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DFT Calculations of Charge Transfer Complexes of N-Aryl-N'-4-(-*p*-anisyl-5-arylazothiazolyl)thiourea Derivatives and Benzoquinones

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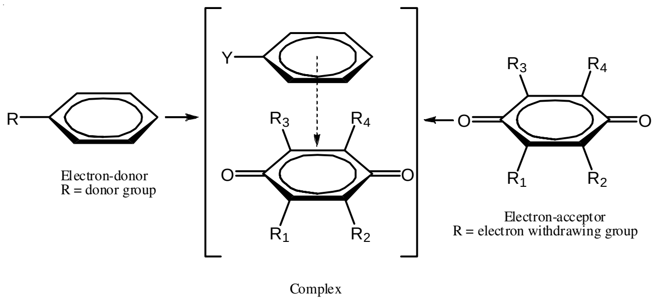
Charge transfer (CT) complexes, consisting of three substituted N-aryl-N'-4-(-*p*-anisyl-5-arylazothiazolyl)thiourea as electron-donor molecules and four benzoquinone derivatives as electron-acceptor molecules, were investigated at the DFT/B3LYP/6-31G(d,p) level of theory. The geometric structures, orbital energies, energy gaps and normal vibrational modes were determined. Quantum chemical parameters, including dipole moment, electronegativity, hardness, softness, electrophilicity index and number of electrons transferred, were calculated. The transition energies of the charge transfer complexes were calculated at the TD-DFT/B3LYP/6-31G(d,p) level of theory. The calculated parameters were comparable to the corresponding experimental parameters and the computational results facilitated the experimental interpretation. The calculated first hyperpolarizabilities demonstrate that those complexes are notably promising candidates as non-linear optical materials.

Keywords: Thiourea, Benzoquinones, Charge transfer complexes, DFT calculations, TD-DFT calculations.

INTRODUCTION

In a donor-acceptor/charge-transfer complex, both molecules are in their ground states. The charge transfer that stabilizes the complex arises from a highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) transfer when the complex is formed. The source molecule from which the charge is transferred is called the electron-donor and the receiving molecule is called the electron-acceptor, hence the name, electron-donor-acceptor/donor-acceptor complex (D-A complex). The nature of the attraction in a D-A complex is not a stable chemical bond and is much weaker than a covalent bond; the attraction is exemplified as a weak electron resonance that can be demonstrated as follows:



Many experimental studies on charge transfer (CT) complexes are found in the literature. These works mainly involve spectroscopic techniques such as IR, ^1H NMR, UV-visible, fluorescence *etc.*[1-7]. Li *et al.*[8] investigated charge transfer complexes made of azobenzene-ethoxy-N-aryl-N′-2-(4-*p*-anisyl-5-aryl-3-methylazothiazolyl)thioureazene-containing cyclopentadienyliron arene complex (Fc-azo) in a combined experimental and DFT study. They compared hydroxyl azobenzene (H-azo) and Fc-azo and found that the change in the electron distribution in Fc-azo compared to that in H-azo improved the first hyperpolarizability value. The experimental and calculated HOMO and LUMO energies demonstrated that the charge transfer occurred within the molecule[8]. Al-Harbi *et al.*[9] studied the charge transfer complexes between substituted aryl Schiff bases as donor molecules and picric acid and *m*-dinitrobenzene as acceptor molecules. They confirmed the ability of theoretical calculations to interpret the normal vibrational frequencies of charge transfer complexes using DFT, CIS-HF and TD-DFT levels of theory[9]. Ganesh *et al.*[10] investigated the charge transfer properties of 1,4-benzoquinones derivatives with L-phenylalanine in aqueous solution. They used many spectral techniques to experimentally study the complex formation. The trend in the experimentally measured association constants of these complexes was well-supported by DFT/B3LYP calculations. Using quantum mechanical calculations, Manna *et al.*[11] determined the structural and electronic properties of the D-A complexes of fullerene derivatives C60 and C70 with azulene and some of its derivatives. They concluded that the LUMO is localized on the fullerene moiety while the HOMO is localized on the azulene. The energy gap of the LUMO levels was strongly dependent on the functional group attached to the azulene as well as the structure of the fullerene-azulene complex[11]. Shukla *et al.*[12] theoretically investigated the ground state structure and charge transfer transitions of a paracetamol and chloranil complex using DFT and TD-DFT methods. They found that the C=O bond length of chloranil was elongated upon complexation and that a considerable amount of charge transfer occurred from paracetamol to chloranil. TD-DFT calculations were used to analyze the observed UV-visible spectrum of the paracetamol-chloranil charge transferred complex. These calculations proved the charge transfer transition and suggested a π-π^* transition in chloranil[12].

To interpret and assist the experimental observations made by El-Mossalmy's study[13] on charge transfer complexes formed between the electron-donor thiourea derivatives 3-chloro-N-aryl-N′-2-(4-*p*-anisyl-5-aryl-3-methylazothiazolyl)thiourea (D1), 4-methoxy-N-aryl-N′-2-(4-*p*-anisyl-5-aryl-3-methoxyazo-thiazolyl)thiourea (D2) and 2-ethoxy-N-aryl-N′-2-(4-*p*-anisyl-5-aryl-3-methylazothiazolyl)thiourea (D3) and the electron-acceptor benzoquinones chloranil (CHL), chloranic acid (CHLA), bromanil (BRL) and 2,3-dichloro-5,6-dicyano-benzoquinones (DDQ), this paper reports extensive quantum chemical calculations including geometric structure, dipole moment, electronegativity, hardness, softness, electrophilicity index, number of electrons transferred, orbital energies, energy gaps, molecular electrostatic potential plots (MEP), vibrational modes, transition energy and first hyperpolarizability value using density functional theory (DFT/B3LYP and TD-DFT) methods with the 6-31G(d,p) basis set. The molecular structures of the studied molecules are demonstrated in Fig. 1.

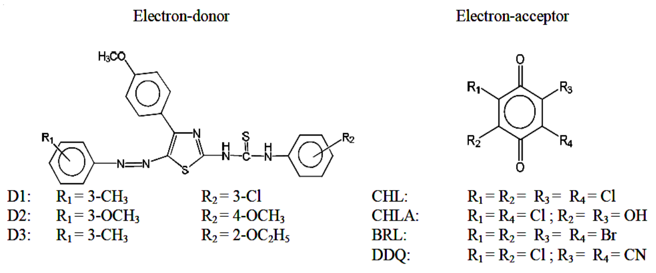


Fig. 1. Molecular structures of the studied electron-donor and electron-acceptor molecules along with their IUPAC names and the abbreviations used in this study

DFT CALCULATIONS

All DFT calculations were performed using the Gaussian 09 suite of programs[14]. Geometry optimizations were conducted using density functional theory (DFT) with Becke's three parameter exchange functional[15], the Lee-Yang-Parr correlation functional[16] (B3LYP) and the 6-31G(d,p) split-valence double zeta basis set with two polarized basis functions (*i.e. d* and *p*). A *d*-type orbital was added to all atoms except hydrogen and a *p*-type orbital was added to all hydrogen atoms. The addition of the higher angular momentum orbitals (polarization orbitals) in the basis set that are empty in the separated atoms was essential for improving the representation of the molecule's electron density.

During geometry optimizations, every bond length, bond angle and dihedral angle was allowed to relax free of constraints. The nature of the stationary points (*i.e.,* minima on the potential energy surface) was confirmed by vibrational frequency analysis to verify that only real frequency (not imaginary frequency) values were obtained for all geometries. The transition energies of the charge transfer complexes were calculated with single-point time-dependent density functional theory (TD-DFT) using the optimized geometries at the B3LYP/6-31G(d,p) level of theory. Visual inspection was carried out using the GuassView program (version 5.0.8)[17].

Geometry optimizations were performed on the ground states of the free donor and free acceptor molecules. To construct the geometry of the resultant charge transfer complex from a pair of donor and acceptor molecules, their optimized geometries were combined together in pairs (*i.e.,* donor-acceptor pairs) to produce the charge transfer complexes. The resultant geometries were again optimized using the same method and basis set. The positioning of the acceptor molecule with respect to the donor molecule was aided by experimentally suggested positions[13].

