Asian Journal of Chemistry; Vol. 28, No. 5 (2016), 947-953

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19190

Theoretical Calculations of Molecular Charge Transfer Complexes of Aryl 2-Azomethine dibenzothiophene with Nitrobenzene Derivatives as π-Acceptors

E.H. EL-MOSSALAMY[1], S. ABDE AAL[1], M. EL-BATOUTI[2,*] and N.F. AL-HARBI[3]

[1]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
[2]Chemistry Department, Faculty of Science, Alexandria University, P.O. 426, Alexandria 21321, Egypt
[3]Chemistry Department, Faculty of Science and Arts, Qassim University, Al-Qassim, Saudi Arabia

*Corresponding author: E-mail: mervette_b@yahoo.com

Received: 10 March 2015; *Accepted*: 18 January 2016; *Published online*: 30 January 2016; AJC-17723

Charge transfer complexes of aryl 2-azomethine dibenzothiophene with π-acceptors *viz.*, 1,3-dinitrobenzene, 2,4-dinitrophenol and picric acid were synthesized and characterized by spectroscopic techniques *viz.*, IR, ^{1}H NMR and elemental analysis. The equilibrium constant (k) was determined using modified Benesi-Hildelbrand methods. The stoichiometries of the reactions were determined using photometric titration methods. The thermodynamic parameters Gibbs free energy (ΔG), enthalpy (ΔH) and entropy change (ΔS) were also calculated. Theoretical calculations have been carried out by density functional theory (DFT) and time-dependent density functional theory calculations.

Keywords: Charge transfer complexes, Aryl 2-azomethine-dibenzothiophene, Picric acid, density functional theory.

INTRODUCTION

Charge transfer complexes are being regarded as important materials due to their several applications [1-3]. Such complexes have been reported as important reaction intermediates in many chemical reactions [4] and play a considerable role in drug interactions [5-8]. The question of participation of charge transfer complexes in organic syntheses and in understanding reaction mechanisms has long been debated since the classical work of Benesi and Hildebrand [9].

The study of charge transfer complexes formed in the reaction of aromatic electron acceptors (π-acceptor) with various electron donors have attracted considerable interests and growing importance owing to their significant physical and chemical properties [10-12]. Some of the charge transfer complexes show interesting applications in the field of analytical chemistry [13,14]. Herein, the present article reported the synthesis and characterization of charge transfer complexes of aryl 2-azomethine dibenzothiophene as donors with 1,3-dinitrobenzene, 2,4-dinitrophenol and picric acid as acceptors. The transition energy (E) and the effects of thermodynamic parameters (ΔG and ΔH) on the stability of complexes are also discussed.

Computational calculations often provide the much needed information on the geometry, electronic structure and molecular properties. The present fully optimized geometries of structural variables of the donor, acceptors, charge transfer-complexes DA_1, DA_2, DA_3 were carried out at the DFT level (B3LYP) and the basis set (SDD). The electronic absorption spectra and the contributions of singly excited-state configurations to each electronic transition of DA_1, DA_2 and DA_3 complexes were calculated and simulated with TD-DFT method in a vacuum. All calculations are carried out by using Gaussian 09 system and the optimal geometries of molecular skeletons and molecular orbital (MO) densities were visualized by using the corresponding Gauss View software.

EXPERIMENTAL

All the chemicals used in this work were of reagent grade (Aldrich) including 2-aminodibenzothiophene, benzaldehyde, salicylaldehyde, 2,4-dihydroxybenzaldehyde, 1,3-dinitrobenzene, 2,4-dinitrophenol and picric acid .

Synthesis of donor Schiff base compounds: Schiff bases containing primary amine reaction with aldehyde, where the interaction is 2-aminodibenzo-thiophene with benzaldehyde, salicylaldehyde, 2,4-dihydroxybenzaldehyde in 1:1 mol ratio in ethanol and the product isolated for a period of 8 h. Crystallized compounds were collected and dried using petroleum ether: 40-60 °C.

Synthesis of charge transfer complexes: The charge transfer complexes were synthesized using Schiff bases prepared with π-acceptors *viz.*, 1,3-dinitrobenzene, 2,4-dinitrophenol and picric in the presence of ethanol and a mole ratio

of 1:1 and 1:2. The obtained charge transfer complexes in solid form were dried using petroleum ether at 40-60 °C.

RESULTS AND DISCUSSION

The molecular structure of thiophene Schiff bases compounds prepared from interaction of primary amine has been identified. The elemental analysis of Schiff base compounds and charge transfer complexes within picric acid (A_3) are given in Table-1. And comparing these theoretically calculated ratios with those found in practice, was noted that it is close to a large extent. Results of elemental analysis, melting points in addition to the molecular formula in Table-1 clearly points to match the results of the analysis process with the ratios calculated, as can also be charge transfer complexes by 1:1 and 1:2 donor:acceptor.

