

Electron-transfer complexation of morpholine donor molecule with some π – acceptors: Synthesis and spectroscopic characterizations

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Morpholine is an interesting moiety that used widely in several organic syntheses. The intermolecular charge-transfer (CT) complexity associated between morpholine (Morp) donor with (monoiodobromide “IBr”, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone “DDQ”, 2,6-dichloroquinone-4-chloroimide “DCQ” and 2,6-dibromoquinone-4-chloroimide “DBQ”) π -acceptors have been spectrophotometrically investigated in CHCl_3 and/or MeOH solvents. The structures of the intermolecular charge-transfer (CT) were elucidated by spectroscopic methods like, infrared spectroscopy. Also, different analyses techniques such as UV-Vis and elemental analyses were performed to characterize the four morpholine [(Morp)(IBr)], [(Morp)(DDQ)], [(Morp)(DCQ)] and [(Morp)(DBQ)] CT-complexes which reveals that the stoichiometry of the reactions is 1:1. The modified Benesi-Hildebrand equation was utilized to determine the physical spectroscopic parameters such as association constant (K) and the molar extinction coefficient (ϵ).

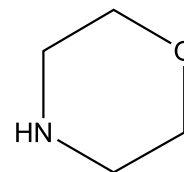
Keywords: Morpholine, π -acceptor, CT complex, photometric titration, infrared, Benesi-Hildebrand.

INTRODUCTION

Morpholine (Scheme 1) is an interesting moiety that used widely in several organic synthesis, also as a building block in the synthesis of antibiotic linezolid, and the anticancer agent¹⁻³. The stable charge transfer complexes associated between some organic cyclic compounds as donor e.g. polysulpher, polyamines and oxygen-nitrogen crown ethers with iodine acceptor were discussed spectrophotometrically⁴⁻⁹.

The chemistry of donor-acceptor (CT) complexation has played a vital role in molecular systems and has turned into a center of attraction for various researchers¹⁰⁻¹⁴. This topic of interactions has gained great attention and considerable interest from chemists and pharmacists as well as biologists. The CT complexations have a broad range of applications not only in chemical and biological fields, but also in many technical and industrial ones. For example, they have been used in optical, electrical, solar energy storage, and magnetic conductivity applications, in studying pharmaceutical receptor binding mechanisms, and in biological applications¹⁵⁻¹⁸. Furthermore, CT complexations were used to obtain and develop simple, efficient, rapid and reliable methods for the determination, detection, or quantitative estimations of drugs in pure and pharmaceutical forms^{19, 20}. The thermal stabilities, crystallographic properties, and effects of several parameters, such as temperature, solvents, reagent concentration, and other parameters, on the properties and characteristics of the obtained CT products have also been intensively investigated and discussed²¹⁻²³.

In continuity of our experimental work in the trend of charge-transfer complexes²⁴⁻³⁰, herein the present article included the spectroscopic investigation of charge-transfer complexes of Morp with different acceptors (σ and π). The physical spectroscopic parameters (association constants “K”, molar extinction coefficient “ ϵ ”, oscillator strength “ f ”) were calculated based on the spectrophotometric analyses. The isolated solid complexes were prepared and well characterized by elemental analysis, infrared, and UV-Vis electronic spectra.



Scheme 1. Structure of Morpholine (I)

EXPERIMENTAL

Chemical materials

Chemicals used throughout this article were of pure grade. Morpholine was received from Merck Co. and the acceptors were received from Aldrich Co. The standard solutions of both Morp or of acceptors were freshly prepared in chloroform and methanol solvents.

2-2-Synthesis of morpholine moniodobromide CT complex

This dark brown solid charge transfer complex has a general formula, [(Morp)(IBr)]. It was synthesized by a mixing of 1 mmol of Morp in 10 mL CHCl_3 with 1 mmol of IBr in the same solvent with stirring for 15

min at room temperature. The mixture solution was allowed to evaporate slowly at room temperature. The solid complex was formed, washed three times with little amounts of chloroform and dried under vacuum over anhydrous CaCl_2 .

2-3-Synthesis of morpholine p-acceptors (DDQ, DCQ and DBQ) CT complexes

The brown solid charge-transfer complexes of [(Morp)(DDQ)], [(Morp)(DCQ)] and [(Morp)(DBQ)] were synthesized by mixing 1 mmol of Morp dissolved in 10 mL of CHCl_3 with 1 mmol of each p-acceptors (DDQ, DCQ and DBQ) in 10 mL CHCl_3 solvent with stirring for 15 min at room temperature. The solid precipitate associated in each case was filtered and washed three times with few drops of CHCl_3 and dried under *vacuo* over anhydrous CaCl_2 .

2-4-Instrumentals and physical measurements

Electronic spectra were scanned using a Jenway 6405 Spectrophotometer within 200–800 nm region. In case of photometric titration measurements the concentrations of Morp donor was kept fixed at 5.0×10^{-4} M, while the concentration of acceptors were ranged from 0.25×10^{-4} to 4×10^{-4} M, so the molar ratio between donor: acceptor is 1:0.25 to 1:4.00. Infrared measurements were performed on a Bruker FT-IR spectrophotometer ($400\text{--}4000 \text{ cm}^{-1}$).