Frontier molecular orbitals (FMO), *i.e.,* the HOMO and LUMO, were calculated. The energies of the HOMO and LUMO orbitals are related to the ionization potential (IP) and the electron affinity (EA), respectively, by the relationships given in eqns. 1 and 2[18]:

$$\text{Ionization potential (IP)} = -E_{HOMO} \tag{1}$$

$$\text{Electron affinity (EA)} = -E_{LUMO} \tag{2}$$

The electronegativity (χ) and hardness (η), of the donor/acceptor molecule are given by eqn. 3 and 4, respectively[19]:

$$\chi = \frac{IP + EA}{2} = \frac{-E_{HOMO} - E_{LUMO}}{2} \tag{3}$$

$$\eta = \frac{IP - EA}{2} = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{4}$$

The softness is the inverse of the hardness (eqn. 5)[19]:

$$\sigma = \frac{1}{\eta} \tag{5}$$

The number of transferred electrons (ΔN) was calculated using eqn. 6[18]:

$$\Delta N = \frac{\chi_A - \chi_D}{2(\eta_A + \eta_D)} \tag{6}$$

where χ_D and χ_A denote the electronegativity of the donor molecule and acceptor molecule, respectively and η_D and η_A denote the hardness of the donor molecule and the acceptor molecule, respectively. The electrophilicity index is given by eqn. 7[20]:

$$\omega = \frac{\mu^2}{2\eta} \tag{7}$$

The total first static hyperpolarizability was calculated in terms of x, y and z components, as shown in eqns. 8 and 9:

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad (8)$$

$$\beta_j = \beta_{jjj} + \sum(\beta_{jii} + 2\beta_{ijj})/3 \quad (i \neq j; i, j = x, y, z) \qquad (9)$$

RESULTS AND DISCUSSION

Free donor and free acceptor

Molecular structures: The free donor and acceptor molecules were optimized at the B3LYP/6-31G(d,p) level of theory (Fig. 2) and a summary of important bond lengths in the optimized geometries are given in Table-1. As shown in Table-1, all bond lengths are within typical ranges and are comparable to the corresponding parameters in similar molecules. With respect to the donor molecules, insignificant differences in the main geometric parameters are observed due to substitutions. A significant difference (0.011 Å) is observed in the O2-C bond length of D2 and D3.

With respect to the acceptor molecules, the bond lengths of chloranil calculated with the 6-31G(d,p) basis set and those calculated with the 6-31++G(d,p) basis set[12] using the same method (BELYP) are not significantly different, indicating that the inclusion of diffuse functions in 6-31++G(d,p) was not essential (Table-1). However, for 2,3-dichloro-5,6-dicyanobenzoquinones, there are slight differences in the geometric parameters calculated at 6-31G(d,p) (this study) and 6-311++G(d,p)[21]. Because experimental values of these geometrical parameters were not available to the authors, using a larger basis set (triple-zeta basis set[21]) is expected to give better description of the molecular geometries than a smaller basis set (double-zeta basis set in this study). However, the present study was restricted by limited computational resources.

HOMO and LUMO analysis: Table-2 shows the calculated frontier molecular orbitals (HOMO and LUMO), the ionization potential (IP), the electron affinity (EA) and the total electronic energy ($E_{D/A}$), of the free donor and acceptor molecules calculated at the B3LYP/6-31G(d,p) level of theory.

Frontier molecular orbitals (FMO): Based on FMO theory, the interactions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the most important. A charge transfer band is usually observed when the energy gap between the HOMO of the donor and the LUMO of the acceptor is relatively small. The electron-donating group increases the energy level of the HOMO and the electron-withdrawing group (EWG) decreases the energy level of the LUMO. Therefore, electron-donating groups contribute to make a better electron-donor and electron-

TABLE-1
CALCULATED GEOMETRICAL BOND DISTANCES OF FREE DONORS AND FREE ACCEPTORS OPTIMIZED AT DFT/B3LYP/6-31G(d,p), REGULAR FONT

Parameter/ Bond length (Å)	Free acceptor			
	CHL	CHLA	BRL	DDQ
Cl–C	1.721; **1.7205**	1.731	–	1.718; *1.7170*
O1=C5	1.213; **1.2147**	1.228	1.214	1.214; *1.2068*
C1–C2	1.500; **1.5003**	1.452	1.499	1.496; *1.4949*
C2–C3	1.500; **1.5003**	1.522	1.499	1.504; *1.5048*
C3–C4	1.351; **1.3526**	1.385	1.349	1.359; *1.3550*
C4–C5	1.500; **1.5003**	1.452	1.499	1.504; *1.5048*
C5–C6	1.500; **1.5003**	1.522	1.499	1.496; *1.4949*
C6–C1	1.351; **1.3526**	1.385	1.349	1.355; *1.3520*
C3–C7	–	–	–	1.427; *1.4237*
O3–C3	–	1.322	–	–
O4–C6	–	1.325	–	–
O3–H1	–	0.986	–	–
O1–H2(*)	–	1.933	–	–
Br–C	–	–	1.878	–
N≡C	–	–	–	1.163; *1.1544*
	Free donor			
	D1	D2	D3	
N1–C1	1.378	1.377	1.376	
N=N	1.270	1.270	1.271	
N3–C11	1.414	1.415	1.414	
N4–C2	1.382	1.382	1.380	
N5–C	1.367	1.367	1.358	
S1–C2	1.745	1.745	1.743	
S2–C	1.670	1.672	1.673	
O1–C10	1.421	1.421	1.421	
Cl1–C23	1.758	–	–	
C14–C17	1.511	–	1.511	
O2–C	–	1.419	1.431	
O3–C25	–	1.420	–	
C25–C26	–	–	1.517	

(*) Hydrogen bonding
Note: Values in bold font are at B3LYP/6-31++G(d,p) from Ref. 1 and in italics font at 6-311++G(d,p) from Ref. 2

TABLE-2
CALCULATED HOMO AND LUMO ENERGIES (IN a.u. units), THE IONIZATION POTENTIALS (IP) AND ELECTRON AFFINITIES (EA), ENERGY GAP (E.G. = (E_{LUMO})-(E_{HOMO}) (IN eV UNITS) AND TOTAL ELECTRONIC ENERGY, $E_{D/A}$, (IN a.u. UNITS) OF THE FREE DONOR AND ACCEPTOR MOLECULES

	E_{HOMO}	E_{LUMO}	IP	EA	E.G.	$E_{D/A}$
CHL	-0.28480	-0.15722	7.75	4.28 (1.37)	3.4715	-2219.81255295
CHLA	-0.25811	-0.14451	7.02	3.93 (1.10)	3.0911	-1451.10450649
BRL	-0.27180	-0.15292	7.40	4.16 (1.41)	3.2347	-10665.85438660
DDQ	-0.30845	-0.18732	8.39	5.10 (1.95)	3.2959	-1485.09435450
D1	-0.20422	-0.09571	5.56 (7.68)	2.60	2.9526	-2532.14890254
D2	-0.19962	-0.09067	5.43	2.47	2.9645	-2262.28427280
D3	-0.19841	-0.08994	5.40	2.45	2.9515	-2226.40513298

Note: Values in parentheses are the experimental values [Ref. 3,4]

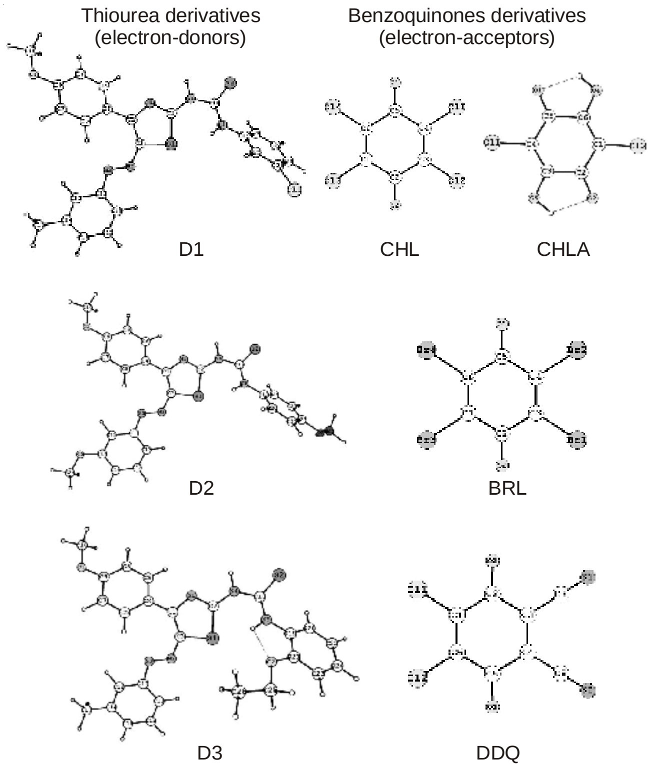


Fig. 2 Optimized geometries of thiourea derivatives (D1, D2 and D3) and benzo-quinones (CHL, CHLA, BRL and DDQ) at the B3LYP/6-31G(d,p) level of theory along with atomic numbering used in this study

withdrawing groups contribute to provide a better electron-acceptor. The HOMO energy of the three donor molecules increases in the following order: D1 < D2 < D3. Thus, D3 is a stronger donor while D1 is a weaker donor. The LUMO energy of the four acceptor molecules decreases in the following order: CHLA > BRL > CHL > DDQ. Thus, 2,3-dichloro-5,6-dicyanobenzoquinones is a stronger acceptor due to the presence of the –C≡N group, which is a strong electron-withdrawing group. Chloranic acid is a weaker acceptor because of the presence of –OH groups that are electron-withdrawing groups inductively but electron-donating groups through resonance.

Ionization potential and electron affinity: The electron donating ability of an electron-donor molecule is measured by its ionization potential, which is the energy required to remove an electron from the HOMO. The electron accepting ability of the electron-acceptor is determined by its electron affinity (EA), which is the energy released when filling the LUMO. The experimental calculated electron affinities of the acceptor molecules decrease in the following order: DDQ (1.95) > IDL (1.65) > BRL (1.41) > CHL (1.37) > CHLA (1.10) eV[22]. These calculated electron affinities show good qualitative agreement with the experimental values; the experimental trend is observed theoretically, but the calculate values are in poor quantitative agreement with the experimental values. The theory over estimates the electron affinities of the acceptor molecules by the following amounts: 3.15, 2.75, 2.91 and 2.83 eV for 2,3-dichloro-5,6-dicyanobenzoquinones, bromanil, chloranil and chloranic acid, respectively. Thus, 2,3-dichloro-5,6-dicyanobenzoquinones with the lowest LUMO energy has also the smallest electron affinity value and, *vice versa* chloranic acid with the highest LUMO energy has the largest electron affinity value.