IR spectra showed all the prepared Schiff bases vibration frequency range azomethine ν(C=N) at 1612-1601 cm^{-1}, while in charge transfer complexes, azomethine group frequency vibration appeared at 1614-1609 cm^{-1}. As shown by absorption of vibration and a broad strong hydroxyl group ν(OH) at 3257 cm^{-1} in compounds and Schiff bases, while at 3525-3374 cm^{-1} in charge transfer complexes. Spectral band appeared range 3260-2886 cm^{-1}, which is due to the aromatic rings protons. ν(C-H) of nitro group appears a set of nice band in the region 1433-1432 cm^{-1} and another in the region 1347-1345 cm^{-1} and the two are special non-symmetrical stretching vibrations and asymmetric, respectively, in all the charge transfer complexes have been observed to appear.

The results of IR spectrum of these complexes and the presence of displacement in the positions of most absorption band compared with the spectrum of donor compounds, where shift vibrations band of various associated molecule donor to the number of wavelengths higher or lower depending on the type of interaction charge transfer [15], which include transmission electron from the HOMO of donor to the LUMO of acceptor. The size of the shift was generally higher in the complexes of 1:2 compared with 1:1 complexes.

^{1}H NMR: ^{1}H NMR confirmed the existence of azomethine (-CH=N-), as appeared signals at 8.56-9.73 ppm in all compounds of Schiff bases. Signals in the range 5.68-7.92 ppm almost back to the ring protons of the benzene ring and may differ from compound to another and according to ring the influential positions of protons in the compound, as different sites after the addition of acceptor compounds to the complex. Also showed proton phenolic OH group in the benzene ring signal at 5.12-9.67 ppm containing compounds in this group and varied locations of these signals before and after add-on, which shows the extent of the impact of synthetic form of the compound on the magnetic field. It also confirmed the existence of an OH- and that after the addition of D_2O where signal disappeared and a new absorption appeared particularly proton water at approximately 4 ppm.

Determination of formation constant of charge transfer complexes in different organic solvents: The formation constant (K_{CT}) and molar extinction coefficient (ε) charge transfer complexes of donor compounds with three receptors A_1, A_2 and A_3 in the presence of organic solvents at four different temperatures (20, 30, 40 and 50 ° C) and these measurements were made on absorption bands in the spectrum of charge transfer systems using modified Benisi-Hildebrand equation [9].

According to modified Benisi-Hildebrand equation:

$$[A]+[D]=\frac{\varepsilon L[A][D]}{d}-\frac{1}{K_{CT}}$$

where [A] = initial molar concentration of acceptor, [D] = initial molar concentration of donor), d = optical density, K_{CT} = equilibrium constant of charge transfer compounds, ε = molar extinction coefficient and L = length of light path in cm.

The cells used have a length of 1 cm light bath. This equation is valid under certain circumstances where [D] > > [A] donor:acceptor is at the molar ratio of 1:1 indicating that ratio of the synthetic complexes studied is 1:1.

The values obtained by each of K_{CT} and ε with increasing temperature of the single-donor compound. Whereas the results of the interaction of donor compounds with acceptor compounds by using different solvents showed that the values of formation constant K_{CT} increases with increasing temperature.

In ethanol at 293 K, 1.825×10^3 L mol^{-1} and reached 1.876×10^3 L mol^- at 303 K, then rise to 1.915×10^3 L mol^{-1} at 313 K and the value of 2×10^3 L mol^{-1} at 323 K. The high temperature causes the ions to activate the viability of the polarization in the solution (polar ability of ions in solution) ($D^{\delta+}$---$A^{\delta-}$) leading to increase the accumulation of ions with each other and this in turn will increase K_{CT} values with a high temperature.

It was observed that the formation constants K_{CT} values were different for all complexes in every solvent because the nature of molecular structure of compounds plays a key role in determining the values of K_{CT}. It was found that the values of K_{CT} of the complexes formed from the acceptor compound A_1 increases clearly with a low polar solvent, in the complex D_1A_1 the value of K_{CT} is equal to 1.825×10^3, 2.5×10^3, 2.833×10^3 and 3.030×10^3 L mol^{-1} in both the ethanol, acetonitrile, dichloromethane and carbon tetrachloride, respectively and this refers to the fact that the charge transfer complexes are stable in low polar solvents. Where there is the dissociation of the complex to radicalize A^- and D^+ in ground state [16]. This means that charge transfer complexes were strong in low polar solvents as compared to polar solvents. It is noted that the values of K_{CT} of complex D_1A_2 is 2.793×10^3 L mol^{-1} in ethanol,