RESULTS AND DISCUSSION

The microanalytical data of the synthesized solid CT complexes of morpholine with IBr, DDQ, DCQ and DBQ acceptors along with their physical properties are summarized in Table 1.

UV-Vis electronic spectra of chemical reactions between (IBr, DDQ, DCQ and DBQ) acceptors and Morp donor in solvents CHCl_3 or CH_3OH (Figs. 1 A–D) displayed distinguish charge transfer bands at 263, 373 nm for Morp-IBr, (401, 553 nm for Morp-DDQ, 320 nm for Morp-DCQ and 300, 396 nm for Morp-DBQ electron transfer systems, these CT bands don't belong to any of both acceptors and Morp. Photometric titrations between Morp donor and respected p-acceptors were operated at selected maximum CT bands mentioned above, when the

concentration of Morp donor was prepared at 0.50×10^{-4} M, while the concentration of the (IBr and DDQ) acceptors was prepared within the range of 0.125×10^{-4} – 1.50×10^{-4} M. In case of DCQ and DBQ acceptors, the concentration of Morp donor is prepared with 0.250×10^{-4} M, while the acceptors concentration was ranged between 0.0625×10^{-4} – 0.7500×10^{-4} M. The 1:1 stoichiometric ratio of CT complex systems (Figs. 2 A–D) was performed using well known method³¹. The association constant “K” and molar extinction coefficients “e” of the CT complex systems were calculated based on the 1:1 modified Benesi-Hildebrand equation (1)³².

$$\frac{C_a^o C_d^o l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^o + C_d^o}{\varepsilon} \quad (1)$$

Where C_a^o and C_d^o are the initial concentrations of the acceptors and Morp donor, respectively, and “A” term is the absorbance of the distinguish CT bands. Straight lines Figs. 3 A–D were obtained by drawing the $(C_a^o C_d^o / A)$ term against

$(C_a^o + C_d^o)$ term. From these straight lines the slope (1/e) and intercept (1/Ke) for the CT reaction mixtures of Morp with p-acceptors in CHCl_3 or CH_3OH were calculated. The physical spectroscopic data (K, e, oscillator strength (f)³³ and transition dipole moment (μ) of the synthesized charge transfer complexes [(Morp)(IBr)], [(Morp)(DDQ)], [(Morp)(DCQ)] and [(Morp)(DBQ)] were calculated and summarized in Table 2³⁴. The charge transfer energy of the $n\text{-}\pi^*$ interaction was calculated as 3.33 eV (IBr), 2.25 eV (DDQ), 3.89 eV (DCQ) and 3.14 eV (DBQ)³⁵. The ionization potential (I_p) of the free donor of the highest filled molecular orbital was calculated from the CT energies of the CT band^{36–38}. Photometric titrations reveal that the stoichiometry of the reaction mixtures is 1:1 which agree with the elemental analysis data of the isolated solid CT-complexes (Table 1).

Infrared spectra of the Morp charge transfer complexes of IBr, DDQ, DCQ and DBQ are illustrated in Figs. 4 A–D and their assignments are listed in Table 3. The outcome data resulted by make a comparison between the infrared of the Morp donor, acceptors (IBr,

Table 1. Elemental analysis and physical data of the synthesized Morp CT complexes

Complexes/ FW	Mwt	C%		H%		N%		Physical data	
		Found	Calc.	Found	Calc.	Found	Calc.	Color	Mp/°C
[(Morp)(IBr)] ($\text{C}_4\text{H}_9\text{NOIBr}$)	293.93	16.11	16.30	2.95	3.06	4.65	4.76	yellow	54
[(Morp)(DDQ)] ($\text{C}_{12}\text{H}_9\text{N}_3\text{Cl}_2\text{O}_3$)	314.13	45.44	45.80	2.74	2.87	13.21	13.40	brown	< 30
[(Morp)(DCQ)] ($\text{C}_{10}\text{H}_{11}\text{N}_2\text{Cl}_3\text{O}_2$)	297.57	40.12	40.30	3.68	3.70	9.35	9.41	brown	< 30
[(Morp)(DBQ)] ($\text{C}_{10}\text{H}_{11}\text{N}_2\text{Br}_2\text{ClO}_2$)	386.49	30.58	31.00	2.80	2.85	7.11	7.24	brown	< 30

Table 2. Physical Spectroscopic data of the Morp CT complexes

Solvent	λ_{max} [nm]	E_{CT} [eV]	K [$\text{l}\cdot\text{mol}^{-1}$]	ε_{max} [$\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$]	f	μ	I_p
IBr	373	3.33	2.16×10^4	1.78×10^4	12.00	30.90	7.44
DDQ	553	2.25	8.34×10^4	1.81×10^4	9.77	33.90	8.51
DCQ	320	3.88	4.76×10^4	3.58×10^4	21.50	38.20	7.83
DBQ	396	3.14	4.25×10^4	2.77×10^4	12.50	32.40	7.31