The calculated ionization potentials of the donor molecules decrease in the following order: D1 (5.56) > D2 (5.43) > D3 (5.40) eV. The only available experimental ionization value is for the D1 molecule (7.68 eV)[13]; in this case, the theory under estimates the ionization potential by 2.12 eV. The reactivity of the donor molecules is expected to decrease as their ionization potentials increase and the reactivity of the acceptor molecules is expected to increase as their electron affinities increase. According to these trends, the reactivity of the acceptor molecules should decrease in the order: DDQ > CHL > BRL > CHLA; and the reactivity of the donor molecules should decrease in the order of: D3 > D2 > D1.

Energy gap: The reactivity/stability can also be deduced from the energy gap calculations (Table-2). Molecules with smaller energy gaps are more reactive. Table-2 shows that D3 is the more reactive donor (from the FMO and IP calculations) and has the smallest energy gap value (2.9515 eV). On the other hand, 2,3-dichloro-5,6-dicyanobenzoquinones is expected to have the smaller energy gap (from the FMO and EA calculations); unexpectedly, however, the acceptor molecule with the smallest energy gap is chloranic acid.

Quantum chemical parameters analysis: Quantum chemical parameters have proven to be useful quantities in chemical reactivity theory. To measure the molecular stability/reactivity of the donor and acceptor molecules, parameters such as dipole moment, electronegativity, hardness, softness and electrophilicity index were calculated and collected in Table-3. The calculation of such parameters has been extensively used to predict the reactivity of various corrosion inhibitors on metal surfaces[23-28]. To the best of our knowledge, this type of calculation for the donor and acceptor molecules of charge transfer complexes are rare in the literature[29].

TABLE-3
CALCULATED QUANTUM CHEMICAL PARAMETERS DIPOLE MOMENT (μ) (IN DEBYE UNITS), ELECTRONEGATIVITY (χ), HARDNESS (η) (IN eV UNITS), SOFTNESS (σ) (IN eV^{-1} UNITS), THE ELECTROPHILICITY INDEX AND ω (IN eV UNITS), OF FREE DONOR AND FREE ACCEPTOR MOLECULES

	μ (Debye)	χ (eV)	η (eV)	σ (eV^{-1})	ω (eV)
CHL	0.000	6.014	1.736	0.576	0.000
CHLA	0.000	5.478	1.546	0.647	0.000
BRL	0.000	5.778	1.617	0.618	0.000
DDQ	4.022	6.745	1.648	0.607	4.908
D1	3.929	4.081	1.476	0.677	5.228
D2	3.371	3.949	1.482	0.675	3.833
D3	4.410	3.923	1.476	0.678	6.589

Dipole moment: The dipole moments (μ) of the donor and acceptor molecules vary from 0.0 to 4.4 Debye. Different substituents generate variation in the dipole moments of the three molecules; the dipole moments of the donor molecules increase in the following order: D2 < D1 < D3. D3 is substituted with an ethoxy and a methyl group at the two opposite ends of the molecule; these groups are both electron-donating groups, but have different donating abilities. On the other hand, D2 is substituted by two identical methoxy groups at the two opposite ends of the molecule. These substituents increase the nucleophilicity of the aromatic rings. D1 is substituted with a methyl group and a chloride group at the two opposite ends of the molecule; the chloride-substituted atom is electron-withdrawing group inductively and electron-donating group through resonance. Thus, the higher dipole moment of D3 suggests that the electronic charge distribution of this molecule is highly asymmetric. In contrast, the lower dipole moment of D2 suggests that the electronic charge distribution of this molecule is symmetrical.

Electronegativity: Electronegativity (χ) is a chemical property that describes the ability of an atom/functional group to attract electrons/electron density towards itself. Thus, it is important to consider the electronegativity of the acceptor molecule as a measure of its reactivity; a larger electronegativity indicates a better acceptor molecule. The electronegativities of the acceptor molecules increase in the following order: CHLA < BRL < CHL < DDQ (Table-3).

Hardness and softness: A hard molecule (η) has a large energy gap, while a soft molecule (σ) has a small energy gap[28]. Tables 2 and 3 validate this statement; comparing acceptor molecules reveals that chloranil, the acceptor molecule with the largest hardness value (1.736 eV) and smallest softness value (0.576 eV^{-1}) also has the largest energy gap (3.4715 a.u.). On the other hand, chloranic acid is the acceptor molecule with the smallest hardness value (1.547 eV), the largest softness value (0.647 eV^{-1}) and the smallest energy gap (3.0911 a.u.).

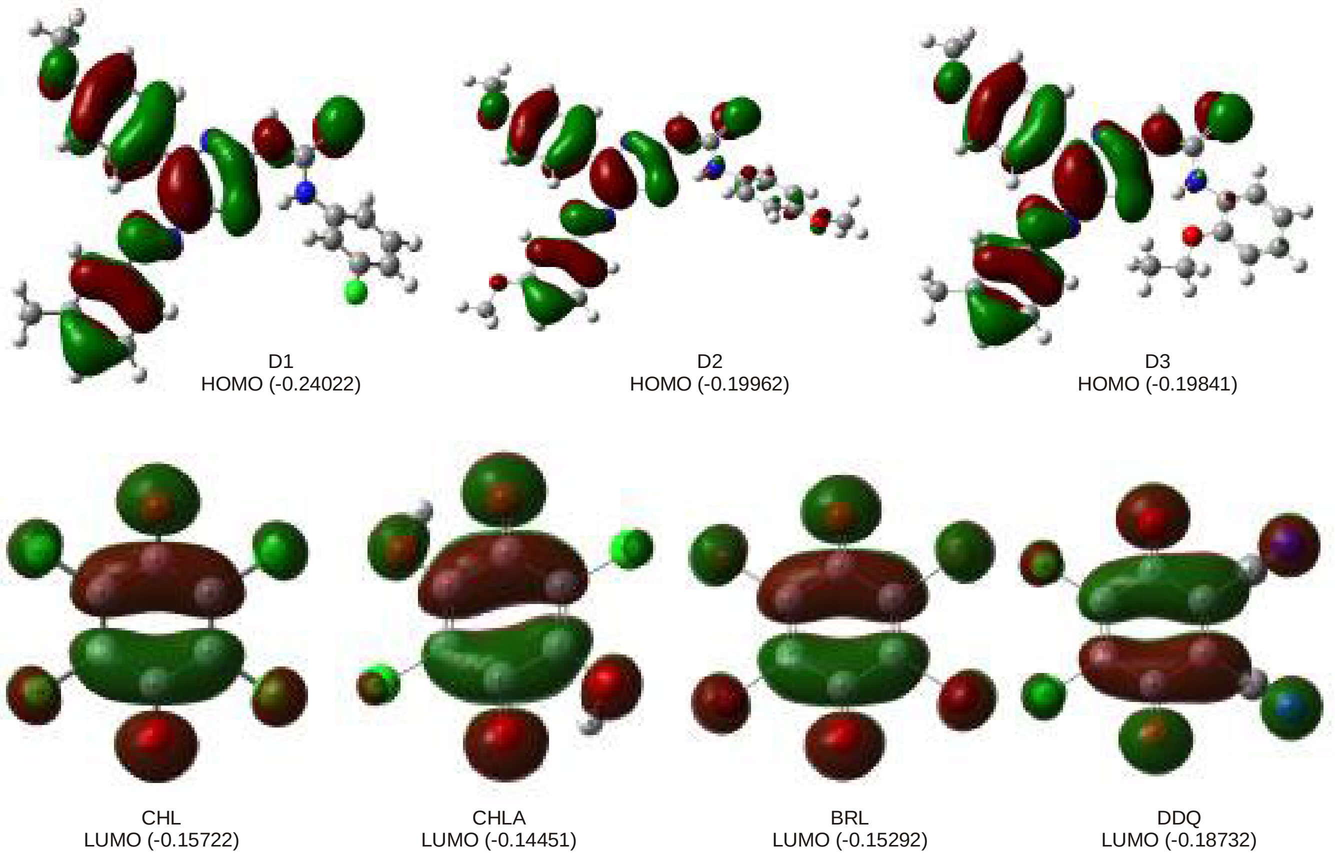
Fig. 3 shows the optimized donor (D1, D2 and D3) geometries along with the HOMOs and LUMOs of the acceptors (chloranil, chloranic acid, bromanil and 2,3-dichloro-5,6-dicyanobenzoquinones). By general inspection, the HOMO is mostly distributed over the donor molecules and an important part of it resides on the hetero atoms (N, S and O atoms) of the rings and substituents groups. Closer inspection reveals that the HOMO is not distributed on a specific part of the donor molecules; for instance, the HOMO of D1 is not distributed on the aromatic ring substituted with chloride atom. Later (donor-acceptor complexes), we determine that the regions in which the HOMOs are not distributed will be excluded in the positioning of the acceptor molecule with respect to the donor molecule. The optimized geometries of the acceptors indicate that the LUMO of chloranil resides on the chlorine and carbon atoms and not on the carbonyl groups. Alternatively, the LUMO of chloranic acid resides on all atoms except hydrogen. In bromanil, the LUMO resides on all atoms without exception. The LUMO of 2,3-dichloro-5,6-dicyanobenzoquinones resides on the chlorine, nitrogen and carbon atoms of the ring but not on the carbon atoms of the cyanide groups.