TABLE-1
PHYSICO-CHEMICAL DATA FOR REPRESENTATIVE SCHIFF BASE AND CHARGE TRANSFER COMPLEXES WITH PICRIC ACID (A_3)

Compound	Elemental analysis (%): Calcd. (Found)				m.p. (°C)
	C	H	N	S	
D_1	79.41 (79.74)	4.56 (4.55)	4.87 (4.34)	11.16 (11.00)	87-90
D_1A_3 (1:1)	58.14 (57.98)	3.12 (3.02)	10.85 (10.39)	6.21 (6.01)	88-91
D_1A_3 (1:2)	49.94 (49.74)	2.57 (2.46)	13.15 (12.85)	4.30 (4.03)	75-77

20×10^3 L mol^{-1} in acetonitrile, 2.457×10^3 L mol^{-1} in dichloro methane and 4.854×10^3 L mol^{-1} in carbon tetrachloride.

In complex D_1A_3, K_{CT} values were equal to 142.857×10^3 L mol^{-1} in ethanol, the values of formation constant (K_{CT}) increase with increasing solvent polarity as the polarity of the medium increases the amount of charge transmitted from donor compound to acceptor compound as a result of increasing overlap between dipolar bond for each donor-acceptor compound and solvent. Therefore, increase the values of K_{CT} is due to the deviation from this phenomenon in some cases as a result of the large molecules of both donor and acceptor, which in turn increases the distance between the molecular charges on both of them ($D^{\delta+}$---$A^{\delta-}$) leading to an incompatibility with the values of K_{CT} with polar solvents.

In general, picric acid (A_3) is the most powerful acceptor and form complexes in different solvents, and have high values of K_{CT}, which refers to the strength of bonding between donor and acceptor and high stability of the resulting complex.

The molar absorption coefficient (ε) of the complex in all the systems decreased, in general with high temperature and can observe slight differences for both molar absorption and temperature. It was also noted that the values of absorption molar coefficient to compound D_1 with receptors of three A_1, A_2 and A_3 increases with increasing the dielectric constant of medium, reaching a value to 46.18×10^2, 405.27×10^2 and 127.75×10^2 L mol^{-1} cm^{-1} and acetonitrile with acceptor compounds A_1, A_2 and A_3, respectively. And in case of carbon tetrachloride, reached to 42.22×10^2, 34.42×10^2 and 33.24×10^2 L mol^{-1} cm^{-1}, respectively.

Theoretical calculations

The charge transfer complexes formed between D and A_1, A_2 and A_3 can be due to the differences in energy between the HOMO of donor and the LUMO of acceptor molecules [17]. The optimized geometry of donor along with HOMO and acceptors along with LUMO are depicted in Fig. 1. The energies of frontier orbitals of donor and acceptors along with the energy (ΔE) corresponds to the charge transfer transition for all the systems are shown in Fig. 2. It is evident (Fig. 2) that ΔE depends on the nature of the substitute as well as the greatest strength of D and A_3 in comparison with DA_1 and DA_2 complexes. As the interaction of D and A_1-A_3 takes place through a charge transfer from HOMO of D to LUMO of A_1-A_3 molecules, smaller the value of HOMO–LUMO gap, the easier the charge transfer and consequently, larger the interaction of charge transfer complexes [18]. The results in Table-2 demonstrate that the interaction of charge transfer complexes between D and A_1-A_3 follows the trend $DA_3 > DA_1 > DA_2$.