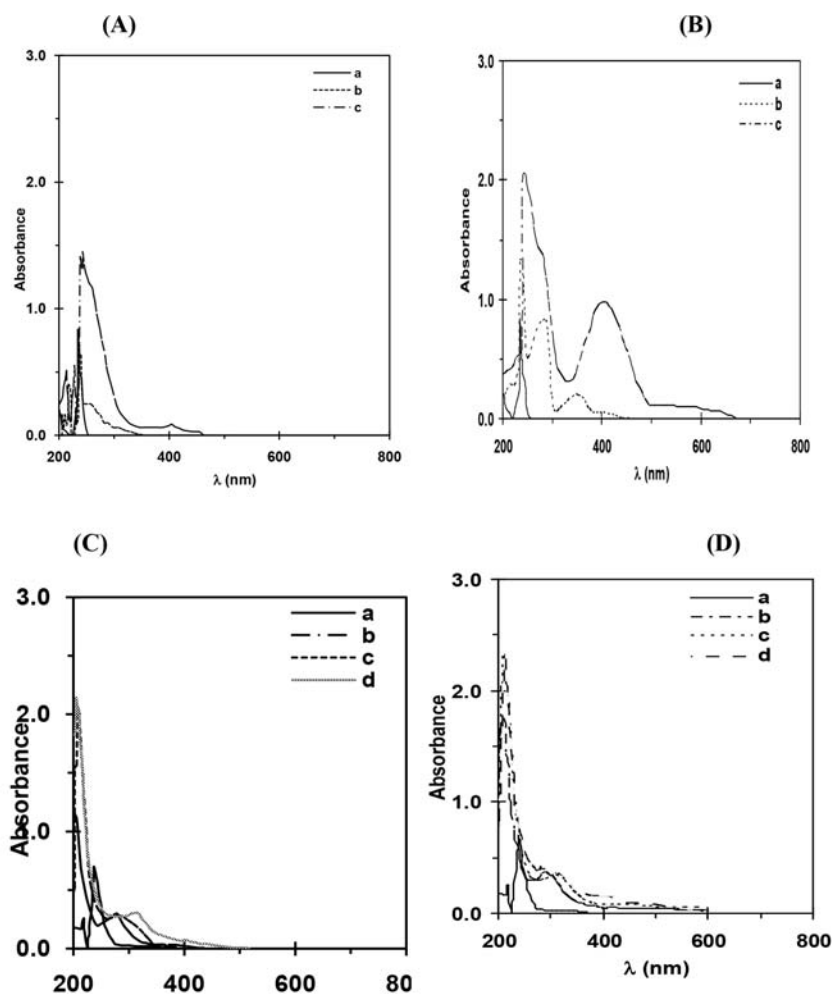


Figure 1. Electronic absorption spectra of (A): Morp/IBr system in CHCl_3 , (B): Morp/DDQ system in CHCl_3 , (C): Morp/DCQ system in CH_3OH and (D): Morp/DBQ system in CH_3OH (a = donor ($1.0 \times 10^{-4}\text{M}$), b = acceptor ($1.0 \times 10^{-4}\text{M}$) and c = CT-complex)

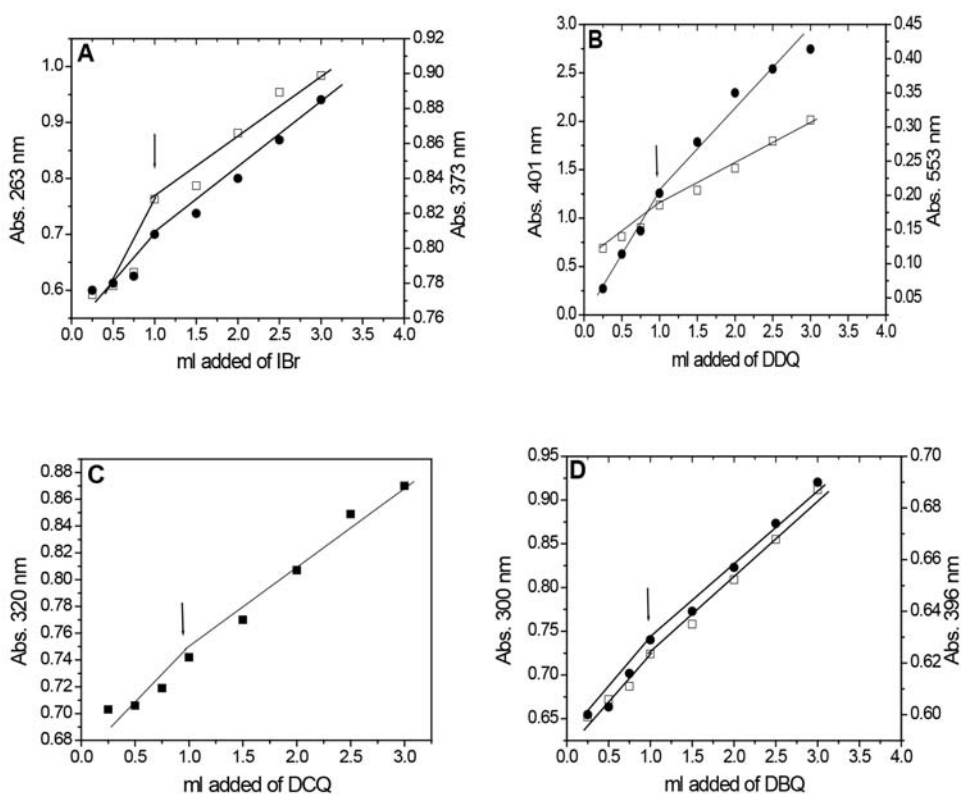


Figure 2. Photometric titration curves for: (A): Morp/IBr system in CHCl_3 at 263 and 373 nm, (B): Morp/DDQ system in CHCl_3 at 401 and 553 nm, (C): Morp/DCQ system in CH_3OH at 320 nm and (D): Morp/DBQ system in CH_3OH at 300 nm and 396 nm