Donor-acceptor complexes

Molecular structures and electronic charge distribution: Fig. 4 shows the optimized geometries of donor-acceptor complexes (D-A complexes) along with atomic numbering on the hetero atoms (N, O, S and Cl). As a representative example, the bond lengths of the optimized geometries of free D1, free CHL and D1-CHL complex are given in Table-4. Upon complexation, one of the C=O bond lengths in chloranil increases by 0.002 Å (from 1.213 to 1.215 Å), while the other C=O bond stays the same length. The Cl-C bonds (1.721 Å) either increase (by 0.001 and 0.002 Å), decrease (by 0.001 Å)

TABLE-4
CALCULATED GEOMETRICAL BOND DISTANCES OF FREE D1, FREE CHL AND D1-CHL COMPLEX OPTIMIZED AT B3LYP/6-31G(d,p)

Parameter/bond length (Å)	D1	CHL	D1-CHL complex
Cl1–C	1.758	–	1.759
Cl2–C	–	1.721	1.722
Cl3–C	–	1.721	1.723
Cl4–C	–	1.721	1.720
Cl5–C	–	1.721	1.721
O1–C	1.421	–	1.422
O2=C	–	1.213	1.213
O3=C	–	1.213	1.215
N1–C1	1.378	–	1.377
N1–C2	1.307	–	1.307
N–N	1.270	–	1.271
N3–C	1.414	–	1.415
N4–C2	1.382	–	1.381
N4–C18	1.387	–	1.388
N5–C18	1.367	–	1.366
N5–C19	1.417	–	1.417
S1–C2	1.745	–	1.744
S1–C3	1.780	–	1.780
S2–C	1.670	–	1.669



D1
HOMO (-0.24022)

D2
HOMO (-0.19962)

D3
HOMO (-0.19841)

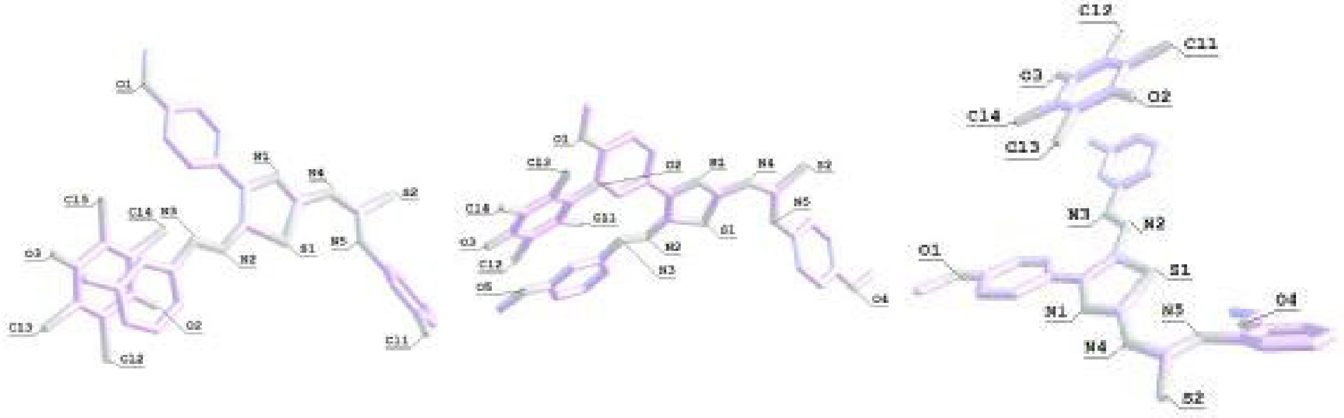
CHL
LUMO (-0.15722)

CHLA
LUMO (-0.14451)

BRL
LUMO (-0.15292)

DDQ
LUMO (-0.18732)

Fig. 3. Optimized geometries of donors along with HOMO and the acceptors along with LUMO



D1-CHL complex

D2-CHL complex

D3-CHL Complex

Fig. 4. Optimized geometries of D-A complexes along with atomic numbering on the hetero atoms *i.e.* N, O, S and Cl atoms. Note: for clarity hydrogen atoms are not shown

or remain the same. In D1, some bond lengths are elongated while others shorten upon complexation; similar observations have been previously reported and were taken as evidence of the charge transfer process[12,30].

To provide more evidence of the charge transfer process, the change in the Mulliken charge on hetero atoms upon moving from free donor or acceptor molecules to the complex was calculated at the B3LYP/6-31G(d,p) level of theory for free D1, D2, D3 and chloranil molecules and D-A complexes (Table-5). With few exceptions, significant changes are observed in the Mulliken charge distribution on hetero atoms between free species and the formed complex, which can be taken as a clear indication of the charge transfer process from the donor molecule to the acceptor molecule. For instance, the charges of N2 atoms are -0.291, -0.289 and -0.292 a.u. in free D1, D2 and D3, respectively, while they are -0.288, -0.286 and -0.290 a.u. in D1-CHL, D2-CHL and D3-CHL, respectively. The charges of S2 atoms are -0.231, -0.249 and -0.247 a.u. in free D1, D2 and D3, respectively, while they are -0.227, -0.245 and -0.242 a.u. in D1-CHL, D2-CHL and D3-CHL, respectively. Furthermore, the charges on the atoms of free donor molecules are generally greater than those of the charge transfer complexes. For the acceptor molecules, the charges on the atoms (O2 and O3) of free acceptor molecules are generally

TABLE-5
MULLIKEN ELECTRONIC CHARGE (a.u.) ON HETERO ATOMS, *i.e.* N, O, S AND Cl ATOMS, OF FREE DONOR MOLECULES, *i.e.* D1, D2 AND D3 AND FREE CHL ACCEPTOR MOLECULE AND D-A COMPLEXES

Atom type & number	D1	D2	D3	CHL	D1-CHL	D2-CHL	D3-CHL
N1	-0.510	-0.513	-0.515	–	-0.513	-0.520	-0.515
N2	-0.291	-0.289	-0.292	–	-0.288	-0.286	-0.290
N3	-0.346	-0.349	-0.349	–	-0.348	-0.351	-0.351
N4	-0.550	-0.551	-0.551	–	-0.550	-0.551	-0.550
N5	-0.605	-0.602	-0.619	–	-0.605	-0.602	-0.616
O1 (methoxy)	-0.513	-0.513	-0.514	–	-0.513	-0.513	-0.513
O4 (methoxy)	–	-0.519	–	–	–	-0.519	–
O5 (methoxy)	–	-0.518	–	–	–	-0.518	–
O2	–	–	–	-0.398	-0.403	-0.403	-0.403
O3	–	–	–	-0.398	-0.418	-0.422	-0.419
O (ethoxy)	–	–	-0.566	–	–	–	-0.566
Cl1	0.015	–	–	–	-0.016	–	–
Cl2	–	–	–	0.102	0.093	0.093	0.091
Cl3	–	–	–	0.102	0.089	0.086	0.088
Cl4	–	–	–	0.102	0.100	0.106	0.104
Cl5	–	–	–	0.102	0.100	0.094	0.094
S1	0.246	0.243	0.248	–	0.250	0.247	0.253
S2	-0.231	-0.249	-0.247	–	-0.227	-0.245	-0.242

TABLE-6
NUMBER OF ELECTRONS TRANSFERRED (ΔN) OF DONOR-ACCEPTOR COMPLEXES

	CHL	CHLA	BRL	DDQ
D1	0.3009	0.2312	0.2744	0.4264
D2	0.3207	0.2950	0.2950	0.4465
D3	0.3255	0.2573	0.2999	0.4517

smaller than those of the charge transfer complexes; for instance, the charge of O2 in free chloranil is -0.398 a.u., while it is -0.403 a.u. in D1-CHL, D2-CHL and D3-CHL. The increase in the Mulliken charges for some atoms of chloranil (electron-acceptor) along with the decrease in the Mulliken charges for some atoms in electron-donor molecules is clear evidence of the nature of reactivity in these species; a similar conclusion has been drawn in previous studies[12,30].

Table-6 summarizes the number of electrons transferred (ΔN) from the donor molecule (mainly from HOMO) to the acceptor molecule (mainly to LUMO) of the charge transfer complexes calculated using eqn. 6. The largest ΔN (more transferred electrons) is associated with cases where the donor molecules are combined with the acceptor 2,3-dichloro-5,6-dicyanobenzoquinones. In contrast, the smallest ΔN (less transferred electrons) correspond to cases where the donor molecules are combined with the acceptor chloranic acid. Additionally, with only one exception, ΔN increases with the same trend for all donor molecules: D-CHLA < D-BRL < D-CHL < D-DDQ. For the three series D-CHL, D-BRL and D-DDQ, D3-A has the maximum ΔN, while D2-CHLA has the maximum ΔN for the series D-CHLA.