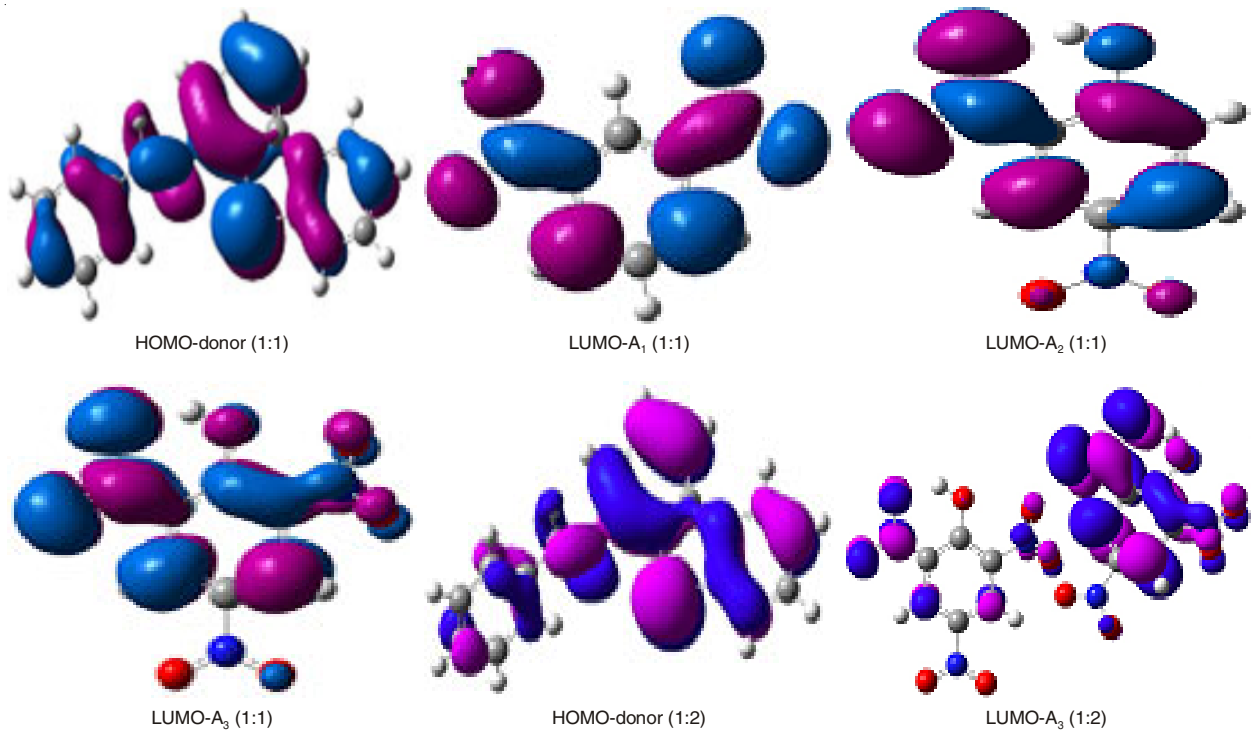


Fig. 1. Optimized structures of the charge transfer complexes by 1:1 and 1:2 donor:acceptor with frontier orbitals

TABLE-2
HOMO, LUMO, ENERGY GAP (E_g), FORMATION ENERGY (ε, eV), IONIZATION POTENTIAL (I, eV), ELECTRON AFFINITY (A, eV), CHEMICAL HARDNESS (η, eV), ELECTRONEGATIVITY (χ, eV) AND ELECTROPHILICITY (ω, eV) OF THE CHARGE TRANSFER COMPLEXES BY 1:1 AND 1:2 DONOR:ACCEPTOR

Compound	HOMO	LUMO	E_g	ε	I	A	η	χ	ω	S
Donor	-5.827	-1.948	3.879	-	5.827	1.948	1.939	3.888	3.896	0.258
DA_1 (1:1)	-5.641	-3.970	1.670	-0.225	5.641	3.970	0.835	4.806	13.827	0.599
DA_2 (1:1)	-5.860	-4.147	1.714	-0.769	5.860	4.147	0.857	5.003	14.609	0.584
DA_3 (1:1)	-5.864	-4.732	1.131	-0.265	5.864	4.732	0.566	5.298	24.809	0.884
DA_3 (1:2)	-5.813	-4.812	1.001	-0.545	5.813	4.771	0.521	5.292	26.876	0.959

