



(Sponsored by Swamy Vivekananda Educational Trust, Hyd.)
(Approved by AICTE, Accredited by NBA & NACC, Affiliated to JNTUH)

CERTIFICATE

FILE AND LINK No: MRP-6946/16 (SERO/UGC)

NAME OF THE PRINCIPAL INVESTIGATOR: Dr. K. Shirish Kumar

Vignana Bharathi Institute of Technology,

Aushapur, Hyderabad, Pin: 501301

TITLE OF THE PROJECT: Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ",

Certified that the project has been successfully completed and Executive summary of the report, Research documents, monograph, academic papers published under Minor research project has been posted on the website of the college.

Signature of the Principal Investigator



Signature of the Principal
With seal and stamp

PRINCIPAL
Vignana Bharathi Institute of Technology
Aushapur(V), Ghatkesar(M), Medchal Dist-501 301

ACCESSION CERTIFICATE

This is to certified that Dr. K. Shirish Kumar, Department of Chemistry, Hyderabad has handed over the following books and journals purchased under the scheme of Minor Research Project to the Library of Vignana Bharathi Institute of Engineering & Technology, Hyderabad. The following are books and journals handed over by Dr. K. Shirish Kumar (MRP-6946/16 (UGC/SERO)). _

| S. No | Item | Qty |
|-------|------------------------------|-----|
| 1 | Charge Transfer complex Book | 1 |
| 2 | Silverstein book | 1 |
| 3 | Atkins book | 1 |
| 4 | Huheey book | 1 |
| 5 | Inorganic book | 1 |
| 6 | Chem.II | 1 |
| 7 | Photo Chemistry | 1 |
| 8 | Green Chemistry | 1 |


Signature of the
Principal Investigator

Signature of the
Librarian


Signature of the
Principal
Vignana Bharathi Institute of Technology
Aushapur(V), Chalkeras(M), Medchal Dist-501 501


ASSETS CERTIFICATE

This is to certify that Dr. K. Shirish Kumar, Department of Chemistry, Hyderabad has handed over the following equipment purchased under the scheme of Minor Research Project to the Department of Chemistry, Vignana Bharathi Institute of Engineering & Technology, Hyderabad. The following are equipments handed over by Dr. K. Shirish Kumar (MRP-6946/16 (UGC/SERO)).

| S. No | Particulars | Company | Qty. |
|-------|---------------------------|----------|------|
| 1 | Magnetic Stirrer | REMI MLH | 1 |
| 2 | Distilled Water | AKSHAYA | 4 |
| 3 | Standard flask 10ml | BOROSIL | 10 |
| 4 | Standard flask 25ml | BOROSIL | 5 |
| 5 | Standard flask 100ml | BOROSIL | 2 |
| 6 | Test Tubes 15*125mm | BOROSIL | 100 |
| 7 | Test tube stand | AKSHAYA | 1 |
| 8 | Magnetic Bead | REMI MLH | 1 |
| 9 | Mask Disp | AKSHAYA | 1 |
| 10 | Nitrile Gloves | AKSHAYA | 1 |
| 11 | NMR Tubes | WILMAD | 2 |
| 12 | Quartz Cuvettes | Q-254 | 4 |
| 13 | HP 15G LAPTOP | HP | 1 |
| 14 | HP Wireless optical mouse | HP | 1 |


Signature of the
Principal Investigator


Signature of the
Head of the Dept.


Signature of the
Principal



Settlement proforma

UTILISATION CERTIFICATE

FILE AND LINK No: MRP-6946/16 (SERO/UGC)

NAME OF THE PRINCIPAL INVESTIGATOR: Dr. K. Shirish Kumar

Vignana Bharathi Institute of Technology,

Aushapur, Hyderabad, Pin: 501301

TITLE OF THE PROJECT: Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ",

Certified that the grant of Rs. 1,60,000/- (Rupees one lakh sixty thousand only) approved by UGC and the grant received Rs 1,55,000/- (Rupees one lakh fifty five thousand only) from the University Grants Commission under the scheme of support for Minor Research Project entitled "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ", vide UGC letter No. F.MRP-6946/16 (SERO/UGC) dated 28/7/2017 has been fully utilized for the purpose for which it was sanctioned and that the balance of Rs.5000 has been spent by institute which has to be released from UGC in accordance with the terms and conditions laid down by the University Grants Commission. If as a result of check or audit objection, some irregularity is noticed at a later stage, action will be taken to refund or regularize the objected amount.


SIGNATURE OF THE

PRINCIPAL INVESTIGATOR


PRINCIPAL w
ith Seal and
Stamp
Vignana Bharathi Institute of Technology
Aushapur (V. Ghatkesar (M), Medchal Dist-501 301)



STATUTORY AUDITOR
with Seal and Stamp


CA. L. JANARDHAN RAO
Chartered Accountant
M.No: 19474

DD/P: 20018474-AAAAA C 5831

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002**

**STATEMENT OF EXPENDITURE IN RESPECT OF MINOR RESEARCH PROJECT
(II YEAR)**

1. Name of Principal Investigator: Dr. K. Shirish kumar

2. Dept. of PI: Chemistry

Name of College: Vignana Bharathi Institute of Engineering & Technology

3. UGC approval Letter No. and Date: MRP-6946/16 (SERO/UGC), 28/7/2017.

4. Title of the Research Project: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ".

4. Effective date of starting the project: 15/08/2017

5. a. Period of Expenditure: From 29-01- 2019 to 07/08/2019

b. Details of Expenditure

| S.No. | Item | Amount Approved (Rs.) | Amount Received (Rs.) | Expenditure Incurred (Rs.) | Amount to be released by UGC |
|---------------------|--|-----------------------------|-----------------------------|----------------------------------|------------------------------------|
| i. | Books & Journals | 00 | 00 | 00 | |
| ii. | Equipment | 00 | 00 | 00 | |
| iii. | Contingency including special needs | 10000 | 8000 | 10000 | 2000 |
| iv. | Field Work/Travel (Give details in the proform) a . | 00 | 00 | 00 | |
| v. | Hiring Services | 00 | 00 | 00 | |
| vi. | Chemicals & Glassware | 15000 | 12000 | 15000 | 3000 |
| GRAND TOTAL. | | 25,000 | 20,000 | 25,000 | 5,000 |

7. if as a result of check or audit objection some irregularity is noticed at later date, action will be taken to refund, adjust or regularize the objected amounts.

8. It is certified that the grant of Rs. **25,000/-** (Rupees twenty five thousand only) approved by UGC and the grant received Rs **20,000** (Rupees twenty thousand only) from the University Grants Commission under the scheme of support for Minor Research Project entitled "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ", vide UGC letter No. F. MRP-6946/16 (SERO/UGC) dated 28/7/2017 has been fully utilized for the purpose for which it was sanctioned and that the balance of Rs. **5,000** has been spent by institute which has to be released from UGC in accordance with the terms and conditions laid down by the University Grants Commission.

SIGNATURE OF PRINCIPAL INVESTIGATOR

PRINCIPAL

PRINCIPAL

Vignana Bhareathi Institute of Techno
Aushapur(V), Ghatkesar(M), Medchal Dist-501

(Seal)



**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002**

Utilization certificate (II YEAR)

Certified that the grant of Rs. 25,000/- (Rupees twenty five thousand only) approved by UGC and the grant received RS 20,000 (Rupees twenty five thousand only) from the University Grants Commission under the scheme of support for Minor Research Project entitled "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ", vide UGC letter No. F. MRP-6946/16 (SERO/UGC) dated 28/7/2017 has been fully utilized for the purpose for which it was sanctioned and that the balance of Rs.5000 has been spent by institute which has to be released from UGC in accordance with the terms and conditions laid down by the University Grants Commission.


SIGNATURE OF THE

PRINCIPAL INVESTIGATOR


PRINCIPAL

PRINCIPAL
(Seal)

Vignana Bharathi Institute of Technology
Aushapur(V), Ghatkesar(M), Medchal Dist-501 301




STATUTORY AUDITOR

(Seal)

CA. L. JANARDHAN RAO
Chartered Accountant
M.No: 18474

UDIN: 20018474 A-AAAA-C5831

Annexure - III**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 002****STATEMENT OF EXPENDITURE IN RESPECT OF MINOR RESEARCH PROJECT
(CONSOLIDATED, I & II Year)**

1.Name of Principal Investigator: Dr. K. Shirish kumar

2.Dept. of PI: Chemistry

Name of College: Vignana Bharathi Institute of Engineering & Technology

3.UGC approval Letter No. and Date: MRP-6946/16 (SERO/UGC), 28/7/2017.

4.Title of the Research Project: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ".

5.Effective date of starting the project: 15/08/2017

6. a. Period of Expenditure: From 10/02/2018 to 07/08/2019

b. Details of Expenditure

| S.No | Item | Amount Approved (Rs.) | Amount Received (Rs) | Expenditure Incurred (Rs.) | Amount to be released by UGC |
|--------------------|---|-----------------------|----------------------|----------------------------|------------------------------|
| i. | Books & Journals | 10,000 | 10,000 | 10,000 | 00 |
| ii. | Equipment | 1,00,000 | 1,00,000 | 1,00,000 | 00 |
| iii. | Contingency including special needs | 20,000 | 18,000 | 20,000 | 2,000 |
| iv. | Field Work/Travel (Give details in the proforma). | 00 | 00 | 00 | 00 |
| v. | Hiring Services | 00 | 00 | 00 | 00 |
| vi. | Chemicals & Glassware | 30,000 | 27,000 | 30,000 | 3,000 |
| GRAND TOTAL | | 1,60,000 | 1,55,000 | 1,60,000 | 5,000 |

7. If as a result of check or audit objection some irregularity is noticed at later date, action will be taken to refund, adjust or regularize the objected amounts.

8. It is certified that the grant of Rs. 1,60,000/- (Rupees one lakh sixty thousand only) approved by UGC and the grant received Rs.155,000/- from the University Grants Commission under the scheme of support for Minor Research Project entitled "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ", vide UGC letter No. F. MRP-6946/16 (SERO/UGC) dated 28/7/2017 has been fully utilized for the purpose for which it was sanctioned and that the balance of Rs.5000 has been spent by institute which has to be released from UGC in accordance with the terms and conditions laid down by the University Grants Commission.


SIGNATURE OF PRINCIPAL INVESTIGATOR


PRINCIPAL
PRINCIPAL
Vignana Bharathi Institute of Technol
Aushapur(V), Ghatkesar(M), Medchal Dist-501
(Seal)



UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Utilization certificate (Consolidated, I & II Year)

Certified that the grant of Rs. 1,60,000/- (Rupees one lakh sixty thousand only) approved by UGC and the grant received Rs1,55,000/(Rupees one lakh fifty five thousand only) from the University Grants Commission under the scheme of support for Minor Research Project entitled "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBO", vide UGC letter No. F. MRP-6946/16 (SERO/UGC) dated 28/7/2017 has been fully utilized for the purpose for which it was sanctioned and that the balance of Rs.5000 has been spent by institute which has to be released from UGC in accordance with the terms and conditions laid down by the University Grants Commission.


SIGNATURE OF THE
PRINCIPAL INVESTIGATOR


PRINCIPAL
PRINCIPAL
Vignana Bharathi Institute of Technology
(Seal)
Aushapur(V), Ghatkesar(M), Medchal Dist-501 301

Aushapur (V),
Ghatkesar (M)
Medchal Dist-
501 301


STATUTORY AUDITOR

(Seal)
CA. L. JANARDHAN RAO
Chartered Accountant
M.No: 18474

UDIN: 20018474AAAAC5831

DETAILED STATEMENT OF EXPENDITURE FOR CONTINGENCY (incl. Special needs) (II Yr)

UGC Reference No. F: MRP-6946/16 (SERO/UGC)

Name of the Principal Investigator: Dr. K. Shirish Kumar

Title of research project: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ"

| S.No | Item | Qty. | Bill.No. | Date | Amount |
|------|--------------------------|------|-------------------|-------------|------------------|
| 1 | IR , UV and NMR analysis | | VCP182A/2018-19 | 07-06-2019 | 6,757.00 |
| 2 | Kaspersky Antivirus | | 12144904607 | 27-07-2019 | 1,429.35 |
| 3 | ICDD | | MOJO9129F00A58423 | 29-01- 2019 | 1,500.00 |
| 4 | Xerox and spiral binding | | 864 | 03-11-2018 | 87.00 |
| 5 | Stationery | | 234 | 07-07-2019 | 226.65 |
| | GRAND TOTAL | | | | 10,000.00 |

Signature of the Principal Investigator

Signature of the Principal

Signature of the Statutory Auditor

PRINCIPAL
Vignana Bharathi Institute of Technology
Aushapur(V), Ghatkesar(M), Medchal Dist-501 301

CA. L. JANARDHAN RAO
Chartered Accountant
M.No: 18474

DETAILED STATEMENT OF EXPENDITURE FOR CONTINGENCY (incl. Special needs) I & II YEAR

UGC Reference No. F: MRP-6946/16 (SERO/UGC)

Name of the Principal Investigator: Dr. K. Shirish Kumar

Title of research project: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ"

I YEAR

| S.No | Item | Qty. | Bill.No. | Date | Amount |
|------|-----------------------------|------|----------------|------------|------------------|
| 1 | CISC Conference | | 215 | 19-12-2017 | 5,000.00 |
| 2 | IR and UV | | VCP150/2018-19 | 18-06-2018 | 2,773.00 |
| 3 | H1NMR, C13 NMR, UV SPECTRUM | | 18-19/637 | 27-06-2018 | 2,218.40 |
| 4 | CD | | 314 | 24-06-2018 | 9.00 |
| | GRAND TOTAL | | | | 10,000.00 |

II YEAR

| S.No | Item | Qty. | Bill.No. | Date | Amount |
|------|--------------------------|------|----------------------|------------|------------------|
| 1 | IR, UV and NMR analysis | | VCP182A/2018-19 | 07-06-2019 | 6,757.00 |
| 2 | Kaspersky Antivirus | | 12144904607 | 27-07-2019 | 1,429.35 |
| 3 | ICDD | | MOJO9129F00A58423004 | 29-01-2019 | 1,500.00 |
| 4 | Xerox and spiral binding | | 864 | 03-11-2018 | 87.00 |
| 5 | Stationery | | 234 | 07-07-2019 | 226.65 |
| | GRAND TOTAL | | | | 10,000.00 |

GRAND TOTAL (I & II YEAR) = 20,000/-

Signature of the Principal Investigator

Signature of the Principal

Signature of the Statutory Auditor

Vignana Bharathi Institute of Technology
Aushapur(V), Chittoor(M), Medical Dist-501 201CA. L. JANARDHAN RAO
Chartered Accountant
M.No: 18474

DETAILED STATEMENT OF EXPENDITURE FOR CHEMICALS (II Yr)

BILL NO. GST/18/19/012

Date : 04-06-2019

GST-36AFOPB6054N221

UGC Reference No. F: MRP-6946/16 (SERO/UGC)

Name of the Principal Investigator: Dr. K. Shirish Kumar

Title of research project: "Spectrophotometric, Thermodynamic and Molecular Modelling studies of Novel Crizotinib with N

| S.No | Item | Pack | QTY | Discount | | Taxable Amt | CGST | | SGST | | Amount |
|-------------|-----------------------------|-------|-----|----------|----------|-------------|------|---------|------|---------|----------|
| | | | | % | Amount | | % | Amount | % | Amount | |
| 1 | 2,6-dibromoquinone-4-chloro | 5GM | 1 | 0.00 | 12000.00 | 12000.00 | 9.00 | 1080.00 | 9.00 | 1080.00 | 14160.00 |
| 2 | DISTILLED WATER | 5LT | 1 | 0.00 | 130.00 | 130.00 | 9.00 | 11.70 | 9.00 | 11.70 | 153.40 |
| 3 | ETHANOL | 500ML | 1 | 0.00 | 582.00 | 582.00 | 9.00 | 52.38 | 9.00 | 52.38 | 686.76 |
| | Total | | | | | 12712.00 | | 1144.08 | | 1144.08 | 15000.00 |
| GRAND TOTAL | | | | | | | | | | | 15000 |

Signature of the Principal Investigator


PRINCIPAL
Vignana Bharathi Institute of Technology
Aushapur(V), Ghatkesar(M), Medchal Dist-501 301

Signature of the Statutory Auditor


CA. L. JANARDHAN RAO
Chartered Accountant
M.No: 18474

DETAILED STATEMENT OF EXPENDITURE FOR CHEMICALS (I & II Year)

UGC Reference No. F: MRP-6946/16 (SERO/UGC)

Name of the Principal Investigator: Dr. K. Shirish Kumar

Title of research project: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ"

I YEAR

BILL NO. GST/17/18/0275

Date: 15-05-2018

| S.No | Item | Pack | QTY | Discount | | Taxable Amt | CGST | | SGST | | Amount |
|-------------|------------------------|------|-----|----------|---------|-------------|------|---------|------|--------|---------|
| | | | | % | Amount | | % | Amount | % | Amount | |
| 1 | N-BROMOSUCCINIMIDE | 100 | 1 | 410.00 | 410.00 | 0.00 | 0.00 | 410.00 | 9.00 | 36.90 | 483.80 |
| 2 | DISTIL WATER | 5LT | 1 | 130.00 | 130.00 | 0.00 | 0.00 | 130.00 | 9.00 | 11.70 | 153.40 |
| 3 | DIMETHYL SULPHOXIDEAR | 500 | 2 | 495.00 | 990.00 | 0.00 | 0.00 | 990.00 | 9.00 | 89.10 | 1168.20 |
| 4 | ACETONE AR | 500 | 1 | 275.00 | 275.00 | 0.00 | 0.00 | 275.00 | 9.00 | 24.75 | 324.50 |
| 5 | HCL AR | 500 | 1 | 202.00 | 202.00 | 0.00 | 0.00 | 202.00 | 9.00 | 18.18 | 238.36 |
| 6 | SULPHURIC ACID AR | 500 | 1 | 250.00 | 250.00 | 0.00 | 0.00 | 250.00 | 9.00 | 22.50 | 295.00 |
| 7 | CRIZOTINIB | | 3 | 2032.30 | 6097.00 | 0.00 | 0.00 | 6097.00 | 9.00 | 540.00 | 7177.00 |
| 8 | DICHLOROMETHANE | 500 | 2 | 640.00 | 1280.00 | 0.00 | 0.00 | 1280.00 | 9.00 | 115.00 | 1510.00 |
| 9 | BEAKER 100 ML | EACH | 2 | 63.00 | 126.00 | 0.00 | 0.00 | 126.00 | 9.00 | 11.34 | 148.68 |
| 10 | BEAKER 50ML | EACH | 2 | 59.00 | 118.00 | 0.00 | 0.00 | 118.00 | 9.00 | 10.62 | 139.24 |
| 11 | BURETT 10ML-2122 | EACH | 1 | 498.00 | 498.00 | 0.00 | 0.00 | 498.00 | 9.00 | 44.82 | 587.64 |
| 12 | TISSUE ROLL | EACH | 1 | 35.00 | 35.00 | 0.00 | 0.00 | 35.00 | 9.00 | 3.15 | 41.30 |
| 13 | GRAD PIPPET 1 ML | EACH | 2 | 122.00 | 244.00 | 0.00 | 0.00 | 244.00 | 9.00 | 21.96 | 287.92 |
| 14 | GRAD PIPPET 5 ML | EACH | 2 | 140.00 | 280.00 | 0.00 | 0.00 | 280.00 | 9.00 | 25.20 | 330.40 |
| 15 | GRAD PIPPET 10ML | EACH | 2 | 150.00 | 300.00 | 0.00 | 0.00 | 300.00 | 9.00 | 27.00 | 354.00 |
| 16 | M.C 10 ML 3021 | EACH | 2 | 231.00 | 462.00 | 0.00 | 0.00 | 462.00 | 9.00 | 41.58 | 545.16 |
| 17 | M.C 25ML | EACH | 2 | 275.00 | 550.00 | 0.00 | 0.00 | 550.00 | 9.00 | 49.50 | 649.00 |
| 18 | PLASTIC TRAY450/350/75 | EACH | 1 | 340.00 | 340.00 | 0.00 | 0.00 | 340.00 | 9.00 | 30.60 | 401.20 |
| 19 | R.B FLASK10ML 4380 | EACH | 1 | 140.00 | 140.00 | 0.00 | 0.00 | 140.00 | 9.00 | 12.60 | 165.20 |
| Total | | | | | | 12727 | | 1139.5 | | 1139.5 | |
| GRAND TOTAL | | | | | | | | | | | 15000 |

II YEAR

BILL NO. GST/18/19/012

Date: 04-06-2019

| S.No | Item | Pack | QTY | Discount | | Taxable Amt. | CGST | | SGST | | Amount |
|-------------|----------------------------|-------|-----|----------|----------|--------------|------|---------|------|---------|----------|
| | | | | % | Amount | | % | Amount | % | Amount | |
| 1 | 2,6-dibromoquinone-4-chlor | 5GM | 1 | 0.00 | 12000.00 | 12000.00 | 9.00 | 1080.00 | 9.00 | 1080.00 | 14160.00 |
| 2 | DISTILLED WATER | 5LT | 1 | 0.00 | 130.00 | 130.00 | 9.00 | 11.70 | 9.00 | 11.70 | 153.40 |
| 3 | ETHANOL | 500ML | 1 | 0.00 | 582.00 | 582.00 | 9.00 | 52.38 | 9.00 | 52.38 | 686.76 |
| Total | | | | | | 12712.00 | | 1144.08 | | 1144.08 | 15000.00 |
| GRAND TOTAL | | | | | | | | | | | 15000 |

GRAND TOTAL

(I & II YEAR)

30,000/-

Signature of the Principal Investigator

Signature of the Principal

Signature of the Statutory Auditor

PRINCIPAL
Vignana Bharathi Institute of Technology
Aushapur(V), Chaiteswar(M), Madhwal Dist-591

CA. L. JANARDHAN RAO
Chartered Accountant
M.No: 18474

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.**

**Final Report of the work done on the Minor Research Project. (Report
to be submitted within 6 weeks after completion of each year)**

1. Project report No. Final: Second (After two years) dated: 25/09/2019
2. UGC Reference No. F: MRP-6946/16 (SERO/UGC)
3. Period of report: from: 15/08/2017 to 07/08/2019
4. Title of research project: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ"
5. (a) Name of the Principal Investigator: Dr. K. Shirish Kumar
(b) Deptt: Chemistry
(c) College where work has progressed: Vignana Bharathi Institute of Technology
6. Effective date of starting of the project: 15/08/2017
7. Grant approved and expenditure incurred during the period of the report:
 - a. Total amount approved Rs. 1,60,000/-
 - b. Total expenditure Rs. 1,60,000/-
 - c. Report of the work done: (Copy attached)
- i. Brief objective of the project:
 1. To find out the Molecular interactions between Crizotinib and π -acceptors (NBS and DBQ).
 2. To characterize Charge Transfer Complexes formed between Crizotinib and π -acceptors (NBS and DBQ) by IR, ¹H-NMR and UV-Visible spectroscopic techniques.
 3. To find out the Charge Transfer complexes formed between Crizotinib and π -acceptors (NBS and DBQ) through Molecular Orbital calculations.
- Work done so far and results achieved and publications, if any, resulting from the work (Give details of the papers and names of the journals in which it has been published or accepted for publication:

ii. Publication/Communication:

- Synthesis, Spectrophotometric, Thermodynamic and Spectroscopic studies of CT complexes of novel crizotinib with 2,6-dibromoquinone-4-chloroimide as π – acceptor **Shirish Kumar Kodadi**, Swetha Kovuri *International Journal of Emerging Technologies and Innovative Research* (UGC Approved), ISSN:2349-5162, Vol.6, Issue 6, page no. pp874-887, June-2019.
- Charge Transfer Reaction of Novel Crizotinib with N – Bromo succinimide: A Spectrophotometric and Spectroscopic Study **shirish kumar kodadi**, srikanth chandupatla, swetha kovuri *Journal of Molecular Structure*, Elsevier Publication (**Under review**).

Presentation:

- Participated and presented the paper entitled "Charge Transfer Reaction Of Novel Crizotinb With N-Bromo Succinimide: A Spectrophotometric, Spectroscopic And Computational Study" in three day International Conference for Development Discourse organized by Research for Resurgence Foundation on 8th, 9th & 10th Feb – 2019 at Hyderabad, Telangana, India, sponsored by UGC, AICTE, NAAC, ICSSR in association with IICT, CSIR, ICFAI, ICMR, NIN, OU, EFL etc.
- iii. Has the progress been according to original plan of work and towards achieving the objective. YES.
- iv. Please enclose a summary of findings of the study. One bound copy of the final report of work done may also be sent to the concerned Regional Office of the UGC.

SIGNATURE OF THE PRINCIPAL INVESTIGATOR

PRINCIPAL

(Seal)



Principal Institute of Technology
Aushapur(V), Ghatkesar(M), Medchal Dist-501 301

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG NEW
DELHI – 110 002

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL
REPORT OF THE WORK DONE ON THE PROJECT

1. Title of the Project: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ"
2. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR: Dr. K. Shirish Kumar, VBIT, Hyderabad.
3. NAME AND ADDRESS OF THE INSTITUTION: Vignana Bharathi Institute of Technology, Aushapur, Hyderabad
4. UGC APPROVAL LETTER NO. AND DATE: MRP-6946/16 (SERO/UGC), 28/7/2017
5. DATE OF IMPLEMENTATION: 15/08/2017
6. TENURE OF THE PROJECT : Two years
7. TOTAL GRANT ALLOCATED: 1,60,000/-
8. TOTAL GRANT RECEIVED: 1,55,000/-
9. FINAL EXPENDITURE: 1,60,000/-
10. TITLE OF THE PROJECT: "Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ"

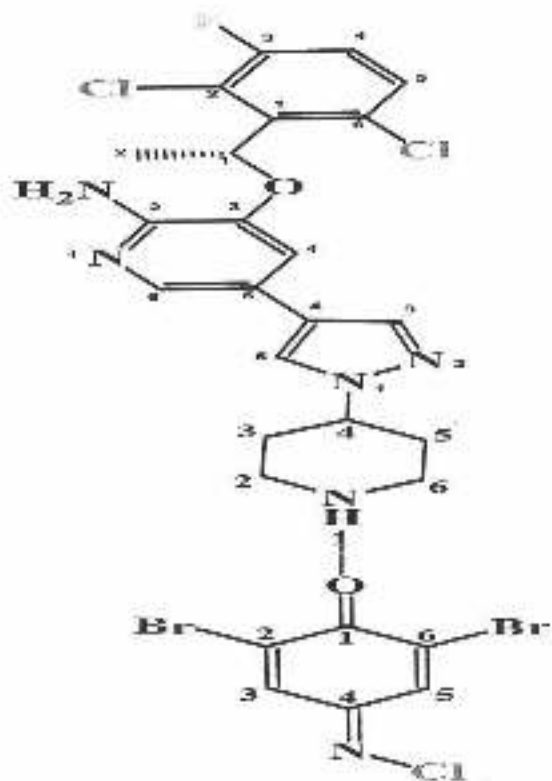
11. OBJECTIVES OF THE PROJECT:

1. To find out the Molecular interactions between Crizotinib and π -acceptors (NBS and DBQ).
2. To characterize Charge Transfer Complexes formed between Crizotinib and π -acceptors (NBS and DBQ) by IR, ¹H-NMR and UV-Visible spectroscopic techniques.
3. To find out the Charge Transfer complexes formed between Crizotinib and π -acceptors (NBS and DBQ) through Molecular Orbital calculations.

12. WHETHER OBJECTIVES WERE ACHIEVED: YES

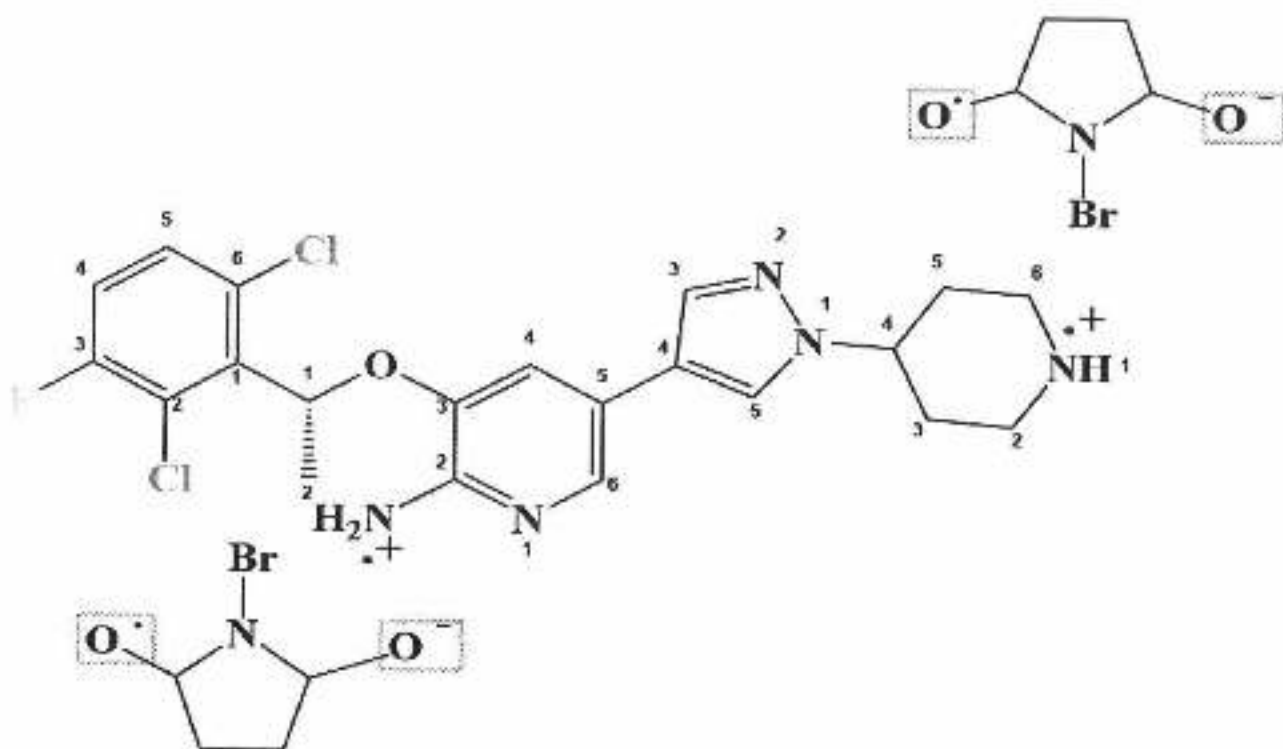
Based upon this valuable information obtained from spectrophotometric and spectroscopic studies, the following plausible interaction (**scheme-1**) between the CZT (donor) and DBQ (acceptor) has been proposed:

Scheme-1



Based upon this valuable information obtained from spectrophotometric and spectroscopic studies, the following plausible interaction (**scheme-2**) between the CZT (donor) and NBS (acceptor) has been proposed:

Scheme-2



ACHIEVEMENTS FROM THE PROJECT: The study enables medical fraternity to pay attention towards the importance of this novel drug, which may potentially contribute to the knowledge in the medicinal field.

SUMMARY OF THE FINDINGS

The CT reaction of CZT as electron donor and NBS, DBQ as electron acceptor has been studied for the first time. The study includes the use of spectrophotometry in the comprehensive manner. A single solvent DMSO has been used to avoid solvent interactions with CZT (donor) and NBS, DBQ (acceptor). The FT-IR and $^1\text{H-NMR}$ is used to characterize the formed complex between CZT and NBS, DBQ. Spectral data acquired from spectral analysis has suggested that CZT acted as an electron donor when interacted with NBS, DBQ (π - acceptor). Hence, the biological activity of CZT may be due its donating ability as is evident from the association constant (K) and standard Gibbs free energy (ΔG^θ) values. The spectroscopic parameters like Ionization Potential (IP), Energy of the complex, E_{CT} (eV), and Resonance Energy (R_N) values also support the strong interaction of CZT with DBQ. Accordingly, plausible interaction between CZT and NBS, DBQ has been proposed.

Therefore, the mechanism for the interaction of the studied CZT is useful in understanding the binding of this bioactive molecule under real pharmacokinetic conditions, which enables medical fraternity to pay attention towards the importance of this novel drug, which may potentially contribute to the knowledge in the medicinal field.

CONTRIBUTION TO THE SOCIETY: The study enables medical fraternity to pay attention towards the importance of this novel drug, which may potentially contribute to the knowledge in the medicinal field.

WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT: NO

NO. OF PUBLICATIONS OUT OF THE PROJECT: One (paper is attached)


(PRINCIPAL INVESTIGATOR)


(PRINCIPAL)
PRINCIPAL
(Seal)
Vignana Bharathi Institute of Techn
Aushapur(V), Chetkesar(M), Madchal Dist-51



THESIS

Title of Minor Research Project: Spectrophotometric, Thermodynamic and Molecular Modeling studies of Novel Crizotinib with NBS and DBQ.

Principal Investigator: Dr. K. Shirish Kumar, Assoc. Prof. of Chemistry, Dept. Of Chemistry, Vignana Bharathi Institute of Technology, Aushapur, Hyderabad.

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FINAL REPORT OF THE MINOR RESEARCH PROJECT IN CHEMISTRY

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Abstract

The mechanism of an elemental act is undeniably one of the most fundamental problems in predicting the drug-receptor interaction. This problem has fascinated scientists for quite a long time. Accordingly, charge transfer (CT) phenomenon was contrived. Hence, Charge transfer complex (CTC) reaction of novel anti lung cancer drug Crizotinib (CZT) as electron donor with N – Bromo succinimide (NBS) as electron acceptor was studied for the first time. Spectrophotometric study has been carried out to ascertain the CTC between CZT and NBS, which was well substantiated by the spectroscopic parameters like Association constant (K), Standard Gibbs free energy (ΔG°), Molar extinction coefficient (ϵ_{CT}), Resonance Energy (R_N) and Ionization potential (I_P) and Dissociation energy (W). Photometric titrations and Jobs method of continuous variations suggested that the CTC formed between CZT and NBS is in the ratio of 1:2. The molecular structure, spectroscopic characteristics and the interactive modes have been construed from FT-IR and ^1H -NMR spectroscopy. Based upon the obtained spectroscopic data, the plausible CT interaction between CZT and DBQ was proposed.

INTRODUCTION:

Lung cancer has long been known as the most common vulnerable disease remained as cause of cancer-related deaths worldwide, adding 1.61 million new cases and 1.38 million deaths in 2008 alone, registering 12.7% of additional cancers and 18.2% of cancer mortality¹. Approximately 85% of lung cancers are non-small cell lung cancer (NSCLC) and the majority of patients are diagnosed at an advanced stage²; 5-year survival for patients in the USA with NSCLC is approximately 16%. Current treatments for NSCLC may extend survival but are rarely curative³.

Crizotinib (CZT) 3-[(1R)-1-(2,6-dichloro-3-fluorophenyl) ethoxy]-5-(1-piperidin-4-ylpyrazol-4-yl) pyridin-2-amine is a novel anti lung cancer drug acting as an ALK (Anaplastic Lymphoma Kinase) & ROS 1 (C- ROS, Oncogene 1) inhibitor; it has been approved by FDA on August 26, 2011, under the trade name of xalkori capsules, made by Pfizer, Inc. for the treatment of patients with locally advanced or metastatic Non-Small Cell Lung Cancer (NSCLC) i.e., ALK positive as detected by an FDA approved test.

Further clinical trials on CZT are under process to test its safety and efficacy in Anaplastic Large Cell Lymphoma, Neuroblastoma and other advanced solid tumours in both adults and Children.

CZT is currently used to exert its effects through modulation of the growth; migration and invasion of malignant cells. Furthermore, other studies suggest that CZT might also act via inhibition of Angiogenesis, in malignant tumours, which is of great interest in order to show how this novel CZT is significant.

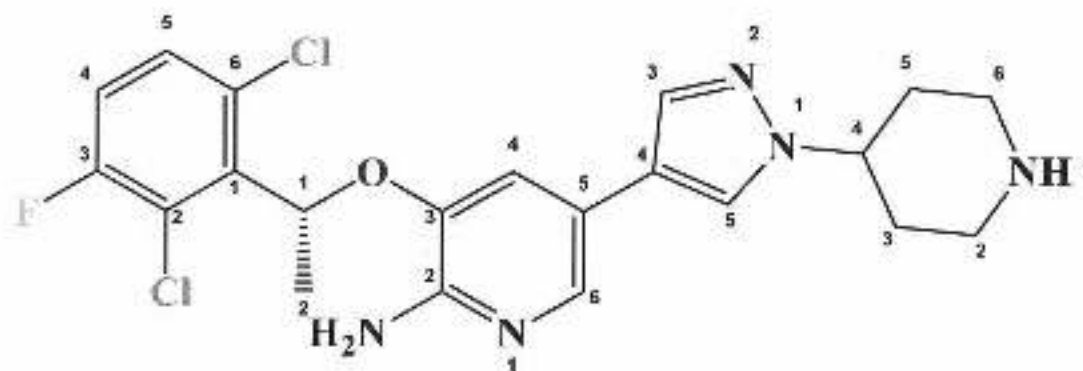
Available literature on this subject reveal that the electron donating properties of CZT and its Charge Transfer (CT) reactions have not been much investigated so far.

These findings about CZT prompted us to investigate the CT reaction of CZT with N-Bromo succinimide, NBS (π - acceptor)

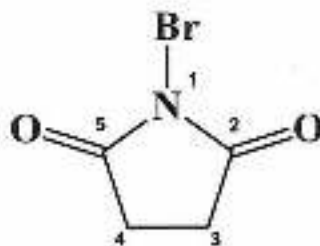
The CT complexes are identified to take part in many chemical reactions like addition, substitution, condensation, etc, Electron donor-acceptor CT interaction is also important in the field of drug receptor binding mechanism⁴, as well as in many biological fields. In view of this, CT reactions of certain π - acceptors have been successfully utilized in pharmaceutical analysis. The CT complexes (CTCs) of organic species are strenuously studied because of their special type of interaction which is accompanied by transfer of electron from donor to acceptor. Also, protonation of donor from acidic receptors are generally rout for the formation of the ion pair adducts. The π -acceptors have numerous applications as analytical reagents. They have been used for the spectrophotometric determination of many drugs in pharmaceutical formulations.

Inasmuch all these aspects, it is proposed to investigate the charge transfer complex (CTC) of CZT with NBS.

Structures of CZT and NBS



CRIZOTINIB (CZT)



N-BROMOSUCCINIMIDE (NBS)

1 Experimental Methodologies

1.1 Chemicals

All the chemicals were used of analytical grade. NBS (Finar, India, purity > 98%) and Dimethyl sulfoxide, DMSO (Finar, India, purity > 99.9%) were used without further purification. The CZT was procured from Meruvax pharmaceuticals, Hyderabad. The purity of CZT as specified by the makers was >99%, which was confirmed by its melting temperature. The CZT was used as received without any further purification.