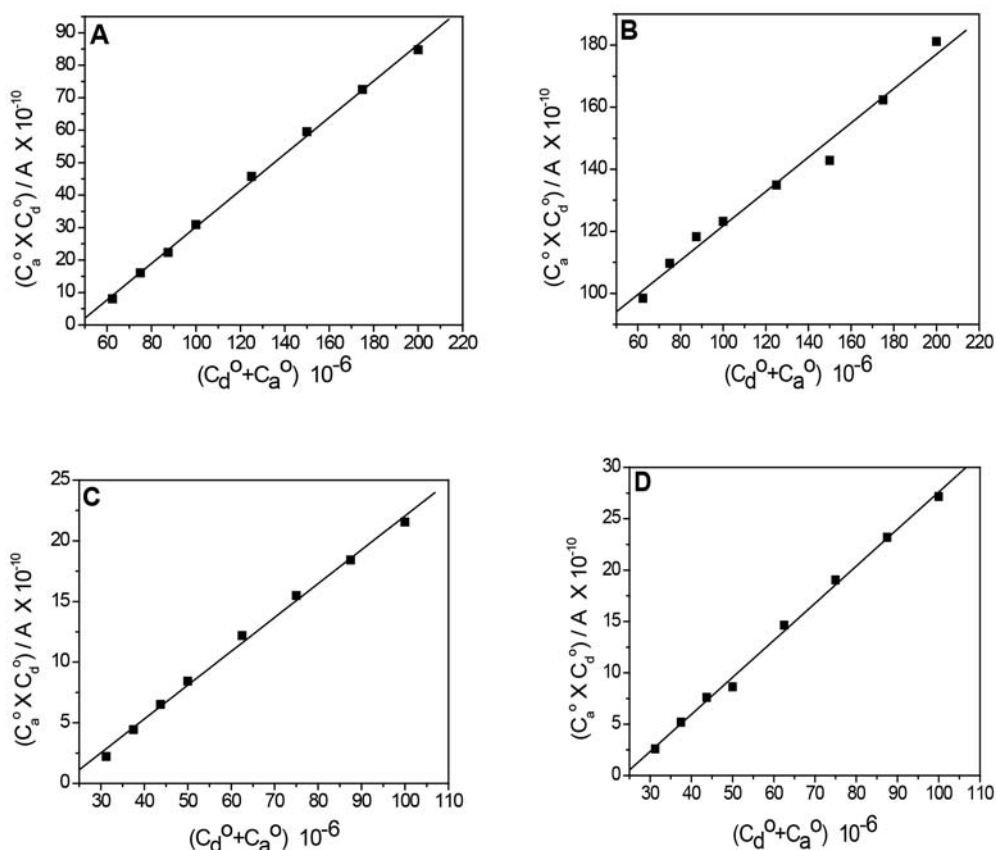


Figure 3. The plot of $(C_d^0 + C_a^0)$ values against $(C_d^0 \cdot C_a^0/A)$ values for: (A): Morp/IBr system in CHCl_3 at 373 nm, (B): Morp/DDQ system in CHCl_3 at 553 nm, (C): Morp/DCQ system in CH_3OH at 320 nm and (D): Morp/DBQ system in CH_3OH at 396 nm

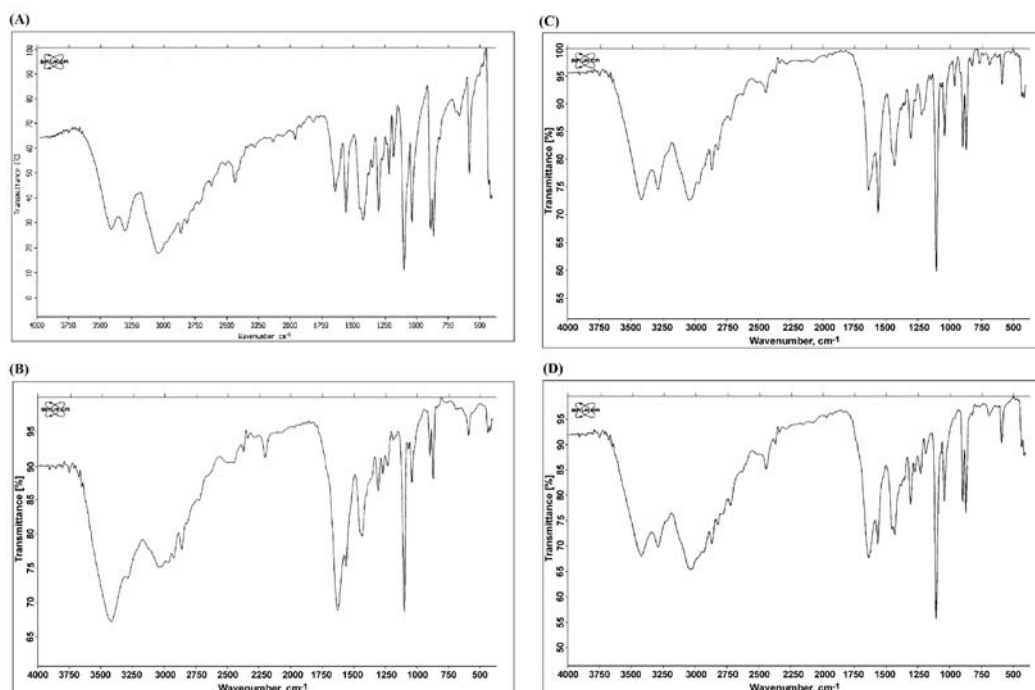


Figure 4. Infrared spectra of (A): [(Morp)(IBr)], (B): [(Morp)(DDQ)], (C): [(Morp)(DCQ)] and (D): [(Morp)(DBQ)] charge transfer complexes