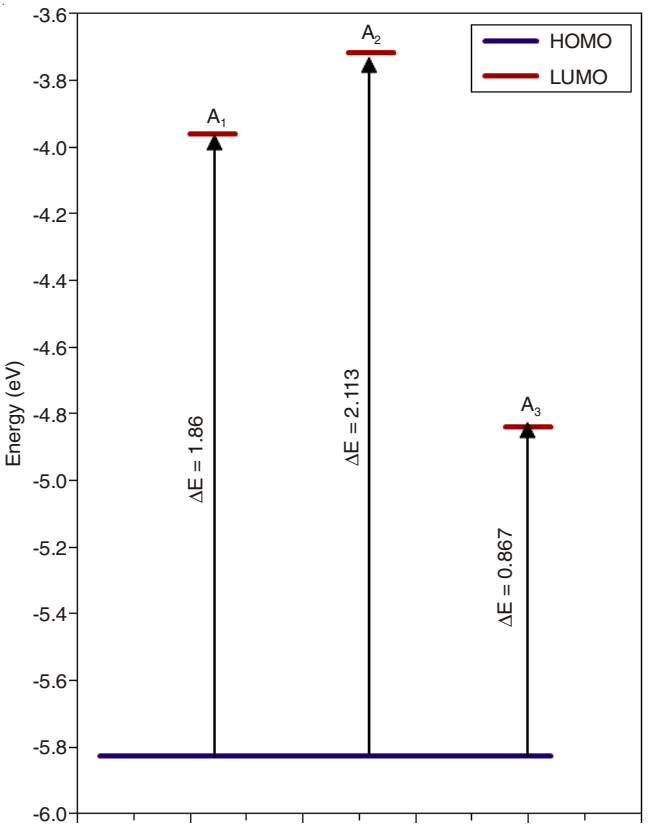
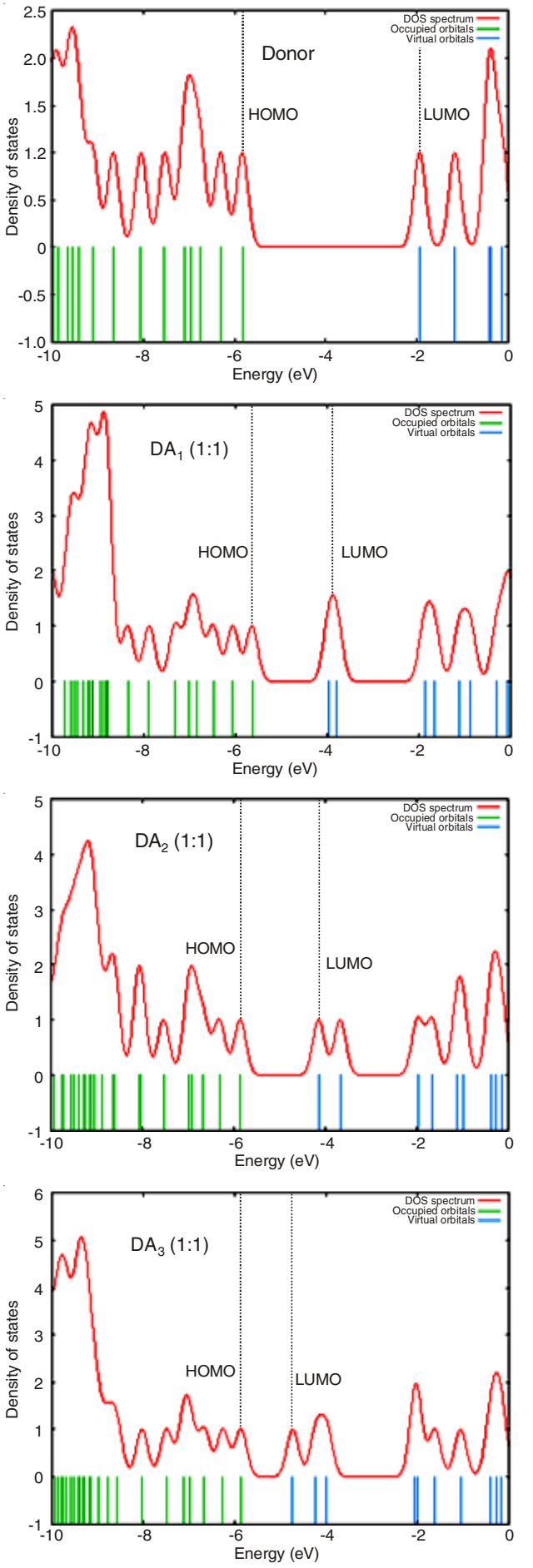


Fig. 2. HOMO of donor and LUMO of acceptors A_1-A_3

The binding energies (Eb) of donor and acceptor on the charge transfer complexes have been calculated as the difference between total energy of DA_n system and the sum of energies for separated fragments D and A_n, where n = 1,2 or 3:

$$Eb = E(DA_n)-[E(D) + E(A_n)]; \quad \text{where } n = 1, 2 \text{ or } 3$$

The negative values correspond to exothermic processes. The interaction energies of donor that interacting with acceptors surface were performed using the DFT-B3LYP level [19]. It is concludedthat the interaction energies in triplet configurations depend somewhat on acceptors. Moreover, different binding energies computed for charge transfer complexes arise principally from the very different local electric fields at charge transfer complexes. The most stable configuration is DA_2 in the charge transfer complexes having binding energy -0.769 which corresponds to the largest band gap 1.714 eV. The density of state (DOS) of charge transfer complexes describes the number of states per interval of energy at each energy level which are available to be occupied by electrons. A high density of state at a specific energy level means that there are many states available for occupation and therefore scales linearly with the interaction of charge transfer complexes. In Fig. 3, calculated values of DOS of D, DA_1, DA_2 and DA_3 are presented, where A_3 is the most favourable acceptor. Density of state as well as Fermi levels were calculated by using Gauss Sum 2.2.5 program [19] at the B3LYP/SDD level of theory. As shown, the DOS become more abundant near Fermi levels going from donor (D) to charge transfer complexes. The trend of DOS follows the order $DA_3 > DA_1 > DA_2$ under the effect of A_1 to A_3 acceptor molecule where extra deep values beyond the LUMO levels in charge transfer complexes have been observed.