HOMO, LUMO and energy gap analysis: Table-7 summarizes the energies of the HOMO and LUMO orbitals, the energy change (ΔE_{CTC}) and the heat of formation (ΔH_{CTC}) for the D-A complexes. The energy change (ΔE_{CTC}) is estimated as the difference between the total electronic energy of the complex (E_{D-A}) and the sum of the total electronic energies of the free donor and free acceptor molecules ($E_D + E_A$), resulting in eqn. 10:

$$\Delta E_{CTC} = E_{D-A} - (E_D + E_A) \qquad (10)$$

The heat of formation (ΔH_{CTC}) is estimated as the difference between the enthalpy change of the complex (ΔH_{D-A}) and the sum of the change of enthalpies of the free donor and acceptor molecules ($\Delta H_D + \Delta H_A$), resulting in eqn. 11:

$$\Delta H_{CTC} = \Delta H_{D-A} - (\Delta H_D + \Delta H_A) \qquad (11)$$

The charge transfer complexes are significantly more stable compared to their components; for instance, D2-CHL and D2-CHLA complexes are 10.04 and 30.96 kJ/mol more stable than their components (D2 and chloranil or chloranic acid), respectively. For the series D-CHL, ΔE_{CTC} for the formation of the charge transfer complexes has the trend: D2-CHL > D3-CHL > D1-CHL. This indicates that D1 has the

TABLE-7
CALCULATED ENERGIES OF THE FRONTIER MOLECULAR ORBITALS OF HOMO AND LUMO, THE TOTAL ELECTRONIC ENERGY (E_{D-A}), (IN a.u. UNITS), THE CALCULATED ENERGY CHANGE (ΔE_{CTC}) AND HEAT OF FORMATION (ΔH_{CTC}), OF DONOR-ACCEPTOR COMPLEXES (IN kJ/mol UNITS) AT DFT/B3LYP/6-31G(d,p)

D-A complex	E_{HOMO}	E_{LUMO}	E_{D-A}	ΔE_{CTC}	ΔH_{CTC}
D1-CHL	-0.20753	-0.15103	-4751.964805540	-8.80	-3.64
D2-CHL	-0.20262	-0.14865	-4482.100650700	-10.04	-4.72 (-9.23)
D2-CHLA	-0.20216	-0.13489	-3713.400570530	-30.96	-25.75 (-10.68)
D2-BRL	-0.20379	-0.14302	-12928.14834820	-25.44	-20.45 (-3.76)
D2-DDQ	-0.20618	-0.16632	-3747.385493640	-18.03	-12.98 (-20.62)
D3-CHL	-0.20149	-0.14904	-4446.221184380	-9.19	-4.37

Note: Values in parentheses are the experimental values from Ref. 4

weakest interaction with chloranil, *i.e.*, it is the least efficient molecule that acts as a donor. With respect to the series D2-A, the energy changes have the trend D2-CHLA > D2-BRL > D2-DDQ > D2-CHL, indicating that chloranil has the weakest interaction with D molecules, *i.e.*, it is the least efficient molecule that acts as an acceptor.

Charge transfer complex heats of formation (ΔH_{CTC}) are negative values, indicating that complex formation is an exothermic process, as observed experimentally[13]. For the series D-CHL complexes, the reaction becomes more exothermic (more negative value) in the order: D1-CHL < D3-CHL < D2-CHL. For the series D2-A complexes, the reaction becomes more exothermic in the following order: D2-CHL < D2-DDQ < D2-BRL< D2-CHLA. Poor agreements with experimental values and trends were found because the parameters were calculated in vacuum (gas phase); the inclusion of solvent may improve the accuracy. As reported[31], the experimental acceptor-solvent interaction affects the correlation between charge transfer intensities and the complex heats of formation. This observation may also be valid to apply to the theoretical calculations.

Because it is expected that more reactive complexes (less stable) have smaller energy gaps and *vice versa*, two equations were used to calculate the energy gap (E.G.) values of D-A complexes to investigate their reactivity/stability. According to eqn. 12, the energy gap is calculated by:

$$\text{Energy gap (E.G.)} = (E_{LUMO})_A - (E_{HOMO})_D \qquad (12)$$

Energy gap is the difference between the energy of the lowest unoccupied molecular orbital of the free acceptor molecule $(E_{LUMO})_A$ and the highest occupied molecular orbital of the free donor molecule $(E_{HOMO})_D$ (Table-8).

TABLE-8
CALCULATED ENERGY GAP (E.G.) USING THE EQUATION ENERGY GAP = $(E_{LUMO})_A$-$(E_{HOMO})_D$, REGULAR FONT AND USING THE EQUATION ENERGY GAP = $(E_{LUMO})_{D-A}$-$(E_{HOMO})_{D-A}$, BOLD FONT, (IN eV UNITS) AT B3LYP/6-31G(d,p)

	D1	D2	D3
CHL	1.2789	1.1537	1.1208
	1.5374	**1.4685**	**1.4272**
CHLA	1.6248	1.4996	1.4667
	–	**1.8305**	–
BRL	1.3959	1.2707	1.2378
	–	**1.6536**	–
DDQ	0.4599	0.3347	0.3018
	–	**1.0846**	–

For the series D1-A, D2-A and D3-A (the acceptor molecule is chloranil, chloranic acid or bromanil), the energy gap values increase in the following order: D3-A < D1-A < D2-A. For the series D-DDQ, the energy gap values increase in the following order: D3-DDQ < D2-DDQ < D1-DDQ. In contrast, for the series D-CHL, D-CHLA, D-BRL and D-DDQ (the donor molecule is D2 or D3), the energy gap values increase in the order: D-DDQ < D-BRL < D-CHLA < D-CHL. When the donor molecule is D1, the trend of increasing the energy gap values is: D-BRL < D-CHLA < D-CHL < D-DDQ. These results clearly indicate the large impact of the substituent groups of the donor and acceptor molecules on the reactivity/stability of the formed complexes.

According to eqn. 13, the energy gap is calculated by:

$$\text{E.G.} = (E_{LUMO})_{D-A} - (E_{HOMO})_{D-A} \qquad (13)$$

where energy gap is the difference between the energy of the lowest unoccupied molecular orbital of the D-A complex $(E_{LUMO})_{D-A}$ and the highest occupied molecular orbital of the D-A complex $(E_{HOMO})_{D-A}$ (Table-8). Table-8 shows that the energy gap values of the charge transfer complexes decrease in the following order: D1-CHL > D2-CHL > D3-CHL. Because the acceptor in these three charge transfer complexes is the same molecule (CHL), the effect on the stability/reactivity of the formed complex depends on the reactivity of the donor molecule *i.e.,* its ability to donate electron to the acceptor molecule. As mentioned previously, the D3 molecule (from FMO and IP calculations) is the most reactive donor molecule and, at the same time, forms the complex with the smallest energy gap. Thus, the complex formed is the less stable and the more chemically reactive, demonstrating that more reactive species (here the donor is D3) do not necessarily form stable complexes. Table-8 shows that the energy gaps calculated by the two equations decrease in the following order: D1-A > D2-A > D3-A; the reactivity of the formed complexes therefore increases in the reverse order. The energy gaps of each donor with different acceptors decrease in the following order: D-CHLA > D-BRL > D-CHL > D-DDQ.

From the determination of donor and acceptor molecule FMO (HOMO and LUMO analysis), the raising of the HOMO energies of the donor molecules (D3 > D2 > D1) along with the lowering of the LUMO energies of the acceptor molecules (DDQ < CHL < BRL < CHLA) should lead to better interaction between the donor and acceptor molecule due to the formation of a complex with smaller energy gap Fig. 5(a) shows the plots charge transfer complex energy gap *vs.* donor molecule HOMO energy for the series D-CHL; a linear relationship with a very good correlation coefficient ($R^2 = 0.968$) is obtained. Similar plots of charge transfer complex energy gap *vs.* acceptor molecule LUMO energy also give a linear relationship with a very good correlation coefficient ($R^2 = 0.958$) for the series D2-A complexes [Fig. 5(b)].

The experimentally determined association constants (K) for the series D2-A reported in El- Mossalamy's study[13] show K decreases in the following order: D2-DDQ > D2-BRL > D2-CHL > D2-CHLA. The K value for the highest stability complex (D2-DDQ) is 12.01 L/mol, while that of the lowest stability complex (D2-CHLA) is 4.78 L/mol. The energy gap values calculated by Equation 12 and Equation 13 for the same series show a good agreement with the experimental K values; the most stable complex (D2-DDQ) has the lowest energy gaps (0.3347 and 1.0846 eV from Equations 12 and 13, respectively), while the least stable complex (D2-CHLA) has the largest energy gaps (1.4996 and 1.8305 eV). It is necessary to mention, however, that there is no linear relationship between the theoretical energy gap values and the experimental K values.

Fig. 6 shows as a representative example of the spatial orientation of the FMO (HOMO and LUMO) of the studied D-CHL complexes calculated at the B3LYP/6-31G(d,p) level.

