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TCNE-aniline charge transfer complex: *ab initio* and TDDFT investigations in gas phase

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Abstract The geometric and electronic structure of tetracyanoethylene (TCNE)-aniline (donor-acceptor type) complex has been investigated in gas phase using *ab initio* and time dependent density functional theory calculations. Both the above calculations predict a composed structure for the complex, in which the interacting site is a C≡N and C=C bond center in the TCNE and, –NH$_2$ and π-electrons of aniline. The N atom of aniline is oriented toward the TCNE molecule. The charge transfer transition energy, estimated by calculating the ground-to-excited state transition electric dipole moments of the complex, agree well with the reported experimental value in chloroform medium.

Keywords *Ab initio* · Aniline · CT complex · DFT and TDDFT investigations · Molecular electrostatic potential maps · TCNE

Introduction

Electron donor–acceptor (EDA) complexes have been extensively studied in widespread fields from biological to materials science [1]. The association behavior of the complexes and the absorption property of intermolecular charge-transfer (CT) transition are dependent on the ionization potential of the donor, the electron affinity of the acceptor and environmental conditions. Molecular assemblies held together by CT interactions show peculiar optical

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[2–4], electrical [5] and magnetic properties [6, 7], which depend on the magnitude of the intermolecular CT interactions, the complex stoichiometry as well as the organization characteristics (spatial arrangement, relative orientation, etc.) of the electron donor and acceptor. In addition, the EDA complexes have attracted interest as organic conductors because they exhibit unique conducting behavior in the solid state [8]. The conductivity is controlled by molecular stacking structures and CT interactions between the donor and the acceptor molecules. Ethylenetetracarbonitrile, commonly known as tetracyanoethylene (TCNE), no less than other good organic electron acceptor molecules, readily participate in this type of intermolecular association with various electron donors [9–11]. The required close approach of donor and acceptor being favored by the perfect planarity of the TCNE molecule. TCNE has been of special interest for a variety of reasons. It is a simple system with only two types of atoms, namely carbon and nitrogen, and has peculiar phase transitions involving crystalline and amorphous form [12]. TCNE is also one of the simplest molecules having a strong coupling of the intra- and intermolecular vibrations [13] leading to complex phonon spectrum and distortion of the molecular geometry in various solid phases. After the pioneering work on electron transfer phenomena in TCNE-hexamethylbenzene CT complex [14] by Mulliken and others, it has been revealed that the theoretical justifications on energies and types of CT transitions play a crucial role in interpreting the UV-Vis spectral behavior of such molecule. Recently, Miller et al. extensively studied the characteristic geometries and vibrational absorptions of various numerous structural aspects of TCNE [15]. However, till date, there is no such report on theoretical prediction on the ground and excited state complexation phenomena between TCNE and some other molecule having electron donation capability. The aim of the present article is to emphasize the role of the

Table 1 Optimized bond length (r), dihedral angle, Mulliken charge and dipole moment of TCNE after HF/3-21G and DFT (B3LYP/6-31G*) calculations in ground state

Parameters	Method	
	HF	B3LYP
r(C1–C2) (Å)	1.358	1.358
r(C1-C5 or C1-C6 or C2-C4 or C2-C3) (Å)	1.425	1.425
r(C4-N4 or C3-N1 or C5-N3 or C6-N2) (Å)	1.159	1.159
∠(C5,C1,C2,C4) (degree)	0.00	0.00
∠(C6,C1,C2,C3) (degree)	0.00	0.00
∠(C1,C2,C3,N1) (degree)	180.00	180.00
∠(C1,C2,C4,N4) (degree)	180.00	180.00
∠(N2,C6,C1,C2) (degree)	180.00	180.00
∠(C2,C1,C5,N3) (degree)	180.00	180.00
∠(C4,C2,C3) (degree)	115.19	115.19
∠(C5,C1,C6) (degree)	115.19	115.19
∠(C5,C1,C2) (degree)	122.40	122.40
∠(C1,C2,C3) (degree)	122.40	122.40
Mulliken charge on N atom		
N1	−0.428	−0.420
N2	−0.428	−0.420
N3	−0.428	−0.420
N4	−0.428	−0.420
Dipole moment (Debye)	0.00	0.00

charge transfer (CT) interaction between TCNE and aniline in TCNE-aniline CT complex, for which the experimental CT transition energy ($h\nu_{CT}$) is already known [16], by means of *ab initio* and time dependent density functional theory (TDDFT) calculations.