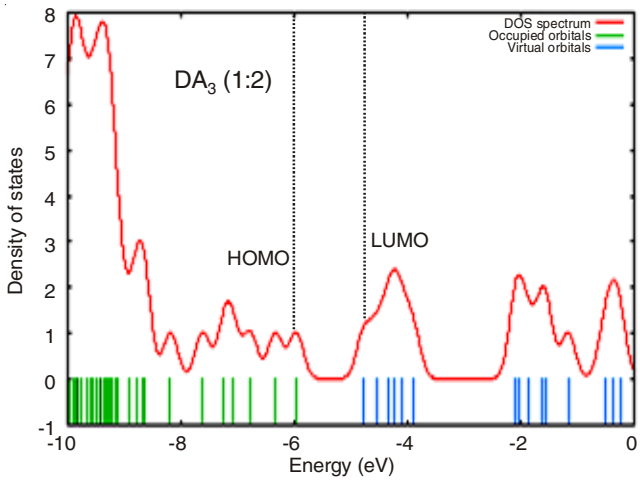


Fig. 3. Densities of states (DOS) of donor, DA_1, DA_2 and DA_3 transfer complexes by 1:1 and 1:2 donor:acceptor

The molecular electrostatic potentials (MEPs) have been established extensively as a guide to the interpretation and prediction of molecular behaviour [20]. The molecular electrostatic potentials (MEPs) are either negative, low potentials that are characterized by an abundance of electrons and reactive with electrophiles, or positive, high potentials that are characterized by the absence of electrons and reactive with nucleophiles. The molecular electrostatic potential contours in planes containing the donor and acceptor molecules are given in Fig. 4. As shown, intensity of the contours increases noticeably with charge transfer complexes. However, the negative

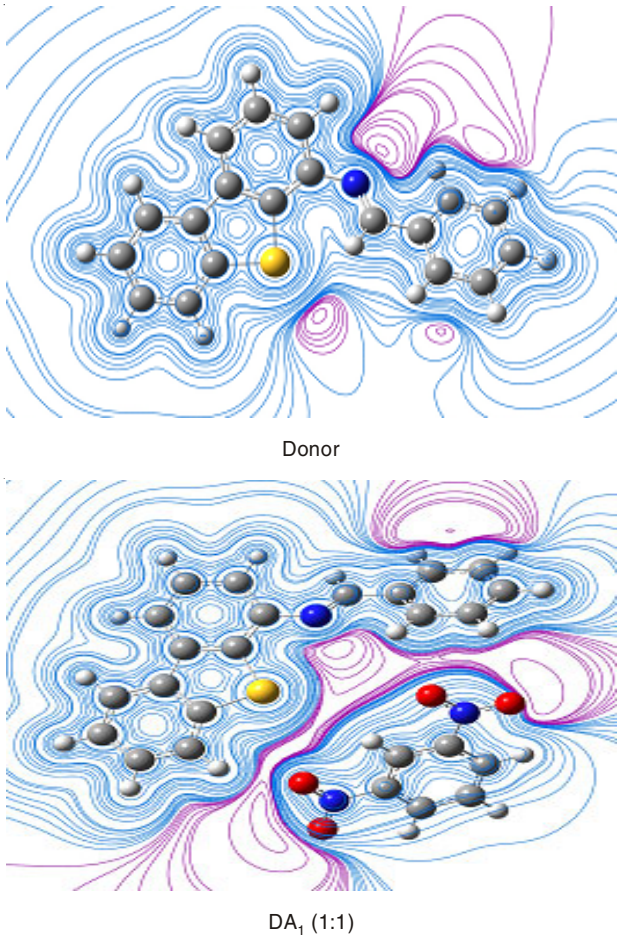


Fig. 4. Molecular electrostatic potential (MEP) surfaces of donor, DA_1, DA_2 and DA_3 charge transfer complexes by 1:1 and 1:2 donor: acceptor

molecular electrostatic potential contours grown up at the terminal ends of the acceptor and phenyl groups of donor in charge transfer complexes. This looks consistent with the nature of charge transfer between the donor and the acceptor molecules.