DDQ, DCQ and DBQ) and isolated solid charge transfer complexes can be summarized as follows:

Concerning of [(Morp)(IBr)] complex, the stretching frequency $\nu(\text{N-H})$ of the $-\text{NH}$ Morp donor which was observed at 3424 and 3300 cm^{-1} is shifted to 3416 and 3306 cm^{-1} in case of CT complex. There are frequencies bands presence at 3044, 2863, 2816 and 2723 cm^{-1} due

to $\nu_s(\text{C-H})$ and $\nu_{as}(\text{C-H})$ vibrations. These vibration bands were small shifted to higher wavenumbers with decreasing in the intensities compared with the Morp free donor. The new weak vibration bands observed at the range of 2600–2400 cm^{-1} for the IBr/Morp complex can be assigned to hydrogen bonding³⁹. The vibrations bands of $\delta(\text{N-H})$, $\nu(\text{C-N})$, CNC deformation show clearly

Table 3. Infrared frequencies^(a) (cm⁻¹) and tentative assignments for charge transfer Morp complexes

[(Morp)(acceptor)] CT-complexes				Assignments ^(b)
IBr	DDQ	DCQ	DBQ	
3416 ms 3306 ms	3423 s, br 3307 w	3418 s 3288 s	3418 s 3287 s	$\nu(\text{O-H})$; H ₂ O of KBr $\nu(\text{N-H})$
3044 s, br 2863 w 2816 vw 2723 vw	3037 w, br 2975 vw 2928 w 2864 ms 2750 vw	3042 s, br 2950 vw 2912 vw 2866 ms 2821 vw	3032 s, br 2865 ms 2819 w	$\nu_s(\text{C-H}) + \nu_{as}(\text{C-H})$
2624 vw 2514 vw 2439 ms	2712 vw 2625 w 2448 ms	2724 w 2625 vw 2444 ms	2719 w 2630 vw 2442 ms	Hydrogen bonding
-	2202 ms	-	-	$\nu(\text{C}\equiv\text{N})$; DDQ
-	1632 vs	-	-	$\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{N})$; DDQ, DCQ and DBQ
1645 s	1623 vs	1637 s	1633 s	$\delta_{\text{def}}(\text{N-H})$ Ring breathing bands
1560 s 1423 s	1564 ms 1437 s	1561 vs 1432 s	1562 s 1450 vw 1420 w	$\nu(\text{C}=\text{C})$; DDQ, DCQ and DBQ C-H deformation
1351 vw 1303 s 1220 ms 1185 s 1101vs 1039 s	1308 ms 1272 mw 1234 mw 1188 w 1105 vs 1069 w 1041 ms	1357 vw 1307 s 1222 s 1150 vw 1104 vs 1068 vw 1042 s	1306 s 1273 w 1228 ms 1188 ms 1103 vs 1041 s	$\nu(\text{C-C}) + \nu(\text{C-N}) + \nu(\text{C-O-C})$ CH, in-plane bend
892 s 869 s 819 vw	898 ms 872 s 846 vw	964 s 887 s 872 s 828 w 770 w	897 s 871 s 791 vw	δ_{rock} ; NH CH-deformation $\nu(\text{C-Cl}) + \nu(\text{C-Br})$; DDQ, DCQ and DBQ
665 m 586 vs	592 ms	690 w 630 vw 593 s	691 ms 593 s	skeletal vibration CH bend
432 vw 414 s	439 vw 421 vw	487 vw 462 vw 437 vw 420 vw	437 vw 415 w	CH out of plane bend Skeletal vibration CNC def.

(a): s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad.

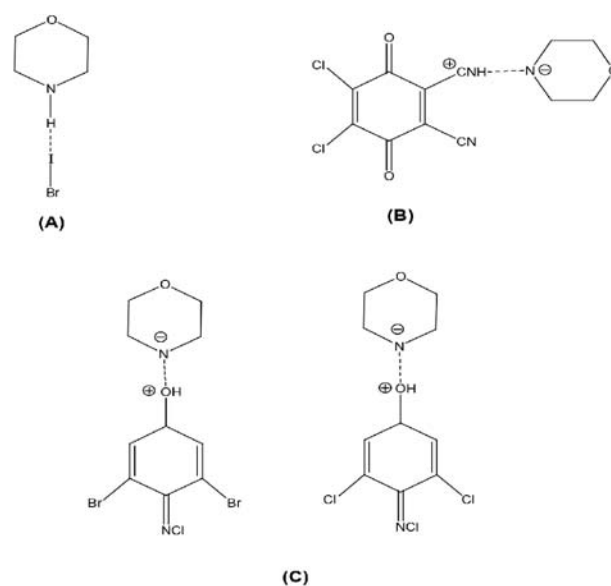
(b): ν , stretching; δ , bending.

changes in comparable with free Morp donor (Table 3). This observation confirm that the charge transfer chelation between Morp and IBr takes place through the formation of hydrogen bonding between -NH group of morpholine and IBr acceptor (Scheme 2).