Model and numerical method

The optimized geometries and energies of all the structural variables were obtained by using the self-consistent Hartree-Fock (HF) method. All the theoretical calculations were performed using the SPARTAN '06 program Windows version [17]. The molecular structure is energetically optimized to reach a stable structure using HF/3-21G level of theory. After geometry optimization by HF/3-21G method, the energy calculations in ground state were done using single point calculations by both HF and DFT methods. CT transition energy of the complex in gas phase was calculated by the restricted configuration interaction singlets (RCIS) method using the ground state optimized geometry of the complex. DFT calculations have been performed by using combination of the Becke's three parameter hybrid [18] exchange potential with the correlation function of Lee et al. [19] (B3LYP). The other levels of DFT which were implemented in the present investigations are BP, BLYP and EDF1 [20–24]. The 6-31G* basis set was used in the present work to determine the excited state energies and related parameters for all the *ab initio* and TDDFT calculations.

Results and discussion

Results of ground state optimization in gas phase

The structural parameters obtained at the HF and DFT (B3LYP) calculations for TCNE, in ground state, were listed in Table 1. The optimized C=C bond length (labeled as C1 & C2 in Fig. 1(a)) value of TCNE in gas phase is 1.358Å as calculated by HF and DFT method (B3LYP). It is also observed that all the four C≡N bond distances are the same as obtained by both HF and DFT (B3LYP) calculations. The dihedral angle connecting the set of carbon and nitrogen atoms comprising of C5(C6),C1,C2,C4(C3) and N4,C4,C2, C3 (Fig. 1(a)) are estimated to be 0.00⁰. These parameters undergo appreciable change when TCNE undergoes complexation with aniline (Table 2). The important structural
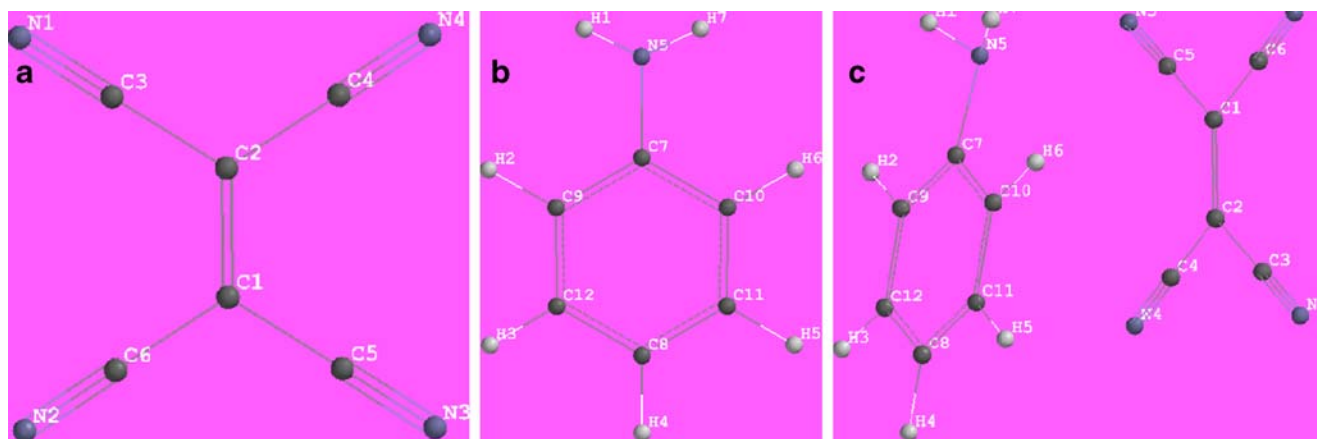

Fig. 1 B3LYP optimized geometric structure of (a) TCNE, (b) aniline and (c) TCNE-aniline complex in ground state

Table 2 Optimized bond length (r), dihedral angle, Mulliken charge and dipole moment of aniline after HF/3-21G and DFT (B3LYP/6-31G*) calculations in ground state

Parameters	Method	
	HF	B3LYP
r(C1–C2) (Å)	1.406	1.395
r(C1–C6) (Å)	1.406	1.395
r(C2–C3) (Å)	1.387	1.380
r(C3–C4) (Å)	1.391	1.384
r(C4–C5) (Å)	1.391	1.384
r(C5–C6) (Å)	1.387	1.380
r(C1-N1) (Å)	1.400	1.376
Mulliken charge on N atom	−0.960	−0.836
Dipole moment (Debye)	1.47	1.92

parameters and dipole moment component of the TCNE-aniline complex in its ground state as obtained after optimization using these two levels of theory are given in Table 3. The most interesting observation in case of TCNE-aniline complex is the considerable change in the dihedral angle. Figure 1(b) nicely demonstrates the noticeable change in the dihedral angle (Table 3) which clearly indicates that the perfect symmetry of TCNE molecule was not maintained

Table 3 Optimized bond length (r), dihedral angle, dipole moment, Mulliken charge and enthalpy of formation value for the TCNE-aniline complex after HF and DFT (B3LYP) calculations, using 3-21G and 6-31G* basis sets, respectively, in ground state