1.2 Synthesis of CZT–NBS CT complex

The CZT and NBS of 1 mmol each (1:1) were accurately weighed on Dhona 160 D analytical balance and transferred them into porcelain mortar and truncated the mixture scrupulously in the presence of a few drops of methylene chloride solvent. Then dried the obtained reaction mixture by continuous suction and transferred them into a dry beaker. The beaker was stored overnight in a desiccator filled with activated anhydrous calcium chloride, then transferred the dried solid brown coloured powder containing CZT–NBS CTC into a clean vial. The vial was capped well to protect from moist air.

2 Instruments

The electronic absorption spectra of the CZT, NBS and resulting CTC were recorded over a wavelength range of 200–800 nm using an UV-2600 Shimadzu UV-VIS Spectrophotometer.

The instrument was equipped with a quartz cell with a 1.0 cm path length. The FT-IR spectra within the range of 4000–250 cm^{-1} for the solid powder of free CZT and its CT Complex with NBS were recorded on a Shimadzu FT-IR Prestige-21 spectrophotometer with 40 scans at 4 cm^{-1} resolution. ^1H -NMR spectra were recorded using Bruker Biospin advance-III 400 MHz Fourier Transform Digital NMR Spectrometer with DMSO as solvent, chemical shift values are given in ppm relative to tetramethyl silane.

3 Spectrophotometric Study

3.1 Preparation of Experimental Solutions

Stock solutions of CZT (donor) and NBS (acceptor) at a concentration of $5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ were freshly prepared before each series of measurement by dissolving accurately weighed amounts in an appropriate volume of DMSO. The stock solutions of donor and acceptor were protected from light. The solutions for spectrophotometric measurements were freshly prepared by mixing appropriate volumes of donor and acceptor stock solutions immediately before recording the spectra.

3.2 Experimental Measurements

To determine the stoichiometry of the CZT (donor) and NBS (acceptor) interactions, various molar ratios were examined by applying Job's method of continuous variations⁵⁻⁶ and photometric titration measurements. These titrations monitored the detectable CT bands during the reactions of NBS with donor. Briefly, 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 mL of a standard solution ($5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) of the appropriate donor in DMSO solvent was added to 1.00 mL of the acceptor at $5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, dissolved in the same solvent. The final volume of the mixture was made to 5 mL. The concentration of the acceptor (C_a^0) was maintained constant at $5.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, while the concentration of the donor (C_d^0) varied from $0.25 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ to $4.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ to produce

solutions with a (donor: acceptor) molar ratio that varied from 1:4 to 4:1, for the 1:2 complex. The absorbance of complex was plotted against the volume of the added acceptor.

3.3 Calculations – Background

The physical spectroscopic data of the resulted CT complexes were computed, the association constant (K) and the molar extinction coefficient (ϵ_{max}) were determined spectrophotometrically using the Modified 1:2 Benesi–Hildebrand equation⁷ for the 1:2 CT complex with NBS.

Table 1 Benesi–Hildebrand data of the CZT-NBS CT complex

| $C_a^0 \times 10^{-4}$ | $C_d^0 \times 10^{-4}$ | Absorbance | $(C_a^0)^2 C_d^0 / A \times 10^{-12}$ | $C_a^0 (4C_d^0 + C_a^0) \times 10^{-8}$ |
|------------------------|------------------------|------------|---------------------------------------|---|
| 0.25 | 5 | 0.657 | 2.097 | 5.062 |
| 0.5 | 5 | 0.750 | 7.530 | 10.250 |
| 0.75 | 5 | 0.835 | 15.368 | 15.562 |
| 1.0 | 5 | 0.926 | 25.000 | 21.000 |
| 1.5 | 5 | 0.938 | 48.900 | 32.250 |
| 2.0 | 5 | 0.956 | 76.920 | 44.000 |
| 2.5 | 5 | 0.968 | 97.170 | 56.250 |
| 3.0 | 5 | 0.976 | 150.000 | 69.000 |
| 3.5 | 5 | 0.985 | 189.620 | 82.250 |
| 4.0 | 5 | 0.998 | 231.880 | 96.000 |

Modified Benesi–Hildebrand (1:2) equation

$$(C_a^0)^2 C_d^0 / A = 1/K\epsilon + 1/\epsilon C_a^0 (4C_d^0 + C_a^0) \text{ ----- (2)}$$

Where, C_a^0 and C_d^0 are the initial concentrations of the acceptor and donor, respectively, and A is the absorbance of the CT band. By plotting the $(C_a^0)^2 C_d^0 / A$ for the 1:2 CT complex as a function of the corresponding values $C_a^0 (4C_d^0 + C_a^0)$, a straight line is obtained with a slope of $1/\epsilon$ and an intercept at $1/K\epsilon$.

4. Results and discussion

4.1 Electronic Spectra

The UV-Vis spectra of CZT (donor) display two absorption bands at $\lambda = 274\text{nm}$ and 326nm and NBS (acceptor) display one absorption band at 258 nm in DMSO solvent (Figure 1). While, UV-Vis spectra of the CZT-NBS CTC in the same solvent (Figure 1) display two absorption bands at $\lambda = 280\text{ nm}$ and 306 nm . The UV-Vis spectra of CZT and NBS shows no absorption bands in this spectral region. The absorption bands which appeared at 280 and 306 nm for the CTC were presumably due to the interaction of CZT (donor) with NBS (acceptor) and are indicative of the formation of a CT complex. This observation suggests the CT from CZT (donor) to the NBS (acceptor), which is well supported by the FT-IR and spectroscopy. The band at $\lambda = 280\text{ nm}$ was selected for the further spectrophotometric study because it has highest absorption intensity (Figure 1). Polar solvent such as DMSO has been chosen as the solvent to promote the complete transfer of electron from CZT (donor) to the NBS (acceptor).

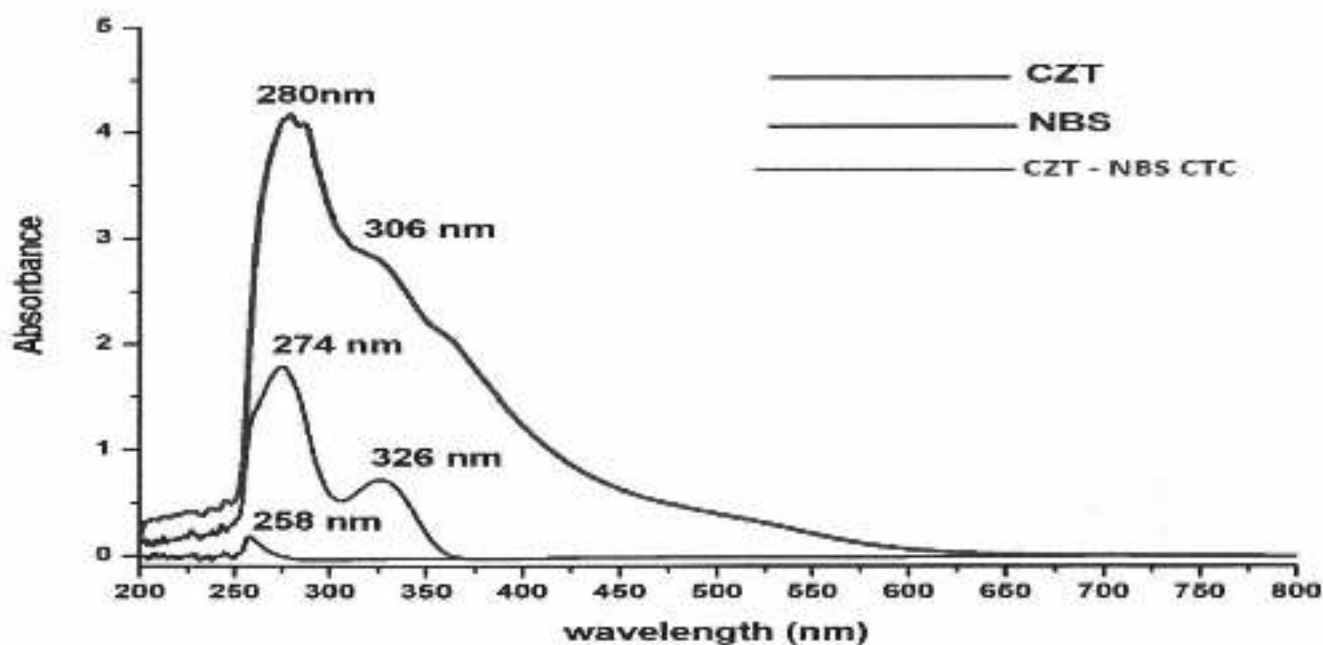


Fig.1. Electronic spectra of CZT-NBS (5×10^{-3})

4.2 Conductance measurements of freshly prepared experimental solutions

Conductimetry has often been employed to study the interactions of CT complexes^{8,9}. In the present study, the conductivity measurements of CZT (donor) and its synthesized CT complex with NBS were performed in DMSO solvent at 5×10^{-3} M using Systronics 304 conductivity meter. The conductance values of free donor was found to be $7 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ and for free acceptor NBS was found to be $20 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ while, the conductance values of CZT-NBS complex was found to be $92 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ respectively, this result suggest that the resulted complex have electrolytic behaviour. This data reveals the formation of dative $D^+ - A^-$ complex between CZT (donor) and NBS (acceptor) under the acid-base theory.

4.3. Effect of reaction time

The optimum reaction time was determined by observing the light-yellow colour development at ambient temperature ($25 \pm 1^\circ \text{C}$). The complete colour development was attained instantaneously with compound investigated, and the colour remained stable for 24 hrs. And it is observed that as the time increases absorbance values increase, which suggest the stability of the CZT-NBS complex.

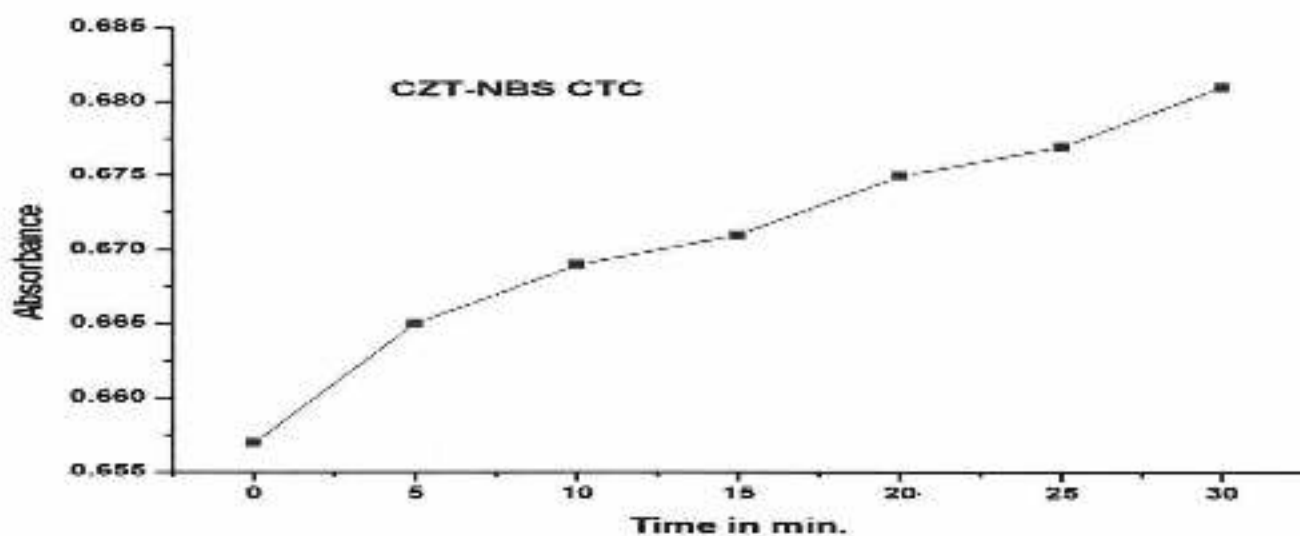


Fig. 2. Effect of time on the stability of the CZT-NBS (5×10^{-4} M) in DMSO at 280nm

4.4. Stoichiometry of the interaction

The stoichiometry of the formed CZT-NBS complex was determined by applying Job's method of continuous variations (**Fig.3.**), the symmetrical curves with a maximum at 0.4 mole fraction indicated the formation of 1:2 complex (**Fig.3.**). The spectrophotometric titration measurements were also performed for the determination of stoichiometry of the formed CT complex. The electronic spectra of the CZT-NBS complex was recorded with varying concentrations of acceptor, while, concentration of donor is kept constant. The stoichiometry of the complex was determined graphically by plotting the absorbance as a function of the volume of donor (in mL.), where two straight lines are produced intercepting at 1:2 ratio for complex. Representative spectrophotometric titration plot based on the characterized absorption bands are shown in **Fig. 3.** The results show the good interaction between NBS acceptor and CZT donor considered in the study.

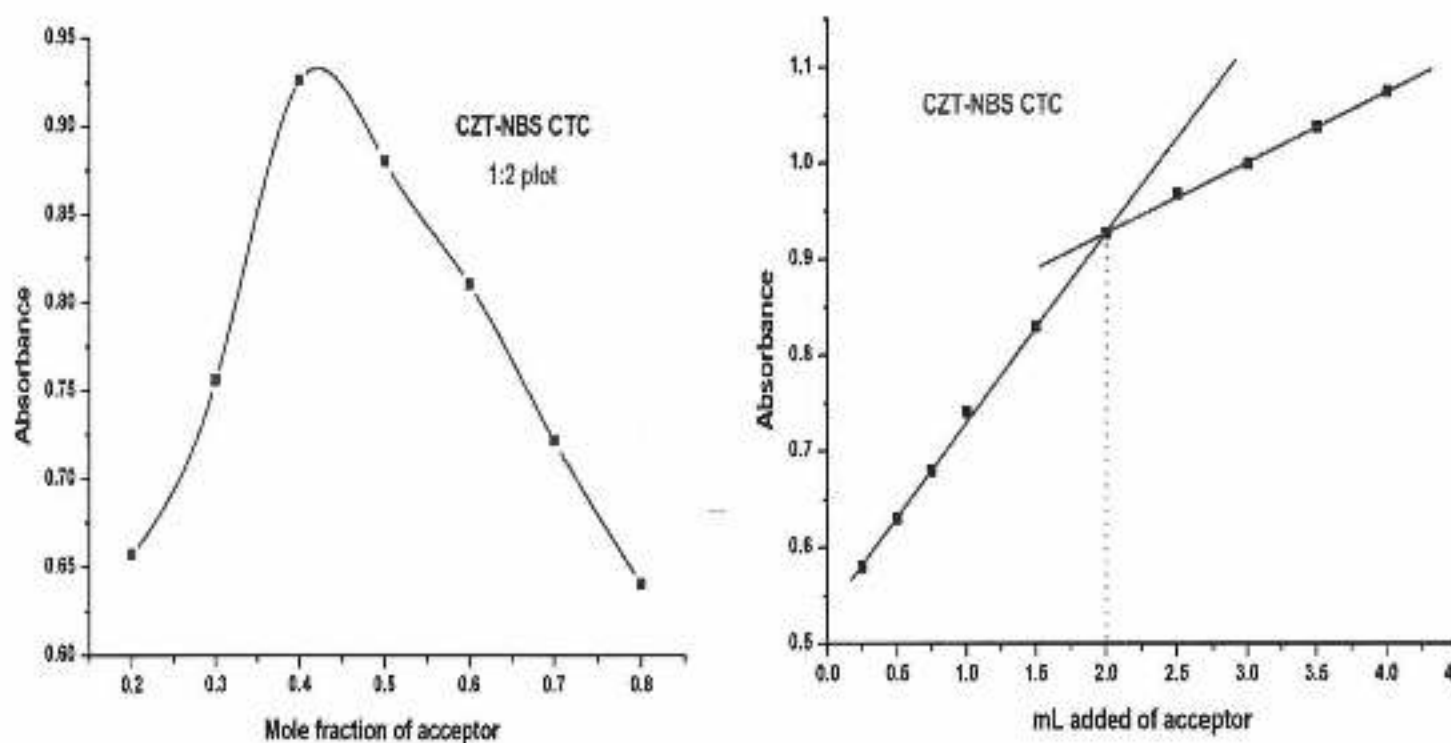


Fig. 3. Jobs plot and Spectrophotometric curve of the CZT-NBS CTC (5×10^{-4} M)

4.5. Association constant of CZT-NBS CT complex

Representative Benesi-Hildebrand plot is shown in (Fig.4) and the values of both K and ϵ are thus determined and are compiled in (Table-2) along with the other spectroscopic parameters data. In general, the 1:2 complexes exhibit high association constant values (K), accordingly, the CZT-NBS complex shown higher K value. This high K value indicates a strong interaction between the CZT and NBS.

High association constant value which was obtained by Benesi-Hildebrand 1:2 equation, suggest the good binding affinity between n -donor CZT and acceptor NBS. The high association constant values are common in n -electron donors, where the intermolecular overlap may be considerable¹⁰.

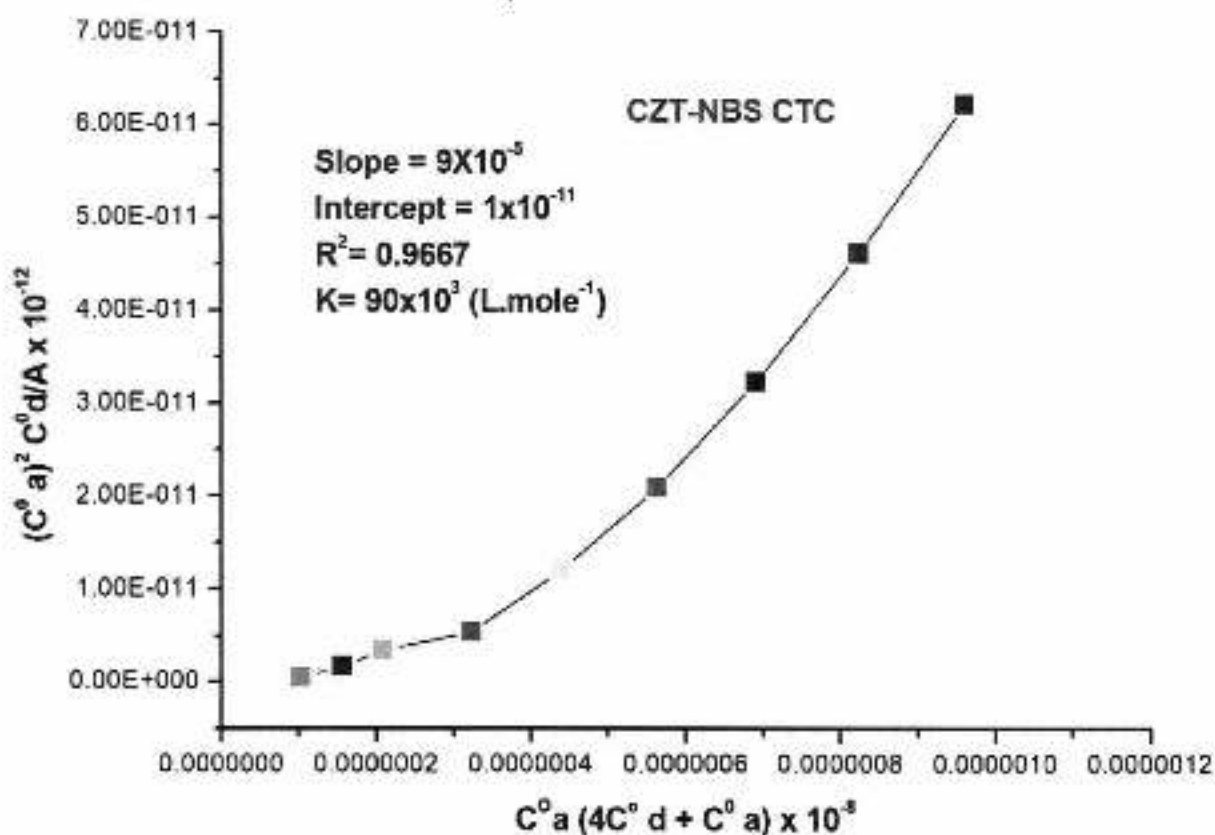


Fig. 4. The 1:2 Benesi-Hildebrand plot for CZT-NBS CTC

5. Calculation of spectroscopic Parameters

In order to support the formation and nature of CZT-NBS CT complex, spectroscopic parameters like, Ionization potential (IP), Energy of the charge transfer complexes (E_{CT}), Resonance Energy (R_N), Dissociation energy (W) and Standard free energy changes (ΔG^0) of the CT Complexes were calculated.

5.1. Ionization Potential (IP)

The ionization potential (IP) of the highest filled molecular orbital of the donor was estimated from CT energies of its complexes with the acceptor making use of the following empirical Aloisi and Pignataro equation¹¹. The calculated IP values for molecular orbital participating in CT interaction of the donors are compiled in the **Table -2**.

$$h\nu_{CT} = a IP^D + b$$

Where, $a = 0.87$ and $b = -3.6$, $h\nu_{CT}$ is the energy of CT complex. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital.

5.2. Energy of the charge transfer complexes (E_{CT})

The energy (E_{CT}) of the CT Complexes were calculated using the following equation¹² and the values are compiled in the **Table -2**.

$$E_{CT} = (h\nu_{CT}) = 1243.667 / \lambda_{CT} \text{ (nm)}$$

Where, λ_{CT} is the wavelength of the complexation band.

5.3. Resonance Energy (R_N)

Resonance Energy (R_N) of CT Complexes were determined by the following theoretically derived equation by Briegleb and Czckalla¹³ and the values were compiled in the **Table -2**.

$$\epsilon_{\max} = 7.7 \times 10^4 / [h\nu_{CT} / |R_N| - 3.5]$$

Where, ϵ_{\max} is the molar absorptivity of the CTC at maximum charge transfer band, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state, which is obviously a contributing factor to the stability constant of the complex.

5.4. Dissociation energy (W)

Further evidence of the nature of CT interaction in the present CT complexes is the calculation of the dissociation energy (W) of the CT excited state of the complex. The dissociation energy (W) of the formed CT complex was calculated from the corresponding CT energy (E_{CT}), ionization potential of the donor (IP) and electron affinity of the acceptor (EA) using the following relationship¹⁴ and the calculated values of W are compiled in (**Table -2**.)

$$h\nu_{CT} = IP - EA - W$$

Where, $h\nu_{CT}$ is the energy of CT complex, IP is the ionization potential of the donor and EA is the electron affinity of the acceptor.

5.5. Standard free energy changes (ΔG^θ)

To add more conformation for the nature of CT interaction, standard free energy change values (ΔG^θ) were calculated and are compiled in **Table-2**, the higher negative values suggest that the CT complexes formed between β -AB and I_2 are exothermic. Generally, the values of ΔG^θ

become more negative as the value of K increases where the CT interactions between the donor and acceptor become strong. Thus, the components (donor and acceptor) are subjected to more physical strain or loss of degree of freedom and the values of ΔG^0 become more negative¹⁵.

The standard free energy changes of complexation (ΔG^0) were calculated from the association constant values by the following equation.

$$\Delta G^0 = - RT \ln K$$

Where, ΔG^0 is the free energy change of the CT Complexes (KJmol^{-1}), R is the gas constant ($1.987\text{calmol}^{-1}\text{K}^{-1}$), T is the temperature in Kelvin and K is the association constant of the CT Complexes at room temperature.

Table - 2. Spectroscopic parameters of the CZT-NBS CT Complex

| | CZT-NBS |
|---|----------------------|
| Wavelength: λ_{max} (nm) | 280 |
| Extinction coefficient: ϵ_{max} ($\text{L mole}^{-1} \text{cm}^{-1}$) | 11×10^3 |
| Association constant: K (L mole^{-1}) | 90×10^3 |
| Energy: $h\nu_{\text{CT}}$ (eV) | 4.416 |
| Ionization Potential: IP (eV) | 9.2432 |
| Resonance Energy: R_N (eV) | 1.261 |
| Dissociation energy : W (eV) | 2.2716 |
| Gibbs free energy: ΔG^0 (KJmol^{-1}) | -6.755×10^3 |

The calculated spectroscopic parameters values like Energy of the CT complex ($h\nu_{CT}$), Ionization Potential (IP), Resonance Energy (R_N), Dissociation energy (W) and Standard Gibbs free energy (ΔG^0) suggests that the investigated CZT-NBS complex was reasonably strong and stable under the studied conditions.

The association constant is strongly dependent on the nature of the acceptor used including the type of electron withdrawing substituents to it such as bromo and carbonyl groups of NBS (acceptor). The association constant value is equal to 90×10^3 L/mol (Table-2), that reflects the relatively higher electron acceptance ability for NBS. The number of donating atoms available in the donor is another important factor that affects the stability of charge transfer complexes¹⁶. High association constant value (Table-2) of CZT-NBS suggests the strong interaction between CZT (donor) and NBS (acceptor). Since in the process of molecular complexation, it is reasonably assumed that the charge density is donated from the donor to acceptor, the increased number of nitrogens in the donor (CZT) is expected to increase the donor acceptor interaction in solution. The effective overlapping of donor-acceptor orbitals involves the proper spatial positions of donor and acceptor molecules. This also needs specific conformation of donor. During complexation, some energy is consumed for the conversion of most stable conformation of free donor to a conformation which is suitable for complex formation.

6. Spectral Characterization

6.1. FT-IR spectroscopy

FT-IR spectroscopy is widely used in organic chemistry for the identification of functional groups of organic compounds as well as the studies on molecular conformation, reaction kinetics, etc¹⁸. Assignment for complex systems can be propounded on the basis of frequency agreement between

the computed harmonics and the observed fundamentals. Therefore, FT-IR spectra of the CZT, NBS and their respective CTC (CZT-NBS) were measured in the range of 4000–250 cm^{-1} .

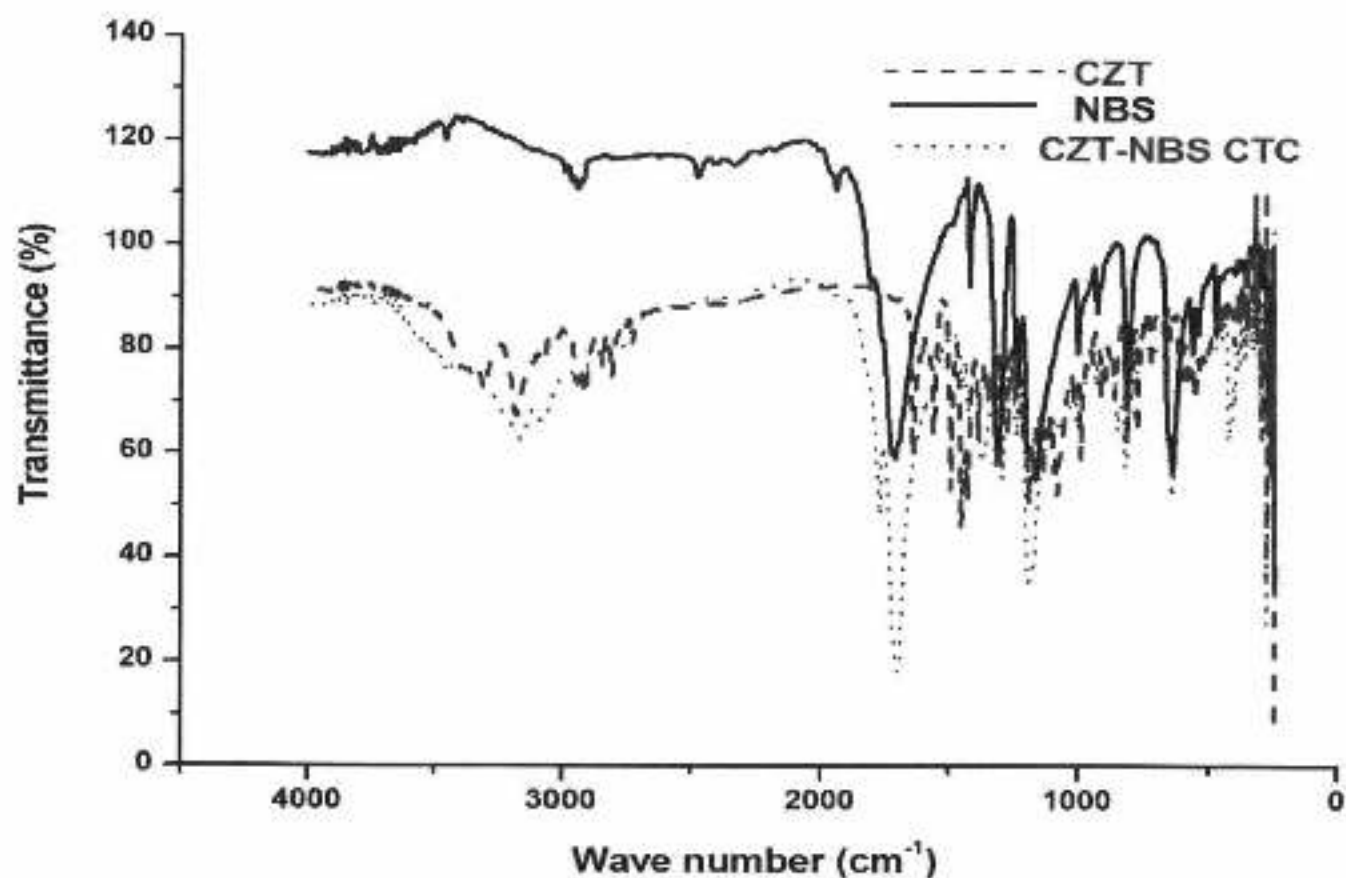


Fig.5. FT-IR spectra of CT complex

The FT-IR spectra of three are shown in Fig. 5. A comparison of the relevant infrared spectral bands of the CZT free donor and NBS acceptor and their respective CTC (CZT-NBS) clearly indicate that the characteristic bands of CZT show some shift in the frequencies (Table-3), as well as some change in their band intensities. This could be attributed to the expected symmetry and electronic structure changes upon the formation of the charge transfer complex, which Suggest

that the CT complex is formed through $n-\pi^*$ charge migration from HOMO of the donor to the LUMO of the acceptor. It is noteworthy to say that the spectra of CZT-NBS complex have a sharp broadening with distortion in the stretching vibration bands.

The frequency of N-H bands, ν (N-H) which were 3379.29 cm^{-1} , 3305.99 cm^{-1} (CZT) before the complexation are shifted to 3458.37 cm^{-1} , 3300.05 cm^{-1} (CZT-NBS) after the complexation, ν (C-H) which were 2956 cm^{-1} , 29142 cm^{-1} , 2849 cm^{-1} (CZT) before the complexation are shifted to 3077 cm^{-1} , 2848 cm^{-1} , 2791 cm^{-1} , 2953 cm^{-1} (CZT-NBS) after the complexation, Aromatic Hydrogens which were 3023 cm^{-1} , 3066 cm^{-1} , 3083 cm^{-1} (CZT) before the complexation are shifted to 3021 cm^{-1} , 3077 cm^{-1} , 3078 cm^{-1} (CZT-NBS) after the complexation, ν (C-O) which was 1673 cm^{-1} (NBS) before the complexation is shifted to 1777 cm^{-1} (CZT-NBS) after the complexation. Moreover, there is a slight change in frequency values of the remaining functional groups, which suggest the CT from CZT to NBS.

Table-3. Important Infrared absorption frequencies (cm^{-1}) and tentative assignments of CZT and CZT-NBS CT complex

| CZT | NBS | CZT-NBS | Assignments |
|--------------------|------------------|------------------------|----------------------------|
| 3379.29, 3305.99 | 3079, 3052 | 3458.37, 3300.05 | ν (N-H) |
| 2956, 29142, 2849, | 2925, 2869, 2854 | 3077, 2848, 2791, 2953 | ν (C-H) |
| 773.46 | - | 775.50 | ν (C-Cl) |
| 1388.75 | - | 1369.46 | ν (C-CH ₃) |
| 1273.02 | - | 1242.16 | ν (C-F) |
| 3023, 3066, 3083 | - | 3021, 3077, 3078 | Aromatic hydrogens |

| | | | |
|------------------|------|------------|---------------------------|
| 1080.14 | - | 1068.56 | ν (C-O-C) |
| 1496.76, 1564.27 | | 1458, 1531 | C=N+ (conjugated, cyclic) |
| | 1673 | 1777, 1703 | ν (C=O), ν (C=C) |

6.1. ^1H -NMR spectroscopy

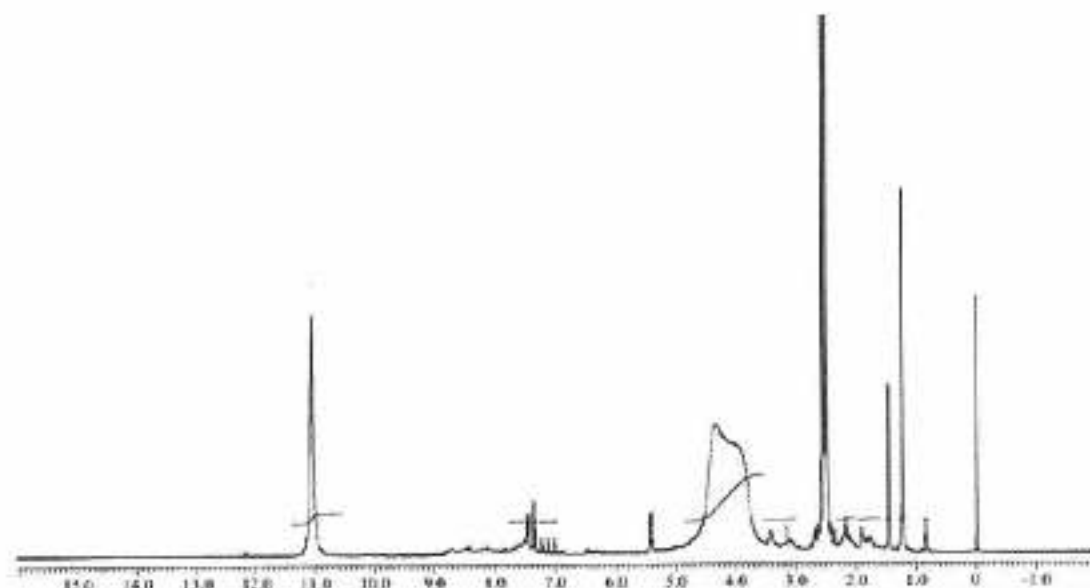


Fig.6. ^1H -NMR spectra of CT complex

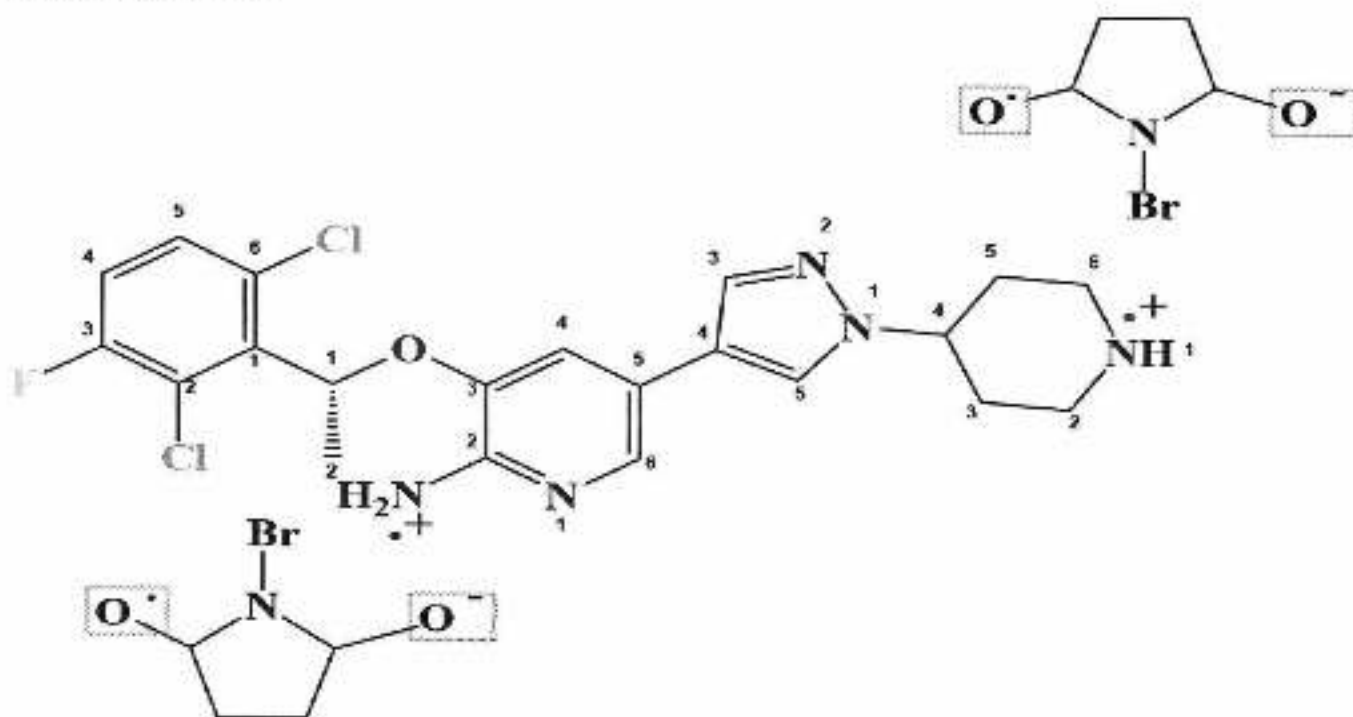
The ^1H NMR spectra of the CT complex CZT-NBS was recorded in DMSO and shown in Fig.6. The ^1H NMR spectrum of this CT complex was compared with the free CZT (donor), and the proton peak of -NH group was detected at 11 ppm, indicating the involvement of the nitrogen atom of -NH groups in complexation. The group of signals within 2.40–2.80 ppm and 6.40–8.80 ppm ranges are assigned to 4H of NBS and 14H of CZT donor, these signals are shifted to lower field

after complexation. The formation of the complex was confirmed by the appearance of new signals in the spectrum.

Apparently, the results obtained from spectrophotometric study, FT-IR spectra met in the same point with ^1H -NMR spectra to construe the mode of interaction between CZT and NBS.

Based upon on the results obtained from spectrophotometric study, FT-IR spectra and ^1H -NMR spectra, following plausible interaction is proposed between CZT and NBS.

Plausible interaction



7. *In silico* study

7.1. *Molecular structure and optimized geometry*

In order to obtain a clue about the structural features of the resulting CT complex, *In silico* study has been carried out using GAMESS computations as a package of ChemBio3D Ultra 14.0; which includes energy optimization, estimation of the stabilization energy, computation of the optimized parameters (bond lengths, bond angles, bond orders and electron densities), Mulliken, Lowdin and Huckel charge computations of the free CZT (donor), NBS (acceptor) and their respective CT complex. MM2 method has been applied at RHF/3-21G level for energy optimization in all the cases.

The stabilization energy of the donor CZT and the acceptor NBS recorded **44.1590** kcal. mol⁻¹, and **11.4742** kcal. mol⁻¹, respectively. The stabilization energy of the formed complex recorded **47.5367** kcal.mol⁻¹, confirming the high stability of the obtained complex in accordance with experimental spectroscopic data.