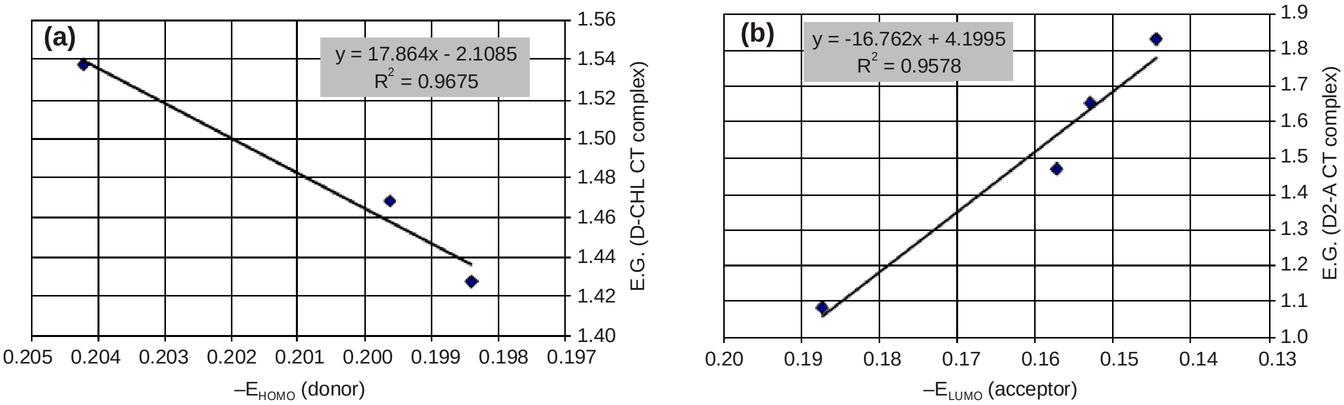


Fig. 5. Complexes of D-CHL (a) and D2-A (b): plot of energy gap (E.G.) of the charge transfer complexes *vs.* (a) E_{HOMO} of donors and (b) E_{LUMO} of acceptors

The HOMO of the D-CHL complex is spread over a large region of the donor molecule only, while the LUMO spreads only over the chloranil molecule. This result is strong evidence of charge transfer process from the donor part (mainly HOMO) to the acceptor part (mainly the LUMO), resulting in the construction of the charge transfer complex. Fig. 6 also shows the various HOMOs and LUMOs of the D-CHL complexes at the B3LYP/6-31G(d,p) level. It is interesting to note that the HOMOs (*i.e.,* HOMO, HOMO-1 and HOMO-2) are generally delocalized on the donor side. On the other hand, most of the LUMOs (*i.e.,* LUMO, LUMO +2 in D2-CHL and D3-CHL) are delocalized over the chloranil moiety. Greater delocalization of the HOMO orbitals over the donor part and the LUMO orbitals over the acceptor part of the D-A complex make the electron transfer process more applicable[12,30].

Table-9 summarizes the energies of the HOMO and LUMO levels for D-CHL complexes. As reported[12,30], the energies values of the complex HOMO levels are generally nearer to the energy values of the HOMO levels of the specific donor molecule in that charge transfer complex. Similarly, the energy values of the charge transfer complex LUMO levels are generally nearer to the energy values of the LUMO levels of the specific acceptor molecule in that charge transfer complex. For instance, the HOMO energy of the D2-CHL complex (-0.20262 a.u.) agrees well with the HOMO energy of D2 (-0.19962 a.u.) and is significantly different from that of chloranil (-0.28480 a.u.). Correspondingly, the LUMO energy of the D2-CHL complex (-0.14865 a.u.) agrees well with the LUMO energy of chloranil (-0.15722 a.u.) and is significantly different from that of D2 (-0.09067 a.u.). This observation could be generalized to almost all HOMO and LUMO levels of the charge transfer complexes.

Many articles[11,12,29,30,32] reported the ease of using the electrostatic potential map (MEP), *i.e.*, the total electron density mapped with the electrostatic potential (ESP), to correlate the relative position of the acceptor molecule with respect to the donor molecule in charge transfer complexes. As representative examples, maps for free D1, D2, D3 and chloranil as well as the D-CHL complexes calculated at the B3LYP/6-31G(d,p) level are shown in Fig. 7. A charge transfer complex is formed when an electrostatic interaction occurs between two oppositely charged pairs, *i.e.*, high and low density charge regions[11]. In Fig. 7, high electron density is represented by red and low electron density is represented by blue; the electron density decreases in the following order: red > orange > yellow > green > blue.

The electrostatic potential map of the chloranil molecule shows that low electron density (blue color) is delocalized on the center region of the aromatic ring; zero electron density (green color) is delocalized along the four C-Cl bonds, which may be attributed to the ED and EW nature of the chloride atoms. High electron density is delocalized along the C=O bonds (red color). For the D1 molecule, the high electron densities are delocalized on several regions: the methoxy group substituent, the thiourea-sulfur atom and the center of the methyl-substituted aromatic ring (electron-donating group). In the introduction, we stated that the nature of the interaction between the donor and acceptor in the charge transfer complex can be represented as the electron resonance between two regions: one with high-electron density and one with low-electron region. From the previous discussion and from Fig. 6, it is clear that the methyl-substituted aromatic ring represents the region of high-electron density. For the charge transfer complex D1-CHL, the chloranil molecule is attracted to this region due to its low-electron density region (the center of the

TABLE-9
HOMOS AND LUMOS ENERGIES (IN a.u. UNITS) OF D-CHL COMPLEXES CALCULATED AT B3LYP/6-31G(d,p)

Orbital type	Free D/A				D-A complex		
	CHL	D1	D2	D3	D1-CHL	D2-CHL	D3-CHL
HOMO	-0.28480 (60)	-0.20422 (128)	-0.19962 (132)	-0.19841 (132)	-0.20753 (188)	-0.20262 (192)	-0.20149 (192)
HOMO–1	-0.30560 (59)	-0.22397 (127)	-0.20871 (131)	-0.21269 (131)	-0.22560 (187)	-0.20980 (191)	-0.21397 (191)
HOMO–2	-0.30704 (58)	-0.22763 (126)	-0.21643 (130)	-0.21605 (130)	-0.23039 (186)	-0.21806 (190)	-0.21766 (190)
LUMO	-0.15722 (61)	-0.09571 (129)	-0.09067 (133)	-0.08994 (133)	-0.15103 (189)	-0.14865 (193)	-0.14904 (193)
LUMO+1	-0.05741 (62)	-0.05438 (130)	-0.04322 (134)	-0.04552 (134)	-0.09945 (190)	-0.09445 (194)	-0.09381 (194)
LUMO+2	-0.03569 (63)	-0.02172 (131)	-0.01160 (135)	-0.01077 (135)	-0.05656 (191)	-0.04876 (195)	-0.04956 (195)