For the [(Morp)(DDQ)] CT complex, the infrared frequencies of both $\nu(\text{C}\equiv\text{N})$ cyano group, $\nu(\text{C}=\text{O})$ and $\nu(\text{C-Cl})$ in case of complex are shifted to lower wave-number values in comparison with free DDQ acceptor. The stretching vibration band of $\nu(\text{C}\equiv\text{N})$ is occurred at 2250 and 2231 cm⁻¹ in case of free DDQ acceptor, this bands were shifted to lower frequencies at 2202 cm⁻¹ in case of charge transfer complex. While the $\nu(\text{C}=\text{O})$ vibration band for the free DDQ is observed at 1673 cm⁻¹, this was shifted to lower value 1632 cm⁻¹ in case of charge transfer complex. The new bands presence in case of charge transfer complex within the 2600–2400 cm⁻¹ range are assigned to the association of hydrogen bonding through the deprotonation of -NH group of Morp to one of the CN groups of DDQ acceptor (Scheme 2).

Regarding the IR spectra of two [(Morp)(DCQ)] and [(Morp)(DBQ)] charge transfer complexes, there are few weak bands at the range of 2400–2800 cm⁻¹ which didn't present in the spectra of the reactants. These bands are assigned to the stretching vibration of hydrogen bonding³⁹, which were formed through the -NH of Morp donor and the oxygen atom of the carbonyl group of acceptors (DCQ and DBQ). The stretching

vibration bands of $\nu(\text{C}=\text{O})$ group are located at 1696, 1686, 1658 and 1656 cm⁻¹ in case of the free acceptors. These bands are shifted to 1637 cm⁻¹ in case of DCQ and at 1633 cm⁻¹ for DBQ acceptor, respectively. This led to confirm that the carbonyl group is participated in the charge transfer complexation (Scheme 2).



Scheme 2. Mode of charge transfer chelating of: (A): [(Morp)(IBr)], (B): [(Morp)(DDQ)], (C): [(Morp)(DCQ)] and [(Morp)(DBQ)] complexes

CONCLUSIONS

Considerable attention and interest have been devoted to the chemistry of CT interactions especially with major moieties presence in many drugs. This interest is due to the potentially useful of the obtained products in a wide range of applications. The results reported in this paper are demonstrated the spectroscopic and structural studies of the CT products derived from the reaction of Morp donor which is an essential molecule in synthetic drugs with four acceptors (IBr, DDQ, DBQ and DCQ). The CT products were synthesized in CHCl_3 solvent, isolated and characterized spectroscopically using UV-Vis and IR spectroscopy. Results obtained by elemental analysis and titrations confirmed that the reaction stoichiometry is 1:1, and the formed products has the general formula: [(Morp)(acceptor)]. The complexation between the donor and the acceptor was taking place by the formation of intermolecular hydrogen bond coupled.

CONFLICT OF INTEREST

The authors declare no potential conflicts of interest with respect to the research, authorship, and publication of this article.

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LITERATURE CITED

- Behmadi, H., Moghaddam, Z.A., Poormorteza, N., Beyramabadi, S.A. & Nezhad, M.A.A. (2017). A four Components, One-Pot Synthesis of New Imidazole Molecular Tweezers Based on 2,4,6-Triarylpyridine as Hinge Region. *Iran. J. Chem. Chem. Eng. (IJCCE)*, 36(1), 11–17.
- Weigelt, J., Itani, K., Stevens, D., Lau, W., Dryden, M., Knirsch, C. & Group, L.C.S. (2005). Linezolid versus Vancomycin in Treatment of Complicated Skin and Soft Tissue Infections. *Antimicrob. Agents. Chemother.*, 49(6), 2260–2266. DOI: 10.1128/AAC.49.6.2260-2266.2005.
- McKeage, K. (2015). Finafloxacin: First Global Approval. *Drugs*, 75(6), 687–693. DOI://doi.org/10.1007/s40265-015-0384-z.
- Mizuno, M., Tanaka, J. & Harada, I. (1981). Electronic spectra and structures of polyiodide chain complexes. *J. Phys. Chem.*, 85, 1789–1794. https://doi.org/10.1021/j150613a006.
- Nour, E.M., Chen, L.H. & Laane, J. (1986). Resonance Raman and far-infrared studies of charge-transfer complexes of iodine. *J. Raman, Spectrosc.*, 17, 467–469. https://doi.org/10.1002/jrs.1250170608.
- Nour, E.M., Chen, L.H. & Laane, J. (1986). Far-infrared and Raman spectroscopic studies of polyiodides. *J. Phys. Chem.*, 90, 2841–2846. https://doi.org/10.1021/j100404a014.
- Mulazzi, E., Pollini, I., Piseri, L. & Tubino, R. (1981). Selective resonant Raman enhancement in polyiodide chains. *Phys. Rev.*, (B) 24, 3555–3563. DOI: https://doi.org/10.1103/PhysRevB.24.3555.
- Nour, E.M. (2000). Resonance Raman study of the polyiodide complex formed in the reaction of iodine with the polysulphur cyclic base 1,4,7,10,13,16-hexathiacyclooctadecane. *Spectrochim. Acta.*, 56A, 167–170. https://doi.org/10.1016/S1386-1425(99)00130-4.
- Nour, E.M. & Shahada, L.A. (1988). Electronic spectral studies and solvent effects on the reaction of iodine with