The optimized structures of NBS (acceptor), CZT (donor) and CZT- NBS CT complex with atomic number are presented. The optimized geometrical structural parameters (bond lengths and angles) are listed in **Table-4 & 5** for the CZT and CZT-NBS CT complex respectively.

i.(a) Optimized geometrical structural parameters

Table 4 Bond lengths of CZT and CZT- NBS CT complex

| CZT | | NBS | | CZT-NBS | |
|--------------|-----------------|-------------|-----------------|--------------|-----------------|
| | Bond length (Å) | Atoms | Bond length (Å) | Atoms | Bond length (Å) |
| O(19)-Lp(57) | 0.595 | O(7)-Lp(16) | 0.599 | O(37)-Lp(73) | 0.599 |
| O(19)-Lp(56) | 0.601 | O(7)-Lp(15) | 0.6 | O(37)-Lp(72) | 0.6 |
| N(13)-Lp(55) | 0.601 | O(6)-Lp(14) | 0.599 | O(36)-Lp(71) | 0.599 |
| N(9)-Lp(54) | 0.601 | O(6)-Lp(13) | 0.6 | O(36)-Lp(70) | 0.6 |
| N(6)-Lp(53) | 0.602 | C(4)-H(12) | 1.114 | O(19)-Lp(69) | 0.6 |
| C(26)-H(52) | 1.104 | C(4)-H(11) | 1.114 | O(19)-Lp(68) | 0.598 |
| C(25)-H(51) | 1.103 | C(3)-H(10) | 1.114 | N(13)-Lp(67) | 0.601 |
| C(21)-H(50) | 1.111 | C(3)-H(9) | 1.114 | N(9)-Lp(66) | 0.601 |
| C(21)-H(49) | 1.115 | N(1)-C(5) | 1.38 | N(6)-Lp(65) | 0.602 |
| C(21)-H(48) | 1.114 | C(4)-C(5) | 1.518 | C(34)-H(64) | 1.115 |
| C(20)-H(47) | 1.124 | C(3)-C(4) | 1.544 | C(34)-H(63) | 1.114 |
| C(18)-H(46) | 1.115 | C(2)-C(3) | 1.518 | C(33)-H(62) | 1.114 |
| C(18)-H(45) | 1.116 | N(1)-C(2) | 1.38 | C(33)-H(61) | 1.114 |
| C(17)-H(44) | 1.116 | N(1)-Br(8) | 1.818 | C(26)-H(60) | 1.104 |
| C(17)-H(43) | 1.116 | C(5)-O(7) | 1.209 | C(25)-H(59) | 1.102 |
| C(16)-H(42) | 1.118 | C(2)-O(6) | 1.209 | C(21)-H(58) | 1.109 |
| C(15)-H(41) | 1.116 | | | C(21)-H(57) | 1.115 |
| C(15)-H(40) | 1.116 | | | C(21)-H(56) | 1.113 |
| C(14)-H(39) | 1.115 | | | C(20)-H(55) | 1.119 |
| C(14)-H(38) | 1.116 | | | C(18)-H(54) | 1.115 |
| N(13)-H(37) | 1.051 | | | C(18)-H(53) | 1.116 |
| C(12)-H(36) | 1.094 | | | C(17)-H(52) | 1.116 |
| C(10)-H(35) | 1.097 | | | C(17)-H(51) | 1.116 |
| N(7)-H(34) | 1.05 | | | C(16)-H(50) | 1.119 |
| N(7)-H(33) | 1.049 | | | C(15)-H(49) | 1.116 |
| C(5)-H(32) | 1.102 | | | C(15)-H(48) | 1.116 |
| C(3)-H(31) | 1.094 | | | C(14)-H(47) | 1.115 |
| C(22)-C(27) | 1.356 | | | C(14)-H(46) | 1.116 |
| C(26)-C(27) | 1.345 | | | N(13)-H(45) | 1.047 |
| C(25)-C(26) | 1.337 | | | C(12)-H(44) | 1.095 |
| C(24)-C(25) | 1.338 | | | C(10)-H(43) | 1.097 |
| C(23)-C(24) | 1.349 | | | N(7)-H(42) | 1.049 |
| C(22)-C(23) | 1.359 | | | N(7)-H(41) | 1.049 |
| N(13)-C(18) | 1.462 | | | C(5)-H(40) | 1.102 |
| C(17)-C(18) | 1.535 | | | C(3)-H(39) | 1.1 |

| | |
|--------------|-------|
| C(16)-C(17) | 1.536 |
| C(15)-C(16) | 1.536 |
| C(14)-C(15) | 1.535 |
| N(13)-C(14) | 1.462 |
| C(4)-C(5) | 1.344 |
| N(6)-C(5) | 1.263 |
| C(1)-N(6) | 1.266 |
| C(2)-C(1) | 1.351 |
| C(3)-C(2) | 1.347 |
| C(4)-C(3) | 1.346 |
| C(10)-N(9) | 1.266 |
| N(8)-N(9) | 1.234 |
| C(12)-N(8) | 1.27 |
| C(11)-C(12) | 1.343 |
| C(10)-C(11) | 1.345 |
| C(2)-O(19) | 1.376 |
| C(20)-C(22) | 1.542 |
| C(23)-Cl(30) | 1.74 |
| C(27)-Cl(29) | 1.732 |
| C(24)-F(28) | 1.326 |
| O(19)-C(20) | 1.415 |
| C(20)-C(21) | 1.532 |
| C(4)-C(11) | 1.347 |
| N(8)-C(16) | 1.482 |
| C(1)-N(7) | 1.269 |

| | |
|--------------|-------|
| N(31)-C(35) | 1.38 |
| C(34)-C(35) | 1.518 |
| C(33)-C(34) | 1.544 |
| C(32)-C(33) | 1.518 |
| N(31)-C(32) | 1.379 |
| C(22)-C(27) | 1.354 |
| C(26)-C(27) | 1.344 |
| C(25)-C(26) | 1.338 |
| C(24)-C(25) | 1.338 |
| C(23)-C(24) | 1.348 |
| C(22)-C(23) | 1.357 |
| N(13)-C(18) | 1.462 |
| C(17)-C(18) | 1.535 |
| C(16)-C(17) | 1.537 |
| C(15)-C(16) | 1.537 |
| C(14)-C(15) | 1.535 |
| N(13)-C(14) | 1.462 |
| C(4)-C(5) | 1.344 |
| N(6)-C(5) | 1.264 |
| C(1)-N(6) | 1.267 |
| C(2)-C(1) | 1.35 |
| C(3)-C(2) | 1.347 |
| C(4)-C(3) | 1.344 |
| C(10)-N(9) | 1.266 |
| N(8)-N(9) | 1.234 |
| C(12)-N(8) | 1.27 |
| C(11)-C(12) | 1.343 |
| C(10)-C(11) | 1.345 |
| N(31)-Br(38) | 1.817 |
| C(35)-O(37) | 1.212 |
| C(32)-O(36) | 1.210 |
| C(2)-O(19) | 1.374 |
| C(20)-C(22) | 1.539 |
| C(23)-Cl(30) | 1.738 |
| C(27)-Cl(29) | 1.729 |
| C(24)-F(28) | 1.326 |
| O(19)-C(20) | 1.414 |
| C(20)-C(21) | 1.532 |
| C(4)-C(11) | 1.346 |
| N(8)-C(16) | 1.482 |
| C(1)-N(7) | 1.269 |

Pertaining to bond lengths, one can observe from **Table 4**, the bond length of NBS increased slightly to **1.212 Å** upon complexation with CZT, relative to **1.209 Å** for free NBS. This finding can be interpreted based on the π -electron transfer from the HOMO of CZT to the LUMO of NBS. This transfer led to the expansion of bond lengths because of the increase of electron density of NBS in the CZT- NBS CT complex compared to NBS alone. Logically the decrease of electron density on CZT (donor) moiety of the complex led to the contraction of bond lengths compared to donor alone (**Table 4**), particularly N(13)-H(37) value decreased from **1.051 Å** to **1.047 Å**, concerning other bonds no significant change was observed, these small changes in the bond length values could not reveal much information about the CT process from CZT to NBS, hence further computations were made to evaluate other parameters to support the CT process.

Table 5 Bond angles of CZT and CZT-NBS CT complex

| CZT | | NBS | | CZT-NBS | |
|--------------------|------------|--------------------|------------|---------------------|------------|
| Atoms | Bond angle | Atoms | Bond angle | Atoms | Bond angle |
| C(22)-C(27)-C(26) | 121.621 | lp(16)-O(7)-lp(15) | 124.445 | lp(73)-O(37)-lp(72) | 124.544 |
| C(22)-C(27)-Cl(29) | 125.246 | lp(16)-O(7)-C(5) | 117.844 | lp(73)-O(37)-C(35) | 117.769 |
| C(26)-C(27)-Cl(29) | 113.134 | lp(15)-O(7)-C(5) | 117.71 | lp(72)-O(37)-C(35) | 117.687 |
| H(52)-C(26)-C(27) | 121.501 | lp(14)-O(6)-lp(13) | 124.444 | lp(71)-O(36)-lp(70) | 123.749 |
| H(52)-C(26)-C(25) | 117.592 | lp(14)-O(6)-C(2) | 117.846 | lp(71)-O(36)-C(32) | 118.189 |
| C(27)-C(26)-C(25) | 120.906 | lp(13)-O(6)-C(2) | 117.71 | lp(70)-O(36)-C(32) | 118.01 |
| H(51)-C(25)-C(26) | 120.439 | N(1)-C(5)-C(4) | 110.591 | N(31)-C(35)-C(34) | 110.492 |
| H(51)-C(25)-C(24) | 120.377 | N(1)-C(5)-O(7) | 124.944 | N(31)-C(35)-O(37) | 124.894 |
| C(26)-C(25)-C(24) | 119.178 | C(4)-C(5)-O(7) | 124.466 | C(34)-C(35)-O(37) | 124.614 |
| C(25)-C(24)-C(23) | 119.735 | H(12)-C(4)-H(11) | 109.706 | H(64)-C(34)-H(63) | 109.818 |
| C(25)-C(24)-F(28) | 118.3 | H(12)-C(4)-C(5) | 109.677 | H(64)-C(34)-C(35) | 108.734 |
| C(23)-C(24)-F(28) | 121.965 | H(12)-C(4)-C(3) | 111.92 | H(64)-C(34)-C(33) | 111.395 |
| C(24)-C(23)-C(22) | 122.511 | H(11)-C(4)-C(5) | 109.593 | H(63)-C(34)-C(35) | 110.651 |
| C(24)-C(23)-Cl(30) | 115.204 | H(11)-C(4)-C(3) | 111.872 | H(63)-C(34)-C(33) | 112.309 |
| C(22)-C(23)-Cl(30) | 122.282 | C(5)-C(4)-C(3) | 103.914 | C(35)-C(34)-C(33) | 103.748 |
| C(27)-C(22)-C(23) | 116.013 | H(10)-C(3)-H(9) | 109.706 | H(62)-C(33)-H(61) | 109.704 |
| C(27)-C(22)-C(20) | 124.953 | H(10)-C(3)-C(4) | 111.911 | H(62)-C(33)-C(34) | 111.608 |
| C(23)-C(22)-C(20) | 119.02 | H(10)-C(3)-C(2) | 109.673 | H(62)-C(33)-C(32) | 108.796 |

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|---------------------|---------|-----------------|---------|---------------------|---------|
| H(50)-C(21)-H(49) | 104.913 | H(9)-C(3)-C(4) | 111.88 | H(61)-C(33)-C(34) | 112.313 |
| H(50)-C(21)-H(48) | 109.915 | H(9)-C(3)-C(2) | 109.597 | H(61)-C(33)-C(32) | 110.571 |
| H(50)-C(21)-C(20) | 113.517 | C(4)-C(3)-C(2) | 103.914 | C(34)-C(33)-C(32) | 103.668 |
| H(49)-C(21)-H(48) | 105.226 | C(3)-C(2)-N(1) | 110.591 | C(33)-C(32)-N(31) | 110.598 |
| H(49)-C(21)-C(20) | 110.506 | C(3)-C(2)-O(6) | 124.467 | C(33)-C(32)-O(36) | 124.498 |
| H(48)-C(21)-C(20) | 112.197 | N(1)-C(2)-O(6) | 124.942 | N(31)-C(32)-O(36) | 124.897 |
| H(47)-C(20)-C(22) | 102.312 | C(5)-N(1)-C(2) | 110.989 | C(35)-N(31)-C(32) | 110.861 |
| H(47)-C(20)-O(19) | 104.288 | C(5)-N(1)-Br(8) | 124.505 | C(35)-N(31)-Br(38) | 124.744 |
| H(47)-C(20)-C(21) | 101.034 | C(2)-N(1)-Br(8) | 124.506 | C(32)-N(31)-Br(38) | 124.381 |
| C(22)-C(20)-O(19) | 114.176 | | | C(22)-C(27)-C(26) | 121.636 |
| C(22)-C(20)-C(21) | 123.59 | | | C(22)-C(27)-Cl(29) | 124.133 |
| O(19)-C(20)-C(21) | 108.469 | | | C(26)-C(27)-Cl(29) | 114.22 |
| Lp(57)-O(19)-Lp(56) | 128.163 | | | H(60)-C(26)-C(27) | 121.385 |
| Lp(57)-O(19)-C(2) | 100.198 | | | H(60)-C(26)-C(25) | 117.95 |
| Lp(57)-O(19)-C(20) | 103.259 | | | C(27)-C(26)-C(25) | 120.664 |
| Lp(56)-O(19)-C(2) | 100.962 | | | H(59)-C(25)-C(26) | 120.328 |
| Lp(56)-O(19)-C(20) | 104.16 | | | H(59)-C(25)-C(24) | 120.307 |
| C(2)-O(19)-C(20) | 122.32 | | | C(26)-C(25)-C(24) | 119.362 |
| H(46)-C(18)-H(45) | 106.98 | | | C(25)-C(24)-C(23) | 119.721 |
| H(46)-C(18)-N(13) | 109.342 | | | C(25)-C(24)-F(28) | 118.467 |
| H(46)-C(18)-C(17) | 110.099 | | | C(23)-C(24)-F(28) | 121.809 |
| H(45)-C(18)-N(13) | 108.962 | | | C(24)-C(23)-C(22) | 122.261 |
| H(45)-C(18)-C(17) | 110.019 | | | C(24)-C(23)-Cl(30) | 115.962 |
| N(13)-C(18)-C(17) | 111.331 | | | C(22)-C(23)-Cl(30) | 121.775 |
| H(44)-C(17)-H(43) | 107.363 | | | C(27)-C(22)-C(23) | 116.352 |
| H(44)-C(17)-C(18) | 110.131 | | | C(27)-C(22)-C(20) | 124.134 |
| H(44)-C(17)-C(16) | 109.942 | | | C(23)-C(22)-C(20) | 119.501 |
| H(43)-C(17)-C(18) | 109.009 | | | H(58)-C(21)-H(57) | 104.599 |
| H(43)-C(17)-C(16) | 109.746 | | | H(58)-C(21)-H(56) | 108.695 |
| C(18)-C(17)-C(16) | 110.586 | | | H(58)-C(21)-C(20) | 114.177 |
| H(42)-C(16)-C(17) | 107.655 | | | H(57)-C(21)-H(56) | 106.552 |
| H(42)-C(16)-C(15) | 107.794 | | | H(57)-C(21)-C(20) | 110.944 |
| H(42)-C(16)-N(8) | 109.726 | | | H(56)-C(21)-C(20) | 111.396 |
| C(17)-C(16)-C(15) | 109.5 | | | H(55)-C(20)-C(22) | 106.379 |
| C(17)-C(16)-N(8) | 111.14 | | | H(55)-C(20)-O(19) | 104.817 |
| C(15)-C(16)-N(8) | 110.911 | | | H(55)-C(20)-C(21) | 99.88 |
| H(41)-C(15)-H(40) | 107.358 | | | C(22)-C(20)-O(19) | 112.047 |
| H(41)-C(15)-C(16) | 109.947 | | | C(22)-C(20)-C(21) | 120.29 |
| H(41)-C(15)-C(14) | 110.115 | | | O(19)-C(20)-C(21) | 111.353 |
| H(40)-C(15)-C(16) | 109.673 | | | Lp(69)-O(19)-Lp(68) | 127.942 |
| H(40)-C(15)-C(14) | 109.07 | | | Lp(69)-O(19)-C(2) | 101.901 |
| C(16)-C(15)-C(14) | 110.613 | | | Lp(69)-O(19)-C(20) | 104.091 |
| H(39)-C(14)-H(38) | 106.983 | | | Lp(68)-O(19)-C(2) | 103.447 |

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|--------------------|---------|
| H(39)-C(14)-C(15) | 110.078 |
| H(39)-C(14)-N(13) | 109.339 |
| H(38)-C(14)-C(15) | 110.014 |
| H(38)-C(14)-N(13) | 108.956 |
| C(15)-C(14)-N(13) | 111.363 |
| Lp(55)-N(13)-H(37) | 107.073 |
| Lp(55)-N(13)-C(18) | 109.359 |
| Lp(55)-N(13)-C(14) | 109.346 |
| H(37)-N(13)-C(18) | 108.889 |
| H(37)-N(13)-C(14) | 108.905 |
| C(18)-N(13)-C(14) | 113.089 |
| H(36)-C(12)-N(8) | 122.958 |
| H(36)-C(12)-C(11) | 130.305 |
| N(8)-C(12)-C(11) | 106.737 |
| C(12)-C(11)-C(10) | 102.027 |
| C(12)-C(11)-C(4) | 128.748 |
| C(10)-C(11)-C(4) | 129.224 |
| H(35)-C(10)-N(9) | 120.297 |
| H(35)-C(10)-C(11) | 127.958 |
| N(9)-C(10)-C(11) | 111.745 |
| Lp(54)-N(9)-C(10) | 126.86 |
| Lp(54)-N(9)-N(8) | 127.503 |
| C(10)-N(9)-N(8) | 105.637 |
| N(9)-N(8)-C(12) | 113.853 |
| N(9)-N(8)-C(16) | 126.311 |
| C(12)-N(8)-C(16) | 119.836 |
| H(34)-N(7)-H(33) | 120.122 |
| H(34)-N(7)-C(1) | 119.347 |
| H(33)-N(7)-C(1) | 120.53 |
| Lp(53)-N(6)-C(5) | 120.226 |
| Lp(53)-N(6)-C(1) | 120.151 |
| C(5)-N(6)-C(1) | 119.623 |
| H(32)-C(5)-C(4) | 122.056 |
| H(32)-C(5)-N(6) | 113.479 |
| C(4)-C(5)-N(6) | 124.465 |
| C(5)-C(4)-C(3) | 114.825 |
| C(5)-C(4)-C(11) | 122.46 |
| C(3)-C(4)-C(11) | 122.714 |
| H(31)-C(3)-C(2) | 118.52 |
| H(31)-C(3)-C(4) | 119.192 |
| C(2)-C(3)-C(4) | 122.288 |
| C(1)-C(2)-C(3) | 115.542 |
| C(1)-C(2)-O(19) | 118.563 |

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|--------------------|---------|
| Lp(68)-O(19)-C(20) | 104.761 |
| C(2)-O(19)-C(20) | 115.4 |
| H(54)-C(18)-H(53) | 106.99 |
| H(54)-C(18)-N(13) | 109.393 |
| H(54)-C(18)-C(17) | 110.145 |
| H(53)-C(18)-N(13) | 108.948 |
| H(53)-C(18)-C(17) | 110.046 |
| N(13)-C(18)-C(17) | 111.216 |
| H(52)-C(17)-H(51) | 107.469 |
| H(52)-C(17)-C(18) | 110.011 |
| H(52)-C(17)-C(16) | 110.033 |
| H(51)-C(17)-C(18) | 108.75 |
| H(51)-C(17)-C(16) | 109.839 |
| C(18)-C(17)-C(16) | 110.673 |
| H(50)-C(16)-C(17) | 107.187 |
| H(50)-C(16)-C(15) | 108.9 |
| H(50)-C(16)-N(8) | 108.141 |
| C(17)-C(16)-C(15) | 109.17 |
| C(17)-C(16)-N(8) | 112.437 |
| C(15)-C(16)-N(8) | 110.877 |
| H(49)-C(15)-H(48) | 107.27 |
| H(49)-C(15)-C(16) | 110.331 |
| H(49)-C(15)-C(14) | 109.669 |
| H(48)-C(15)-C(16) | 109.278 |
| H(48)-C(15)-C(14) | 109.442 |
| C(16)-C(15)-C(14) | 110.778 |
| H(47)-C(14)-H(46) | 106.994 |
| H(47)-C(14)-C(15) | 109.998 |
| H(47)-C(14)-N(13) | 109.297 |
| H(46)-C(14)-C(15) | 110.017 |
| H(46)-C(14)-N(13) | 108.946 |
| C(15)-C(14)-N(13) | 111.476 |
| Lp(67)-N(13)-H(45) | 107.099 |
| Lp(67)-N(13)-C(18) | 109.38 |
| Lp(67)-N(13)-C(14) | 109.351 |
| H(45)-N(13)-C(18) | 108.907 |
| H(45)-N(13)-C(14) | 108.917 |
| C(18)-N(13)-C(14) | 113.012 |
| H(44)-C(12)-N(8) | 122.745 |
| H(44)-C(12)-C(11) | 130.655 |
| N(8)-C(12)-C(11) | 106.599 |
| C(12)-C(11)-C(10) | 102.192 |
| C(12)-C(11)-C(4) | 128.505 |

| | |
|-----------------|---------|
| C(3)-C(2)-O(19) | 125.858 |
| N(6)-C(1)-C(2) | 123.254 |
| N(6)-C(1)-N(7) | 120.323 |
| C(2)-C(1)-N(7) | 116.423 |

| | |
|-------------------|---------|
| C(10)-C(11)-C(4) | 129.3 |
| H(43)-C(10)-N(9) | 120.542 |
| H(43)-C(10)-C(11) | 127.829 |
| N(9)-C(10)-C(11) | 111.629 |
| Lp(66)-N(9)-C(10) | 126.792 |
| Lp(66)-N(9)-N(8) | 127.539 |
| C(10)-N(9)-N(8) | 105.669 |
| N(9)-N(8)-C(12) | 113.91 |
| N(9)-N(8)-C(16) | 127.312 |
| C(12)-N(8)-C(16) | 118.777 |
| H(42)-N(7)-H(41) | 119.611 |
| H(42)-N(7)-C(1) | 120.208 |
| H(41)-N(7)-C(1) | 120.179 |
| Lp(65)-N(6)-C(5) | 120.068 |
| Lp(65)-N(6)-C(1) | 119.922 |
| C(5)-N(6)-C(1) | 120.003 |
| H(40)-C(5)-C(4) | 121.771 |
| H(40)-C(5)-N(6) | 113.705 |
| C(4)-C(5)-N(6) | 124.521 |
| C(5)-C(4)-C(3) | 114.527 |
| C(5)-C(4)-C(11) | 123.26 |
| C(3)-C(4)-C(11) | 122.21 |
| H(39)-C(3)-C(2) | 117.267 |
| H(39)-C(3)-C(4) | 120.49 |
| C(2)-C(3)-C(4) | 122.243 |
| C(1)-C(2)-C(3) | 115.957 |
| C(1)-C(2)-O(19) | 122.688 |
| C(3)-C(2)-O(19) | 120.531 |
| N(6)-C(1)-C(2) | 122.464 |
| N(6)-C(1)-N(7) | 120.041 |
| C(2)-C(1)-N(7) | 117.488 |

The CZT- DBQ CT complex is further confirmed from the changes in its bond angle values compared to the reactant alone. One can observe from **Table-5**, the bond angle values of the atoms involving in the CT decreased relative to free CZT. It seems the lowered electron density of CZT (**Table 6**) due to CT process led to the retrenchment of bond angle values.

Table 6: Electron density values of CZT, NBS and CZT-NBS CT complex

| CZT | | | NBS | | | CZT-NBS | | |
|--------|------------|-----------|-------|------------|-----------|---------|------------|-----------|
| Atom | Atom Type | E D (A.U) | Atom | Type | E D (A.U) | Atom | Atom Type | E D (A.U) |
| Atom | Atom Type | 93.9881 | C(1) | C Carbonyl | 94.023 | C(1) | C Alkane | 93.9794 |
| C(1) | C Alkane | 94.1444 | O(2) | O Carbonyl | 233.871 | C(2) | C Alkane | 94.0778 |
| C(2) | C Alkane | 233.57 | C(3) | C Alkane | 94.1422 | O(3) | O Enol | 233.589 |
| O(3) | O Enol | 94.0297 | C(4) | C Alkane | 94.1049 | C(4) | C Alkene | 94.0346 |
| C(4) | C Alkene | 94.0934 | C(5) | C Carbonyl | 94.051 | C(5) | C Alkene | 94.1087 |
| C(5) | C Alkene | 94.0584 | O(6) | O Carbonyl | 233.857 | C(6) | C Alkene | 94.1235 |
| C(6) | C Alkene | 93.9729 | N(7) | N Amide | 153.487 | C(7) | C Alkene | 93.977 |
| C(7) | C Alkene | 153.818 | Br(8) | Br | 22231.6 | N(8) | N Pyridine | 153.821 |
| N(8) | N Pyridine | 94.0232 | H(9) | H | 0.396347 | C(9) | C Alkene | 94.0385 |
| C(9) | C Alkene | 153.203 | H(10) | H | 0.363816 | N(10) | N Enamine | 153.135 |
| N(10) | N Enamine | 94.1485 | H(11) | H | 0.357475 | C(11) | C Alkene | 94.1425 |
| C(11) | C Alkene | 93.9888 | H(12) | H | 0.353898 | C(12) | C Alkene | 93.9713 |
| C(12) | C Alkene | 153.427 | | | | N(13) | N Pyrrole | 153.474 |
| N(13) | N Pyrrole | 153.826 | | | | N(14) | N Imine | 153.911 |
| N(14) | N Imine | 94.0064 | | | | C(15) | C Alkene | 93.9875 |
| C(15) | C Alkene | 94.112 | | | | C(16) | C Alkane | 94.1332 |
| C(16) | C Alkane | 94.0983 | | | | C(17) | C Alkane | 94.0964 |
| C(17) | C Alkane | 94.0225 | | | | C(18) | C Alkane | 94.0359 |
| C(18) | C Alkane | 153.387 | | | | N(19) | N Amine | 153.37 |
| N(19) | N Amine | 94.0393 | | | | C(20) | C Alkane | 94.039 |
| C(20) | C Alkane | 94.0771 | | | | C(21) | C Alkane | 94.09 |
| C(21) | C Alkane | 94.1358 | | | | C(22) | C Alkene | 94.0983 |
| C(22) | C Alkene | 94.0823 | | | | C(23) | C Alkene | 94.1179 |
| C(23) | C Alkene | 2405.25 | | | | Cl(24) | Cl | 2405.19 |
| Cl(24) | Cl | 94.0843 | | | | C(25) | C Alkene | 94.0863 |
| C(25) | C Alkene | 94.035 | | | | C(26) | C Alkene | 94.0665 |
| C(26) | C Alkene | 94.0128 | | | | C(27) | C Alkene | 93.9879 |
| C(27) | C Alkene | 337.567 | | | | F(28) | F | 337.572 |
| F(28) | F | 94.0982 | | | | C(29) | C Alkene | 94.0973 |
| C(29) | C Alkene | 2405.19 | | | | Cl(30) | Cl | 2405.19 |
| Cl(30) | Cl | 0.333416 | | | | C(31) | C Carbonyl | 94.0201 |
| H(31) | H | 0.329703 | | | | O(32) | O Carbonyl | 233.858 |
| H(32) | H | 0.360851 | | | | C(33) | C Alkane | 94.1167 |
| H(33) | H | 0.401103 | | | | C(34) | C Alkane | 94.1142 |
| H(34) | H | 0.371579 | | | | C(35) | C Carbonyl | 94.0347 |
| H(35) | H | 0.379245 | | | | O(36) | O Carbonyl | 233.872 |
| H(36) | H | 0.373743 | | | | N(37) | N Amide | 153.488 |
| H(37) | H Amine | 0.334708 | | | | Br(38) | Br | 22231.5 |

| | | |
|-------|---------|----------|
| H(38) | H Amine | 0.37024 |
| H(39) | H | 0.365479 |
| H(40) | H | 0.363519 |
| H(41) | H | 0.376807 |
| H(42) | H | 0.347279 |
| H(43) | H | 0.367804 |
| H(44) | H | 0.362172 |
| H(45) | H | 0.339834 |
| H(46) | H Amine | 0.364857 |
| H(47) | H | 0.380356 |
| H(48) | H | 0.359412 |
| H(49) | H | 0.345856 |
| H(50) | H | 0.346597 |
| H(51) | H | 0.367624 |

| | | |
|-------|---------|----------|
| H(39) | H | 0.364745 |
| H(40) | H | 0.350905 |
| H(41) | H | 0.343693 |
| H(42) | H | 0.352618 |
| H(43) | H | 0.371581 |
| H(44) | H | 0.368941 |
| H(45) | H Amine | 0.347356 |
| H(46) | H Amine | 0.349279 |
| H(47) | H | 0.371241 |
| H(48) | H | 0.3602 |
| H(49) | H | 0.36285 |
| H(50) | H | 0.35587 |
| H(51) | H | 0.350141 |
| H(52) | H | 0.364627 |
| H(53) | H | 0.373181 |
| H(54) | H Amine | 0.346801 |
| H(55) | H | 0.361764 |
| H(56) | H | 0.377712 |
| H(57) | H | 0.359775 |
| H(58) | H | 0.347845 |
| H(59) | H | 0.355523 |
| H(60) | H | 0.37502 |
| H(61) | H | 0.350839 |
| H(62) | H | 0.363584 |
| H(63) | H | 0.358498 |
| H(64) | H | 0.344578 |

i.(b) Atomic charges

To add more support for the formed CZT- NBS CT complex, Mulliken atomic charges were computed and the results are compiled in **Table 7**, where one can observe the increase in charge on the atoms of acceptor (NBS) from **0.866498** to **0.923633** (C Carbonyl) and from **-0.57226** to **-0.60557** (O Carbonyl), indicating the charge transfer process. Concerning the donor CZT, the decrease of effective atomic charges of its atoms than the free donor molecule (CZT) support the charge transfer from CZT to NBS. Huckel and Lowdin atomic charges were also computed, in order to support Mulliken charges and are tabulated in the **Table 8-9**, which are in good agreement with Mulliken charges.

Table 7 Mulliken charges (MC) of CZT, NBS and CZT-NBS CT complex

| CZT | | | NBS | | | CZT-NBS | | |
|--------|------------|----------|-------|------------|----------|---------|------------|----------|
| Atom | Atom Type | MC | Atom | Type | MC | Atom | Atom Type | MC |
| Atom | Atom Type | -0.62412 | C(1) | C Carbonyl | 0.866498 | C(1) | C Alkane | -0.59684 |
| C(1) | C Alkane | 0.081177 | O(2) | O Carbonyl | -0.57226 | C(2) | C Alkane | 0.049456 |
| C(2) | C Alkane | -0.72873 | C(3) | C Alkane | -0.53304 | O(3) | O Enol | -0.71407 |
| O(3) | O Enol | 0.262181 | C(4) | C Alkane | -0.53101 | C(4) | C Alkene | 0.26726 |
| C(4) | C Alkene | -0.09766 | C(5) | C Carbonyl | 0.904271 | C(5) | C Alkene | -0.09494 |
| C(5) | C Alkene | -0.21982 | O(6) | O Carbonyl | -0.56879 | C(6) | C Alkene | -0.28186 |
| C(6) | C Alkene | 0.169361 | N(7) | N Amide | -1.12173 | C(7) | C Alkene | 0.203498 |
| C(7) | C Alkene | -0.82267 | Br(8) | Br | 0.433654 | N(8) | N Pyridine | -0.84513 |
| N(8) | N Pyridine | 0.884254 | H(9) | H | 0.297918 | C(9) | C Alkene | 0.852504 |
| C(9) | C Alkene | -1.01143 | H(10) | H | 0.287978 | N(10) | N Enamine | -0.97587 |
| N(10) | N Enamine | -0.49424 | H(11) | H | 0.26859 | C(11) | C Alkene | -0.43518 |
| C(11) | C Alkene | 0.323571 | H(12) | H | 0.267934 | C(12) | C Alkene | 0.369489 |
| C(12) | C Alkene | -0.67434 | | | | N(13) | N Pyrrole | -0.6692 |
| N(13) | N Pyrrole | -0.36974 | | | | N(14) | N Imine | -0.36162 |
| N(14) | N Imine | 0.316679 | | | | C(15) | C Alkene | 0.250393 |
| C(15) | C Alkene | 0.047144 | | | | C(16) | C Alkane | 0.025293 |
| C(16) | C Alkane | -0.38746 | | | | C(17) | C Alkane | -0.3926 |
| C(17) | C Alkane | -0.17621 | | | | C(18) | C Alkane | -0.19753 |
| C(18) | C Alkane | -0.699 | | | | N(19) | N Amine | -0.71979 |
| N(19) | N Amine | -0.19772 | | | | C(20) | C Alkane | -0.19514 |
| C(20) | C Alkane | -0.38741 | | | | C(21) | C Alkane | -0.4032 |
| C(21) | C Alkane | 0.00384 | | | | C(22) | C Alkene | -0.00948 |
| C(22) | C Alkene | -0.35951 | | | | C(23) | C Alkene | -0.41181 |
| C(23) | C Alkene | 0.148465 | | | | Cl(24) | Cl | 0.216527 |
| Cl(24) | Cl | -0.16297 | | | | C(25) | C Alkene | -0.15984 |
| C(25) | C Alkene | -0.27646 | | | | C(26) | C Alkene | -0.27615 |
| C(26) | C Alkene | 0.531306 | | | | C(27) | C Alkene | 0.53458 |
| C(27) | C Alkene | -0.39152 | | | | F(28) | F | -0.38907 |
| F(28) | F | -0.4913 | | | | C(29) | C Alkene | -0.44128 |
| C(29) | C Alkene | 0.278546 | | | | Cl(30) | Cl | 0.261697 |
| Cl(30) | Cl | 0.217146 | | | | C(31) | C Carbonyl | 0.923633 |
| H(31) | H | 0.249781 | | | | O(32) | O Carbonyl | -0.60557 |
| H(32) | H | 0.223265 | | | | C(33) | C Alkane | -0.53022 |
| H(33) | H | 0.290091 | | | | C(34) | C Alkane | -0.54207 |
| H(34) | H | 0.257414 | | | | C(35) | C Carbonyl | 0.902349 |
| H(35) | H | 0.241835 | | | | O(36) | O Carbonyl | -0.59386 |
| H(36) | H | 0.366486 | | | | N(37) | N Amide | -1.10976 |
| H(37) | H Amine | 0.373298 | | | | Br(38) | Br | 0.422532 |

| | | |
|-------|---------|----------|
| H(38) | H Amine | 0.266155 |
| H(39) | H | 0.256757 |
| H(40) | H | 0.220163 |
| H(41) | H | 0.217599 |
| H(42) | H | 0.233006 |
| H(43) | H | 0.223419 |
| H(44) | H | 0.150169 |
| H(45) | H | 0.286861 |
| H(46) | H Amine | 0.224766 |
| H(47) | H | 0.177379 |
| H(48) | H | 0.25748 |
| H(49) | H | 0.212001 |
| H(50) | H | 0.287451 |
| H(51) | H | 0.293254 |

| | | |
|-------|---------|----------|
| H(39) | H | 0.216725 |
| H(40) | H | 0.242466 |
| H(41) | H | 0.200585 |
| H(42) | H | 0.266653 |
| H(43) | H | 0.257972 |
| H(44) | H | 0.249071 |
| H(45) | H Amine | 0.371376 |
| H(46) | H Amine | 0.360505 |
| H(47) | H | 0.268946 |
| H(48) | H | 0.247446 |
| H(49) | H | 0.222472 |
| H(50) | H | 0.216653 |
| H(51) | H | 0.245106 |
| H(52) | H | 0.236079 |
| H(53) | H | 0.171143 |
| H(54) | H Amine | 0.311428 |
| H(55) | H | 0.230066 |
| H(56) | H | 0.1787 |
| H(57) | H | 0.245747 |
| H(58) | H | 0.217863 |
| H(59) | H | 0.299665 |
| H(60) | H | 0.288883 |
| H(61) | H | 0.27572 |
| H(62) | H | 0.277724 |
| H(63) | H | 0.276171 |
| H(64) | H | 0.297675 |