Note: The orbital number is written in parenthesis

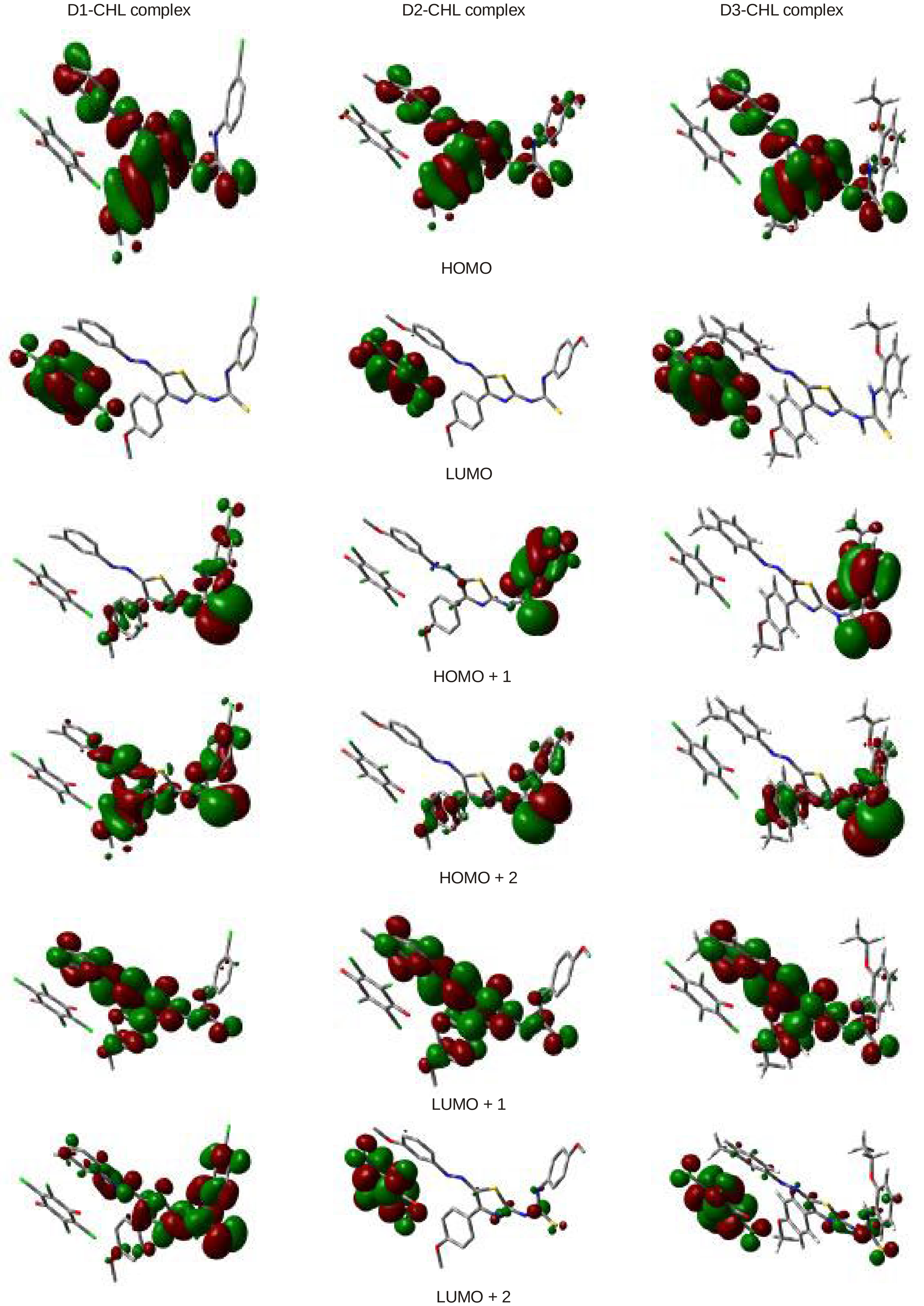


Fig. 6. Molecular orbital distribution for HOMO, HOMO - n (n = 1, 2) and LUMO, LUMO + n (n = 1, 2) of D-CHL complexes calculated at B3LYP/6-31G(d,p). Note: for clarity the hydrogen atoms are not shown

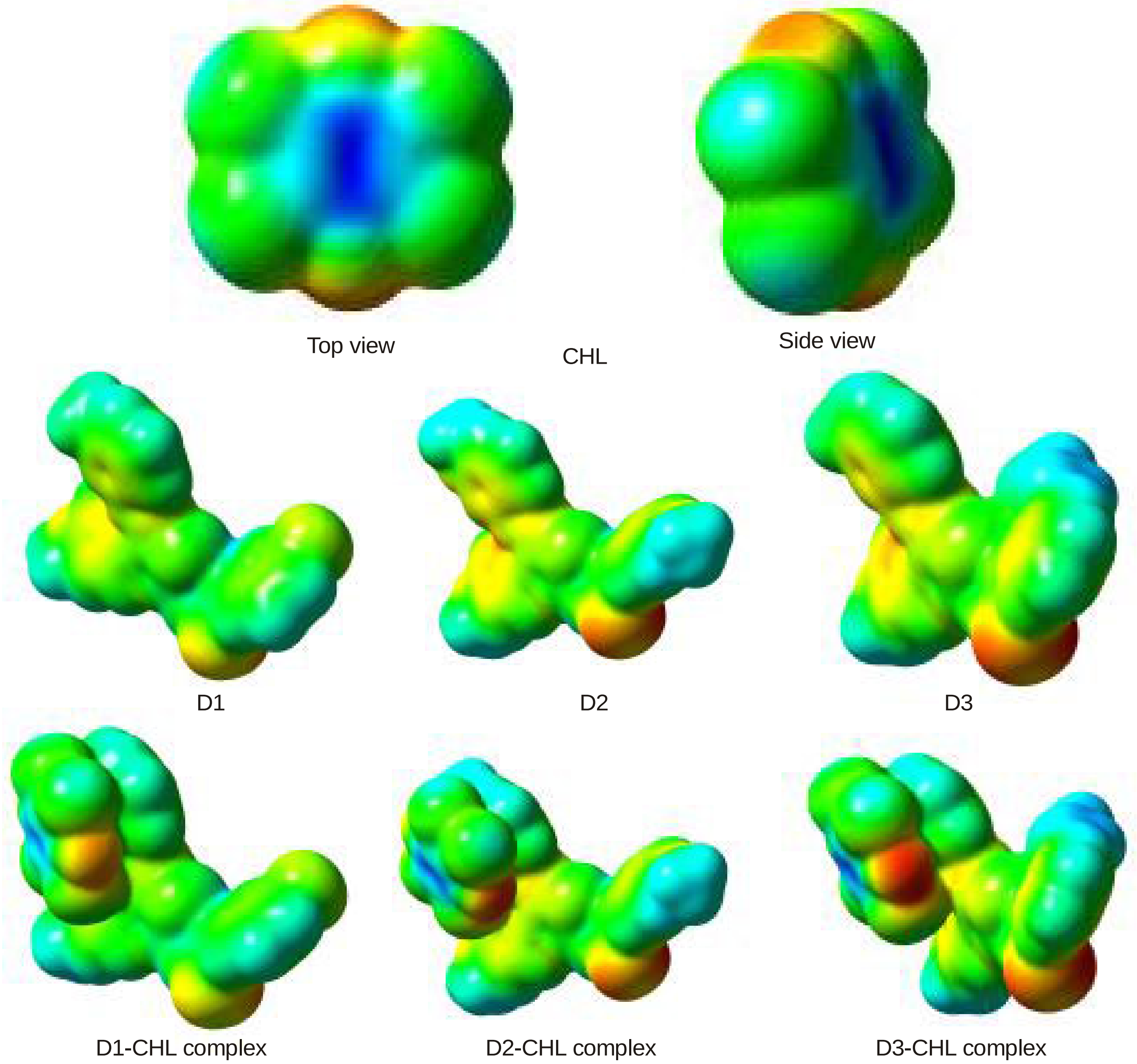


Fig. 7. Molecular electrostatic potentials (MEPs) of free donor molecules, free CHL and D-CHL complexes mapped at B3LYP/6-31G(d,p)

aromatic ring), which is similar to a cavity being filled. This observation confirms the charge transfer process and indicates that the positioning of the acceptor molecule with respect to the donor molecule was accurate, supporting the experimentally suggested positioning[13]. The same treatment can be extended to the D2-CHL and D3-CHL charge transfer complexes along with the other complexes investigated in this study.

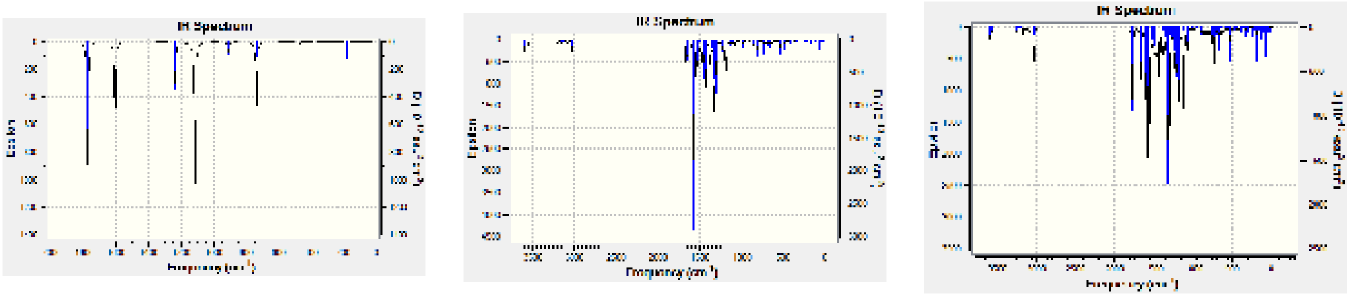
Assignments of vibrational frequencies: Experimentally investigating infrared (IR) vibrational frequencies of charge transfer complexes can be tedious and imprecise because the resultant spectra are crowded with overlapped bands. For this reason, vibrational frequency calculations assist in assigning spectra features[29,32]. If the acceptor molecule is non-acidic, *i.e.,* chloranil, bromanil and 2,3-dichloro-5,6-dicyanobenzoquinones[13,33], the complex formation interaction involves only electron transfer from the donor molecule to the acceptor molecule. As a representative example, the IR frequencies bands of free chloranil and the D1-CHL complex are shown in Fig. 8 and Table-10. The calculations overestimate the experimental frequencies. This may be attributed to the fact that the calculated values are harmonic frequencies (from the simple harmonic oscillation model), while the experimental values are inharmonic frequencies[9] (real systems deviate from harmonicity). The discrepancy may also be attributed to the fact that the experimental values were calculated from solutions, while the theoretical values were calculated in the gas phase. For instance, the experimental $\bar{\nu}_{C=O}$ values in the free chloranil molecule are 1686 and 1695 cm^{-1}, whereas the calculated values are 1773 and 1777 cm^{-1}. The experimental $\bar{\nu}_{C\equiv N}$ values in the free 2,3-dichloro-5,6-dicyano-benzoquinones molecule are 2235 cm^{-1}, while the calculated values are 2348.59 and 2358.47 cm^{-1}. The $\bar{\nu}_{C\equiv N}$ value in the D1-DDQ complex (1:1) is: 2210 cm^{-1}, lower than the calculated values of 2345.41 and 2356.47 cm^{-1}.