In order to understand the electronic transitions of donor and charge transfer complexes, time dependent density functional theory (TD-DFT) calculations of the electronic absorption spectra in vacuum were performed. A minimum of

five lowest spin-allowed singlet-singlet transitions were taken into account. The results are shown in Table-3 and the calculations were carried out at the B3LYP/SDD level of theory. The absorption in visible and near-UV regions is the most important regions for charge transfer complexes, so the singlet to singlet transitions of the absorption bands and wavelengths longer than 400 nm were considered. The maximum absorption bands of donor in vacuum near 376 nm resulted from the electronic transitions from the initial states that are contributed by HOMO to the final states which are mainly contributed by LUMO (Fig. 5). The absorption bands that correspond to the absorption of free donor in vacuum are red shifted under the

TABLE-3
CALCULATED ABSORPTION WAVELENGTH (λ, nm), EXCITATION ENERGIES (E, eV) AND OSCILLATOR STRENGTHS (*f*) OF DONOR, DA_1, DA_2 AND DA_3 CALCULATED BY THE B3LYP/SDD METHOD

Gas			Ethanol			Dichloromethane			Carbon tetrachloride			Acetonitrile		
E (eV)	λ (nm)	*f*	E (eV)	λ (nm)	*f*	E (eV)	λ (nm)	*f*	E (eV)	λ (nm)	*f*	E (eV)	λ (nm)	*f*
D_1														
5.4547	227.3	0.1729	5.4339	228.17	0.1959	5.4274	228.44	0.2199	5.4158	228.93	0.2648	5.4354	228.11	0.1902
4.3722	283.58	0.5136	4.3084	287.77	0.6069	4.3031	288.13	0.6050	4.3042	288.05	0.5891	4.3101	287.66	0.6066
3.2955	376.23	0.2526	3.2795	378.06	0.3424	3.2722	378.90	0.3514	3.2605	380.27	0.3518	3.2813	377.85	0.3398
D_1A_1														
4.3377	285.83	0.2570	4.3752	283.38	0.8214	4.3736	283.48	0.8208	4.2939	288.74	0.2769	4.3770	283.26	0.7987
3.2072	386.58	0.2067	3.2856	377.35	0.2959	3.2649	379.75	0.3133	3.2130	385.89	0.3039	3.2901	376.84	0.2918
D_1A_2														
4.2049	294.86	0.2202	4.1598	298.05	0.3653	4.1768	296.84	0.4058	4.1873	296.10	0.2731	4.1572	298.24	0.3676
3.3633	368.63	0.1405	3.3202	373.42	0.2841	3.3089	374.70	0.3621	3.2959	376.18	0.3589	3.3206	373.38	0.1980
D_1A_3														
3.2704	379.11	0.2146	3.3081	374.78	0.2958	3.2923	376.59	0.3164	3.2578	380.58	0.3224	3.3115	374.40	0.2891