Table 8 Huckle charges (HC) of CZT, NBS and CZT-NBS CT complex

| CZT | | | NBS | | | CZT-NBS | | |
|-------|------------|----------|-------|------------|----------|---------|------------|---------|
| Atom | Atom Type | HC | Atom | Type | HC | Atom | Atom Type | HC |
| Atom | Atom Type | 0.247397 | C(1) | C Carbonyl | 0.483148 | C(1) | C Alkane | 0.2475 |
| C(1) | C Alkane | 0.123527 | O(2) | O Carbonyl | 0.43466 | C(2) | C Alkane | 0.11234 |
| C(2) | C Alkane | -0.18345 | C(3) | C Alkane | -0.11145 | O(3) | O Enol | -0.1272 |
| O(3) | O Enol | -0.11855 | C(4) | C Alkane | -0.11145 | C(4) | C Alkene | -0.1198 |
| C(4) | C Alkene | 0.008622 | C(5) | C Carbonyl | 0.434661 | C(5) | C Alkene | 0.05914 |
| C(5) | C Alkene | -0.43383 | O(6) | O Carbonyl | -0.71362 | C(6) | C Alkene | -0.3411 |
| C(6) | C Alkene | 0.114145 | N(7) | N Amide | -0.71363 | C(7) | C Alkene | 0.06435 |
| C(7) | C Alkene | 0.693456 | Br(8) | Br | 0.096684 | N(8) | N Pyridine | 0.7230 |
| N(8) | N Pyridine | -0.35682 | H(9) | H | 0.050415 | C(9) | C Alkene | -0.3247 |
| C(9) | C Alkene | -0.124 | H(10) | H | 0.050076 | N(10) | N Enamine | -0.1092 |
| N(10) | N Enamine | -0.12293 | H(11) | H | 0.050441 | C(11) | C Alkene | -0.1495 |

| | | | | | | | | |
|--------|-----------|----------|-------|---|----------|--------|------------|---------|
| C(11) | C Alkene | -0.20443 | H(12) | H | 0.050049 | C(12) | C Alkene | -0.1912 |
| C(12) | C Alkene | -0.21373 | | | | N(13) | N Pyrrole | -0.2035 |
| N(13) | N Pyrrole | 0.035663 | | | | N(14) | N Imine | 0.03400 |
| N(14) | N Imine | -0.06406 | | | | C(15) | C Alkene | -0.0630 |
| C(15) | C Alkene | 0.066228 | | | | C(16) | C Alkene | 0.05185 |
| C(16) | C Alkene | -0.06272 | | | | C(17) | C Alkene | -0.0720 |
| C(17) | C Alkene | 0.03435 | | | | C(18) | C Alkene | 0.03388 |
| C(18) | C Alkene | -0.24908 | | | | N(19) | N Amine | 0.2991 |
| N(19) | N Amine | 0.209027 | | | | C(20) | C Alkene | 0.19453 |
| C(20) | C Alkene | -0.49628 | | | | C(21) | C Alkene | -0.1643 |
| C(21) | C Alkene | -0.06557 | | | | C(22) | C Alkene | -0.1189 |
| C(22) | C Alkene | 0.033153 | | | | C(23) | C Alkene | 0.08208 |
| C(23) | C Alkene | 0.257196 | | | | Cl(24) | Cl | 0.26395 |
| Cl(24) | Cl | -0.18377 | | | | C(25) | C Alkene | -0.1252 |
| C(25) | C Alkene | -0.18743 | | | | C(26) | C Alkene | -0.1469 |
| C(26) | C Alkene | 0.068485 | | | | C(27) | C Alkene | 0.11140 |
| C(27) | C Alkene | -0.13404 | | | | F(28) | F | -0.1554 |
| F(28) | F | 0.254072 | | | | C(29) | C Alkene | 0.01907 |
| C(29) | C Alkene | 0.075045 | | | | Cl(30) | Cl | 0.02838 |
| Cl(30) | Cl | 0.089052 | | | | C(31) | C Carbonyl | 0.48184 |
| H(31) | H | 0.007867 | | | | O(32) | O Carbonyl | 0.43645 |
| H(32) | H | 0.092648 | | | | C(33) | C Alkene | -0.1117 |
| H(33) | H | 0.092792 | | | | C(34) | C Alkene | -0.1102 |
| H(34) | H | 0.011955 | | | | C(35) | C Carbonyl | 0.43436 |
| H(35) | H | 0.025054 | | | | O(36) | O Carbonyl | -0.7117 |
| H(36) | H | 0.104409 | | | | N(37) | N Amide | -0.7142 |
| H(37) | H Amine | 0.020679 | | | | Br(38) | Br | 0.09693 |
| H(38) | H Amine | 0.003593 | | | | H(39) | H | 0.02119 |
| H(39) | H | 0.028553 | | | | H(40) | H | -0.006 |
| H(40) | H | 0.027875 | | | | H(41) | H | 0.09071 |
| H(41) | H | 0.017941 | | | | H(42) | H | 0.09288 |
| H(42) | H | 0.0284 | | | | H(43) | H | 0.00202 |
| H(43) | H | 0.027858 | | | | H(44) | H | 0.01382 |
| H(44) | H | 0.020938 | | | | H(45) | H Amine | 0.10073 |
| H(45) | H | 0.003843 | | | | H(46) | H Amine | 0.02002 |
| H(46) | H Amine | 0.019088 | | | | H(47) | H | 0.00215 |
| H(47) | H | 0.17107 | | | | H(48) | H | 0.02878 |
| H(48) | H | 0.041723 | | | | H(49) | H | 0.0269 |
| H(49) | H | 0.092416 | | | | H(50) | H | 0.01865 |
| H(50) | H | 0.028451 | | | | H(51) | H | 0.02916 |
| H(51) | H | 0.024125 | | | | H(52) | H | 0.02674 |
| | | | | | | H(53) | H | 0.01976 |
| | | | | | | H(54) | H Amine | 0.00200 |

| | | |
|-------|---|---------|
| H(55) | H | 0.02266 |
| H(56) | H | 0.04507 |
| H(57) | H | 0.04054 |
| H(58) | H | 0.04548 |
| H(59) | H | 0.02363 |
| H(60) | H | 0.01794 |
| H(61) | H | 0.04624 |
| H(62) | H | 0.05387 |
| H(63) | H | 0.04546 |
| H(64) | H | 0.05399 |

Table 9 Lowdin charges (LC) of CZT, NBS and CZT-NBS CT complex

| CZT | | | NBS | | | CZT-NBS | | |
|--------|------------|----------|-------|------------|----------|---------|------------|----------|
| Atom | Atom Type | LC | Atom | Type | LC | Atom | Atom Type | LC |
| Atom | Atom Type | -0.29229 | C(1) | C Carbonyl | 0.302673 | C(1) | C Alkane | -0.28126 |
| C(1) | C Alkane | 0.150605 | O(2) | O Carbonyl | -0.27399 | C(2) | C Alkane | 0.108804 |
| C(2) | C Alkane | -0.29378 | C(3) | C Alkane | -0.20592 | O(3) | O Enol | -0.27058 |
| O(3) | O Enol | 0.026809 | C(4) | C Alkane | -0.22801 | C(4) | C Alkene | 0.042584 |
| C(4) | C Alkene | -0.06382 | C(5) | C Carbonyl | 0.28763 | C(5) | C Alkene | -0.06194 |
| C(5) | C Alkene | -0.09725 | O(6) | O Carbonyl | -0.24973 | C(6) | C Alkene | -0.10091 |
| C(6) | C Alkene | 0.036719 | N(7) | N Amide | -0.45654 | C(7) | C Alkene | 0.049164 |
| C(7) | C Alkene | -0.27324 | Br(8) | Br | 0.314292 | N(8) | N Pyridine | -0.23122 |
| N(8) | N Pyridine | 0.163607 | H(9) | H | 0.1277 | C(9) | C Alkene | 0.158554 |
| C(9) | C Alkene | -0.34201 | H(10) | H | 0.133571 | N(10) | N Enamine | -0.38584 |
| N(10) | N Enamine | -0.12866 | H(11) | H | 0.123694 | C(11) | C Alkene | -0.12879 |
| C(11) | C Alkene | -0.04784 | H(12) | H | 0.12463 | C(12) | C Alkene | -0.04397 |
| C(12) | C Alkene | -0.04277 | | | | N(13) | N Pyrrole | -0.02393 |
| N(13) | N Pyrrole | -0.08221 | | | | N(14) | N Imine | -0.12726 |
| N(14) | N Imine | -0.0904 | | | | C(15) | C Alkene | -0.07946 |
| C(15) | C Alkene | 0.048946 | | | | C(16) | C Alkane | 0.050102 |
| C(16) | C Alkane | 0.1764 | | | | C(17) | C Alkane | -0.17321 |
| C(17) | C Alkane | -0.04693 | | | | C(18) | C Alkane | -0.05239 |
| C(18) | C Alkane | -0.34043 | | | | N(19) | N Amine | -0.35034 |
| N(19) | N Amine | -0.04716 | | | | C(20) | C Alkane | 0.04849 |
| C(20) | C Alkane | -0.16329 | | | | C(21) | C Alkane | -0.16884 |
| C(21) | C Alkane | -0.04065 | | | | C(22) | C Alkene | -0.06167 |
| C(22) | C Alkene | -0.08527 | | | | C(23) | C Alkene | 0.10608 |
| C(23) | C Alkene | -0.0043 | | | | Cl(24) | Cl | 0.044214 |
| Cl(24) | Cl | -0.07756 | | | | C(25) | C Alkene | -0.08369 |
| C(25) | C Alkene | 0.13647 | | | | C(26) | C Alkene | 0.13923 |
| C(26) | C Alkene | 0.207561 | | | | C(27) | C Alkene | 0.195726 |
| C(27) | C Alkene | -0.16251 | | | | F(28) | F | -0.13221 |

| | | |
|--------|----------|----------|
| F(28) | F | -0.15735 |
| C(29) | C Alkene | 0.088675 |
| Cl(30) | Cl | 0.110501 |
| H(31) | H | 0.123403 |
| H(32) | H | 0.100517 |
| H(33) | H | 0.104204 |
| H(34) | H | 0.104411 |
| H(35) | H | 0.089963 |
| H(36) | H | 0.20748 |
| H(37) | H Amine | 0.234987 |
| H(38) | H Amine | 0.105967 |
| H(39) | H | 0.100885 |
| H(40) | H | 0.081539 |
| H(41) | H | 0.087223 |
| H(42) | H | 0.103661 |
| H(43) | H | 0.088608 |
| H(44) | H | 0.038056 |
| H(45) | H | 0.173205 |
| H(46) | H Amine | 0.090005 |
| H(47) | H | 0.051021 |
| H(48) | H | 0.113247 |
| H(49) | H | 0.094074 |
| H(50) | H | 0.131664 |
| H(51) | H | 0.135055 |

| | | |
|--------|------------|----------|
| C(29) | C Alkene | -0.13529 |
| Cl(30) | Cl | 0.080089 |
| C(31) | C Carbonyl | 0.31681 |
| O(32) | O Carbonyl | -0.31079 |
| C(33) | C Alkane | -0.21437 |
| C(34) | C Alkane | -0.22243 |
| C(35) | C Carbonyl | 0.305823 |
| O(36) | O Carbonyl | -0.29267 |
| N(37) | N Amide | -0.42226 |
| Br(38) | Br | 0.309459 |
| H(39) | H | 0.098634 |
| H(40) | H | 0.108277 |
| H(41) | H | 0.094638 |
| H(42) | H | 0.108878 |
| H(43) | H | 0.104259 |
| H(44) | H | 0.095499 |
| H(45) | H Amine | 0.215702 |
| H(46) | H Amine | 0.219076 |
| H(47) | H | 0.105621 |
| H(48) | H | 0.098 |
| H(49) | H | 0.084693 |
| H(50) | H | 0.092955 |
| H(51) | H | 0.106451 |
| H(52) | H | 0.093605 |
| H(53) | H | 0.048895 |
| H(54) | H Amine | 0.184604 |
| H(55) | H | 0.092854 |
| H(56) | H | 0.051237 |
| H(57) | H | 0.100985 |
| H(58) | H | 0.096648 |
| H(59) | H | 0.134818 |
| H(60) | H | 0.127148 |
| H(61) | H | 0.129417 |
| H(62) | H | 0.126591 |
| H(63) | H | 0.127741 |
| H(64) | H | 0.140543 |

7.2 Electronic properties

The most important orbitals in a molecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps

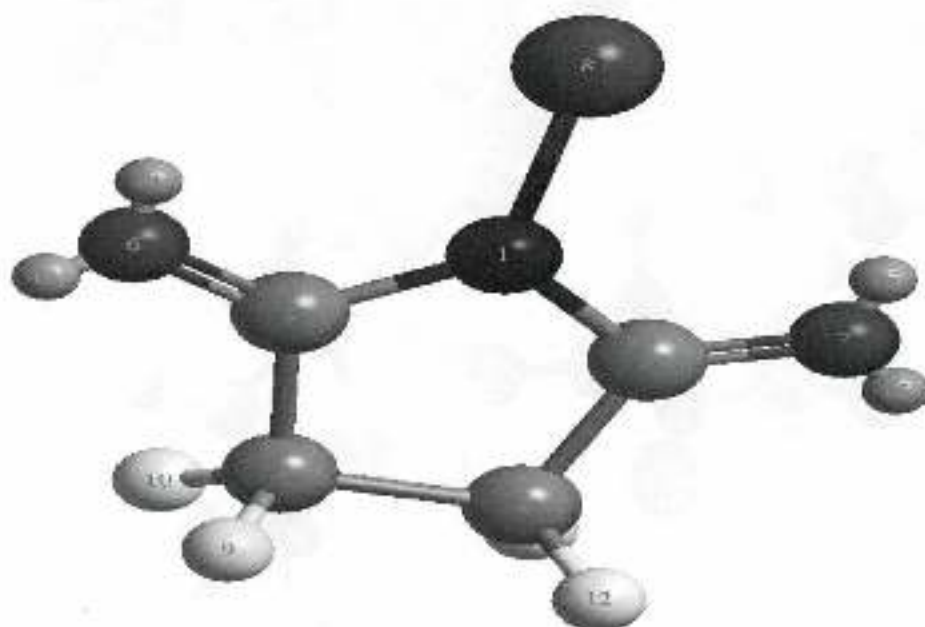
to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule. The lower value for frontier orbital gap in case of CT complexes makes it more reactive and less stable (**Table 10**). The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital acts as the electron acceptor. The 3D plots of the frontier orbitals HOMO, LUMO of CZT CT complex with NBS show that the HOMO is distributed uniformly on the NBS (**Figs.17-22**).

The LUMO in case of CT complex is found to spread over nitrogen moieties. The HOMO and LUMO maps in case of studied CT complex clearly suggests that the potential swings significantly on nitrogen atoms in particular, followed by benzene atoms to some extent, by observing these, one can easily conclude how the introduction of the NBS modifies the properties of the donor molecules, during CT formation between the two species.

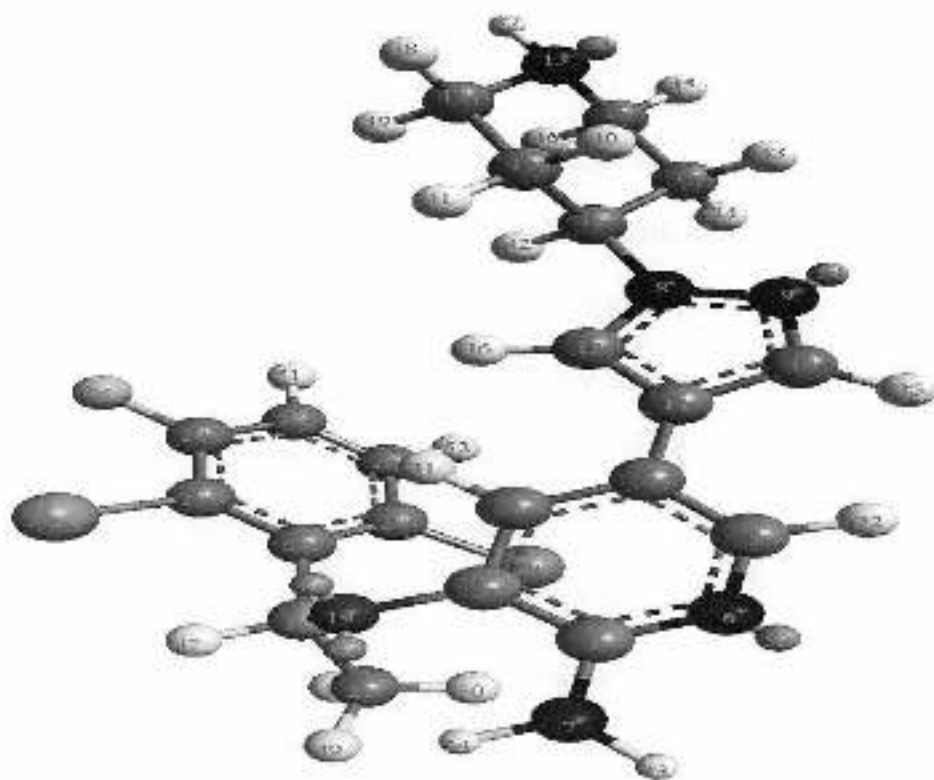
The values of the extreme potentials for HOMO and LUMO maps of all complexes have been taken for the sake of comparison and drawing the conclusions. The electronic properties of the calculated frontier orbital gap, for the complex are in **Table 10**.

i Energy optimised molecular structures

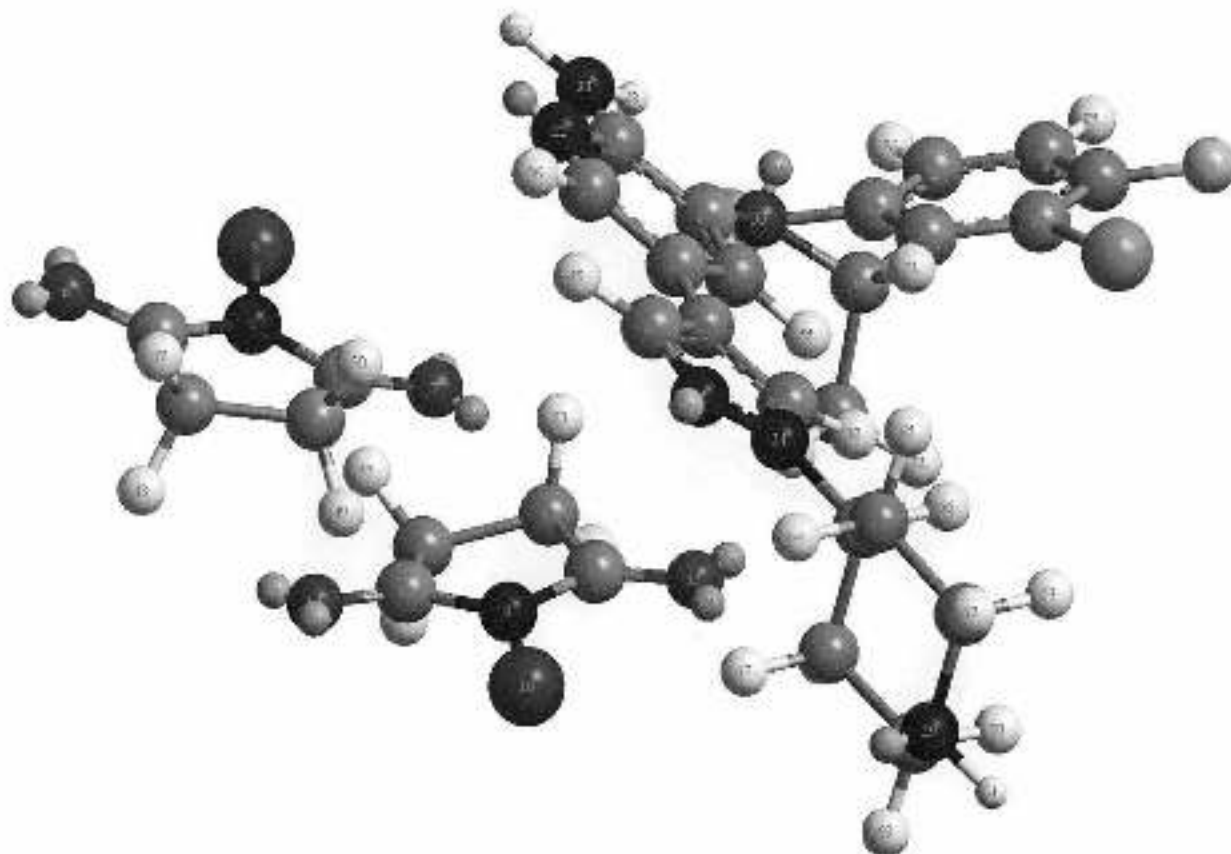
Optimized structure of NBS



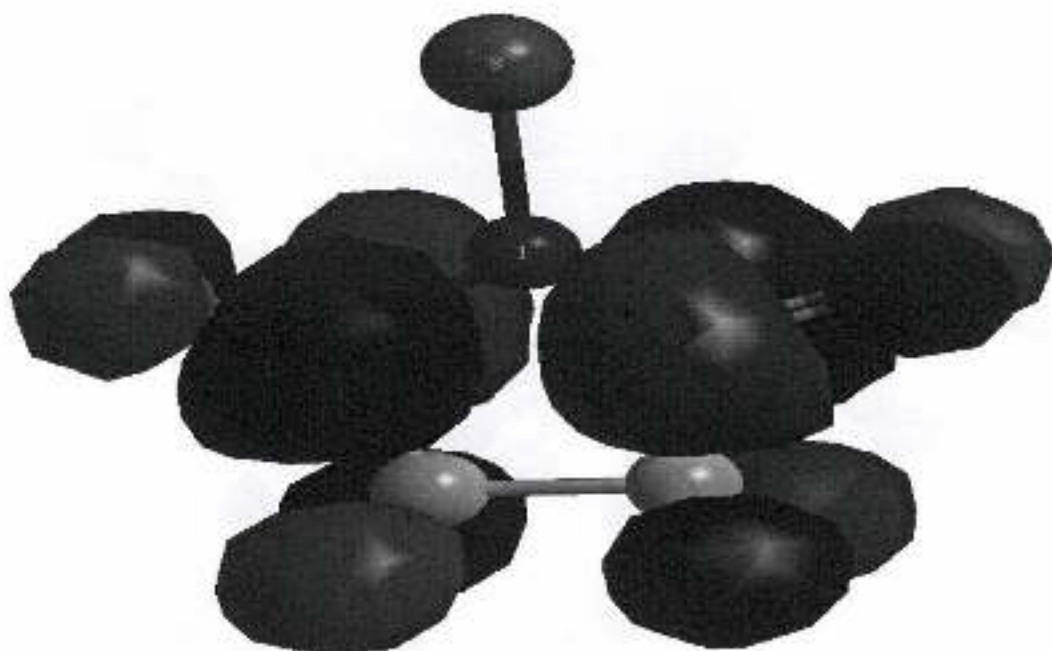
Optimized structure of CZT



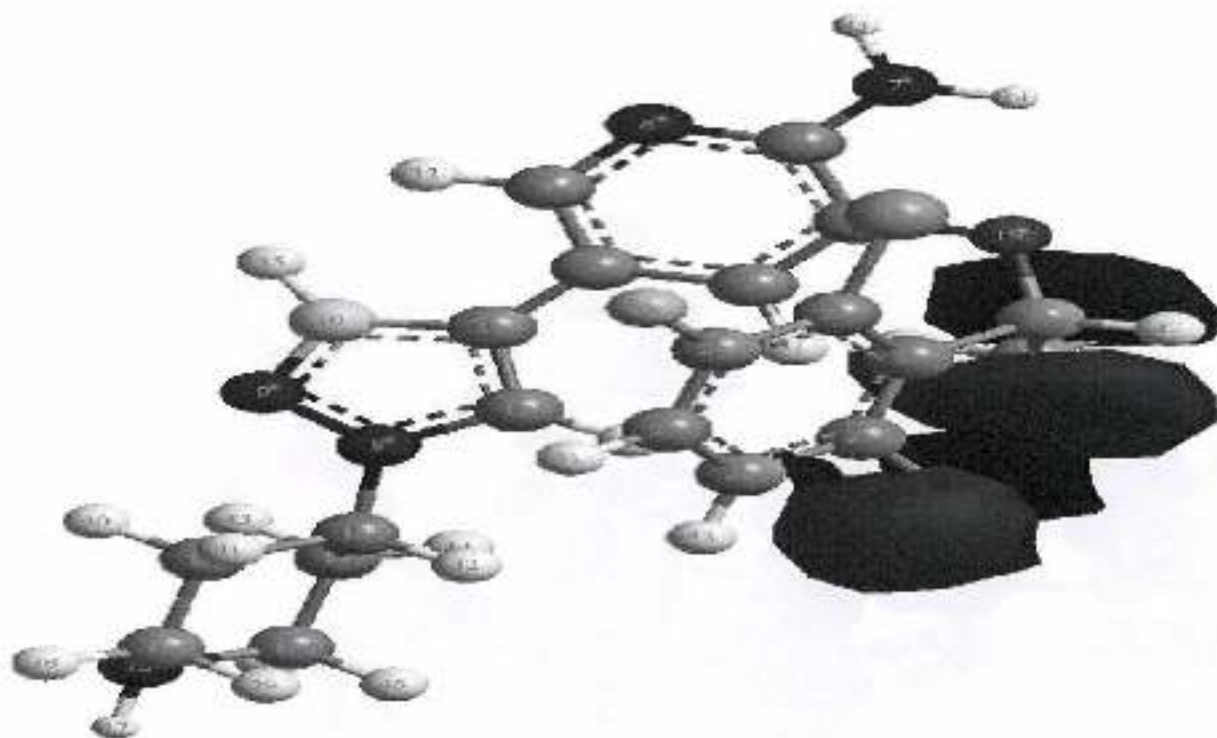
Optimized structure of CZT-NBS CTC



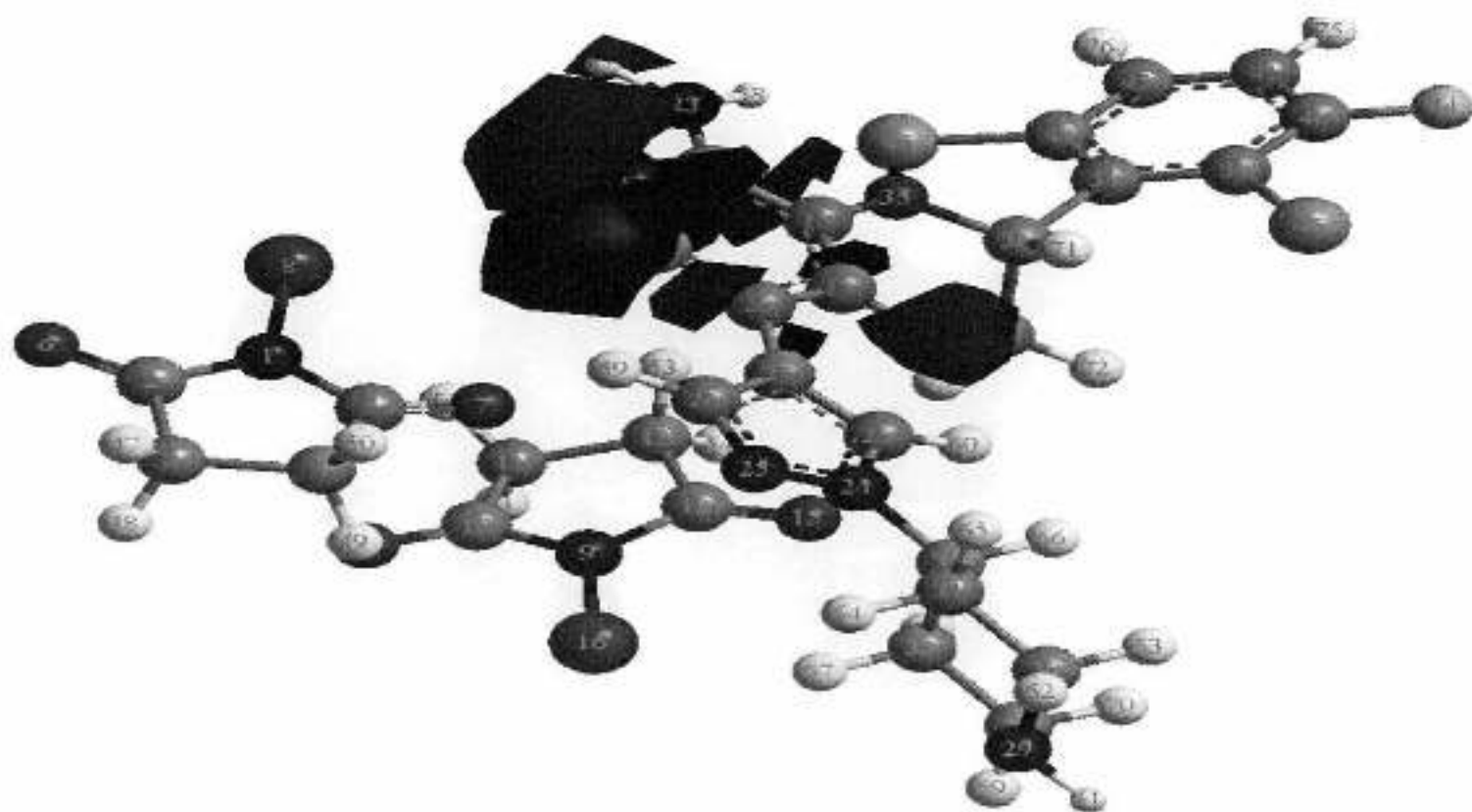
LUMO of NBS



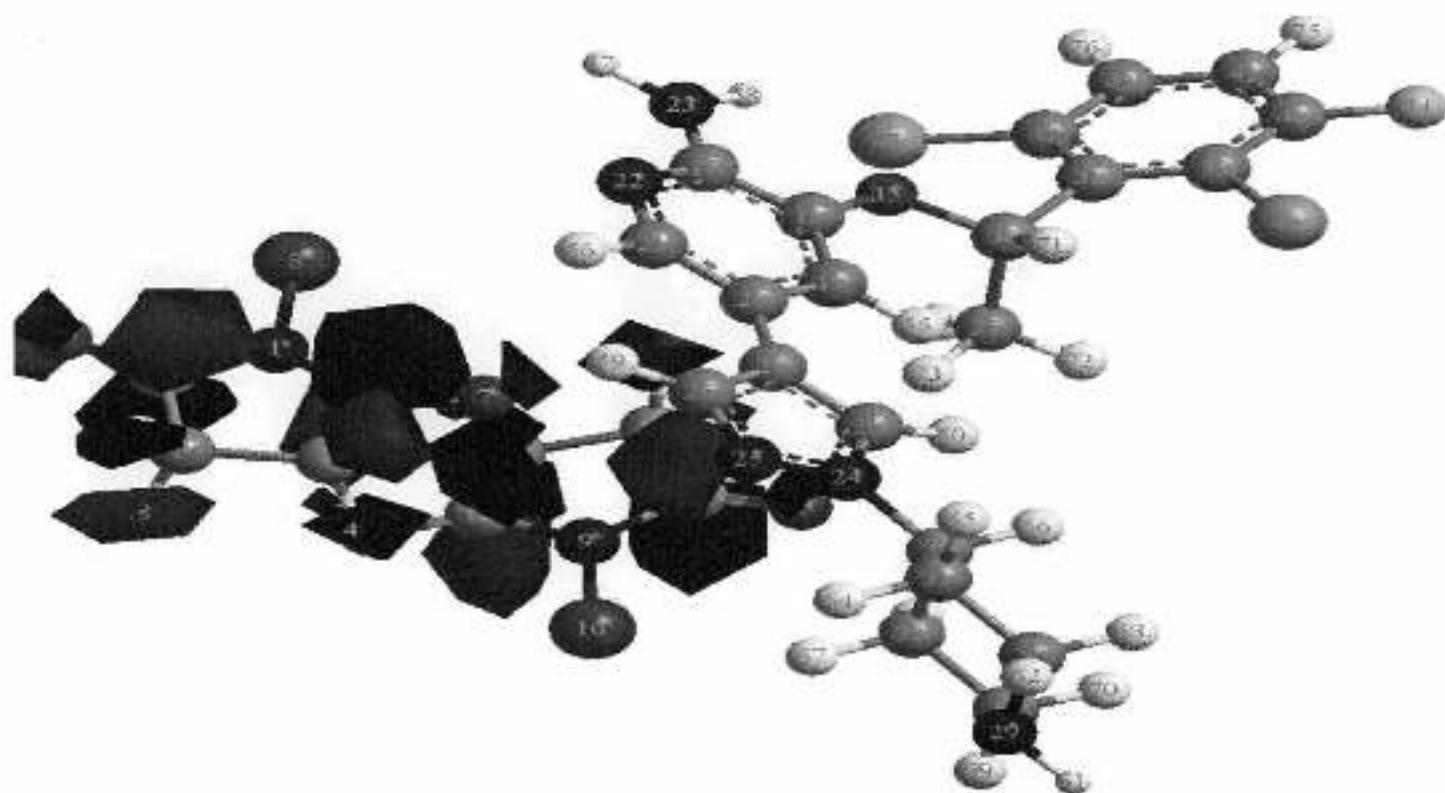
HOMO of CZT



HOMO of CZT-NBS



LUMO of CZT-NBS



7. Conclusion

The CT reaction of CZT as electron donor and NBS as electron acceptor has been studied for the first time. The study includes the use of spectrophotometry in the comprehensive manner. A single solvent DMSO has been used to avoid solvent interactions with CZT (donor) and NBS (acceptor). The FT-IR and $^1\text{H-NMR}$ is used to characterize the formed complex between CZT and NBS. Spectral data acquired from spectral analysis has suggested that CZT acted as an electron donor when interacted with NBS (π - acceptor). Hence, the biological activity of CZT may be due its donating ability as is evident from the association constant (K) and standard Gibbs free energy (ΔG°) values. The spectroscopic parameters like Ionization Potential (IP), Energy of the complex, E_{CT} (eV), and Resonance Energy (R_N) values also support the strong interaction of CZT with NBS. Accordingly, plausible interaction between CZT and NBS has been proposed.

Therefore, the mechanism for the interaction of the studied CZT is useful in understanding the binding of this bioactive molecule under real pharmacokinetic conditions, which enables medical fraternity to pay attention towards the importance of this novel drug, which may potentially contribute to the knowledge in the medicinal field.

**SYNTHESIS, SPECTROPHOTOMETRIC, THERMODYNAMIC AND
SPECTROSCOPIC STUDIES OF CT COMPLEXES OF NOVEL CRIZOTINIB WITH
2,6-DIBROMOQUINONE-4-CHLOROIMIDE AS π -ACCEPTOR**

Abstract : Understanding the charge transfer process between bioactive molecules and inorganic or organic molecules is significant as this interaction can be used to interpret bioactive molecule–receptor interactions. A comprehensive spectrophotometric study has been performed to explore the complexation chemistry of the Crizotinib (CZT) with 2,6-dibromoquinone-4-chloroimide (DBQ) as π - acceptor. The molecular structure, spectroscopic characteristics and the interactive modes have been deduced from UV -Vis, FT-IR and ^1H NMR spectra. The binding ratio of complexation has been determined to be 1:1 for CZT with DBQ. Benesi–Hildebrand method was applied to estimate the spectroscopic and physical data. The association constant (K), extinction coefficient (ϵ_{max}), ionization potential (IP), energy of the charge transfer complex (E_{CT}), resonance energy (R_N), dissociation energy (W) and standard Gibbs energy (ΔG^0) have been computed. Based upon the obtained spectroscopic data, the plausible CT mechanism between CZT and DBQ was proposed.

I. INTRODUCTION

Crizotinib (CZT) is a novel anti-lung cancer drug acting as an ALK (Anaplastic Lymphoma Kinase) & ROS 1 (C- ROS, Oncogene 1) inhibitor; it has been approved by FDA on August 26, 2011, under the trade name of xalkori capsules, made by Pfizer, Inc. for the treatment of patients with locally advanced or metastatic Non-Small Cell Lung Cancer (NSCLC) i.e., ALK positive as detected by an FDA approved test.

CZT is currently used to exert its effects through modulation of the growth; migration and invasion of malignant cells. Furthermore, other studies suggest that CZT might also act via

inhibition of Angiogenesis, in malignant tumours, which is of great interest in order to show how this novel CZT is significant.

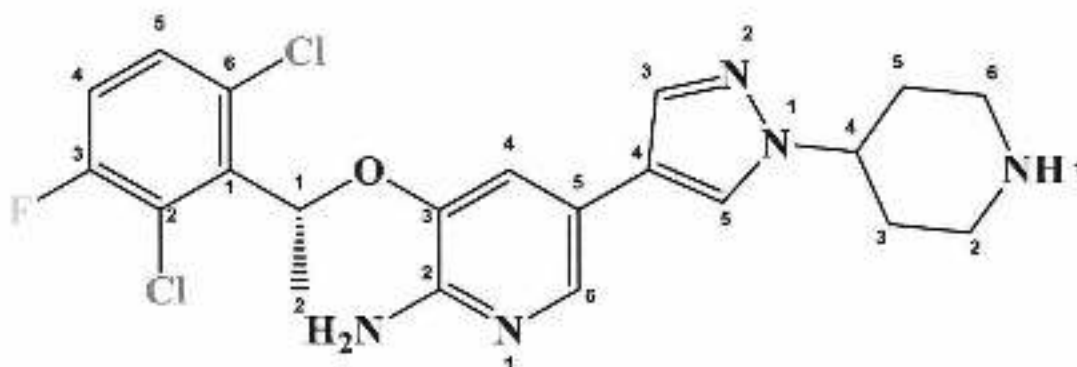
Available literature on this subject reveal that the electron donating properties of CZT & its Charge Transfer (CT) reactions have not been much investigated so far.

These findings about CZT prompted us to investigate the CT reaction of CZT with 2,6-dibromoquinone-4-chloroimide (DBQ) as π - acceptor.

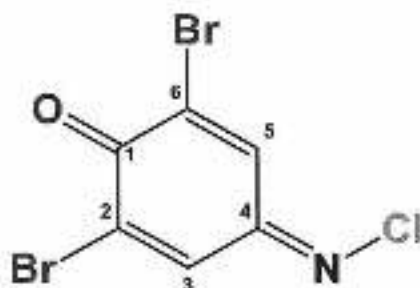
The CT complexes are identified to take part in many chemical reactions like addition, substitution, condensation etc, Electron donor-acceptor CT interaction is also important in the field of drug receptor binding mechanism, as well as in many biological fields. In view of this, CT reactions of certain π - acceptors have been successfully utilized in pharmaceutical analysis. The CT complexes (CTCs) of organic species are strenuously studied because of their special type of interaction which is accompanied by transfer of electron from donor to acceptor. Also, protonation of donor from acidic receptors are generally rout for the formation of the ion pair adducts. The π -acceptors have numerous applications as analytical reagents. They have been used for the spectrophotometric determination of many drugs in pharmaceutical formulations.

Considering all these aspects, it is proposed to investigate the charge transfer complex (CTC) of CZT with DBQ.

Structures of CZT and DBQ



CRIZOTINIB (CZT)



2, 6-dibromoquinone-4-chloroimide (DBQ)

1. Experimental Methodologies

1.1 Chemicals

All the chemicals were used of analytical grade. DBQ (TCI, India, purity > 98%) and Ethanol, (Finar, India, purity > 99.9%) were used without further purification. The CZT was procured from Meruvax pharmaceuticals, Hyderabad. The purity of CZT as specified by the makers

was >99%, which was confirmed by its melting temperature. The CZT was used as received without any further purification.

1.2 Synthesis of CZT–DBQ CT complex

The CZT and DBQ of 1 mmol each (1:1) were accurately weighed on Dhona 160 D analytical balance and transferred them into porcelain mortar and truncated the mixture scrupulously in the presence of a few drops of methylene chloride solvent. Then dried the obtained reaction mixture by continuous suction and transferred them into a dry beaker. The beaker was stored overnight in a desiccator filled with activated anhydrous calcium chloride, then transferred the dried solid brown coloured powder containing CZT–DBQ CTC into a clean vial. The vial was capped well to protect from moist air.

2. Instruments

The electronic absorption spectra of the CZT, DBQ and resulting CTC were recorded over a wavelength range of 200–800 nm using an UV-2600 Shimadzu UV-VIS Spectrophotometer. The instrument was equipped with a quartz cell with a 1.0 cm path length. The FT-IR spectra within the range of 4000–250 cm^{-1} for the solid powder of free CZT and its CT Complex with DBQ were recorded on a Shimadzu FT-IR Prestige-21 spectrophotometer with 40 scans at 4 cm^{-1} resolution. ^1H -NMR spectra were recorded using Bruker Biospin advance-III 400 MHz Fourier Transform Digital NMR Spectrometer with DMSO as solvent, chemical shift values are given in ppm relative to tetramethyl silane.

3. Spectrophotometric Study

3.1 Preparation of Experimental Solutions

Stock solutions of CZT (donor) and DBQ (acceptor) at a concentration of $5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ were freshly prepared before each series of measurement by dissolving accurately weighed amounts

in an appropriate volume of ethanol. The stock solutions of donor and acceptor were protected from light. The solutions for spectrophotometric measurements were freshly prepared by mixing appropriate volumes of donor and acceptor stock solutions immediately before recording the spectra.