TABLE-10
CALCULATED IR NORMAL VIBRATIONAL MODES (cm^{-1}) AND TRANSITION ENERGY (E_{CT}) (eV) OF CHARGE TRANSFER COMPLEXES OF D1, D2 AND D3, WITH BENZOQUINONES

	Ratio D:A	C–O	C–H (methoxy)	O–H	C≡N	–NH	C=O	C–Cl	E_{CT}
D1	Free	1071.47	1518.48	–	–	3552.59, 3595.08	–	739.98	–
D2	Free	1072.04, 1075.44, 1082.10	1518.05, 1518.69, 1520.89	–	–	3555.87, 3598.20	–	–	–
D3	Free	1072.38	1518.88	–	–	3529.23, 3594.32	–	–	–
CHL	Free	–	–	–	–	–	1773.14, 1777.05 (1686, 1695)	738.00	–
CHLA	Free	–	–	3512.83, 3520.67	–	–	1741.84, 1746.18 (1637, 1670)	913.05	–
BRL	Free	–	–	–	–	–	1766.07, 1771.67 (1640, 1685)	–	–
DDQ	Free	–	–	–	2348.59, 2358.47 (2235)	–	1768.70, 1773.86 (1674)	799.98	–
D1-CHL	1:1	1071.49	1517.68	–	–	3553.03, 3595.35	1767.04, 1776.64	735.00	1.076 (2.89)
	1:2	1070.35	1518.23	–	–	3563.85, 3598.26	1767.26, 1768.24, 1771.40, 1772.59	735.90, 737.37	0.975 (2.67)
D1-BRL	1:1	1071.44	1517.97	–	–	3554.35, 3594.79	1761.92, 1768.22	740.25	(2.89)
D1-DDQ	1:1	1070.51	1518.08	–	2345.41, 2356.47 (2210)	3554.86, 3592.69	1754.66, 1768.07	795.96	(2.59)
D2-CHL	1:1	1070.44, 1075.57, 1075.79	1517.66, 1518.70, 1518.94	–	–	3556.02, 3596.31	1765.76, 1776.44	735.17	1.053 (2.04)
	1:2	1068.11, 1070.73, 1075.18	1517.38, 1518.38, 1523.52	–	–	3565.29, 3597.80	1765.71, 1766.54, 1770.03, 1771.01	735.43, 735.58	0.977 (–)
D2-CHLA	1:1	1070.08, 1075.44, 1075.67	1517.36, 1518.75, 1521.24	3433.67, 3508.80 (3210)	–	3557.57, 3596.73	1736.79, 1749.37	911.63	–
D2-BRL	1:1	1072.21, 1074.69, 1075.87	1517.53, 1518.55, 1518.95	–	–	3555.13, 3596.24	1756.52, 1767.88	–	–
D2-DDQ	1:1	1069.74, 1071.02, 1075.50	1517.13, 1518.13, 1519.03	–	2345.35, 2355.17	3557.43, 3593.03	1747.92, 1761.46	794.85	–
D3-CHL	1:1	1071.40	1518.32	–	–	3531.26, 3594.36	1766.02, 1777.02	735.09	–
	1:2	1071.92	1518.34	–	–	3536.50, 3595.38	1766.73, 1768.89, 1771.78, 1775.71	735.50, 736.44	–

Note: Values in parentheses are the experimental values of IR frequencies

The conclusions from experimentally determined IR frequencies can be summarized in two points: (1) Most IR bands of the charge transfer complexes are shifted compared to those of their free components and (2) this shift is generally higher in the 1:1 (ratio) complexes than in the 1:2 (ratio) complexes, which is attributed to resonance inhibition in the 1:2 complexes[13]. The results of the calculations in this study agree with these two points; for instance, the $\bar{\nu}_{C=O}$ values of the free chloranil molecule are different from those in the D1-CHL complexes (1:1 and 1:2 ratios). The $\bar{\nu}_{C=O}$ in chloranil are 1773.14 and 1777.05 cm^{-1}, while they are 1767.04 and 1776.64 cm^{-1} in D1-CHL (1:1) and 1767.26, 1768.24, 1771.40 and 1772.59 cm^{-1} in D1-CHL (1:2). The same observation holds for $\bar{\nu}_{C-Cl}$; the $\bar{\nu}_{C-Cl}$ values are 738.00 in free chloranil, 735.17 in D2-CHL (1:1) and 735.43 and 735.58 cm^{-1} in D2-CHL (1:2). For the free D1 molecule, the $\bar{\nu}_{C-H}$ (methoxy)



CHL D1-CHL complex (1:1 ratio) D1-CHL (1:2 ratio)

Fig. 8. IR spectra of selected free CHL and its charge transfer complexes by B3LYP/6-31G(d,p)

values are different than those in the D1-CHL complexes, which have $\overline{\nu}_{C-H}$ values of 1518.48, 1517.68 and 1518.23 for D1, D1-CHL (1:1) and D1-CHL (1:2), respectively. Generally, the IR bands of the acceptor molecules were shifted to lower values in their corresponding complexes while the IR bands of the donor molecules were shifted to higher values in their corresponding complexes. This observation is similar to the one in the literature, where the shifts were explained as a characteristic of the π-π^* charge transfer interaction (πHOMO$_D$ – π^*LUMO$_A$)[9]. The transition energies (E_{CT}) for the charge transfer complexes were calculated at the TD-DFT/B3LYP/6-31G(d,p) level and are given in Table-10. The calculated values do not agree very well with the available corresponding experimental values; for instance, the difference between the experimental and calculated energy values for the D1-CHL complex (1:1) is 1.814 eV.

First hyperpolarizability: The dipole moments and the first total hyperpolarizability of charge transfer complexes calculated at the DFT/B3LYP/6-31G(d,p) level of theory are given in Table-11. The dipole moments of the charge transfer complexes are generally different from the dipole moments of their constituent donor and acceptor molecules. This result is a clear indication of the charge transfer process from the donor molecule to the acceptor molecule, as previously reported[12]. The dipole moments of the charge transfer complexes are generally lower than those of their constituent donor molecules; for instance, the dipole moments of the free donor molecules D1, D2 and D3 are 3.93, 3.37 and 4.41 Debye, respectively, while those of their charge transfer complexes D1-CHL, D2-CHL and D3-CHL are 3.24, 2.19 and 3.94 Debye, respectively. In addition, the donor with larger dipole moment (more polar) forms a complex with a larger dipole moment. For the series D2-A complexes, the dipole moments increase in the following order: D2-BRL (2.04 Debye) < D2-CHL (2.19 Debye) < D2-CHLA (3.09 Debye) < D2-DDQ (3.73 Debye). As expected, 2,3-dichloro-5,6-dicyanobenzoquinones, the only acceptor molecule with a net dipole moment (4.02 Debye), forms the complex with the highest dipole moment.

Non-linear optical (NLO) activity was extensively investigated by calculating the first hyperpolarizability parameter. A large first hyperpolarizability (B_{tot}) , indicates a good NLO material[8,34-37]. The charge transfer complexes in this study show significantly large B_{tot} values ranging from 4.4×10^{-29} to 95×10^{-29} esu. Therefore, these charge transfer complexes make good candidates as NLO materials. For the series D-CHL complexes, D1-CHL has the largest B_{tot} value, while the D2-CHL complex has the smallest. For the series D2-A complexes, the largest B_{tot} value is that of D2-DDQ (the complex of maximum μ value) and the smallest is that of D2-CHLA; the trend in increasing B_{tot} values is: D2-CHLA < D2-BRL < D2-CHL < D2-DDQ.

TABLE-11
CALCULATED DIPOLE MOMENT (μ) AND TOTAL HYPERPOLARIZABILITY (B_{tot}) OF D-A COMPLEXES

	μ (Debye)	B_{tot} (a.u.)	$B_{tot} \times 10^{-29}$ (esu)
D1-CHL	3.24	5088.50	4.4
D2-CHL	2.19	26806.48	23.2
D2-CHLA	3.09	3444.71	2.97
D2-BRL	2.04	23220.73	20.06
D2-DDQ	3.73	110099.78	95.12
D3-CHL	3.94	16956.37	14.6

Conclusions

In this study, the following goals have been achieved at the DFT/B3LYP/6-31G(d,p) and TD-DFT/B3LYP/6-31G(d,p) levels of theory:

(1) The geometries of the N-aryl-N′-4-(-*p*-anisyl-5-arylazothiazolyl)thiourea derivatives and benzoquinone derivatives were calculated.

(2) The capabilities of the N-aryl-N′-4-(-*p*-anisyl-5-arylazothiazolyl)thiourea derivatives to act as electron-donor molecules and the benzoquinone derivatives to act as electron-acceptor molecules were demonstrated.

(3) Quantum chemical properties of the free donor and acceptor molecules such as HOMO, LUMO, energy gap, ionization potential, electron affinity *etc.* were used to identify the reactivity of these molecules toward complexation and the results assisted in the inter-pretation of experimental findings. Generally, the reactivity of the studied donor molecules toward complexation had the trend D1 < D2 < D3, while the trend for the acceptor molecules (mainly from the LUMO and energy gap calculations) was CHLA < BRL < CHL < DDQ.

(4) The charge transfer process was demonstrated using FMO and Mulliken charge distribution calculations.

(5) The suggested positioning of the acceptor molecule with respect to the donor molecule[13] was confirmed theoretically from the HOMO, LUMO and electrostatic potential map calculations of the charge transfer complexes.

(6) The calculated IR vibrational frequencies agreed well with experiment and justify the type of the interaction (electron transfer only) between the donor and acceptor molecules with non-acidic character.

(7) First hyperpolarizability calculations demonstrated that these charge transfer complexes are active NLO materials.

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