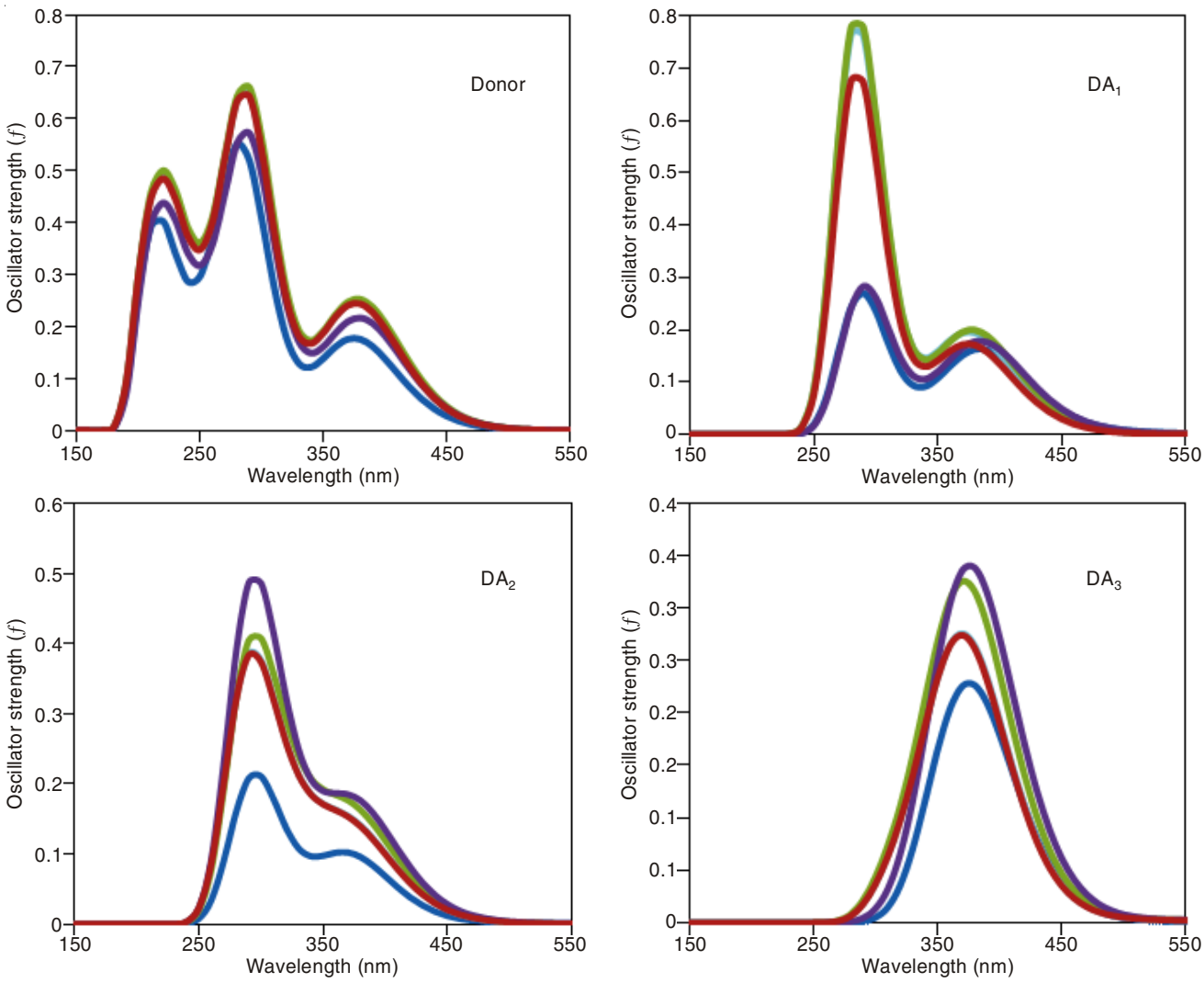


Fig. 5. Calculated UV-spectra for donor, DA_1, DA_2 and DA_3 in various solvents

effect of acceptors. The absorption bands of DA_1, DA_2 and DA_3 complexes result from the electronic transitions take place from the initial states that are mainly contributed by HOMOs (at donor) to the final states that are mainly contributed by LUMOs (at acceptors). These absorption bands in the visible region are typical π-π^* transitions. Usually, if the absorption bands are close to infrared region, it is expected that the charge transfer complexes have higher electron transfer. Moreover, given the data indicate that the absorptions are photo-induced electron transfer processes.

REFERENCES

1. I.M. Khan and A. Ahmad, *J. Mol. Struct.*, **977**, 189 (2010).
2. P.J. Trotter and P.A. White, *Appl. Spectrosc.*, **32**, 323 (1978).
3. E.M. Nour and L.A. Shahada, *Spectrochim. Acta A*, **44**, 1277 (1988).
4. G.A. Bowmaker and R.J. Knappstein, *J. Chem. Soc., Dalton Trans.*, 1928 (1977).
5. M.J. Jenita, A.A.M. Prabhu and N. Rajendiran, *Indian J. Chem*., **51A**, 1686 (2012).
6. M.V. Rekharsky and Y. Inoue, *Chem. Rev*., **98** 1875 (1998).
7. L. Seridi and A. Boufelfel, *J. Mol. Liq*., **158**, 151 (2011).
8. S. Chaudhuri, S. Chakraborty and P.K. Sengupta, *J. Mol. Struct*., **975**, 160 (2010).
9. H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc*., **71**, 2703 (1949).
10. N. Alizadeh and S. Dehganikhah, *J. Solution Chem*., **45**, 42 (2016).
11. R.M. Issa, M.M. Ayad, G.B. EI-Hefnawey and H.F. Rizk, *Indian J. Chem*., **42A**, 84 (2003).
12. M.M. Ayad, G.B. EI-Hefnawey, S.A. Amer and R.M. Issa, *Proc. Pakistan Acad. Sci*., **27**, 169 (1989).
13. H. Salem, *J. Pharm. Biomed. Anal.*, **29**, 527 (2002).
14. D.A. Skoog, F.J. Holler and T.A. Nieman, Principle of Instrumental Analysis, Saunders College Publishing, New York, vol. 347, edn 5 (1992).
15. M. Arslan and H. Duymus, *Spectrochim. Acta A*, **67**, 573 (2007).
16. M. Pandeeswaran and K.P. Elango, *Spectrochim. Acta A*, **65**, 1148 (2006).
17. M. Sterrer, M. Yulikov, T. Risse, H.-J. Freund, J. Carrasco, F. Illas, C. Di Valentin, L. Giordano and G. Pacchioni, *Angew. Chem. Int. Ed.*, **45**, 2633 (2006).
18. A. Markovits, J.C. Paniagua, N. López, C. Minot and F. Illas, *Phys. Rev. B*, **67**, 115417 (2003).
19. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford CT (2009).
20. N.M. O'Boyle, A.L. Tenderholt and K.M. Langner, *J. Comput. Chem.*, **29**, 839 (2008).