3.2 Experimental Measurements

To determine the stoichiometry of the CZT (donor) and DBQ (acceptor) interactions, various molar ratios were examined by applying Job's method of continuous variations and photometric titration measurements. These titrations monitored the detectable CT bands during the reactions of DBQ with donor. Briefly, 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 mL of a standard solution ($5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) of the donor in ethanol solvent was added to 1.00 mL of the acceptor at $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, dissolved in the same solvent. The final volume of the mixture was made to 5 mL. The concentration of the acceptor (C_a^0) was maintained constant at $5.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, while the concentration of the donor (C_d^0) varied from $0.25 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ to $4.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ to produce solutions with a (donor: acceptor) molar ratio that varied from 1:4 to 4:1, for the complex. The absorbance of complex was plotted against the volume of the added acceptor.

3.3 Calculations – Background

The physical spectroscopic data of the resulted CT complexes were computed, the association constant (K) and the molar extinction coefficient (ϵ_{max}) were determined spectrophotometrically using the 1:1 Benesi-Hildebrand equation.

Table 1: Benesi–Hildebrand data of the CZT-DBQ CT complex

| $C_a^0 \times 10^{-4}$ | $C_d^0 \times 10^{-4}$ | Absorbance | $C_a^0 C_d^0 / A \times 10^{-7}$ | $(C_a^0 + C_d^0) \times 10^{-4}$ |
|------------------------|------------------------|------------|----------------------------------|----------------------------------|
| 0.25 | 5 | 0.632 | 0.197 | 5.25 |
| 0.5 | 5 | 0.650 | 0.384 | 5.5 |
| 0.75 | 5 | 0.666 | 0.563 | 5.75 |
| 1.0 | 5 | 0.683 | 0.732 | 6.0 |
| 1.5 | 5 | 0.718 | 1.044 | 6.5 |
| 2.0 | 5 | 0.751 | 1.331 | 7.0 |
| 2.5 | 5 | 0.769 | 1.625 | 7.5 |
| 3.0 | 5 | 0.783 | 1.915 | 8.0 |
| 3.5 | 5 | 0.797 | 2.195 | 8.5 |
| 4.0 | 5 | 0.816 | 2.450 | 9.0 |

Benesi–Hildebrand (1:1) equation

$$(C_a^0 C_d^0) / A = 1/K\varepsilon + (C_a^0 + C_d^0) / \varepsilon$$

Where, C_a^0 and C_d^0 are the initial concentrations of the acceptor and donor, respectively, and A is the absorbance of the CT band. By plotting the $(C_a^0 C_d^0) / A$ values for the 1:1 CT complex as a function of the corresponding $(C_a^0 + C_d^0)$ values, a straight line is obtained with a slope of $1/\varepsilon$ and an intercept at $1/K\varepsilon$.

4. Results and discussion

4.1 UV-Vis spectra

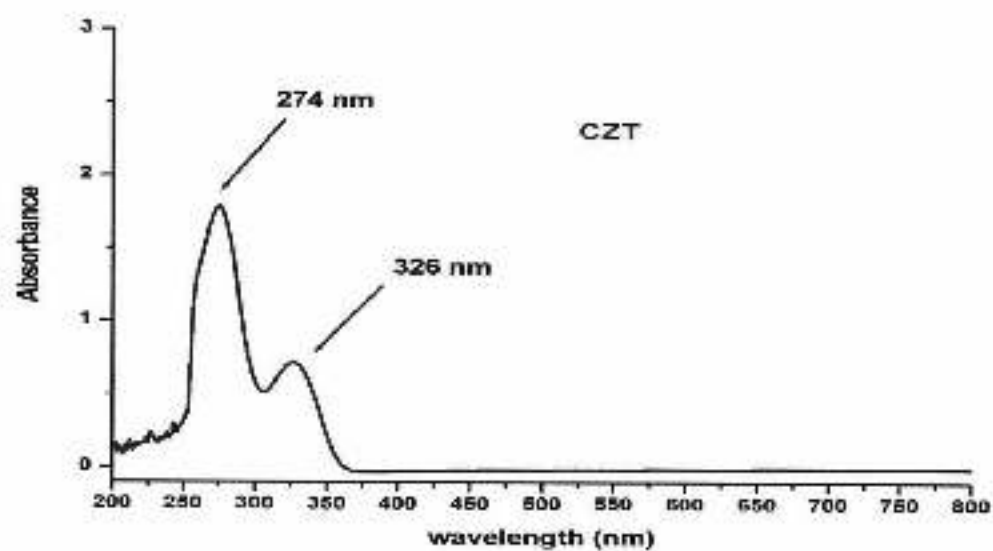


Figure 1. UV-Vis spectra of CZT (5×10^{-3} M)

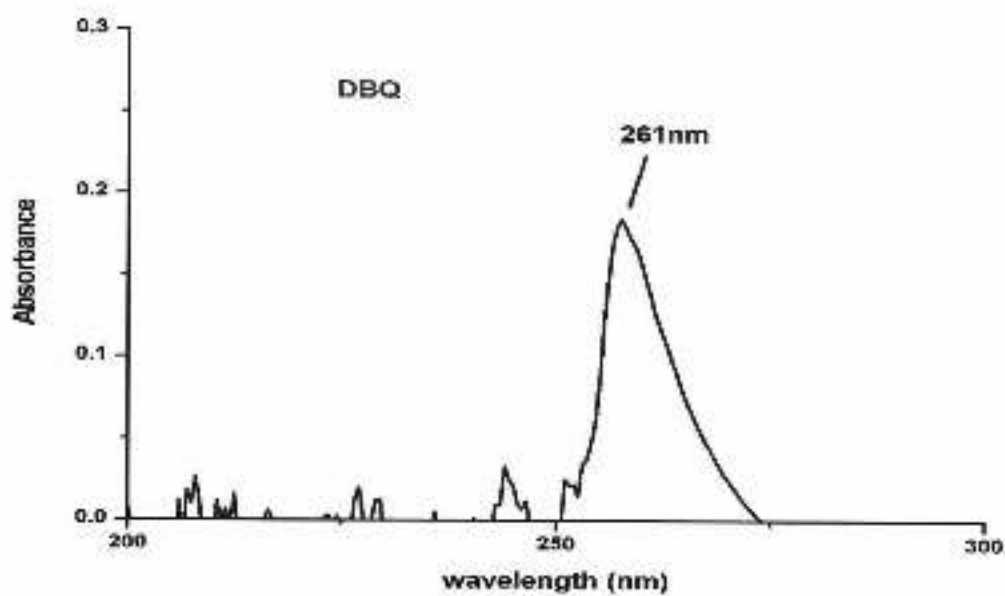


Figure 2. UV-Vis spectra of DBQ (5×10^{-5} M)

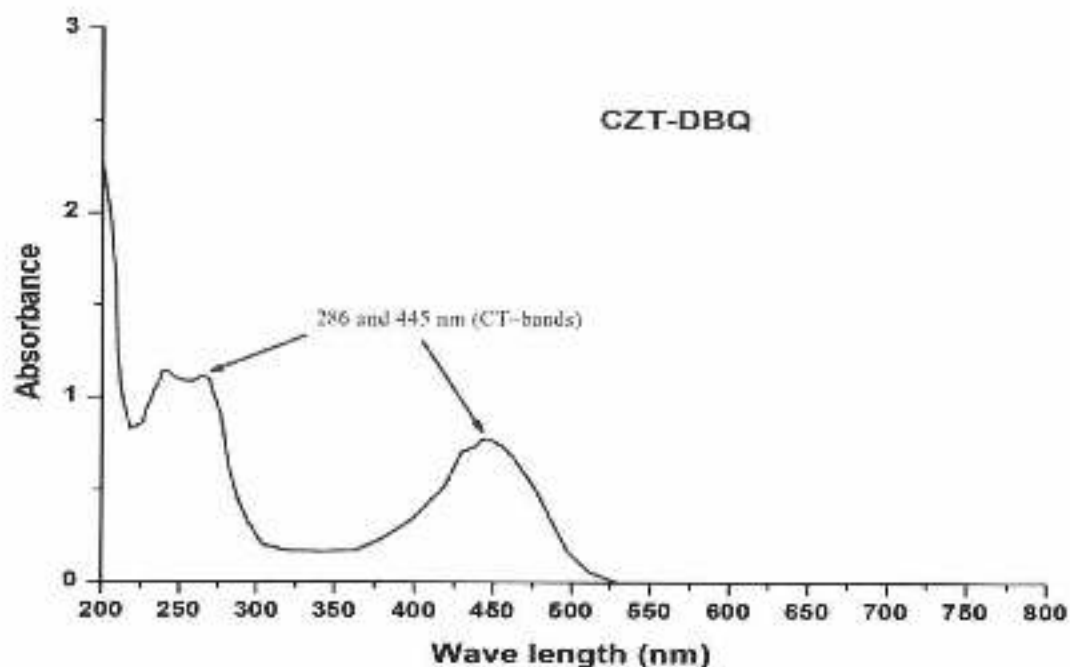


Figure 3. UV-Vis spectra of CZT-DBQ (5×10^{-3} M)

The UV-Vis spectra of CZT (donor) display two absorption bands at $\lambda = 274$ nm and 326 nm and DBQ (acceptor) display one absorption band at 261 nm in ethanol solvent (Fig.1 & 2 respectively). While, UV-Vis spectra of the CZT- DBQ CTC in the same solvent (Fig.3) display two absorption bands at $\lambda = 286$ nm and 445 nm. The UV-Vis spectra of CZT and DBQ shows no absorption bands in this spectral region. The absorption bands which appeared at 286 and 445 nm for the CTC were presumably due to the interaction of CZT (donor) with DBQ (acceptor) and are indicative of the formation of a CT complex. This observation suggests the CT from CZT (donor) to the DBQ (acceptor), which is well supported by the FT-IR and ^1H -NMR spectroscopy. The band at $\lambda = 286$ nm was selected for the further spectrophotometric study because it has highest absorption intensity. Polar solvent such as ethanol has been chosen as the solvent to promote the complete transfer of electron from CZT (donor) to the DBQ (acceptor).

4.2 Conductance measurements of freshly prepared experimental solutions

Conductimetry has often been employed to study the interactions of CT complexes. In the present study, the conductivity measurements of CZT (donor) and its synthesized CT complexes with DBQ were performed in ethanol solvent at 5×10^{-3} M using Systronics 304 conductivity meter. The conductance values of free donor was found to be $8.5 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ and for free acceptor DBQ was found to be $23 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ while, the conductance values of CZT- DBQ complex was found to be $98 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ respectively, this result suggest that the resulted complex have electrolytic behaviour. This data reveals the formation of dative $D^+ - A^-$ complex between CZT (donor) and DBQ (acceptor) under the acid-base theory.

4.3. Effect of reaction time

It is observed that as the time increases absorbance values increase, which suggest the stability of the CZT-DBQ complex.

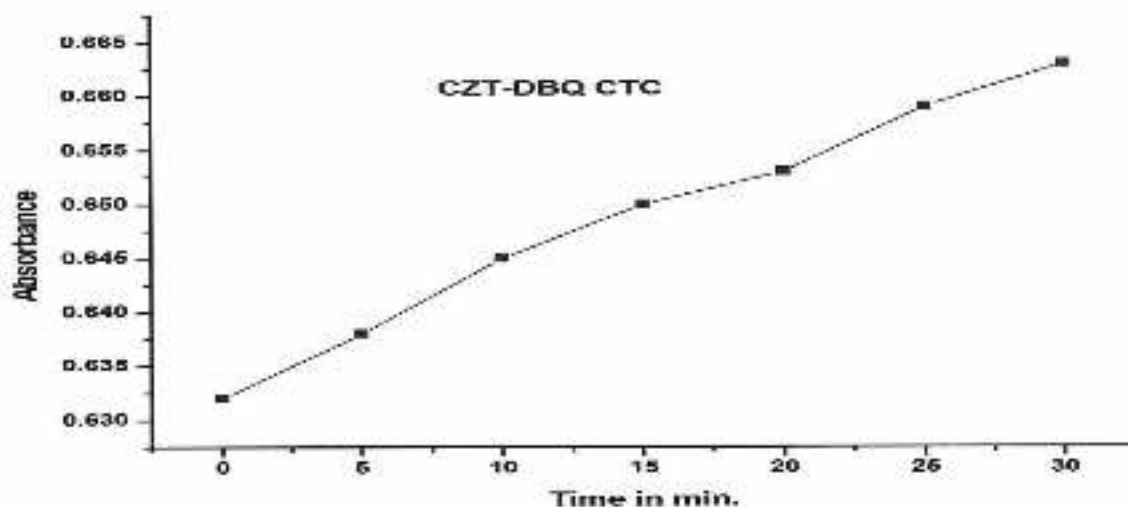


Figure 4. Effect of time on the stability of the CZT-DBQ (5×10^{-4} M) in ethanol at 286nm

4.4. Stoichiometry of the interaction

The stoichiometry of the formed CZT-DBQ complex was determined by applying Job's method of continuous variations (Fig.5.), the symmetrical curves with a maximum at 0.5 mole fraction indicated the formation of 1:1 complex (Fig.5.). The spectrophotometric titration measurements were also performed for the determination of stoichiometry of the formed CT complex (Fig.6.). The UV-Vis spectra of the CZT-DBQ complex was recorded with varying concentrations of acceptor, while, concentration of donor is kept constant. The stoichiometry of the complex was determined graphically by plotting the absorbance as a function of the volume of donor (in mL), where two straight lines are produced intercepting at 1:1 ratio for complex. Representative spectrophotometric titration plot based on the characterized absorption bands are shown in Fig. 6. The results show the good interaction between DBQ (acceptor) and CZT (donor) considered in the study.

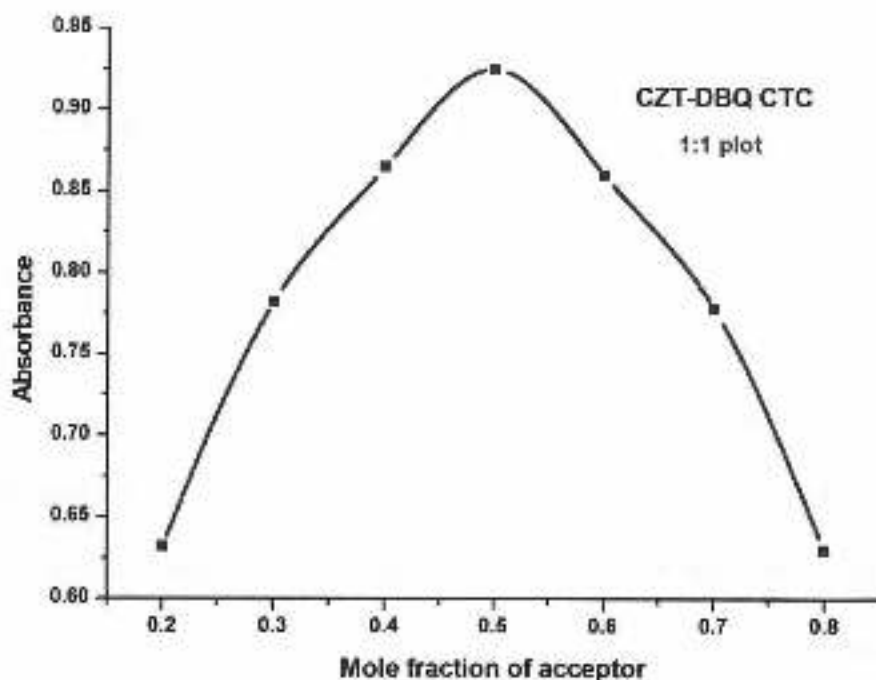


Figure. 5. Jobs plot of the CZT-DBQ CTC (5×10^{-4} M)

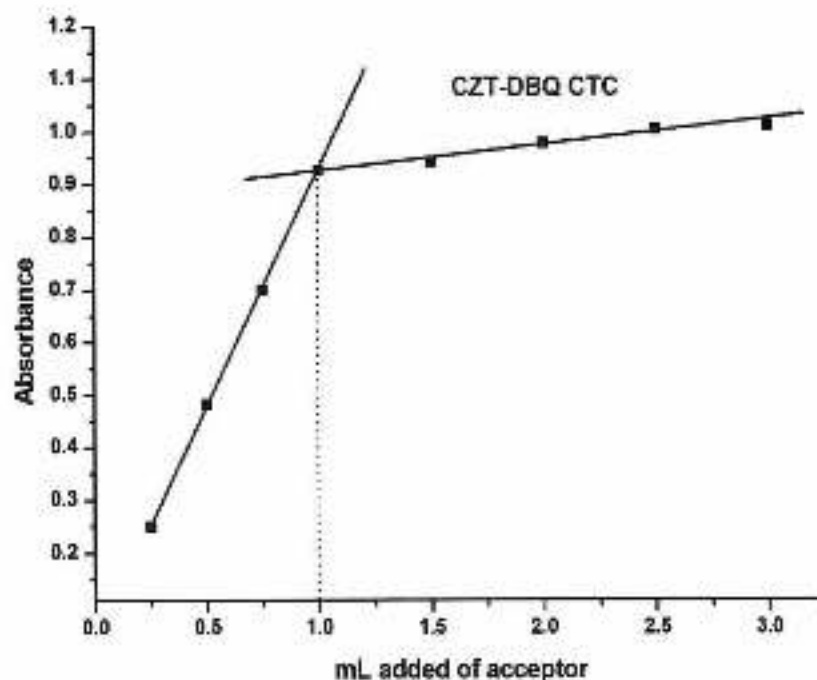


Figure 6. Spectrophotometric curve of the CZT-DBQ CTC (5×10^{-4} M)

4.5. Association constant of CZT-DBQ CT complex

Representative Benesi–Hildebrand plot is shown in (Fig.7) and the values of both K and ϵ are thus determined and are compiled in (Table-2) along with the other spectroscopic parameters data. The high K value indicates a strong interaction between the CZT and DBQ.

High association constant value which was obtained by Benesi–Hildebrand 1:1 equation, suggest the good binding affinity between n -donor CZT and acceptor DBQ. The high association constant values are common in n -electron donors, where the intermolecular overlap may be considerable.

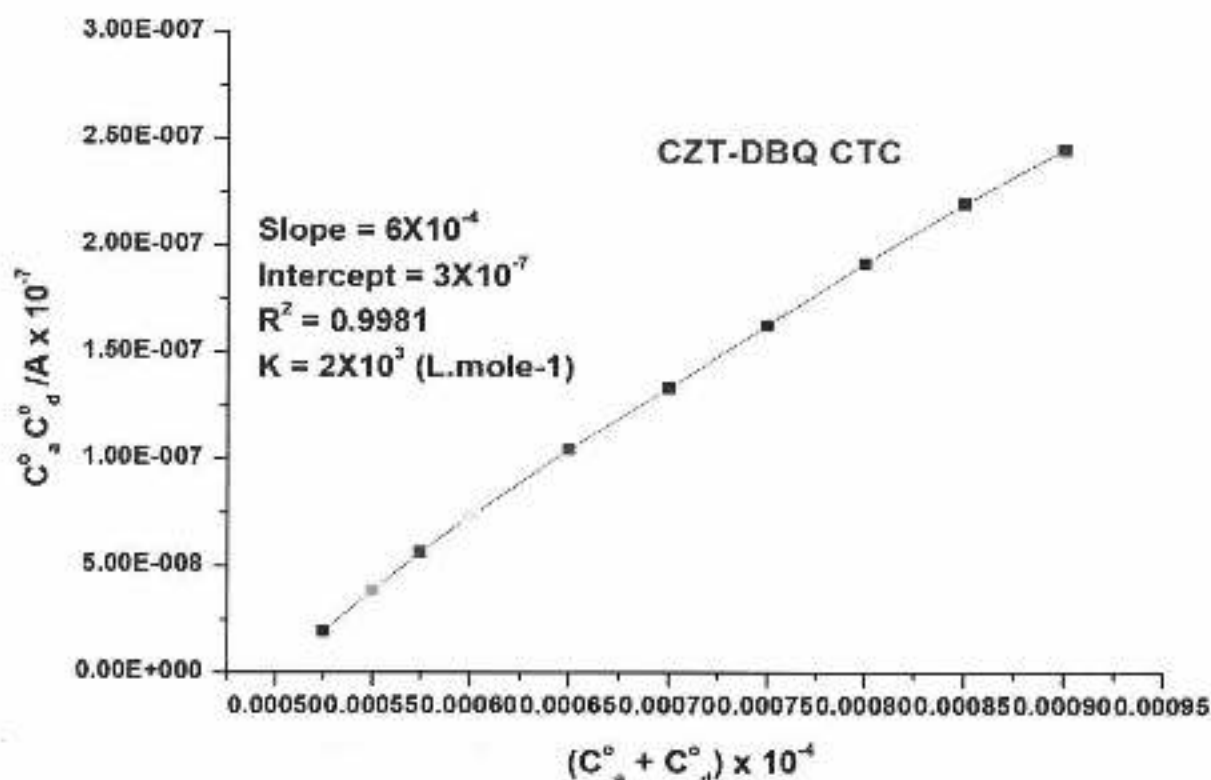


Figure 7. The 1:1 Benesi-Hildebrand plot for CZT-DBQ CTC

5. Calculation of spectroscopic Parameters

In order to support the formation and nature of CZT-DBQ CT complex, spectroscopic parameters like, Ionization potential (IP), Energy of the charge transfer complexes (E_{CT}), Resonance Energy (R_N), Dissociation energy (W) and Standard free energy changes (ΔG^0) of the CT Complexes were calculated.

5.1. Ionization Potential (IP)

The ionization potential (IP) of the highest filled molecular orbital of the donor was estimated from CT energies of its complexes with the acceptor making use of the following empirical Aloisi and Pignataro equation. The calculated IP values for molecular orbital participating in CT interaction of the donors are compiled in the **Table -2**.

$$h\nu_{CT} = a IP^D + b$$

Where, $a = 0.87$ and $b = -3.6$, $h\nu_{CT}$ is the energy of CT complex. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital.

5.2. Energy of the charge transfer complexes (E_{CT})

The energy (E_{CT}) of the CT Complexes were calculated using the following equation and the values are compiled in the **Table -2**.

$$E_{CT} = (h\nu_{CT}) = 1243.667 / \lambda_{CT} \text{ (nm)}$$

Where, λ_{CT} is the wavelength of the complexation band.

5.3. Resonance Energy (R_N)

Resonance Energy (R_N) of CT Complexes were determined by the following theoretically derived equation by Briegleb and Czekalla and the values were compiled in the **Table -2**.

$$\epsilon_{max} = 7.7 \times 10^4 / [h\nu_{CT} / [R_N] - 3.5]$$

Where, ϵ_{max} is the molar absorptivity of the CTC at maximum charge transfer band, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state, which is obviously a contributing factor to the stability constant of the complex.

5.4. Dissociation energy (W)

Further evidence of the nature of CT interaction in the present CT complexes is the calculation of the dissociation energy (W) of the CT excited state of the complex. The dissociation energy (W) of the formed CT complex was calculated from the corresponding CT energy (E_{CT}), ionization potential of the donor (IP) and electron affinity of the acceptor (EA) using the following relationship and the calculated values of W are compiled in (Table -2.)

$$h\nu_{CT} = IP - EA - W$$

Where, $h\nu_{CT}$ is the energy of CT complex, IP is the ionization potential of the donor and EA is the electron affinity of the acceptor.

5.5. Standard free energy changes (ΔG^0)

To add more conformation for the nature of CT interaction, standard free energy change values (ΔG^0) were calculated and are compiled in Table-2, the higher negative values suggest that the CT complexes formed between β -AB and I_2 are exothermic. Generally, the values of ΔG^0 become more negative as the value of K increases where the CT interactions between the donor and acceptor become strong. Thus, the components (donor and acceptor) are subjected to more physical strain or loss of degree of freedom and the values of ΔG^0 become more negative.

The standard free energy changes of complexation (ΔG^0) were calculated from the association constant values by the following equation.

$$\Delta G^0 = - RT \ln K$$

Where, ΔG^0 is the free energy change of the CT Complexes (KJmol^{-1}), R is the gas constant ($1.987\text{calmol}^{-1}\text{K}^{-1}$), T is the temperature in Kelvin and K is the association constant of the CT Complexes at room temperature.

Table - 2. Spectroscopic parameters of the CZT-DBQ CT Complex

| | CZT-DBQ |
|---|----------------------|
| Wavelength: λ_{max} (nm) | 286 |
| Extinction coefficient: ϵ_{max} ($\text{L mole}^{-1} \text{cm}^{-1}$) | 1.666×10^3 |
| Association constant: K (L mole^{-1}) | 2×10^3 |
| Energy: $h\nu_{\text{CT}}$ (eV) | 4.348 |
| Ionization Potential: IP (eV) | 9.136 |
| Resonance Energy: R_N (eV) | 1.242 |
| Dissociation energy: W (eV) | 2.301 |
| Gibbs free energy: ΔG^0 (KJmol^{-1}) | -1.231×10^3 |

The calculated spectroscopic parameters values like Energy of the CT complex ($h\nu_{\text{CT}}$), Ionization Potential (IP), Resonance Energy (R_N), Dissociation energy (W) and Standard Gibbs free energy (ΔG^0) suggests that the investigated CZT-DBQ complex was reasonably strong and stable under the studied conditions.

6. Spectral Characterization

6.1. FT-IR spectroscopy

The Infrared spectra of the CZT (donor) and DBQ (acceptor) and their corresponding CTC CZT-DBQ are shown in (Fig. 8,9 &10). Full assignments concerning all the infrared bands were located in the spectra are listed in Table 3. A comparison of the relevant IR spectral bands of the CZT (donor) and DBQ (acceptor) and their corresponding CTC (CZT-DBQ) clearly indicated that the characteristic bands of CZT show some shift in the frequencies (Table 3), as well as some change in their band intensities. This could be attributed to the expected symmetry and electronic structure changes upon the formation of the CTC.

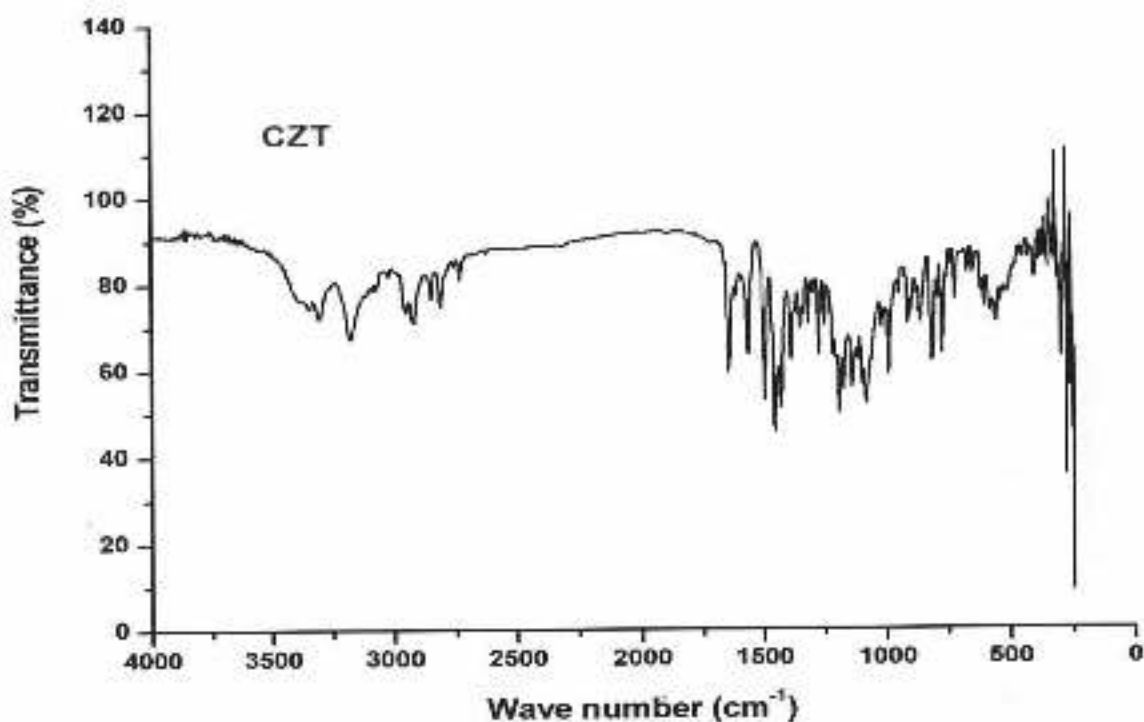


Figure 8. FT-IR spectra of CZT (donor)

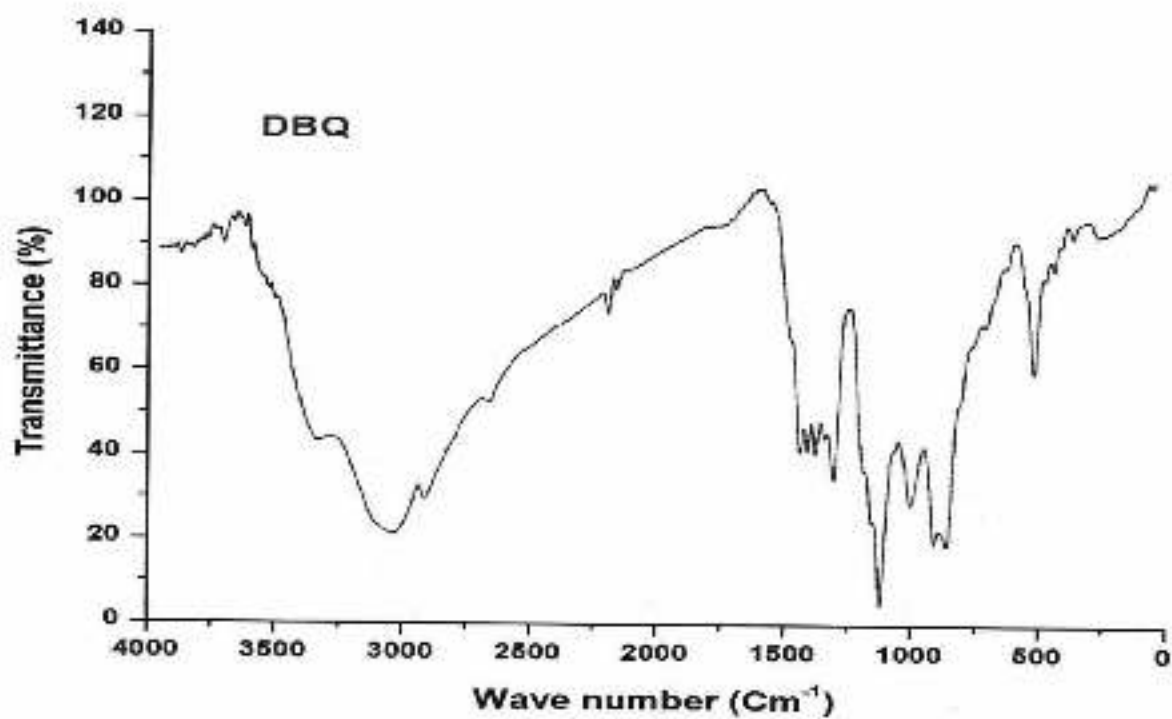


Figure 9. FT-IR spectra of DBQ (acceptor)

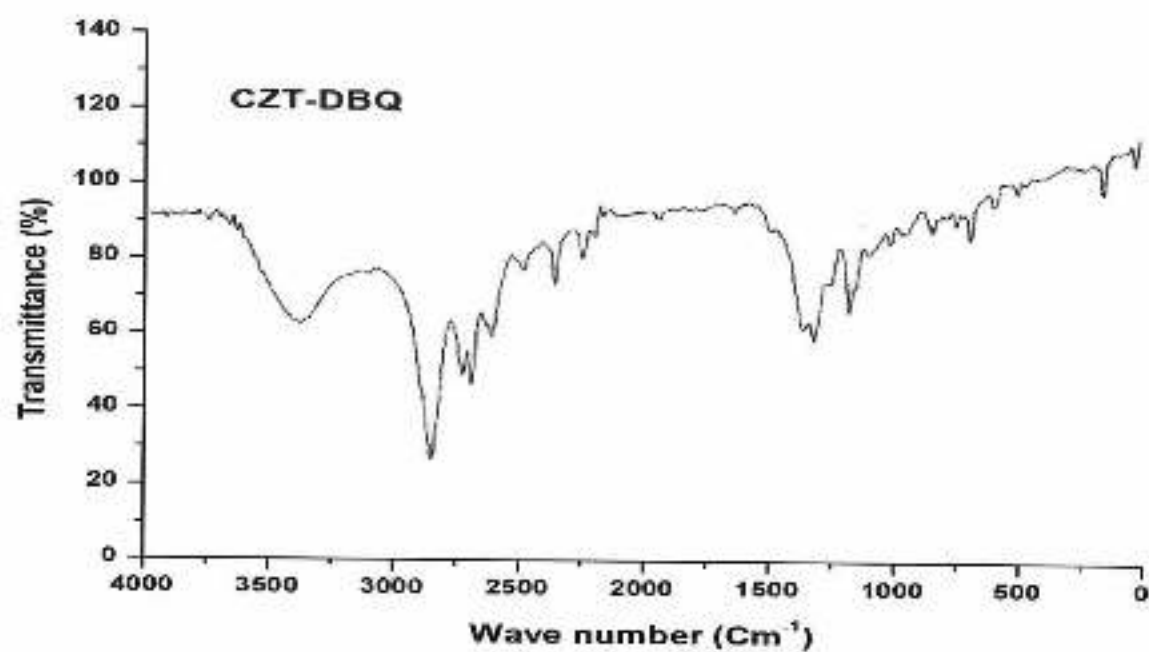


Figure 10. FT-IR spectra of CZT-DBQ (CTC)

To summarize,

The IR spectra of the CZT-DBQ is characterized by a group of bands within the 2415–2805 cm^{-1} range which are not present in the spectra of the free reactants. These bands are due to the stretching mode of a hydrogen bonding. This fact resulted from the hydrogen bond interaction through the proton ($-\text{NH}$) of CZT (donor) and the oxygen atom of the carbonyl group of acceptor. This is further strongly supported by the clear appearance of characteristic peak of the $\nu_{(\text{O}-\text{H})}$ at the wavelength 3422 cm^{-1} for CZT-DBQ CTC. The $\nu_{(\text{C}=\text{O})}$ group appearing at 1684, 1656 and 1630 cm^{-1} are disappeared and shifted to 1622 cm^{-1} in CZT-DBQ CTC, this led us to predict that the carbonyl group is involved in the complexation.

Table-3. Infrared absorption frequencies (cm^{-1}) and tentative assignments of DBQ and CZT-DBQ

| DBQ | CZT-DBQ | Assignments |
|------------|------------|---|
| 3418 s, br | 3422 s, br | $\nu_{(\text{O}-\text{H})}$; H_2O of KBr |
| | | $\nu_{(\text{N}-\text{H})}$ |
| 3140 s, br | 2951 vs | $\nu_{\text{as}}(\text{C}-\text{H}) + \nu_{\text{as}}(\text{C}-\text{H})$ |
| 3030 w | 2842 s | |
| | 2805 s | |
| | 2735 ms | |
| — | 2623 ms | Hydrogen bonding |
| | 2514 s | |
| | 2415 ms | |
| — | — | |
| 1684 w | 1741 vw | $\nu_{(\text{C}=\text{O})}$ |
| 1656 w | | |
| 1630 w | | |
| | 1622 mw | |
| 1595 vw | 1583 ms | $\nu_{(\text{C}-\text{C})}$; |
| 1563 vs | 1452 s | C-H deformation |
| 1399 vs | 1391 w | $(\text{C}-\text{C}) + \nu_{(\text{C}-\text{N})}$ |
| 1292 s | 1313 w | C-H, in-plane bend |
| 1204 w | 1256 w | |
| 1162 w | 1163 ms | |
| | 1079 w | |
| | 1029 ms | |
| 846 s | 941 ms | rock; NH |

778 vw
710 w

860 w
830 vw

CH-deformation
 ν (C-Cl) + ν (C-Br)

623 br

621 vw

Skeletal vibration

421 vw

552 s

CH bend

436 ms

CH out of plane bend

s = Strong, w = weak, m = medium, sh = shoulder, v = very, br = broad

6.2. ^1H -NMR spectroscopy

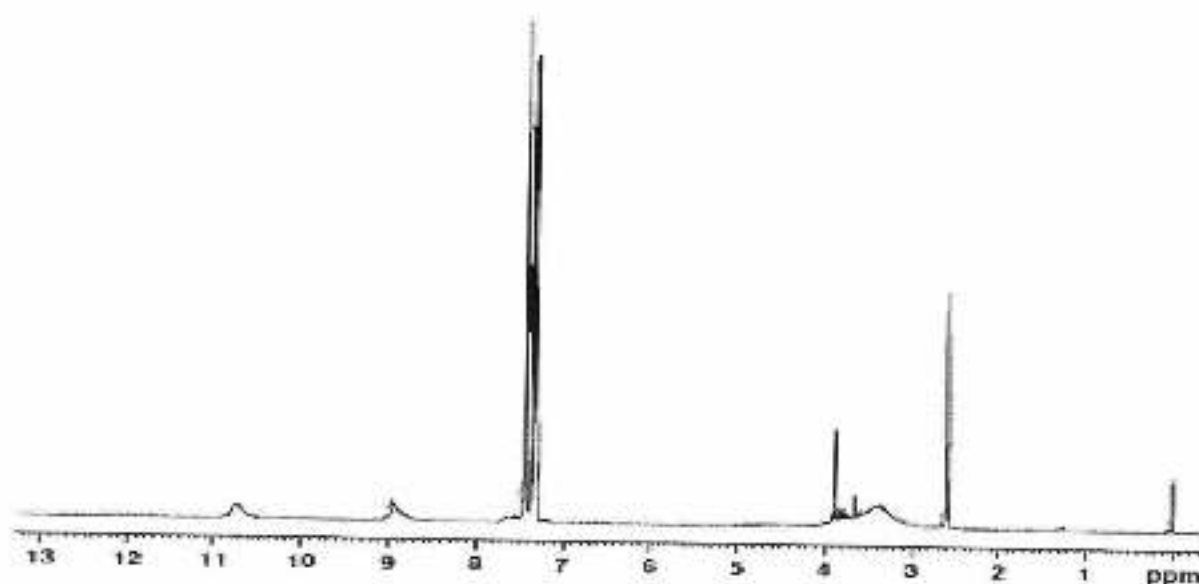


Fig.11. ^1H -NMR spectra of CT complex

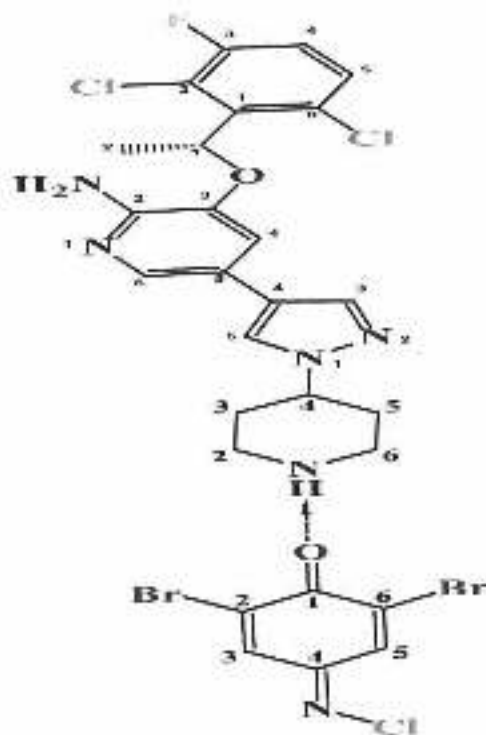
The ^1H NMR spectra of the CT complex CZT-NBS was recorded in DMSO and shown in Fig.11. The ^1H NMR spectrum of this CT complex was compared with the free CZT (donor), and the proton peak of -NH group was detected at 10.50 ppm, indicating the involvement of the nitrogen atom of -NH groups in complexation. The group of signals within 7.27 ppm and 6.40–8.80 ppm

ranges are assigned to 2H of DBQ and 14H of CZT donor. These signals are shifted to lower field after complexation due to the intermolecular charge transfer complexes with different transitions via lone pair of electrons on nitrogen atoms of CZT and the center of accepted groups in the DBQ acceptors.