- 1,4,8,11-tetraazacyclotetradecane. *Spectrochim. Acta.*, 44A, 1277–1280. https://doi.org/10.1016/0584-8539(88)80169-7.
- Singh, N., Khan, I.M., Ahmad, A. & Javed, S. (2014). Preparation, spectral investigation and spectrophotometric studies of proton transfer complex of 2,2'-bipyridine with 3,5-dinitrobenzoic acid in various polar solvents. *J. Mol. Struct.*, 1065–1066, 74–85. https://doi.org/10.1016/j.molstruc.2014.02.017.
- Khan, I.M., Shakya, S. & Singh, N. (2018). Preparation, single-crystal investigation and spectrophotometric studies of proton transfer complex of 2,6-diaminopyridine with oxalic acid in various polar solvents. *J. Mol. Liq.*, 250, 150–161. https://doi.org/10.1016/j.molliq.2017.11.150.
- Khan, I.M., Alam, K., Alam, M.J. & Ahmad, M. (2019). Spectrophotometric and photocatalytic studies of H-bonded charge transfer complex of oxalic acid with imidazole: single crystal XRD, experimental and DFT/TD-DFT studies *New J. Chem.*, 43, 9039–9051. DOI:10.1039/C9NJ00332K.
- Khan, I.M. & Shakya, S. (2019). Exploring Colorimetric Real-Time Sensing Behavior of a Newly Designed CT Complex toward Nitrobenzene and Co^{2+} : Spectrophotometric, DFT/TD-DFT, and Mechanistic Insights. *ACS Omega*, 4, 9983–9995. https://doi.org/10.1021/acsomega.9b01314.
- Singh, N., Khan, I.M., Ahmad, A. & Javed, S. (2016). Synthesis, spectrophotometric and thermodynamic studies of charge transfer complex of 5,6-dimethylbenzimidazole with chloranilic acid at various temperatures in acetonitrile and methanol solvents. *J. Mol. Liq.*, 221, 1111–1120. https://doi.org/10.1016/j.molliq.2016.06.081.
- Almalki, A.S.A., Alhadhrami, A., Adam, A.M.A., Grabchev, I., Almeataq, M., Al-Humaidi, J.Y., Sharshar, T. & Refat, M.S. (2018). Preparation of elastic polymer slices have the semiconductors properties for use in solar cells as a source of new and renewable energy. *J. Photochem. Photobiol.*, A 361, 76–85. https://doi.org/10.1016/j.jphotochem.2018.05.001.
- Almalki, A.S.A., Alhadhrami, A., Obaid, R.J., Alsharif, M.A., Adam, A.M.A., Grabchev, I. & Refat, M.S. (2018). Preparation of some compounds and study their thermal stability for use in dye sensitized solar cells. *J. Mol. Liq.* 261, 565–582. https://doi.org/10.1016/j.molliq.2018.04.057.
- Datta, A.S., Bagchi, S., Chakraborty, A. & Lahiri, S.C. (2015). Studies on the weak interactions and CT complex formations between chloranilic acid, 2,3-dichloro-5,6-dicyano-p-benzoquinone, tetracyanoethylene and papaverine in acetonitrile and their thermodynamic properties, theoretically, spectrophotometrically aided by FTIR. *Spectrochim. Acta A*, 146, 119–128. https://doi.org/10.1016/j.saa.2015.02.064.
- Saravanabhavan, M., Sathya, K., Puranik, V.G. & Sekar, M. (2014). Synthesis, spectroscopic characterization and structural investigations of new adduct compound of carbazole with picric acid: DNA binding and antimicrobial studies. *Spectrochim. Acta A*, 118, 399–406. https://doi.org/10.1016/j.saa.2013.08.115.
- Mohamed, M.E., Frag, E.Y.Z., Hathoot, A.A. & Shalaby, E.A. (2018). Spectrophotometric determination of fenopofen calcium drug in pure and pharmaceutical preparations. Spectroscopic characterization of the charge transfer solid complexes. *Spectrochim. Acta A*, 189, 357–365. https://doi.org/10.1016/j.saa.2017.08.027.
- Shehab, O.R., AlRabiah, H., Abdel-Aziz, H.A. & Mostafa, G.A.E. (2018). Charge-transfer complexes of cefpodoxime proxetil with chloranilic acid and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone: Experimental and theoretical studies. *J. Mol. Liq.* 257, 42–51. https://doi.org/10.1016/j.molliq.2018.02.083.
- Soltani, S., Magri, P., Rogalski, M. & Kadri, M. (2019). Charge-transfer complexes of hypoglycemic sulfonamide with π -acceptors: Experimental and DFT-TDDFT studies. *J. Mol. Struct.*, 1175, 105–116. https://doi.org/10.1016/j.molstruc.2018.07.074.
- Fathima, K.S., Sathiyendran, M. & Anitha, K. (2019). Structure elucidation, biological evaluation and molecular docking studies of 3-aminoquinolinium 2-carboxy benzoate-

A proton transferred molecular complex. *J. Mol. Struct.*, 1176, 238–248. <https://doi.org/10.1016/j.molstruc.2018.08.020>.