Apparently, the results obtained from spectrophotometric study, FT-IR spectra met in the same point with ^1H -NMR spectra to construe the mode of interaction between CZT and NBS.

Based upon this valuable information obtained from spectrophotometric and spectroscopic studies, the following plausible interaction (**scheme-1**) between the CZT (donor) and DBQ (acceptor) has been proposed:

Scheme-1



7. *In silico* study

7.1 Molecular structure and optimized geometry

In order to obtain an evidence about the structural features of the resulting CT complexes, *In silico* study has been carried out using GAMESS (General Atomic and Molecular Electronic

Structure System) computations as a package of ChemBio3D Ultra 14.0; which includes energy optimization, estimation of the stabilization energy, computation of the optimized parameters (bond lengths, bond angles, bond orders and electron densities), Mulliken, Lowdin and Huckel charge computations of the free CZT (donor), DBQ (acceptor) and its respective CT complex with DBQ. MM2 method has been applied at RHF/3-21G level for energy optimization in all the cases.

The stabilization energy of the donor CZT and the acceptor DBQ recorded **46.6455** and **24.8194** kcal. mol⁻¹, respectively. The stabilization energy of the formed complex recorded **43.6013** kcal.mol⁻¹, confirming the noticeable stability of the obtained complex in accordance with experimental spectroscopic data.

The optimized geometrical structural parameters (bond lengths and angles) are listed in **Table-4 & 5** for the CZT and CZT-DBQ CT complex respectively.

i.(a) Optimized geometrical structural parameters

Table 4 Bond lengths of CZT and CZT-DBQ CT complex

| CZT | | DBQ | | CZT-DBQ | |
|--------------|-------------------------------|-------------|-------------------------------|--------------|-------------------------------|
| Atoms | Bond length (Å ^o) | Atoms | Bond length (Å ^o) | Atoms | Bond length (Å ^o) |
| O(19)-Lp(57) | 0.595 | N(8)-Lp(16) | 0.6 | N(38)-Lp(73) | 0.6 |
| O(19)-Lp(56) | 0.601 | O(2)-Lp(15) | 0.599 | O(32)-Lp(72) | 0.599 |
| N(13)-Lp(55) | 0.601 | O(2)-Lp(14) | 0.599 | O(32)-Lp(71) | 0.599 |
| N(9)-Lp(54) | 0.601 | C(6)-H(13) | 1.105 | O(19)-Lp(70) | 0.6 |
| N(6)-Lp(53) | 0.602 | C(4)-H(12) | 1.102 | O(19)-Lp(69) | 0.598 |
| C(26)-H(52) | 1.104 | C(3)-C(1) | 1.367 | N(13)-Lp(68) | 0.601 |
| C(25)-H(51) | 1.103 | C(7)-C(1) | 1.367 | N(9)-Lp(67) | 0.601 |
| C(21)-H(50) | 1.111 | C(6)-C(7) | 1.344 | N(6)-Lp(66) | 0.602 |
| C(21)-H(49) | 1.115 | C(5)-C(6) | 1.345 | C(36)-H(65) | 1.105 |
| C(21)-H(48) | 1.114 | C(4)-C(5) | 1.344 | C(34)-H(64) | 1.102 |
| C(20)-H(47) | 1.124 | C(3)-C(4) | 1.345 | C(26)-H(63) | 1.104 |
| C(18)-H(46) | 1.115 | C(3)-Br(11) | 1.913 | C(25)-H(62) | 1.102 |
| C(18)-H(45) | 1.116 | C(7)-Br(10) | 1.912 | C(21)-H(61) | 1.109 |
| C(17)-H(44) | 1.116 | C(5)-N(8) | 1.269 | C(21)-H(60) | 1.115 |
| C(17)-H(43) | 1.116 | N(8)-Cl(9) | 1.667 | C(21)-H(59) | 1.113 |

| | | | | | |
|--------------|-------|-----------|-------|-------------|-------|
| C(16)-H(42) | 1.118 | C(1)-O(2) | 1.217 | C(20)-H(58) | 1.119 |
| C(15)-H(41) | 1.116 | | | C(18)-H(57) | 1.115 |
| C(15)-H(40) | 1.116 | | | C(18)-H(56) | 1.116 |
| C(14)-H(39) | 1.115 | | | C(17)-H(55) | 1.116 |
| C(14)-H(38) | 1.116 | | | C(17)-H(54) | 1.116 |
| N(13)-H(37) | 1.051 | | | C(16)-H(53) | 1.119 |
| C(12)-H(36) | 1.094 | | | C(15)-H(52) | 1.116 |
| C(10)-H(35) | 1.097 | | | C(15)-H(51) | 1.116 |
| N(7)-H(34) | 1.05 | | | C(14)-H(50) | 1.115 |
| N(7)-H(33) | 1.049 | | | C(14)-H(49) | 1.116 |
| C(5)-H(32) | 1.102 | | | N(13)-H(48) | 1.046 |
| C(3)-H(31) | 1.094 | | | C(12)-H(47) | 1.095 |
| C(22)-C(27) | 1.356 | | | C(10)-H(46) | 1.097 |
| C(26)-C(27) | 1.345 | | | N(7)-H(45) | 1.049 |
| C(25)-C(26) | 1.337 | | | N(7)-H(44) | 1.049 |
| C(24)-C(25) | 1.338 | | | C(5)-H(43) | 1.102 |
| C(23)-C(24) | 1.349 | | | C(3)-H(42) | 1.1 |
| C(22)-C(23) | 1.359 | | | C(33)-C(31) | 1.367 |
| N(13)-C(18) | 1.462 | | | C(37)-C(31) | 1.367 |
| C(17)-C(18) | 1.535 | | | C(36)-C(37) | 1.343 |
| C(16)-C(17) | 1.536 | | | C(35)-C(36) | 1.344 |
| C(15)-C(16) | 1.536 | | | C(34)-C(35) | 1.344 |
| C(14)-C(15) | 1.535 | | | C(33)-C(34) | 1.345 |
| N(13)-C(14) | 1.462 | | | C(22)-C(27) | 1.354 |
| C(4)-C(5) | 1.344 | | | C(26)-C(27) | 1.344 |
| N(6)-C(5) | 1.263 | | | C(25)-C(26) | 1.337 |
| C(1)-N(6) | 1.266 | | | C(24)-C(25) | 1.338 |
| C(2)-C(1) | 1.351 | | | C(23)-C(24) | 1.348 |
| C(3)-C(2) | 1.347 | | | C(22)-C(23) | 1.357 |
| C(4)-C(3) | 1.346 | | | N(13)-C(18) | 1.462 |
| C(10)-N(9) | 1.266 | | | C(17)-C(18) | 1.535 |
| N(8)-N(9) | 1.234 | | | C(16)-C(17) | 1.537 |
| C(12)-N(8) | 1.27 | | | C(15)-C(16) | 1.537 |
| C(11)-C(12) | 1.343 | | | C(14)-C(15) | 1.535 |
| C(10)-C(11) | 1.345 | | | N(13)-C(14) | 1.462 |
| C(2)-O(19) | 1.376 | | | C(4)-C(5) | 1.344 |
| C(20)-C(22) | 1.542 | | | N(6)-C(5) | 1.264 |
| C(23)-Cl(30) | 1.74 | | | C(1)-N(6) | 1.267 |
| C(27)-Cl(29) | 1.732 | | | C(2)-C(1) | 1.35 |
| C(24)-F(28) | 1.326 | | | C(3)-C(2) | 1.347 |
| O(19)-C(20) | 1.415 | | | C(4)-C(3) | 1.344 |
| C(20)-C(21) | 1.532 | | | C(10)-N(9) | 1.266 |
| C(4)-C(11) | 1.347 | | | N(8)-N(9) | 1.234 |

| | |
|------------|-------|
| N(8)-C(16) | 1.482 |
| C(1)-N(7) | 1.269 |

| | |
|--------------|-------|
| C(12)-N(8) | 1.27 |
| C(11)-C(12) | 1.343 |
| C(10)-C(11) | 1.345 |
| C(33)-Br(41) | 1.912 |
| C(37)-Br(40) | 1.912 |
| C(35)-N(38) | 1.269 |
| N(38)-Cl(39) | 1.667 |
| C(31)-O(32) | 1.220 |
| C(2)-O(19) | 1.374 |
| C(20)-C(22) | 1.539 |
| C(23)-Cl(30) | 1.739 |
| C(27)-Cl(29) | 1.73 |
| C(24)-F(28) | 1.326 |
| O(19)-C(20) | 1.415 |
| C(20)-C(21) | 1.532 |
| C(4)-C(11) | 1.346 |
| N(8)-C(16) | 1.482 |
| C(1)-N(7) | 1.269 |

Pertaining to bond lengths, one can observe from **Table 4**, the bond length of DBQ increased slightly to 1.220 \AA upon complexation with CZT, relative to 1.217 \AA for free DBQ. This finding can be interpreted based on the n -electron transfer from the HOMO of CZT to the LUMO of DBQ. This transfer led to the expansion of bond lengths because of the increase of electron density of DBQ in the CZT-DBQ CT complex compared to DBQ alone. Logically the decrease of electron density on CZT (donor) moiety of the complex led to the contraction of bond lengths compared to donor alone (**Table 4**), particularly N(13)-H(37) value decreased from 1.051 \AA to 1.046 \AA , concerning other bonds no significant change was observed, these small changes in the bond length values could not reveal much information about the CT process from CZT to DBQ, hence further computations were made to evaluate other parameters to support the CT process.

Table 5 Bond angles of CZT and CZT-DBQ CT complex

| CZT | | DBQ | | CZT-DBQ | |
|---------------------|------------|--------------------|------------|---------------------|------------|
| Atoms | Bond angle | Atoms | Bond angle | Atoms | Bond angle |
| C(22)-C(27)-C(26) | 121.621 | Lp(16)-N(8)-C(5) | 118.91 | Lp(73)-N(38)-C(35) | 118.876 |
| C(22)-C(27)-Cl(29) | 125.246 | Lp(16)-N(8)-Cl(9) | 115.296 | Lp(73)-N(38)-Cl(39) | 115.374 |
| C(26)-C(27)-Cl(29) | 113.134 | C(5)-N(8)-Cl(9) | 125.795 | C(35)-N(38)-Cl(39) | 125.747 |
| H(52)-C(26)-C(27) | 121.501 | C(1)-C(7)-C(6) | 120.411 | C(31)-C(37)-C(36) | 120.419 |
| H(52)-C(26)-C(25) | 117.592 | C(1)-C(7)-Br(10) | 122.956 | C(31)-C(37)-Br(40) | 123.178 |
| C(27)-C(26)-C(25) | 120.906 | C(6)-C(7)-Br(10) | 116.632 | C(36)-C(37)-Br(40) | 116.385 |
| H(51)-C(25)-C(26) | 120.439 | H(13)-C(6)-C(7) | 119.183 | H(65)-C(36)-C(37) | 119.186 |
| H(51)-C(25)-C(24) | 120.377 | H(13)-C(6)-C(5) | 118.367 | H(65)-C(36)-C(35) | 118.391 |
| C(26)-C(25)-C(24) | 119.178 | C(7)-C(6)-C(5) | 122.45 | C(37)-C(36)-C(35) | 122.419 |
| C(25)-C(24)-C(23) | 119.735 | C(6)-C(5)-C(4) | 117.116 | C(36)-C(35)-C(34) | 117.166 |
| C(25)-C(24)-F(28) | 118.3 | C(6)-C(5)-N(8) | 117.291 | C(36)-C(35)-N(38) | 117.089 |
| C(23)-C(24)-F(28) | 121.965 | C(4)-C(5)-N(8) | 125.593 | C(34)-C(35)-N(38) | 125.742 |
| C(24)-C(23)-C(22) | 122.511 | H(12)-C(4)-C(5) | 119.668 | H(64)-C(34)-C(35) | 119.665 |
| C(24)-C(23)-Cl(30) | 115.204 | H(12)-C(4)-C(3) | 118.205 | H(64)-C(34)-C(33) | 118.242 |
| C(22)-C(23)-Cl(30) | 122.282 | C(5)-C(4)-C(3) | 122.127 | C(35)-C(34)-C(33) | 122.092 |
| C(27)-C(22)-C(23) | 116.013 | C(1)-C(3)-C(4) | 120.685 | C(31)-C(33)-C(34) | 120.671 |
| C(27)-C(22)-C(20) | 124.953 | C(1)-C(3)-Br(11) | 122.767 | C(31)-C(33)-Br(41) | 122.664 |
| C(23)-C(22)-C(20) | 119.02 | C(4)-C(3)-Br(11) | 116.548 | C(34)-C(33)-Br(41) | 116.661 |
| H(50)-C(21)-H(49) | 104.913 | Lp(15)-O(2)-Lp(14) | 124.572 | Lp(72)-O(32)-Lp(71) | 124.645 |
| H(50)-C(21)-H(48) | 109.915 | Lp(15)-O(2)-C(1) | 117.706 | Lp(72)-O(32)-C(31) | 117.769 |
| H(50)-C(21)-C(20) | 113.517 | Lp(14)-O(2)-C(1) | 117.722 | Lp(71)-O(32)-C(31) | 117.586 |
| H(49)-C(21)-H(48) | 105.226 | C(3)-C(1)-C(7) | 117.21 | C(33)-C(31)-C(37) | 117.231 |
| H(49)-C(21)-C(20) | 110.506 | C(3)-C(1)-O(2) | 121.405 | C(33)-C(31)-O(32) | 121.656 |
| H(48)-C(21)-C(20) | 112.197 | C(7)-C(1)-O(2) | 121.385 | C(37)-C(31)-O(32) | 121.113 |
| H(47)-C(20)-C(22) | 102.312 | | | C(22)-C(27)-C(26) | 121.587 |
| H(47)-C(20)-O(19) | 104.288 | | | C(22)-C(27)-Cl(29) | 124.513 |
| H(47)-C(20)-C(21) | 101.034 | | | C(26)-C(27)-Cl(29) | 113.89 |
| C(22)-C(20)-O(19) | 114.176 | | | H(63)-C(26)-C(27) | 121.436 |
| C(22)-C(20)-C(21) | 123.59 | | | H(63)-C(26)-C(25) | 117.844 |
| O(19)-C(20)-C(21) | 108.469 | | | C(27)-C(26)-C(25) | 120.72 |
| Lp(57)-O(19)-Lp(56) | 128.163 | | | H(62)-C(25)-C(26) | 120.299 |
| Lp(57)-O(19)-C(2) | 100.198 | | | H(62)-C(25)-C(24) | 120.366 |
| Lp(57)-O(19)-C(20) | 103.259 | | | C(26)-C(25)-C(24) | 119.331 |
| Lp(56)-O(19)-C(2) | 100.962 | | | C(25)-C(24)-C(23) | 119.733 |
| Lp(56)-O(19)-C(20) | 104.16 | | | C(25)-C(24)-F(28) | 118.362 |
| C(2)-O(19)-C(20) | 122.32 | | | C(23)-C(24)-F(28) | 121.905 |
| H(46)-C(18)-H(45) | 106.98 | | | C(24)-C(23)-C(22) | 122.25 |

| | |
|--------------------|---------|
| H(46)-C(18)-N(13) | 109.342 |
| H(46)-C(18)-C(17) | 110.099 |
| H(45)-C(18)-N(13) | 108.962 |
| H(45)-C(18)-C(17) | 110.019 |
| N(13)-C(18)-C(17) | 111.331 |
| H(44)-C(17)-H(43) | 107.363 |
| H(44)-C(17)-C(18) | 110.131 |
| H(44)-C(17)-C(16) | 109.942 |
| H(43)-C(17)-C(18) | 109.009 |
| H(43)-C(17)-C(16) | 109.746 |
| C(18)-C(17)-C(16) | 110.586 |
| H(42)-C(16)-C(17) | 107.655 |
| H(42)-C(16)-C(15) | 107.794 |
| H(42)-C(16)-N(8) | 109.726 |
| C(17)-C(16)-C(15) | 109.5 |
| C(17)-C(16)-N(8) | 111.14 |
| C(15)-C(16)-N(8) | 110.911 |
| H(41)-C(15)-H(40) | 107.358 |
| H(41)-C(15)-C(16) | 109.947 |
| H(41)-C(15)-C(14) | 110.115 |
| H(40)-C(15)-C(16) | 109.673 |
| H(40)-C(15)-C(14) | 109.07 |
| C(16)-C(15)-C(14) | 110.613 |
| H(39)-C(14)-H(38) | 106.983 |
| H(39)-C(14)-C(15) | 110.078 |
| H(39)-C(14)-N(13) | 109.339 |
| H(38)-C(14)-C(15) | 110.014 |
| H(38)-C(14)-N(13) | 108.956 |
| C(15)-C(14)-N(13) | 111.363 |
| Lp(55)-N(13)-H(37) | 107.073 |
| Lp(55)-N(13)-C(18) | 109.359 |
| Lp(55)-N(13)-C(14) | 109.346 |
| H(37)-N(13)-C(18) | 108.889 |
| H(37)-N(13)-C(14) | 108.905 |
| C(18)-N(13)-C(14) | 113.089 |
| H(36)-C(12)-N(8) | 122.958 |
| H(36)-C(12)-C(11) | 130.305 |
| N(8)-C(12)-C(11) | 106.737 |
| C(12)-C(11)-C(10) | 102.027 |
| C(12)-C(11)-C(4) | 128.748 |
| C(10)-C(11)-C(4) | 129.224 |
| H(35)-C(10)-N(9) | 120.297 |

| | |
|-------------------------|---------|
| C(24)-C(23)-Cl(30) | 115.828 |
| C(22)-C(23)-Cl(30) | 121.914 |
| C(27)-C(22)-C(23) | 116.371 |
| C(27)-C(22)-C(20) | 124.225 |
| C(23)-C(22)-C(20) | 119.38 |
| H(61)-C(21)-H(60) | 104.584 |
| H(61)-C(21)-H(59) | 108.801 |
| H(61)-C(21)-C(20) | 114.319 |
| H(60)-C(21)-H(59) | 106.635 |
| H(60)-C(21)-C(20) | 110.924 |
| H(59)-C(21)-C(20) | 111.117 |
| H(58)-C(20)-C(22) | 106.301 |
| H(58)-C(20)-O(19) | 104.955 |
| H(58)-C(20)-C(21) | 100.053 |
| C(22)-C(20)-O(19) | 111.955 |
| C(22)-C(20)-C(21) | 120.358 |
| O(19)-C(20)-C(21) | 111.203 |
| Lp(70)-O(19)- Lp(69) | 128.07 |
| Lp(70)-O(19)-C(2) | 101.562 |
| Lp(70)-O(19)-C(20) | 103.959 |
| Lp(69)-O(19)-C(2) | 103.438 |
| Lp(69)-O(19)-C(20) | 105.08 |
| C(2)-O(19)-C(20) | 115.421 |
| H(57)-C(18)-H(56) | 107 |
| H(57)-C(18)-N(13) | 109.397 |
| H(57)-C(18)-C(17) | 110.151 |
| H(56)-C(18)-N(13) | 108.941 |
| H(56)-C(18)-C(17) | 110.047 |
| N(13)-C(18)-C(17) | 111.202 |
| H(55)-C(17)-H(54) | 107.473 |
| H(55)-C(17)-C(18) | 110.007 |
| H(55)-C(17)-C(16) | 110.039 |
| H(54)-C(17)-C(18) | 108.745 |
| H(54)-C(17)-C(16) | 109.825 |
| C(18)-C(17)-C(16) | 110.684 |
| H(53)-C(16)-C(17) | 107.169 |
| H(53)-C(16)-C(15) | 108.894 |
| H(53)-C(16)-N(8) | 108.101 |
| C(17)-C(16)-C(15) | 109.19 |
| C(17)-C(16)-N(8) | 112.436 |
| C(15)-C(16)-N(8) | 110.919 |
| H(52)-C(15)-H(51) | 107.27 |

| | |
|-------------------|---------|
| H(35)-C(10)-C(11) | 127.958 |
| N(9)-C(10)-C(11) | 111.745 |
| Lp(54)-N(9)-C(10) | 126.86 |
| Lp(54)-N(9)-N(8) | 127.503 |
| C(10)-N(9)-N(8) | 105.637 |
| N(9)-N(8)-C(12) | 113.853 |
| N(9)-N(8)-C(16) | 126.311 |
| C(12)-N(8)-C(16) | 119.836 |
| H(34)-N(7)-H(33) | 120.122 |
| H(34)-N(7)-C(1) | 119.347 |
| H(33)-N(7)-C(1) | 120.53 |
| Lp(53)-N(6)-C(5) | 120.226 |
| Lp(53)-N(6)-C(1) | 120.151 |
| C(5)-N(6)-C(1) | 119.623 |
| H(32)-C(5)-C(4) | 122.056 |
| H(32)-C(5)-N(6) | 113.479 |
| C(4)-C(5)-N(6) | 124.465 |
| C(5)-C(4)-C(3) | 114.825 |
| C(5)-C(4)-C(11) | 122.46 |
| C(3)-C(4)-C(11) | 122.714 |
| H(31)-C(3)-C(2) | 118.52 |
| H(31)-C(3)-C(4) | 119.192 |
| C(2)-C(3)-C(4) | 122.288 |
| C(1)-C(2)-C(3) | 115.542 |
| C(1)-C(2)-O(19) | 118.563 |
| C(3)-C(2)-O(19) | 125.858 |
| N(6)-C(1)-C(2) | 123.254 |
| N(6)-C(1)-N(7) | 120.323 |
| C(2)-C(1)-N(7) | 116.423 |

| | |
|------------------------|---------|
| H(52)-C(15)-C(16) | 110.338 |
| H(52)-C(15)-C(14) | 109.657 |
| H(51)-C(15)-C(16) | 109.272 |
| H(51)-C(15)-C(14) | 109.446 |
| C(16)-C(15)-C(14) | 110.784 |
| H(50)-C(14)-H(49) | 106.993 |
| H(50)-C(14)-C(15) | 110.006 |
| H(50)-C(14)-N(13) | 109.296 |
| H(49)-C(14)-C(15) | 110.019 |
| H(49)-C(14)-N(13) | 108.946 |
| C(15)-C(14)-N(13) | 111.469 |
| Lp(68)-N(13)- H(48) | 107.097 |
| Lp(68)-N(13)-C(18) | 109.364 |
| Lp(68)-N(13)-C(14) | 109.344 |
| H(48)-N(13)-C(18) | 108.929 |
| H(48)-N(13)-C(14) | 108.93 |
| C(18)-N(13)-C(14) | 113.003 |
| H(47)-C(12)-N(8) | 122.722 |
| H(47)-C(12)-C(11) | 130.671 |
| N(8)-C(12)-C(11) | 106.605 |
| C(12)-C(11)-C(10) | 102.197 |
| C(12)-C(11)-C(4) | 128.487 |
| C(10)-C(11)-C(4) | 129.313 |
| H(46)-C(10)-N(9) | 120.557 |
| H(46)-C(10)-C(11) | 127.827 |
| N(9)-C(10)-C(11) | 111.616 |
| Lp(67)-N(9)-C(10) | 126.786 |
| Lp(67)-N(9)-N(8) | 127.53 |
| C(10)-N(9)-N(8) | 105.683 |
| N(9)-N(8)-C(12) | 113.897 |
| N(9)-N(8)-C(16) | 127.325 |
| C(12)-N(8)-C(16) | 118.777 |
| H(45)-N(7)-H(44) | 119.553 |
| H(45)-N(7)-C(1) | 120.209 |
| H(44)-N(7)-C(1) | 120.237 |
| Lp(66)-N(6)-C(5) | 120.042 |
| Lp(66)-N(6)-C(1) | 119.944 |
| C(5)-N(6)-C(1) | 120.012 |
| H(43)-C(5)-C(4) | 121.76 |
| H(43)-C(5)-N(6) | 113.706 |
| C(4)-C(5)-N(6) | 124.533 |
| C(5)-C(4)-C(3) | 114.575 |

| | |
|-----------------|---------|
| C(5)-C(4)-C(11) | 123.264 |
| C(3)-C(4)-C(11) | 122.161 |
| H(42)-C(3)-C(2) | 117.287 |
| H(42)-C(3)-C(4) | 120.561 |
| C(2)-C(3)-C(4) | 122.149 |
| C(1)-C(2)-C(3) | 116.093 |
| C(1)-C(2)-O(19) | 122.685 |
| C(3)-C(2)-O(19) | 120.775 |
| N(6)-C(1)-C(2) | 122.379 |
| N(6)-C(1)-N(7) | 120.111 |
| C(2)-C(1)-N(7) | 117.508 |

The CZT- DBQ CT complex is further confirmed from the changes in its bond angle values compared to the reactant alone. One can observe from **Table-5**, the bond angle values of the atoms involving in the CT decreased relative to free CZT. It seems the lowered electron density of CZT (**Table 6**) due to CT process led to the retrenchment of bond angle values.

Table 6: Electron density values of CZT, DBQ and CZT-DBQ CT complex

| CZT | | | DBQ | | | CZT-DBQ | | |
|-------|------------|-----------|--------|------------|-----------|---------|------------|-----------|
| Atom | Atom Type | E D (A.U) | Atom | Type | E D (A.U) | Atom | Atom Type | E D (A.U) |
| C(1) | C Alkane | 93.9881 | C(1) | C Carbonyl | 94.1548 | C(1) | C Alkane | 93.9967 |
| C(2) | C Alkane | 94.1444 | O(2) | O Carbonyl | 233.989 | C(2) | C Alkane | 94.0949 |
| O(3) | O Enol | 233.57 | C(3) | C Alkene | 94.1247 | O(3) | O Enol | 233.57 |
| C(4) | C Alkene | 94.0297 | C(4) | C Alkene | 94.1238 | C(4) | C Alkene | 93.9702 |
| C(5) | C Alkene | 94.0934 | C(5) | C Alkene | 94.1066 | C(5) | C Alkene | 94.0975 |
| C(6) | C Alkene | 94.0584 | C(6) | C Alkene | 94.0921 | C(6) | C Alkene | 94.0952 |
| C(7) | C Alkene | 93.9729 | C(7) | C Alkene | 94.1324 | C(7) | C Alkene | 94.0191 |
| N(8) | N Pyridine | 153.818 | N(8) | N Imine | 154.005 | N(8) | N Pyridine | 153.772 |
| C(9) | C Alkene | 94.0232 | Cl(9) | Cl | 2405.54 | C(9) | C Alkene | 94.0765 |
| N(10) | N Enamine | 153.203 | Br(10) | Br | 22231.5 | N(10) | N Enamine | 153.324 |
| C(11) | C Alkene | 94.1485 | Br(11) | Br | 22231.4 | C(11) | C Alkene | 94.1197 |

| | | | | | | | | |
|--------|-----------|----------|-------|---|----------|--------|------------|----------|
| C(12) | C Alkene | 93.9888 | H(12) | H | 0.360009 | C(12) | C Alkene | 93.9721 |
| N(13) | N Pyrrole | 153.427 | H(13) | H | 0.352411 | N(13) | N Pyrrole | 153.497 |
| N(14) | N Imine | 153.826 | | | | N(14) | N Imine | 153.887 |
| C(15) | C Alkene | 94.0064 | | | | C(15) | C Alkene | 93.9891 |
| C(16) | C Alkane | 94.112 | | | | C(16) | C Alkane | 94.1299 |
| C(17) | C Alkane | 94.0983 | | | | C(17) | C Alkane | 94.1004 |
| C(18) | C Alkane | 94.0225 | | | | C(18) | C Alkane | 94.0301 |
| N(19) | N Amine | 153.387 | | | | N(19) | N Amine | 153.414 |
| C(20) | C Alkane | 94.0393 | | | | C(20) | C Alkane | 94.0336 |
| C(21) | C Alkane | 94.0771 | | | | C(21) | C Alkane | 94.0922 |
| C(22) | C Alkene | 94.1358 | | | | C(22) | C Alkene | 94.0756 |
| C(23) | C Alkene | 94.0823 | | | | C(23) | C Alkene | 94.0959 |
| Cl(24) | Cl | 2405.25 | | | | Cl(24) | Cl | 2405.2 |
| C(25) | C Alkene | 94.0843 | | | | C(25) | C Alkene | 94.0616 |
| C(26) | C Alkene | 94.035 | | | | C(26) | C Alkene | 94.054 |
| C(27) | C Alkene | 94.0128 | | | | C(27) | C Alkene | 94.015 |
| F(28) | F | 337.567 | | | | F(28) | F | 337.56 |
| C(29) | C Alkene | 94.0982 | | | | C(29) | C Alkene | 94.099 |
| Cl(30) | Cl | 2405.19 | | | | Cl(30) | Cl | 2405.2 |
| H(31) | H | 0.333416 | | | | C(31) | C Carbonyl | 94.1547 |
| H(32) | H | 0.329703 | | | | O(32) | O Carbonyl | 233.985 |
| H(33) | H | 0.360851 | | | | C(33) | C Alkene | 94.1216 |
| H(34) | H | 0.401103 | | | | C(34) | C Alkene | 94.0875 |
| H(35) | H | 0.371579 | | | | C(35) | C Alkene | 94.1453 |
| H(36) | H | 0.379245 | | | | C(36) | C Alkene | 94.1235 |
| H(37) | H Amine | 0.373743 | | | | C(37) | C Alkene | 94.1145 |
| H(38) | H Amine | 0.334708 | | | | N(38) | N Imine | 154.072 |
| H(39) | H | 0.37024 | | | | Cl(39) | Cl | 2405.47 |
| H(40) | H | 0.365479 | | | | Br(40) | Br | 22231.4 |
| H(41) | H | 0.363519 | | | | Br(41) | Br | 22231.3 |
| H(42) | H | 0.376807 | | | | H(42) | H | 0.335646 |
| H(43) | H | 0.347279 | | | | H(43) | H | 0.361076 |
| H(44) | H | 0.367804 | | | | H(44) | H | 0.355303 |
| H(45) | H | 0.362172 | | | | H(45) | H | 0.341431 |
| H(46) | H Amine | 0.339834 | | | | H(46) | H | 0.359861 |
| H(47) | H | 0.364857 | | | | H(47) | H | 0.393215 |
| H(48) | H | 0.380356 | | | | H(48) | H Amine | 0.284187 |
| H(49) | H | 0.359412 | | | | H(49) | H Amine | 0.312742 |

| | | |
|-------|---|----------|
| H(50) | H | 0.345856 |
| H(51) | H | 0.346597 |
| H(52) | H | 0.367624 |

| | | |
|-------|---------|----------|
| H(50) | H | 0.359618 |
| H(51) | H | 0.359629 |
| H(52) | H | 0.355245 |
| H(53) | H | 0.359729 |
| H(54) | H | 0.354246 |
| H(55) | H | 0.353429 |
| H(56) | H | 0.363685 |
| H(57) | H Amine | 0.339536 |
| H(58) | H | 0.360282 |
| H(59) | H | 0.363627 |
| H(60) | H | 0.359208 |
| H(61) | H | 0.359037 |
| H(62) | H | 0.348763 |
| H(63) | H | 0.387963 |
| H(64) | H | 0.354872 |
| H(65) | H | 0.358453 |

i.(b) Atomic charges

To add more support for the formed CZT- DBQ CT complex. Mulliken and Huckel atomic charges were computed and the results are compiled in **Table 7**, where one can observe the increase in charge on the atoms of acceptor (DBQ) from **0.543783** to **0.549363** (C Carbonyl) and from **-0.52384** to **-0.5394** (O Carbonyl), indicating the charge transfer process. Concerning the donor CZT, the decrease of effective atomic charges of its atoms than the free donor molecule (CZT) support the charge transfer from CZT to DBQ. Huckel and Lowdin atomic charges were also computed, in order to support Mulliken charges and are tabulated in the **Table 8-9**, which are in good agreement with Mulliken charges.

Table 7 Mulliken charges (MC) of CZT, DBQ and CZT-DBQ CT complex

| CZT | | | DBQ | | | CZT-DBQ | | |
|--------|------------|----------|--------|------------|----------|---------|------------|----------|
| Atom | Atom Type | MC | Atom | Type | MC | Atom | Atom Type | MC |
| C(1) | C Alkane | -0.62412 | C(1) | C Carbonyl | 0.543783 | C(1) | C Alkane | -0.57799 |
| C(2) | C Alkane | 0.081177 | O(2) | O Carbonyl | -0.52384 | C(2) | C Alkane | 0.074486 |
| O(3) | O Enol | -0.72873 | C(3) | C Alkene | -0.42912 | O(3) | O Enol | -0.70503 |
| C(4) | C Alkene | 0.262181 | C(4) | C Alkene | -0.09248 | C(4) | C Alkene | 0.210118 |
| C(5) | C Alkene | -0.09766 | C(5) | C Alkene | 0.278707 | C(5) | C Alkene | -0.11502 |
| C(6) | C Alkene | -0.21982 | C(6) | C Alkene | -0.11566 | C(6) | C Alkene | -0.24868 |
| C(7) | C Alkene | 0.169361 | C(7) | C Alkene | -0.41978 | C(7) | C Alkene | 0.240795 |
| N(8) | N Pyridine | -0.82267 | N(8) | N Imine | -0.70051 | N(8) | N Pyridine | -0.81792 |
| C(9) | C Alkene | 0.884254 | Cl(9) | Cl | 0.24029 | C(9) | C Alkene | 0.927344 |
| N(10) | N Enamine | -1.01143 | Br(10) | Br | 0.282846 | N(10) | N Enamine | -1.04663 |
| C(11) | C Alkene | -0.49424 | Br(11) | Br | 0.287385 | C(11) | C Alkene | -0.39737 |
| C(12) | C Alkene | 0.323571 | H(12) | H | 0.328302 | C(12) | C Alkene | 0.362948 |
| N(13) | N Pyrrole | -0.67434 | H(13) | H | 0.320077 | N(13) | N Pyrrole | -0.67936 |
| N(14) | N Imine | -0.36974 | | | | N(14) | N Imine | -0.36319 |
| C(15) | C Alkene | 0.316679 | | | | C(15) | C Alkene | 0.204729 |
| C(16) | C Alkane | 0.047144 | | | | C(16) | C Alkane | 0.031669 |
| C(17) | C Alkane | -0.38746 | | | | C(17) | C Alkane | -0.39209 |
| C(18) | C Alkane | -0.17621 | | | | C(18) | C Alkane | -0.18995 |
| N(19) | N Amine | -0.699 | | | | N(19) | N Amine | -0.70028 |
| C(20) | C Alkane | -0.19772 | | | | C(20) | C Alkane | -0.193 |
| C(21) | C Alkane | -0.38741 | | | | C(21) | C Alkane | -0.40694 |
| C(22) | C Alkene | 0.00384 | | | | C(22) | C Alkene | 0.028488 |
| C(23) | C Alkene | -0.35951 | | | | C(23) | C Alkene | -0.4321 |
| Cl(24) | Cl | 0.148465 | | | | Cl(24) | Cl | 0.242209 |
| C(25) | C Alkene | -0.16297 | | | | C(25) | C Alkene | -0.1578 |
| C(26) | C Alkene | -0.27646 | | | | C(26) | C Alkene | -0.26871 |
| C(27) | C Alkene | 0.531306 | | | | C(27) | C Alkene | 0.51083 |
| F(28) | F | -0.39152 | | | | F(28) | F | -0.38994 |
| C(29) | C Alkene | -0.4913 | | | | C(29) | C Alkene | -0.4287 |
| Cl(30) | Cl | 0.278546 | | | | Cl(30) | Cl | 0.228443 |
| H(31) | H | 0.217146 | | | | C(31) | C Carbonyl | 0.549363 |
| H(32) | H | 0.249781 | | | | O(32) | O Carbonyl | -0.5394 |
| H(33) | H | 0.223265 | | | | C(33) | C Alkene | -0.41526 |
| H(34) | H | 0.290091 | | | | C(34) | C Alkene | -0.08698 |
| H(35) | H | 0.257414 | | | | C(35) | C Alkene | 0.275528 |
| H(36) | H | 0.241835 | | | | C(36) | C Alkene | -0.05338 |

| | | |
|-------|---------|----------|
| H(37) | H Amine | 0.366486 |
| H(38) | H Amine | 0.373298 |
| H(39) | H | 0.266155 |
| H(40) | H | 0.256757 |
| H(41) | H | 0.220163 |
| H(42) | H | 0.217599 |
| H(43) | H | 0.233006 |
| H(44) | H | 0.223419 |
| H(45) | H | 0.150169 |
| H(46) | H Amine | 0.286861 |
| H(47) | H | 0.224766 |
| H(48) | H | 0.177379 |
| H(49) | H | 0.25748 |
| H(50) | H | 0.212001 |
| H(51) | H | 0.287451 |
| H(52) | H | 0.293254 |

| | | |
|--------|----------|----------|
| C(37) | C Alkene | -0.45548 |
| N(38) | N Imine | -0.73157 |
| Cl(39) | Cl | 0.225964 |
| Br(40) | Br | 0.292546 |
| Br(41) | Br | 0.291323 |
| H(42) | H | 0.197648 |
| H(43) | H | 0.243064 |
| H(44) | H | 0.191512 |
| H(45) | H | 0.250249 |
| H(46) | H | 0.2521 |
| H(47) | H | 0.265455 |
| H(48) | H Amine | 0.369764 |
| H(49) | H Amine | 0.359757 |
| H(50) | H | 0.265793 |
| H(51) | H | 0.24584 |
| H(52) | H | 0.215203 |
| H(53) | H | 0.220439 |
| H(54) | H | 0.24903 |
| H(55) | H | 0.228185 |
| H(56) | H | 0.164014 |
| H(57) | H Amine | 0.293086 |
| H(58) | H | 0.216029 |
| H(59) | H | 0.166157 |
| H(60) | H | 0.260168 |
| H(61) | H | 0.228607 |
| H(62) | H | 0.286262 |
| H(63) | H | 0.290809 |
| H(64) | H | 0.308609 |
| H(65) | H | 0.328218 |

Table 8 Huckle charges (HC) of CZT, DBQ and CZT-DBQ CT complex

| CZT | | | DBQ | | | CZT-DBQ | | |
|------|-----------|----------|------|------------|----------|---------|-----------|----------|
| Atom | Atom Type | HC | Atom | Type | HC | Atom | Atom Type | HC |
| C(1) | C Alkane | 0.247397 | C(1) | C Carbonyl | 0.326098 | C(1) | C Alkane | 0.247026 |
| C(2) | C Alkane | 0.123527 | O(2) | O Carbonyl | -0.56803 | C(2) | C Alkane | 0.112402 |
| O(3) | O Enol | -0.18345 | C(3) | C Alkene | 0.048137 | O(3) | O Enol | -0.12664 |
| C(4) | C Alkene | -0.11855 | C(4) | C Alkene | -0.19726 | C(4) | C Alkene | -0.11988 |
| C(5) | C Alkene | 0.008622 | C(5) | C Alkene | 0.060822 | C(5) | C Alkene | 0.058938 |
| C(6) | C Alkene | -0.43383 | C(6) | C Alkene | -0.15529 | C(6) | C Alkene | -0.34087 |
| C(7) | C Alkene | 0.114145 | C(7) | C Alkene | 0.031166 | C(7) | C Alkene | 0.064506 |

| | | | | | | | | |
|--------|------------|----------|--------|---------|----------|--------|------------|----------|
| N(8) | N Pyridine | 0.693456 | N(8) | N Imine | -0.09674 | N(8) | N Pyridine | 0.722892 |
| C(9) | C Alkene | -0.35682 | Cl(9) | Cl | 0.333043 | C(9) | C Alkene | -0.32468 |
| N(10) | N Enamine | -0.124 | Br(10) | Br | 0.076944 | N(10) | N Enamine | -0.10944 |
| C(11) | C Alkene | -0.12293 | Br(11) | Br | 0.085366 | C(11) | C Alkene | -0.1492 |
| C(12) | C Alkene | -0.20443 | H(12) | H | 0.03019 | C(12) | C Alkene | -0.19125 |
| N(13) | N Pyrrole | -0.21373 | H(13) | H | 0.025561 | N(13) | N Pyrrole | -0.20351 |
| N(14) | N Imine | 0.035663 | | | | N(14) | N Imine | 0.034003 |
| C(15) | C Alkene | -0.06406 | | | | C(15) | C Alkene | -0.06317 |
| C(16) | C Alkene | 0.066228 | | | | C(16) | C Alkene | 0.051851 |
| C(17) | C Alkene | -0.06272 | | | | C(17) | C Alkene | -0.07208 |
| C(18) | C Alkene | 0.03435 | | | | C(18) | C Alkene | 0.03387 |
| N(19) | N Amine | -0.24908 | | | | N(19) | N Amine | -0.29917 |
| C(20) | C Alkene | 0.209027 | | | | C(20) | C Alkene | 0.195862 |
| C(21) | C Alkene | -0.49628 | | | | C(21) | C Alkene | -0.16414 |
| C(22) | C Alkene | -0.06557 | | | | C(22) | C Alkene | -0.11859 |
| C(23) | C Alkene | 0.033153 | | | | C(23) | C Alkene | 0.080769 |
| Cl(24) | Cl | 0.257196 | | | | Cl(24) | Cl | 0.264343 |
| C(25) | C Alkene | -0.18377 | | | | C(25) | C Alkene | -0.12608 |
| C(26) | C Alkene | -0.18743 | | | | C(26) | C Alkene | -0.14407 |
| C(27) | C Alkene | 0.068485 | | | | C(27) | C Alkene | 0.111049 |
| F(28) | F | -0.13404 | | | | F(28) | F | -0.15553 |
| C(29) | C Alkene | 0.254072 | | | | C(29) | C Alkene | 0.021126 |
| Cl(30) | Cl | 0.075045 | | | | Cl(30) | Cl | 0.027587 |
| H(31) | H | 0.089052 | | | | C(31) | C Carbonyl | 0.277001 |
| H(32) | H | 0.007867 | | | | O(32) | O Carbonyl | -0.76109 |
| H(33) | H | 0.092648 | | | | C(33) | C Alkene | 0.047383 |
| H(34) | H | 0.092792 | | | | C(34) | C Alkene | -0.12369 |
| H(35) | H | 0.011955 | | | | C(35) | C Alkene | 0.08238 |
| H(36) | H | 0.025054 | | | | C(36) | C Alkene | -0.07167 |
| H(37) | H Amine | 0.104409 | | | | C(37) | C Alkene | 0.02468 |
| H(38) | H Amine | 0.020679 | | | | N(38) | N Imine | -0.04257 |
| H(39) | H | 0.003593 | | | | Cl(39) | Cl | 0.474667 |
| H(40) | H | 0.028553 | | | | Br(40) | Br | 0.024116 |
| H(41) | H | 0.027875 | | | | Br(41) | Br | 0.033159 |
| H(42) | H | 0.017941 | | | | H(42) | H | 0.021445 |
| H(43) | H | 0.0284 | | | | H(43) | H | -0.00615 |
| H(44) | H | 0.027858 | | | | H(44) | H | 0.090699 |
| H(45) | H | 0.020938 | | | | H(45) | H | 0.09251 |
| H(46) | H Amine | 0.003843 | | | | H(46) | H | 0.002036 |
| H(47) | H | 0.019088 | | | | H(47) | H | 0.013868 |
| H(48) | H | 0.17107 | | | | H(48) | H Amine | 0.100699 |
| H(49) | H | 0.041723 | | | | H(49) | H Amine | 0.020046 |
| H(50) | H | 0.092416 | | | | H(50) | H | 0.002142 |

| | | |
|-------|---|----------|
| H(51) | H | 0.028451 |
| H(52) | H | 0.024125 |

| | | |
|-------|---------|----------|
| H(51) | H | 0.028795 |
| H(52) | H | 0.026992 |
| H(53) | H | 0.018722 |
| H(54) | H | 0.029167 |
| H(55) | H | 0.026736 |
| H(56) | H | 0.019778 |
| H(57) | H Amine | 0.001991 |
| H(58) | H | 0.021882 |
| H(59) | H | 0.044268 |
| H(60) | H | 0.040742 |
| H(61) | H | 0.04535 |
| H(62) | H | 0.023588 |
| H(63) | H | 0.018196 |
| H(64) | H | 0.019982 |
| H(65) | H | 0.014221 |

Table 9 Lowdin charges (I.C) of CZT, DBQ and CZT-DBQ CT complex

| CZT | | | DBQ | | | CZT-DBQ | | |
|-------|------------|----------|--------|------------|----------|---------|------------|----------|
| Atom | Atom Type | I.C | Atom | Type | LC | Atom | Atom Type | LC |
| C(1) | C Alkane | -0.29229 | C(1) | C Carbonyl | 0.153741 | C(1) | C Alkane | -0.28038 |
| C(2) | C Alkane | 0.150605 | O(2) | O Carbonyl | -0.20125 | C(2) | C Alkane | 0.111013 |
| O(3) | O Enol | -0.29378 | C(3) | C Alkene | -0.18809 | O(3) | O Enol | -0.28059 |
| C(4) | C Alkene | 0.026809 | C(4) | C Alkene | -0.05744 | C(4) | C Alkene | -0.00784 |
| C(5) | C Alkene | -0.06382 | C(5) | C Alkene | 0.031985 | C(5) | C Alkene | -0.04158 |
| C(6) | C Alkene | -0.09725 | C(6) | C Alkene | -0.09312 | C(6) | C Alkene | -0.13034 |
| C(7) | C Alkene | 0.036719 | C(7) | C Alkene | -0.17685 | C(7) | C Alkene | 0.0604 |
| N(8) | N Pyridine | -0.27324 | N(8) | N Imine | -0.20624 | N(8) | N Pyridine | -0.26617 |
| C(9) | C Alkene | 0.163607 | Cl(9) | Cl | 0.130834 | C(9) | C Alkene | 0.147568 |
| N(10) | N Enamine | -0.34201 | Br(10) | Br | 0.155862 | N(10) | N Enamine | -0.28626 |
| C(11) | C Alkene | -0.12866 | Br(11) | Br | 0.158971 | C(11) | C Alkene | -0.1148 |
| C(12) | C Alkene | -0.04784 | H(12) | H | 0.148282 | C(12) | C Alkene | -0.06559 |
| N(13) | N Pyrrole | -0.04277 | H(13) | H | 0.143311 | N(13) | N Pyrrole | -0.0091 |
| N(14) | N Imine | -0.08221 | | | | N(14) | N Imine | -0.13636 |
| C(15) | C Alkene | -0.0904 | | | | C(15) | C Alkene | -0.09426 |
| C(16) | C Alkane | 0.048946 | | | | C(16) | C Alkane | 0.052992 |
| C(17) | C Alkane | -0.1764 | | | | C(17) | C Alkane | -0.17315 |
| C(18) | C Alkane | -0.04693 | | | | C(18) | C Alkane | -0.05198 |

| | | |
|--------|----------|----------|
| N(19) | N Amine | -0.34043 |
| C(20) | C Alkane | -0.04716 |
| C(21) | C Alkane | -0.16329 |
| C(22) | C Alkene | -0.04065 |
| C(23) | C Alkene | -0.08527 |
| Cl(24) | Cl | -0.0043 |
| C(25) | C Alkene | -0.07756 |
| C(26) | C Alkene | -0.13647 |
| C(27) | C Alkene | 0.207561 |
| F(28) | F | -0.16251 |
| C(29) | C Alkene | -0.15735 |
| Cl(30) | Cl | 0.088675 |
| H(31) | H | 0.110501 |
| H(32) | H | 0.123403 |
| H(33) | H | 0.100517 |
| H(34) | H | 0.104204 |
| H(35) | H | 0.104411 |
| H(36) | H | 0.089963 |
| H(37) | H Amine | 0.20748 |
| H(38) | H Amine | 0.234987 |
| H(39) | H | 0.105967 |
| H(40) | H | 0.100885 |
| H(41) | H | 0.081539 |
| H(42) | H | 0.087223 |
| H(43) | H | 0.103661 |
| H(44) | H | 0.088608 |
| H(45) | H | 0.038056 |
| H(46) | H Amine | 0.173205 |
| H(47) | H | 0.090005 |
| H(48) | H | 0.051021 |
| H(49) | H | 0.113247 |
| H(50) | H | 0.094074 |
| H(51) | H | 0.131664 |
| H(52) | H | 0.135055 |

| | | |
|--------|------------|----------|
| N(19) | N Amine | -0.34271 |
| C(20) | C Alkane | -0.05003 |
| C(21) | C Alkane | -0.17125 |
| C(22) | C Alkene | -0.04273 |
| C(23) | C Alkene | -0.11852 |
| Cl(24) | Cl | 0.059122 |
| C(25) | C Alkene | -0.08728 |
| C(26) | C Alkene | -0.12129 |
| C(27) | C Alkene | 0.191981 |
| F(28) | F | -0.14969 |
| C(29) | C Alkene | -0.12992 |
| Cl(30) | Cl | 0.061503 |
| C(31) | C Carbonyl | 0.162074 |
| O(32) | O Carbonyl | -0.21645 |
| C(33) | C Alkene | -0.16455 |
| C(34) | C Alkene | -0.09297 |
| C(35) | C Alkene | 0.023287 |
| C(36) | C Alkene | -0.03896 |
| C(37) | C Alkene | -0.20734 |
| N(38) | N Imine | -0.20007 |
| Cl(39) | Cl | 0.121922 |
| Br(40) | Br | 0.162819 |
| Br(41) | Br | 0.161381 |
| H(42) | H | 0.096615 |
| H(43) | H | 0.104142 |
| H(44) | H | 0.081859 |
| H(45) | H | 0.102748 |
| H(46) | H | 0.106647 |
| H(47) | H | 0.098137 |
| H(48) | H Amine | 0.243971 |
| H(49) | H Amine | 0.234113 |
| H(50) | H | 0.108003 |
| H(51) | H | 0.099685 |
| H(52) | H | 0.081778 |
| H(53) | H | 0.094519 |
| H(54) | H | 0.104105 |
| H(55) | H | 0.093196 |
| H(56) | H | 0.046402 |
| H(57) | H Amine | 0.176344 |
| H(58) | H | 0.084951 |
| H(59) | H | 0.04759 |
| H(60) | H | 0.10677 |
| H(61) | H | 0.100538 |

| | | |
|-------|---|----------|
| H(62) | H | 0.129681 |
| H(63) | H | 0.127907 |
| H(64) | H | 0.136461 |
| H(65) | H | 0.14995 |

7.2 Electronic properties

The most important orbitals in a molecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule. The lower value for frontier orbital gap in case of CT complexes makes it more reactive and less stable (**Table 10**). The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital acts as the electron acceptor.

The values of the extreme potentials for HOMO and LUMO maps of all complexes have been taken for the sake of comparison and drawing the conclusions. The electronic properties of the calculated frontier orbital gap, for all the complexes are in **Table 10**.

i Energy optimised molecular structures

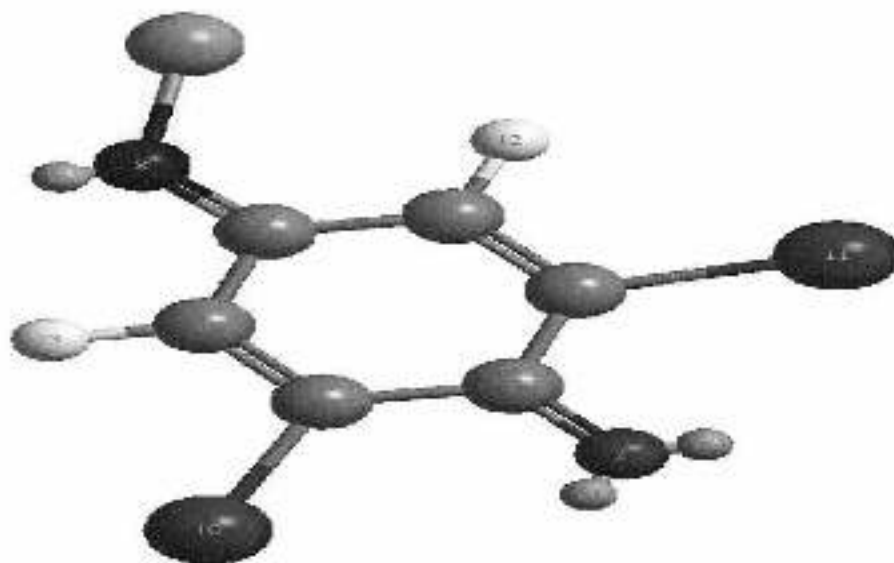


Fig. 12 Energy optimised molecular structure of DBQ (acceptor)

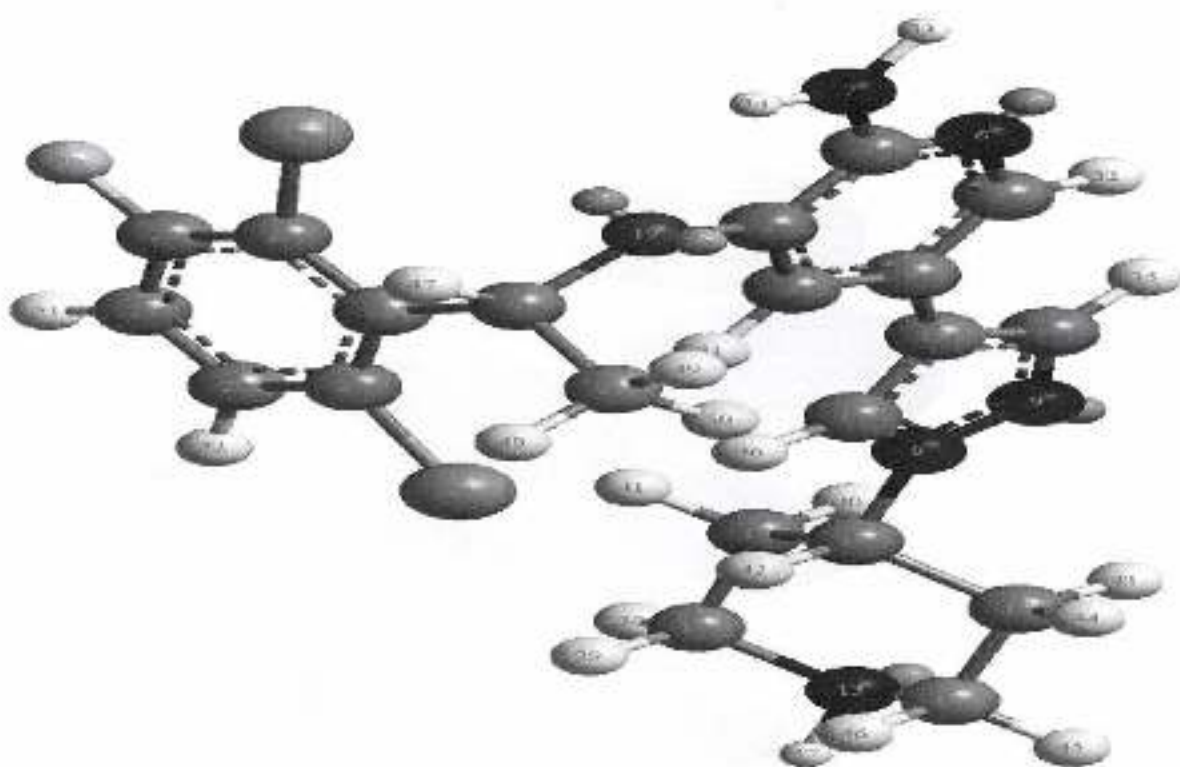


Fig. 13 Energy optimised molecular structure of CZT (donor)

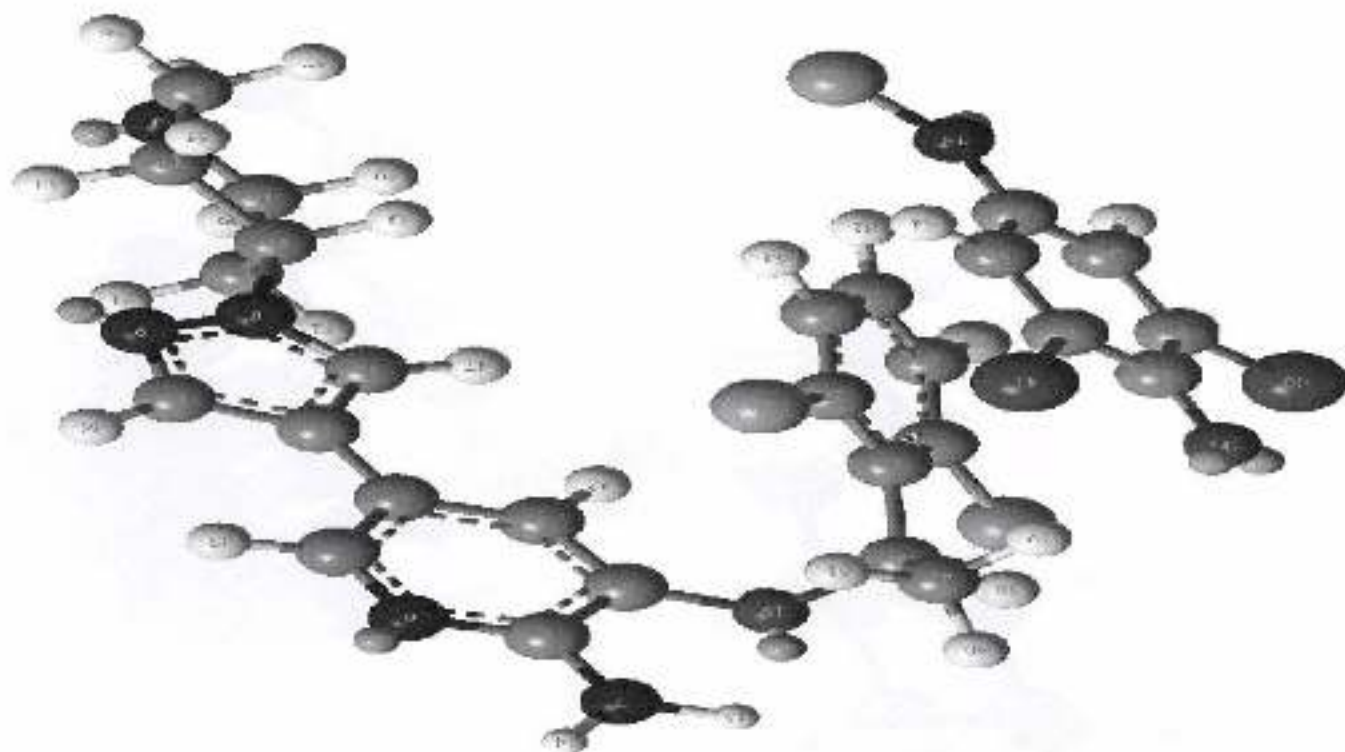


Fig. 14 Energy optimised molecular structure of CZT-DBQ CT complex

ii Molecular orbital surfaces

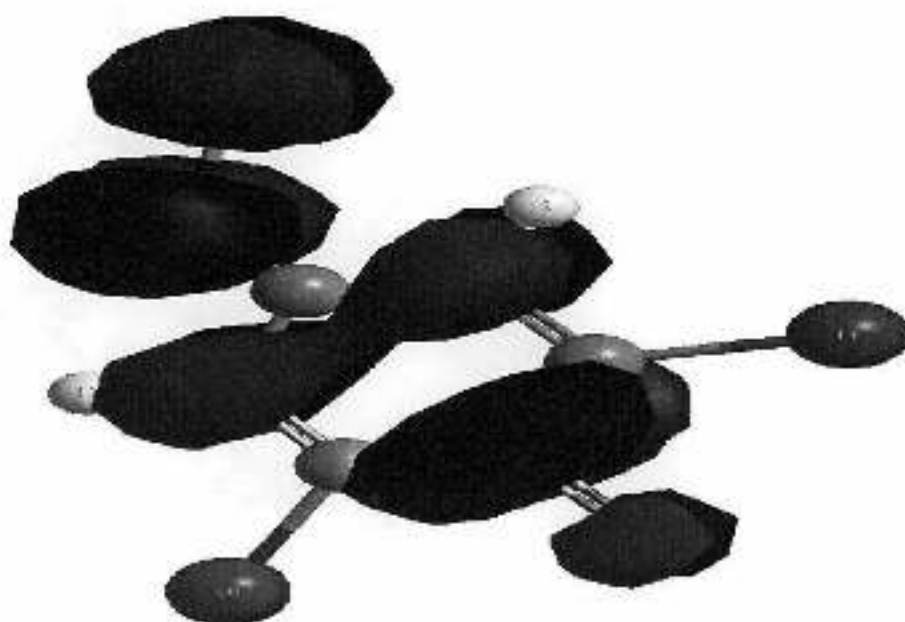


Fig. 15 LUMO molecular orbital surface of DBQ

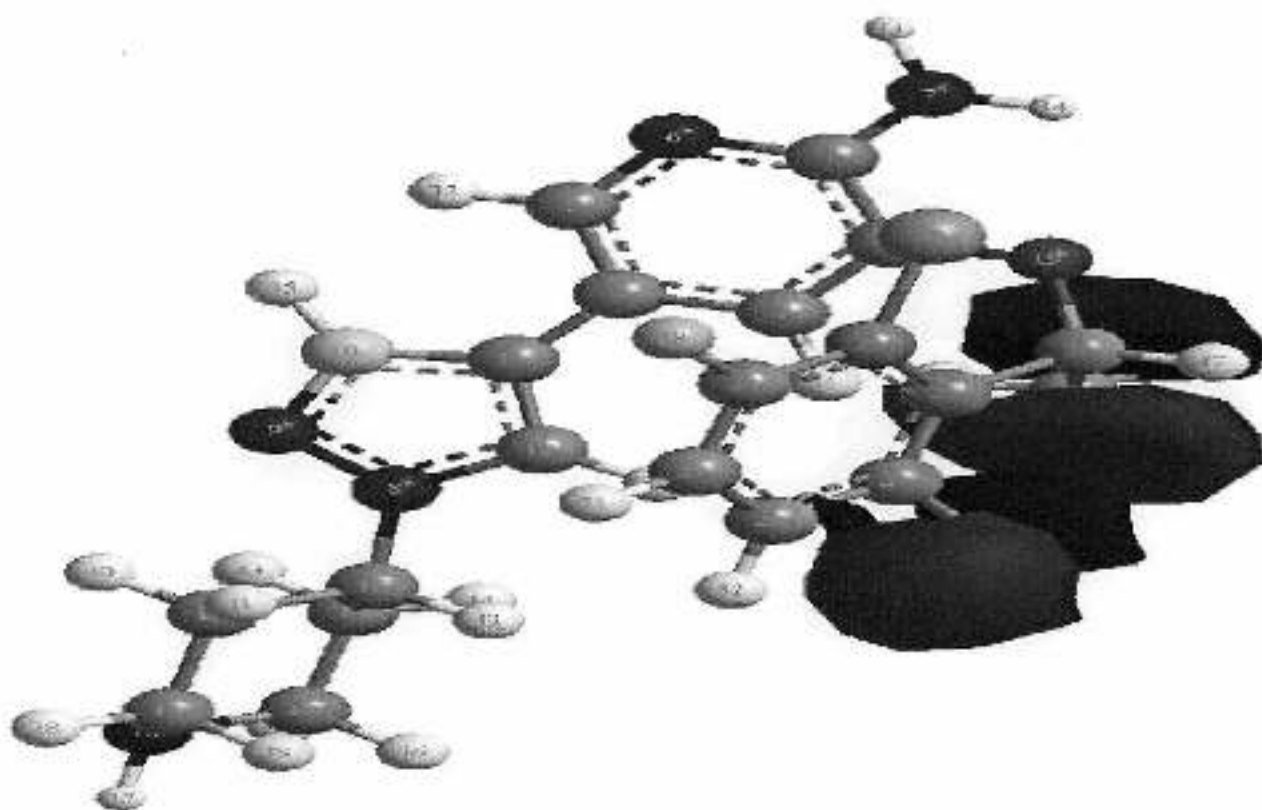


Fig. 16 HOMO molecular orbital surface of CZT

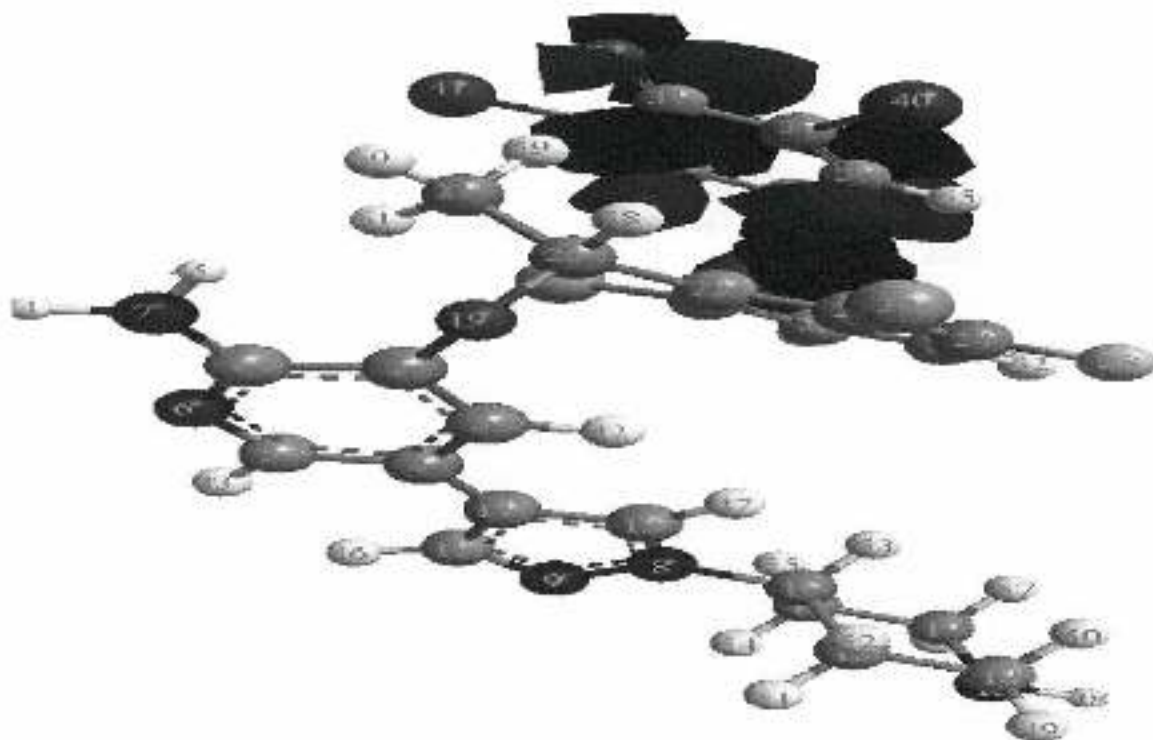


Fig. 19 LUMO molecular orbital surface of CZT-DBQ CT complex



Fig. 20 HOMO molecular orbital surface of CZT-DBQ CT complex

Table 10

| CT complex | Experimental Energy (eV) | Calculated Energy (eV) | Assignment of electronic transition |
|-------------------|---------------------------------|-------------------------------|--|
| CZT-DBQ | 4.348 | 4.342 | HOMO to LUMO |

8. Conclusion

The CT reaction between the CZT with the electron acceptor DBQ is comprehensively studied for the first time.

The present research work has demonstrated the feasibility of the use of UV-Vis spectrophotometry, complexation reaction and the suitability of DBQ as electron acceptor. CZT-DBQ CT complex has been investigated experimentally and theoretically.

Experimental investigation includes the use of spectrophotometry in the comprehensive manner. A single solvent DMSO has been used to avoid solvent interactions with CZT and DBQ considered in the study. The spectroscopic parameters like Ionization Potential (IP), Energy of the complex, (E_{CT}), and Resonance Energy (R_o) values support the perceptible interaction of CZT with DBQ.

The computational analysis has been carried out using GAMESS computations. It includes energy minimization of the CZT, DBQ and CZT- DBQ CT complex utilizing MM2 method, estimation of the stabilization energy, computation of the optimized parameters (bond lengths, bond angles, bond orders and electron densities of atoms), Mulliken charge computations, Huckel charge computations, Lowdin charge computations, presentation of optimised structures of CZT CT complex and also presenting the HOMO and LUMO molecular orbital participating in the electronic transitions.

A good consistency between experimental and computational analysis has been found. In addition, the suggested positioning of the acceptor molecule with respect to the donor molecule (CZT) were confirmed theoretically from the HOMO, LUMO figures.

Therefore, the mechanism for the interaction of the studied CZT is useful in understanding the binding of these bioactive molecules under real pharmacokinetic conditions, which enables medical fraternity to pay attention towards the importance of this novel drug in our country, which may potentially contribute to the knowledge in the medicinal field of our country.

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SYNTHESIS, SPECTROPHOTOMETRIC, THERMODYNAMIC AND SPECTROSCOPIC STUDIES

OF CT COMPLEXES OF NOVEL CRIZOTINIB WITH 2,6-DIBROMOQUINONE-4- CHLOROIMIDE AS π - ACCEPTOR

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Abstract : Understanding the charge transfer process between bioactive molecules and inorganic or organic molecules is significant as this interaction can be used to interpret bioactive molecule-receptor interactions. A comprehensive spectrophotometric study has been performed to explore the complexation chemistry of the Crizotinib (CZT) with 2,6-dibromoquinone-4-chloroimide (DBQ) as π - acceptor. The molecular structure, spectroscopic characteristics and the interactive modes have been deduced from UV-Vis and FT-IR spectra. The binding ratio of complexation has been determined to be 1:1 for DBQ with CZT. Benesi-Hildebrand method was applied to estimate the spectroscopic and physical data. The association constant (K), extinction coefficient (ϵ_{max}), ionization potential (IP), energy of the charge transfer complex (E_{CT}), resonance energy (R_N), dissociation energy (W) and standard Gibbs energy (ΔG^θ) have been computed. Based upon the obtained spectroscopic data, the plausible CT mechanism between CZT and DBQ was proposed.

Keywords - Spectrophotometry, Spectroscopy, CZT, DBQ, Charge transfer complexation, Computational study.

1. INTRODUCTION

Crizotinib (CZT) is a novel anti-lung cancer drug acting as an ALK (Anaplastic Lymphoma Kinase) & ROS 1 (C-ROS, Oncogene 1) inhibitor; it has been approved by FDA on August 26, 2011, under the trade name of xalkori capsules, made by Pfizer, Inc. for the treatment of patients with locally advanced or metastatic Non-Small Cell Lung Cancer (NSCLC) i.e., ALK positive as detected by an FDA approved test.

CZT is currently used to exert its effects through modulation of the growth; migration and invasion of malignant cells. Furthermore, other studies suggest that CZT might also act via inhibition of Angiogenesis, in malignant tumours, which is of great interest in order to show how this novel CZT is significant.

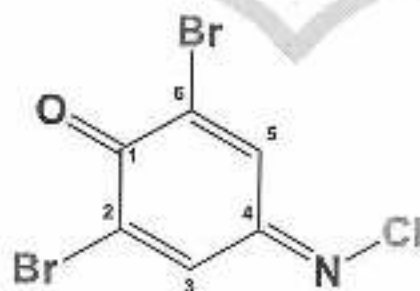
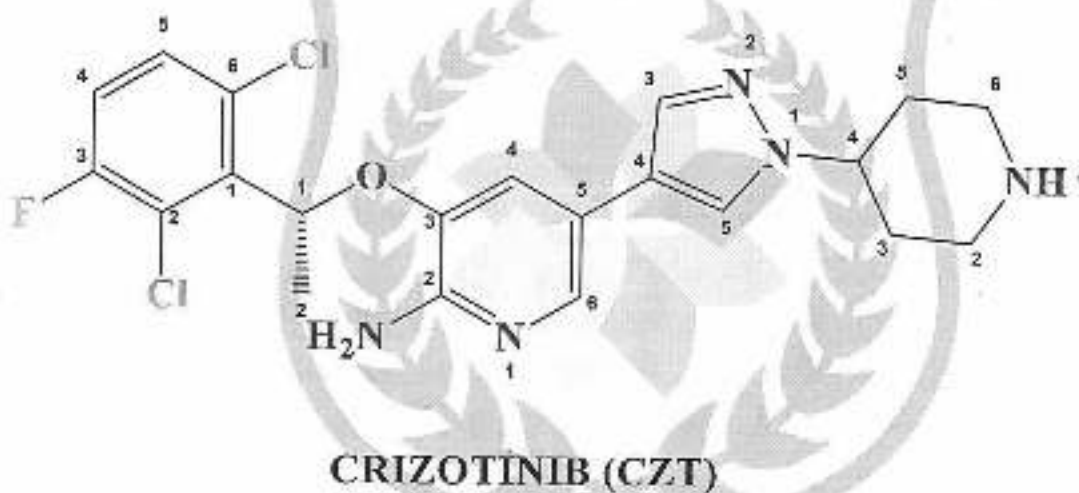
Available literature on this subject reveal that the electron donating properties of CZT & its Charge Transfer (CT) reactions have not been much investigated so far.

These findings about CZT prompted us to investigate the CT reaction of CZT with 2,6-dibromoquinone-4-chloroimide (DBQ) as π - acceptor.

The CT complexes are identified to take part in many chemical reactions like addition, substitution, condensation (Subramanian, 2008) etc. Electron donor-acceptor CT interaction is also important in the field of drug receptor binding mechanism (Shirish Kumar, 2017), as well as in many biological fields. In view of this, CT reactions of certain π - acceptors have been successfully utilized in pharmaceutical analysis. The CT complexes (CTCs) of organic species are strenuously studied because of their special type of interaction which is accompanied by transfer of electron from donor to acceptor. Also, protonation of donor from acidic receptors are generally rout for the formation of the ion pair adducts. The π -acceptors have numerous applications as analytical reagents. They have been used for the spectrophotometric determination of many drugs in pharmaceutical formulations.

Considering all these aspects, it is proposed to investigate the charge transfer complex (CTC) of CZT with DBQ.

Structures of CZT and DBQ



2, 6-dibromoquinone-4-chloroimide (DBQ)

1.1 Chemicals

All the chemicals were used of analytical grade. DBQ (TCL, India, purity > 98%) and Ethanol, (Finar, India, purity > 99.9%) were used without further purification. The CZT was procured from Meruvax pharmaceuticals, Hyderabad. The purity of CZT as specified by the makers was >99%, which was confirmed by its melting temperature. The CZT was used as received without any further purification.

1.2 Synthesis of CZT-DBQ CT complex

The CZT and DBQ of 1 mmol each (1:1) were accurately weighed on Dhona 160 D analytical balance and transferred them into porcelain mortar and truncated the mixture scrupulously in the presence of a few drops of methylene chloride solvent. Then dried the obtained reaction mixture by continuous suction and transferred them into a dry beaker. The beaker was stored overnight in a desiccator filled with activated anhydrous calcium chloride, then transferred the dried solid brown coloured powder containing CZT-DBQ CTC into a clean vial. The vial was capped well to protect from moist air.

2. Instruments

The electronic absorption spectra of the CZT, DBQ and resulting CTC were recorded over a wavelength range of 200–800 nm using an UV-2600 Shimadzu UV-VIS Spectrophotometer. The instrument was equipped with a quartz cell with a 1.0 cm path length. The FT-IR spectra within the range of 4000–250 cm^{-1} for the solid powder of free CZT and its CT Complex with DBQ were recorded on a Shimadzu FT-IR Prestige-21 spectrophotometer with 40 scans at 4 cm^{-1} resolution.

3. Spectrophotometric Study

3.1 Preparation of Experimental Solutions

Stock solutions of CZT (donor) and DBQ (acceptor) at a concentration of $5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ were freshly prepared before each series of measurement by dissolving accurately weighed amounts in an appropriate volume of ethanol. The stock solutions of donor and acceptor were protected from light. The solutions for spectrophotometric measurements were freshly prepared by mixing appropriate volumes of donor and acceptor stock solutions immediately before recording the spectra.

3.2 Experimental Measurements

To determine the stoichiometry of the CZT (donor) and DBQ (acceptor) interactions, various molar ratios were examined by applying Job's method of continuous variations and photometric titration measurements. These titrations monitored the detectable CT bands during the reactions of DBQ with donor. Briefly, 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 mL of a standard solution ($5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) of the donor in ethanol solvent was added to 1.00 mL of the acceptor at $5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, dissolved in the same solvent. The final volume of the mixture was made to 5 mL. The concentration of the acceptor (C_a^0) was maintained constant at $5.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, while the concentration of the donor (C_d^0) varied from $0.25 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ to $4.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ to produce solutions with a (donor: acceptor) molar ratio that varied from 1:4 to 4:1, for the complex. The absorbance of complex was plotted against the volume of the added acceptor.

3.3 Calculations – Background

The physical spectroscopic data of the resulted CT complexes were computed, the association constant (K) and the molar extinction coefficient (ϵ_{max}) were determined spectrophotometrically using the 1:1 Benesi-Hildebrand equation.