23. Man, L., Li, T., Wu, X., Lu, K., Yang, L., Liu, X., Yang, Z., Zhou, J. & Ni, C. (2019). Synthesis, crystal structure, vibrational spectra, nonlinear optical property of an organic charge-transfer compound—4-nitrobenzyl isoquinolinium picrate based on DFT calculations. *J. Mol. Struct.*, 1175, 971–978. <https://doi.org/10.1016/j.molstruc.2018.07.054>.

24. Refat, M.S., Adam, A.M.A., Saad, H.A., Naglah, A.M. & Al-Omar, M.A. (2015). transfer-Charge Complexation and Photostability Characteristics of Iodine with bis-1,8-naphthalimide as a Photosensitive Biologically Active Units in Solution and in the Solid State: Linear Correlation of Photostability and Dissociation Energy. *Int. J. Electrochem. Sci.*, 10, 6405–6421.

25. Refat, M.S., Elfalaky, A., Elesh, E., Naglah, A.M. & Al-Omar, M.A. (2015). Electrical Properties on Charge Transfer Complex of Norfloxacin Drug with Iodine Acceptor. *Int. J. Electrochem. Sci.*, 10, 6433–6443.

26. Naglah, A.M., Al-Omar, M.A., Adam, A.M.A. & Refat, M.S. (2015). Charge-transfer Complexes Formed between the Sweeteners Saccharin Drug and Acido Acceptors: Structural, Thermal and Morphological Features. *Int. J. Pharmacology*, 11(8), 929–937. DOI: 10.3923/ijp.2015.929.937.

27. Refat, M.S., Saad, H.A., Eldaroti, H.H., Adam, A.M.A., Al-Omar, M.A. & Naglah, A.M. (2016). Charge-transfer interactions between nitrogen moieties as a basis for different drugs with a picric acid acceptor. *ScienceAsia*, 42(6), 397–406. doi: 10.2306/scienceasia1513-1874.2016.42.397.

28. Naglah, A.M., Al-Omar, M.A., Ibrahim, O.B., Refat, M.S., Adam, A.M.A., Saad, H.A. & El-Metwaly, N.M. (2016). Charge-transfer complexes of two highly efficient drugs with σ - and π -acceptors: Spectroscopic, thermal, and surface morphology characteristics. *Russ. J. Gen. Chem.*, 86(4), 965–974. <https://doi.org/10.1134/S1070363216040356>.

29. Almalki, A.S.A., Naglah, A.M., Refat, M.S., Hegab, M.S., Adam, A.M.A. & Al-Omar, M.A. (2017). Liquid and solid-state study of antioxidant quercetin donor and TCNE acceptor interaction: Focusing on solvent affect on the morphological properties. *J. Mol. Liq.*, 233, 292–302. <https://doi.org/10.1016/j.molliq.2017.03.033>.

30. Arora, S., Kothiyal, N.C., Kumar, R., Shahab, S., Al-Wasidi, A.S., Al-Jafshar, N.M., Al-Otifi, J.S., Naglah, A.M., Refat, M.S., Alghamdi, M.T. & Adam, A.M.A. (2018). Experimental and Theoretical Studies of Charge Transfer Complex Formed Between the Antibiotic Drug Norfloxacin with Picric Acid: Density Functional Theory Approach. *J. Biobased Materials and Bioenergy*, 12(2), 203–210. <https://doi.org/10.1166/jbmb.2018.1761>.

31. Skoog, D.A. (1985). *Principle of Instrumental Analysis*, 3rd edn., Ch. 7, Saunders College Publishing, New York, USA.

32. Harada, I., Tanaka, J. & Zuno, M.M. (1981). Electronic spectra and structures of polyiodide chain complexes. *J. Phys. Chem.*, 85, 1789–1794. <https://doi.org/10.1021/j150613a006>.

33. Lever, A.B.P. (1985). *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, p. 161.

34. Tsubomura, H. & Lang, R.P. (1961). Molecular Complexes and Their Spectra. XIII. Complexes of Iodine with Amides, Diethyl Sulfide and Diethyl Disulfide. *J. Am. Chem. Soc.*, 83, 2085–2092. <https://doi.org/10.1021/ja01470a013>.

35. McConnel, H.M., Ham, J.J. & Platt, J.R. (1964). Regularities in the Spectra of Molecular Complexes. *J. Chem. Phys.*, 21, 66–70. <https://doi.org/10.1063/1.1698626>.

36. Aloisi, G.G. & Pignataro, S. (1973). Molecular complexes of substituted thiophens with σ and π acceptors. Charge transfer spectra and ionization potentials of the donors. *J. Chem. Soc., Faraday Trans.*, 69, 534–539. DOI:10.1039/F19736900534.

37. Foster, R. (1969). *Organic Charge Transfer Complexes*, Academic Press, London.

38. Wheat, D.C. (1969–1970). *Hand Book of Chemistry and Physics*, 50th ed.

39. Bellamy, L.J. (1975). *The infrared Spectra of Complex Molecules*, Chapman & Hall, London.