Table 1: Benesi-Hildebrand data of the CZT-DBQ CT complex

| $C_a^0 \times 10^{-4}$ | $C_d^0 \times 10^{-4}$ | Absorbance | $C_a^0 C_d^0 / A \times 10^{-7}$ | $(C_a^0 + C_d^0) \times 10^{-4}$ |
|------------------------|------------------------|------------|----------------------------------|----------------------------------|
| 0.25 | 5 | 0.632 | 0.197 | 5.25 |
| 0.5 | 5 | 0.650 | 0.384 | 5.5 |
| 0.75 | 5 | 0.666 | 0.563 | 5.75 |
| 1.0 | 5 | 0.683 | 0.732 | 6.0 |
| 1.5 | 5 | 0.718 | 1.044 | 6.5 |
| 2.0 | 5 | 0.751 | 1.331 | 7.0 |
| 2.5 | 5 | 0.769 | 1.625 | 7.5 |
| 3.0 | 5 | 0.783 | 1.915 | 8.0 |
| 3.5 | 5 | 0.797 | 2.195 | 8.5 |
| 4.0 | 5 | 0.816 | 2.450 | 9.0 |

Benesi-Hildebrand (1:1) equation

$$(C_a^0 C_d^0) / A = 1/K\epsilon + (C_a^0 + C_d^0) / \epsilon$$

Where, C_a^0 and C_d^0 are the initial concentrations of the acceptor and donor, respectively, and A is the absorbance of the CT band. By plotting the $(C_a^0 C_d^0) / A$ values for the 1:1 CT complex as a function of the corresponding $(C_a^0 + C_d^0)$ values, a straight line is obtained with a slope of $1/\epsilon$ and an intercept at $1/K\epsilon$.

4. Results and discussion

4.1 UV-Vis spectra

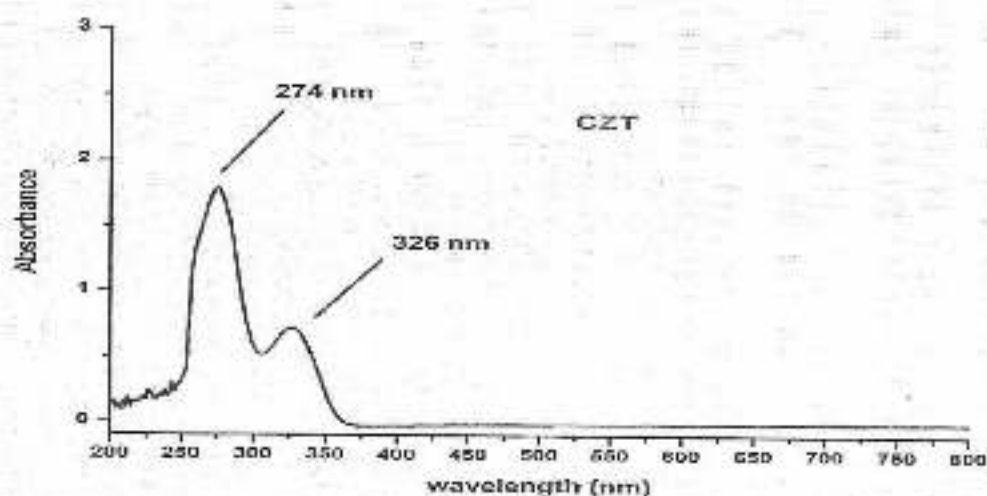


Figure 1. UV-Vis spectra of CZT ($5 \times 10^{-3} M$)

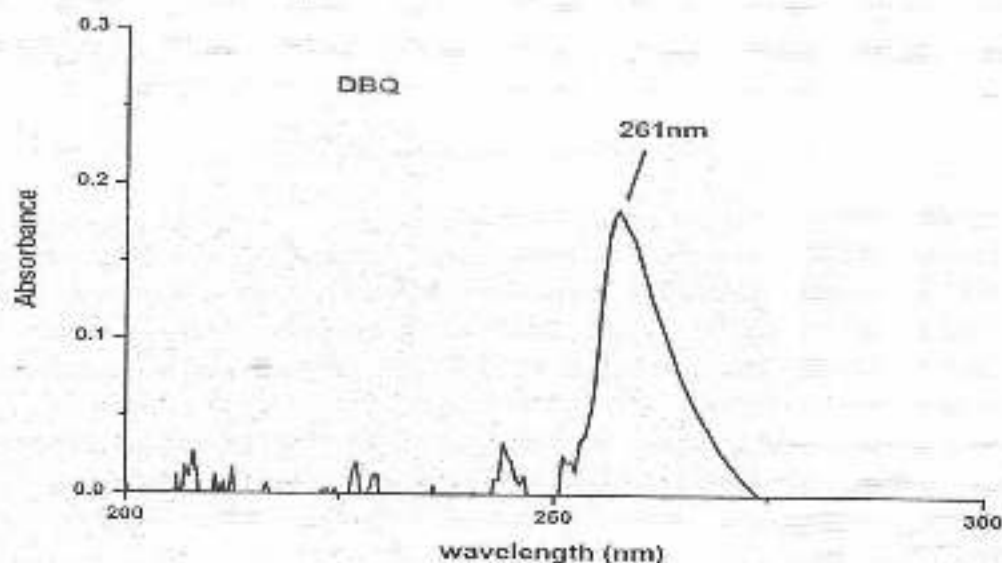


Figure 2. UV-Vis spectra of DBQ (5×10^{-3} M)

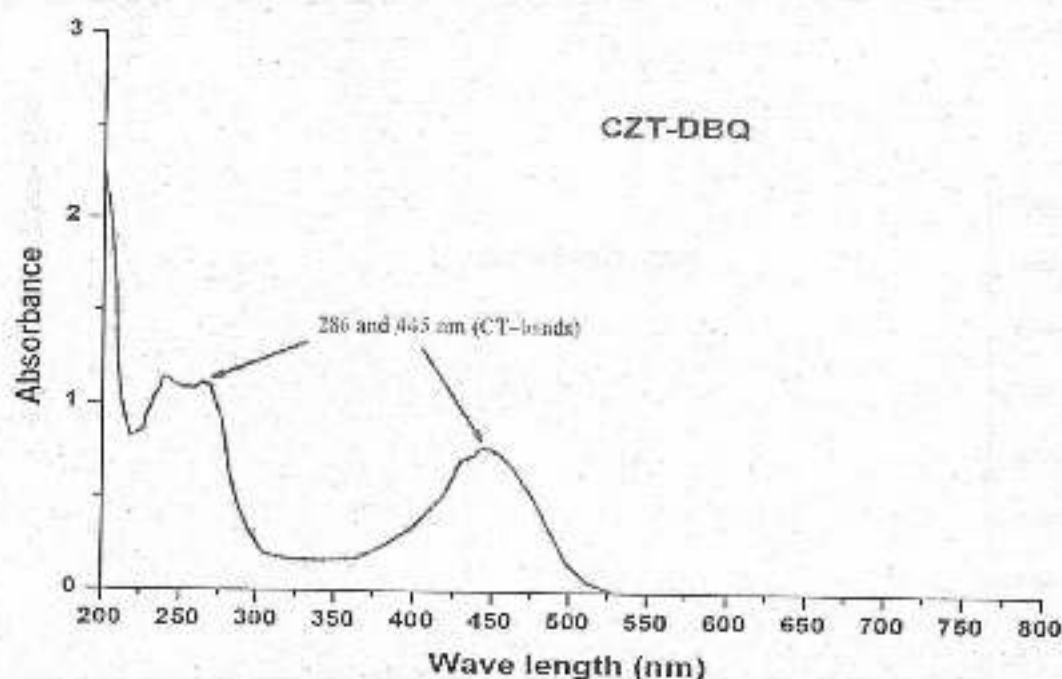


Figure 3. UV-Vis spectra of CZT-DBQ (5×10^{-3} M)

The UV-Vis spectra of CZT (donor) display two absorption bands at $\lambda = 274$ nm and 326 nm and DBQ (acceptor) display one absorption band at 261 nm in ethanol solvent (Fig.1 & 2 respectively). While, UV-Vis spectra of the CZT- DBQ CTC in the same solvent (Fig.3) display two absorption bands at $\lambda = 286$ nm and 445 nm. The UV-Vis spectra of CZT and DBQ shows no absorption bands in this spectral region. The absorption bands which appeared at 286 and 445 nm for the CTC were presumably due to the interaction of CZT (donor) with DBQ (acceptor) and are indicative of the formation of a CT complex. This observation suggests the CT from CZT (donor) to the DBQ (acceptor), which is well supported by the FT-IR and spectroscopy. The band at $\lambda = 286$ nm was selected for the further spectrophotometric study because it has highest absorption intensity. Polar solvent such as ethanol has been chosen as the solvent to promote the complete transfer of electron from CZT (donor) to the DBQ (acceptor).

4.2 Conductance measurements of freshly prepared experimental solutions

Conductimetry has often been employed to study the interactions of CT complexes. In the present study, the conductivity measurements of CZT (donor) and its synthesized CT complexes with DBQ were performed in ethanol solvent at 5×10^{-3} M using Systronics 304 conductivity meter. The conductance values of free donor was found to be $8.5 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ and for free acceptor DBQ was found to be $23 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ while, the conductance values of CZT-DBQ complex was found to be $98 \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$ respectively, this result suggest that the resulted complex have electrolytic behaviour. This data reveals the formation of dative $D^+ \cdot A^-$ complex between CZT (donor) and DBQ (acceptor) under the acid-base theory. The increase in conductivity was observed with elapse of time, may be due to the fact that the CT complex formed between donor and acceptor might have undergone dissociation into ionic intermediate in solvent of sufficient high dielectric constant give rise to appreciable conductivity.

4.3. Effect of reaction time

It is observed that as the time increases absorbance values increase, which suggest the stability of the CZT-DBQ complex.

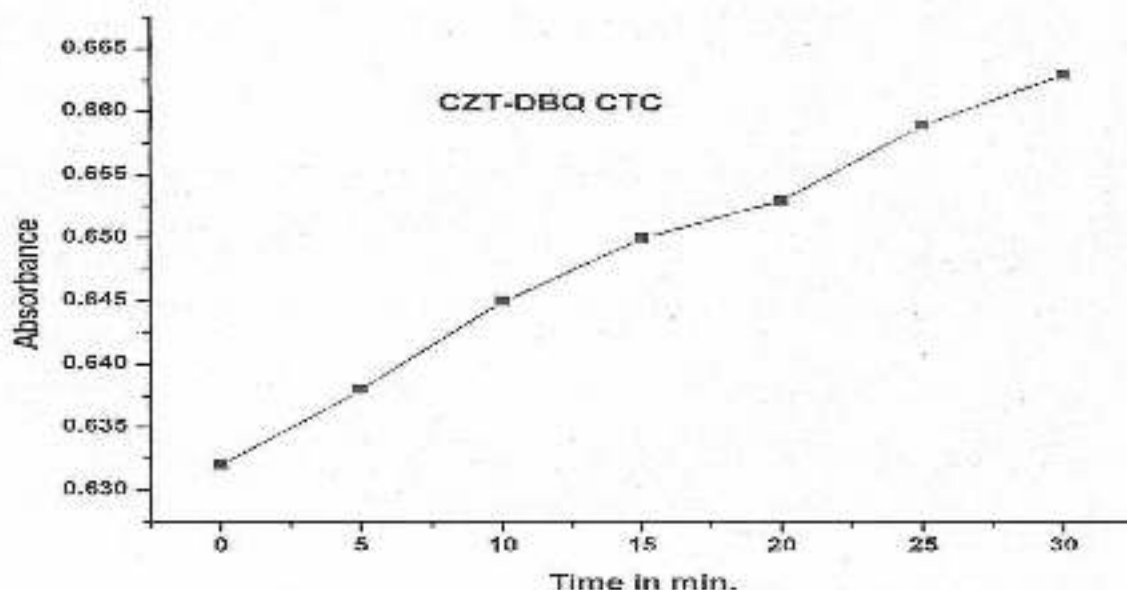


Figure 4. Effect of time on the stability of the CZT-DBQ (5×10^{-3} M) in ethanol at 286nm

4.4. Stoichiometry of the interaction

The stoichiometry of the formed CZT-DBQ complex was determined by applying Job's method of continuous variations (Fig.5.), the symmetrical curves with a maximum at 0.5 mole fraction indicated the formation of 1:1 complex (Fig.5.). The spectrophotometric titration measurements were also performed for the determination of stoichiometry of the formed CT complex (Fig.6.). The UV-Vis spectra of the CZT-DBQ complex was recorded with varying concentrations of acceptor, while, concentration of donor is kept constant. The stoichiometry of the complex was determined graphically by plotting the absorbance as a function of the volume of donor (in mL), where two straight lines are produced intercepting at 1:1 ratio for complex. Representative spectrophotometric titration plot based on the characterized absorption bands are shown in Fig. 6. The results show the good interaction between DBQ acceptor and CZT donor considered in the study.

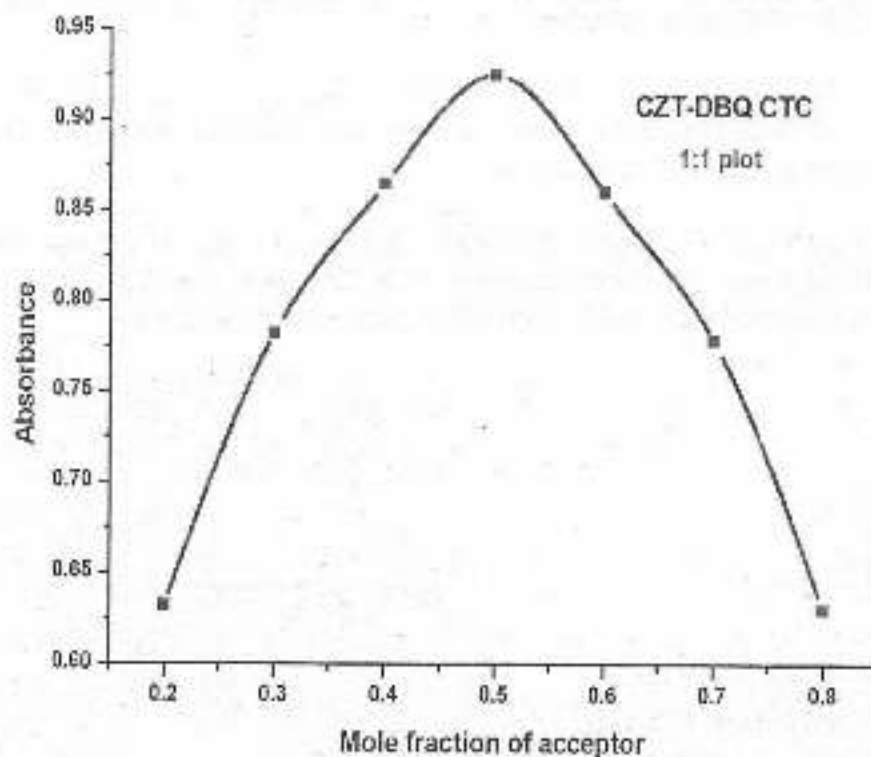


Figure 5. Jobs plot of the CZT-DBQ CTC (5×10^{-4} M)

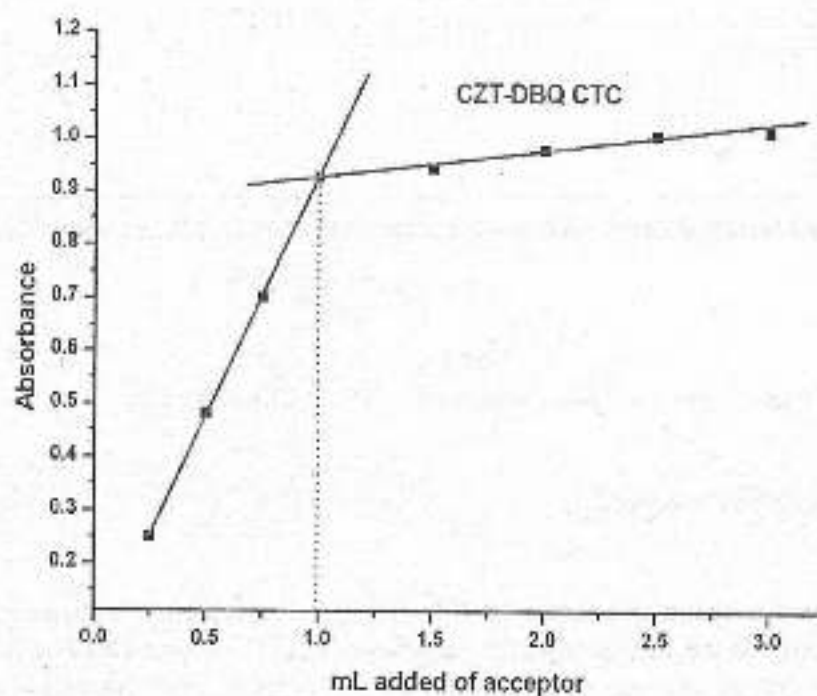


Figure 6. Spectrophotometric curve of the CZT-DBQ CTC (5×10^{-4} M)

4.5. Association constant of CZT-DBQ CT complex

Representative Benesi-Hildebrand plot is shown in (Fig.7) and the values of both K and ϵ are thus determined and are compiled in (Table-2) along with the other spectroscopic parameters data. The high K value indicates a strong interaction between the CZT and DBQ.

High association constant value which was obtained by Benesi-Hildebrand 1:1 equation, suggest the good binding affinity between π -donor CZT and acceptor DBQ. The high association constant values are common in π -electron donors, where the intermolecular overlap may be considerable.

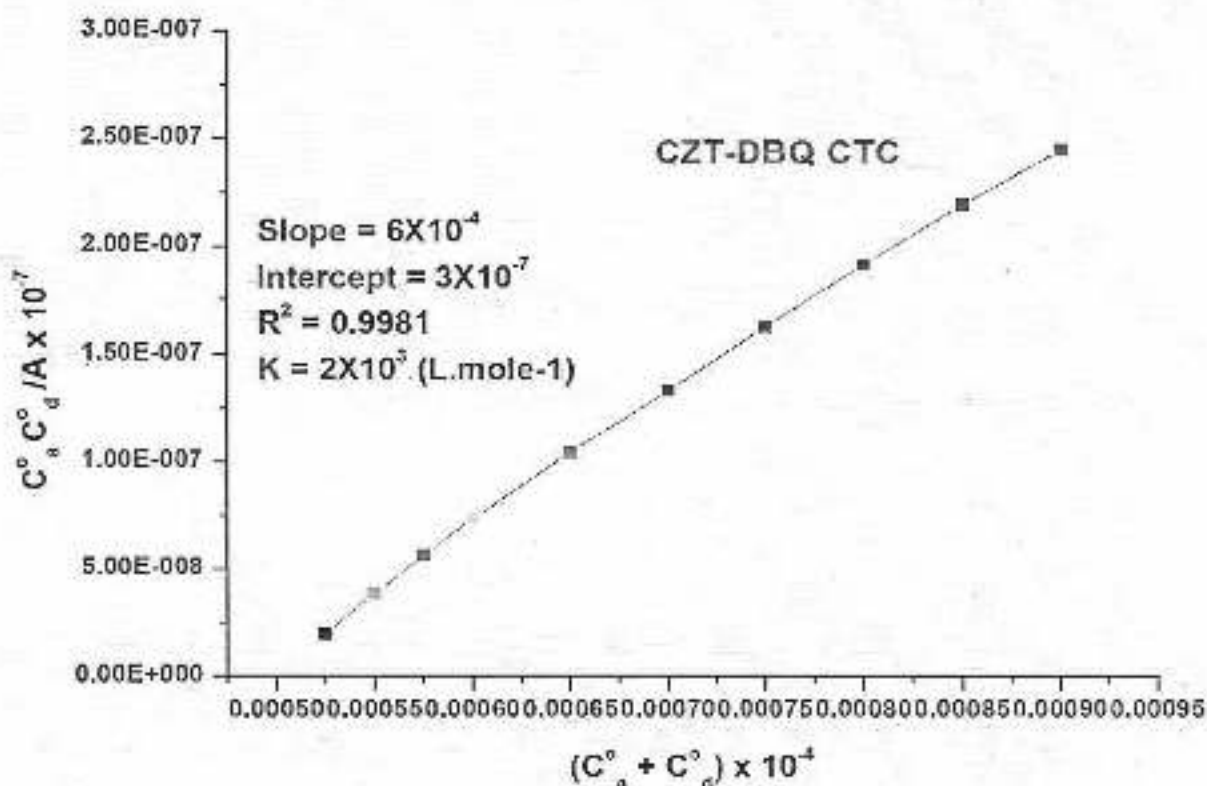


Figure 7. The 1:1 Benesi-Hildebrand plot for CZT-DBQ CTC

5. Calculation of spectroscopic Parameters

In order to support the formation and nature of CZT-DBQ CT complex, spectroscopic parameters like, Ionization potential (IP), Energy of the charge transfer complexes (E_{CT}), Resonance Energy (R_N), Dissociation energy (W) and Standard free energy changes (ΔG°) of the CT Complexes were calculated.

5.1. Ionization Potential (IP)

The ionization potential (IP) of the highest filled molecular orbital of the donor was estimated from CT energies of its complexes with the acceptor making use of the following empirical Aloisi and Pignataro equation (Aloisi, 1972). The calculated IP values for molecular orbital participating in CT interaction of the donors are compiled in the Table -2.

$$h\nu_{CT} = a IP^n + b$$

Where, $a = 0.87$ and $b = -3.6$, $h\nu_{CT}$ is the energy of CT complex. The electron donating power of a donor molecule is measured by its ionization potential which is the energy required to remove an electron from the highest occupied molecular orbital.

5.2. Energy of the charge transfer complexes (E_{CT})

The energy (E_{CT}) of the CT Complexes were calculated using the following equation (Rathone, 1997) and the values are compiled in the **Table -2**.

$$E_{CT} = (h\nu_{CT}) = 1243.667 / \lambda_{CT} \text{ (nm)}$$

Where, λ_{CT} is the wavelength of the complexation band.

5.3. Resonance Energy (R_N)

Resonance Energy (R_N) of CT Complexes were determined by the following theoretically derived equation by Briegleb and Czekalla (Briegleb, 1960) and the values were compiled in the **Table -2**.

$$\epsilon_{max} = 7.7 \times 10^4 / [h\nu_{CT} / (R_N) - 3.5]$$

Where, ϵ_{max} is the molar absorptivity of the CTC at maximum charge transfer band, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state, which is obviously a contributing factor to the stability constant of the complex.

5.4. Dissociation energy (W)

Further evidence of the nature of CT interaction in the present CT complexes is the calculation of the dissociation energy (W) of the CT excited state of the complex. The dissociation energy (W) of the formed CT complex was calculated from the corresponding CT energy (E_{CT}), ionization potential of the donor (IP) and electron affinity of the acceptor (EA) using the following relationship (McConnel, 1953) and the calculated values of W are compiled in (**Table -2**.)

$$h\nu_{CT} = IP - EA - W$$

Where, $h\nu_{CT}$ is the energy of CT complex, IP is the ionization potential of the donor and EA is the electron affinity of the acceptor.

5.5. Standard free energy changes (ΔG^0)

To add more conformation for the nature of CT interaction, standard free energy change values (ΔG^0) were calculated and are compiled in **Table-2**, the higher negative values suggest that the CT complexes formed between β -AB and I_2 are exothermic. Generally, the values of ΔG^0 become more negative as the value of K_{CT} increases where the CT interactions between the donor and acceptor become strong. Thus, the components (donor and acceptor) are subjected to more physical strain or loss of degree of freedom and the values of ΔG^0 become more negative (Person, 1962).

The standard free energy changes of complexation (ΔG^0) were calculated from the association constant values by the following equation,

$$\Delta G^0 = -RT \ln K$$

Where, ΔG^0 is the free energy change of the CT Complexes (KJmol^{-1}), R is the gas constant ($1.987 \text{ calmol}^{-1}\text{K}^{-1}$), T is the temperature in Kelvin and K is the association constant of the CT Complexes at room temperature.

Table - 2. Spectroscopic parameters of the CZT-DBQ CT Complex

| | CZT-DBQ |
|---|----------------------|
| Wavelength: λ_{max} (nm) | 286 |
| Extinction coefficient: ϵ_{max} ($\text{L mole}^{-1} \text{cm}^{-1}$) | 1.666×10^3 |
| Association constant: K (L mole^{-1}) | 2×10^3 |
| Energy: $h\nu_{\text{CT}}$ (eV) | 4.348 |
| Ionization Potential: IP (eV) | 9.136 |
| Resonance Energy: R_N (eV) | 1.242 |
| Dissociation energy: W (eV) | 2.301 |
| Gibbs free energy: ΔG^0 (KJmol^{-1}) | -1.231×10^3 |

The calculated spectroscopic parameters values like Energy of the CT complex ($h\nu_{\text{CT}}$), Ionization Potential (IP), Resonance Energy (R_N), Dissociation energy (W) and Standard Gibbs free energy (ΔG^0) suggests that the investigated CZT-DBQ complex was reasonably strong and stable under the studied conditions.

6. Spectral Characterization

6.1. FT-IR spectroscopy

The Infrared spectra of the CZT (donor) and DBQ (acceptor) and their corresponding CTC CZT-DBQ are shown in (Fig. 8,9 &10). Full assignments concerning all the infrared bands were located in the spectra are listed in Table 3. A comparison of the relevant IR spectral bands of the CZT (donor) and DBQ (acceptor) and their corresponding CTC CZT-DBQ clearly indicated that the characteristic bands of CZT show some shift in the frequencies (Table 3), as well as some change in their band intensities. This could be attributed to the expected symmetry and electronic structure changes upon the formation of the CTC.

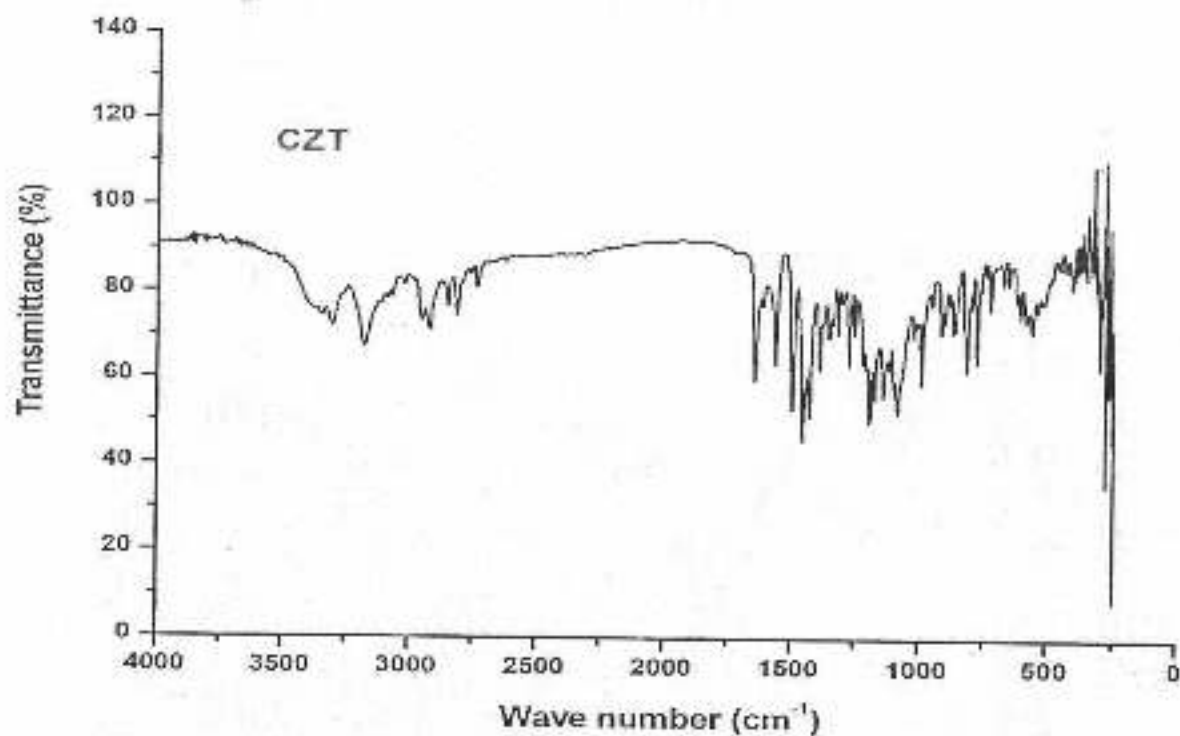


Figure 8. FT-IR spectra of CZT (donor)

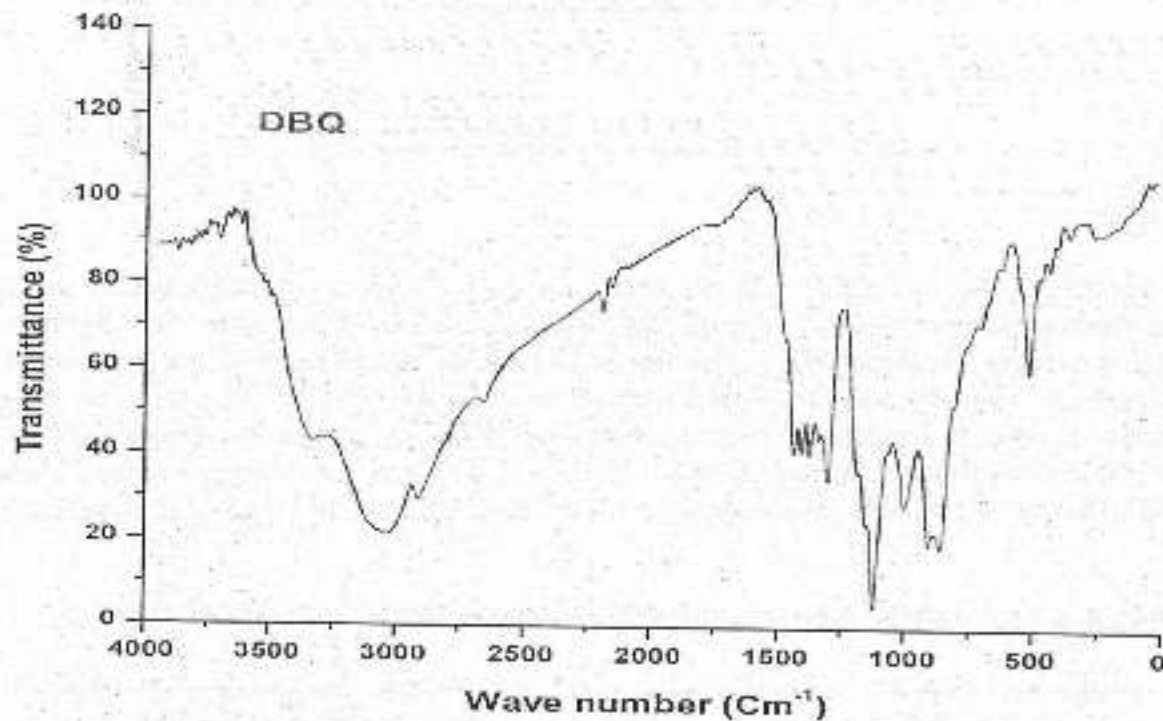


Figure 9. FT-IR spectra of DBQ (acceptor)

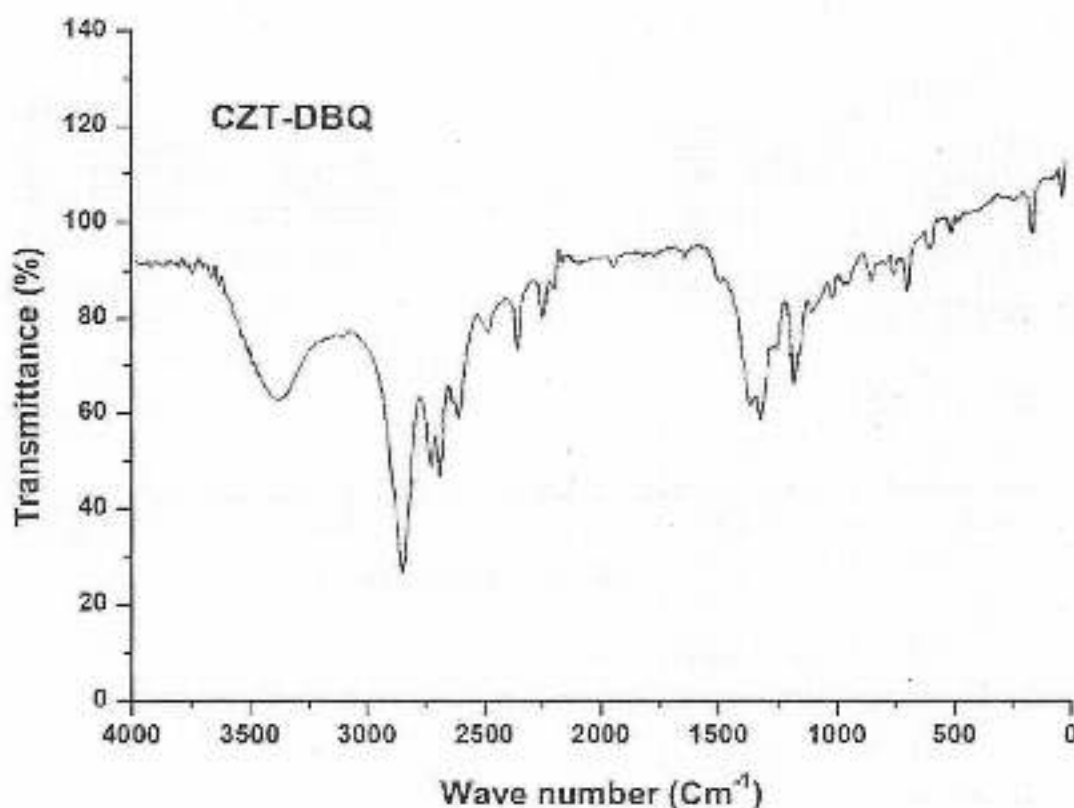


Figure 10. FT-IR spectra of CZT-DBQ (CTC)

To summarize,

The IR spectra of the CZT-DBQ CTC is characterized by a group of bands within the 2415–2805 cm^{-1} range which are not present in the spectra of the free reactants. These bands are due to the stretching mode of a hydrogen bonding (Bellamy, 1975). This fact resulted from the hydrogen bond interaction through the proton ($-\text{NH}$) of CZT (donor) and the oxygen atom of the carbonyl group of acceptor. This is further strongly supported by the clearly appearance of characteristic peak of the $\nu_{\text{O-H}}$ at the wavelength 3422 cm^{-1} for CZT-DBQ CTC. The $\nu_{\text{C=O}}$ group appearing at 1684, 1656 and 1630 cm^{-1} are disappeared and shifted to 1622 cm^{-1} in CZT-DBQ CTC, this led us to predict that the carbonyl group is involved in the complexation.

Table-3. Infrared absorption frequencies (cm^{-1}) and tentative assignments of DBQ and CZT-DBQ

| DBQ | CZT-DBQ | Assignments |
|------------|------------|---|
| 3418 s, br | 3422 s, br | ν (O-H); H_2O of KBr |
| | | ν (N-H) |
| 3140 s, br | 2951 vs | $\nu_{\text{as}}(\text{C-H}) + \nu_{\text{as}}(\text{C-H})$ |
| 3030 w | 2842 s | |
| | 2805 s | |
| | 2735 ms | |
| | 2623 ms | Hydrogen bonding |

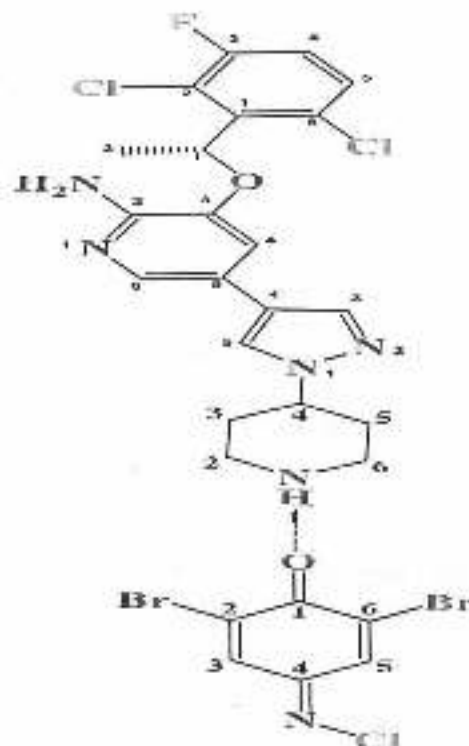
| | | |
|---------|---------|-----------------------------|
| | 2514 s | |
| | 2415 ms | |
| 1684 w | 1741 vw | ν (C=O) |
| 1656 w | | |
| 1630 w | | |
| | 1622 mw | |
| 1595 vw | 1583 ms | ν (C=C); |
| 1563 vs | 1452 s | C-H deformation |
| 1399 vs | 1391 w | (C=C) + ν (C-N) |
| 1292 s | 1313 w | CH, in-plane bend |
| 1204 w | 1256 w | |
| 1162 w | 1163 ms | |
| | 1079 w | |
| | 1029 ms | |
| 846 s | 941 ms | rock; NH |
| 778 vw | 860 w | CH-deformation |
| 710 w | 830 vw | ν (C-Cl) + ν (C-Br) |
| 623 br | 621 vw | Skeletal vibration |
| | 552 s | CH bend |
| 421 vw | 436 ms | CH out of plane bend |

s - Strong, w = weak, m - medium, sh = shoulder, v = very, br = broad.

The UV-Vis and FT-IR data obtained for CZT (donor) and its CTC with DBQ (acceptor) from spectrophotometric and spectroscopic studies suggests that the transfer of charge significantly took place from the piperidine moiety of CZT (donor) to carbonyl moiety of DBQ (acceptor).

Based upon this valuable information obtained from spectrophotometric and spectroscopic studies, the following plausible interaction (scheme-1) between the CZT (donor) and DBQ (acceptor) has been proposed:

Scheme-1



7. Conclusion

The CT reaction of CZT as electron donor and DBQ as electron acceptor has been studied for the first time. The study includes the use of spectrophotometry in the comprehensive manner. A single solvent ethyl alcohol has been used to avoid solvent interactions with CZT (donor) and DBQ (acceptor). The FT-IR is used to characterize the formed complex between CZT and DBQ. Spectral data acquired from spectral analysis has suggested that CZT acted as an electron donor when interacted with DBQ (π - acceptor). Hence, the biological activity of CZT may be due its donating ability as is evident from the association constant (K) and standard Gibbs free energy (ΔG°) values. The spectroscopic parameters like Ionization Potential (IP), Energy of the complex, E_{CT} (eV), and Resonance Energy (R_N) values also support the strong interaction of CZT with DBQ. Accordingly, plausible interaction between CZT and DBQ has been proposed.

Therefore, the mechanism for the interaction of the studied CZT is useful in understanding the binding of this bioactive molecule under real pharmacokinetic conditions, which enables medical fraternity to pay attention towards the importance of this novel drug in our country, which may potentially contribute to the knowledge in the medicinal field of our country.

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