Parameters	Method	
	HF	B3LYP
r(C1–C2) (Å)	1.358	1.358
r(C1-C5 or C1-C6 or C2-C4 or C2-C3) (Å)	1.425	1.425
r(C4-N4 or C3-N1 or C5-N3 or C6-N2) (Å)	1.159	1.159
∠(C5,C1,C2,C4) (degree)	0.09	0.09
R(C1-C7) (Å)	4.189	4.189
r(C5-N5 or C6-N5) (Å)	3.934	3.934
∠(C6,C1,C2,C3) (degree)	−0.09	−0.09
∠(C1,C2,C3,N1) (degree)	173.66	173.66
∠(C1,C2,C4,N4) (degree)	−173.66	−173.66
∠(N2,C6,C1,C2) (degree)	−162.52	−162.52
∠(C2,C1,C5,N3) (degree)	162.52	162.52
r(C7-N5)	1.433	1.433
Dipole moment (Debye)	1.96	2.06
Mulliken charge on N atom		
N1	−0.438	−0.429
N2	−0.442	−0.433
N3	−0.442	−0.433
N4	−0.438	−0.429
N5	−0.862	−0.777
Enthalpy (kcal·mol^{-1})	−1.34	−5.14

Table 4 Enthalpies of formation (ΔH_f^0) values for the TCNE/aniline complex obtained by DFT calculations, using BP, BLYP, and EDF1 methods at 6-31G* basis set

DFT method	ΔH_f^0 (kcal·mol^{-1})
BP	−3.61
BLYP	−3.98
EDF1	−2.37

after complexation with aniline. It has been observed that the amine group of aniline in the TCNE-aniline complex is directed toward the TCNE molecule. It is further observed that in all the levels of calculation, the bond distance between the carbon atom of the benzene ring (marked as C1 in Fig. 1(c)) and the nitrogen atom in aniline (N5) molecule, i.e., 1.400 and 1.376 Å increases appreciably after complexation; e.g., 0.333 and 0.357 Å in HF and DFT calculations, respectively. The direction of the dipole moment vector is originated from aniline and it is pointed toward the TCNE molecule. Mulliken charge calculation reveals that after complexation with TCNE, N atom of aniline molecule becomes more positive which proves that charge transfer takes place from aniline to TCNE (Tables 2 & 3). In addition to that, the Mulliken charge on the N atom of the –CN group of the TCNE molecule is found to be more negative (Table 3) in TCNE-aniline complex than that observed for the isolated TCNE molecule (Table 1). This indicates that some amount of electronic charge has been transferred from aniline to TCNE. The sum of the Mulliken charges on the aniline moiety and that on the TCNE moiety of the complex (Table 3) indicate that with respect to aniline, the TCNE moiety is negatively charged. It has been observed that ~2% of the charge of an electron

Table 5 Comparison of five highest occupied (HOMOs) and five lowest unoccupied molecular orbital (LUMOs) levels of TCNE/aniline system in ground state done by various DFT calculations using 6-31G* basis set

State	Energy, eV		
	BP	BLYP	EDF1
HOMO-4	−8.4626	−8.2283	−8.3213
HOMO-3	−7.9345	−7.6006	−7.7701
HOMO-2	−7.7714	−7.4350	−7.5765
HOMO-1	−6.4205	−6.0818	−6.2223
HOMO	−5.3840	−5.0650	−5.1973
LUMO	−5.0638	−4.7365	−4.8888
LUMO+1	−2.2700	−1.9501	−2.0507
LUMO+2	−2.0174	−1.6934	−1.8259
LUMO+3	−1.2521	−0.9498	−1.0495
LUMO+4	−1.2185	−0.9055	−1.0210

Table 6 Excited state, excitation energy, total energy for each state, multiplicity, transition dipole moments (μ) and oscillator strengths (f) of TCNE in gas phase estimated by HF calculation using 3-21G basis set

Method	Excited state	Excitation energy (eV)	Total energy (eV)	Multiplicity	μ			F
					μ_x	μ_y	μ_z	
HF	1	1.9963	−444.83715	Triplet	0.0000	0.0000	0.0000	0.0000
	2	4.5745	−444.74240	Triplet	0.0000	0.0000	0.0000	0.0000
	3	4.6950	−444.73797	Triplet	0.0000	0.0000	0.0000	0.0000
	4	5.1709	−444.72048	Triplet	0.0000	0.0000	0.0000	0.0000
	5	5.2131*	−444.71893	Singlet	2.2195	0.0000	0.0000	0.6291
	6	5.4316	−444.71090	Triplet	0.0000	0.0000	0.0234	0.0000
	7	5.4722	−444.70941	Triplet	0.0000	0.0000	0.0000	0.0000
	8	5.7209	−444.70027	Singlet	0.0000	0.0000	0.0000	0.0000
	9	6.0644	−444.68765	Singlet	0.0000	0.0000	0.0000	0.0000
	10	6.1801	−444.68339	Singlet	0.0000	0.0000	−0.0014	0.0000
	11	6.6475	−444.66622	Singlet	0.0000	0.7758	0.0000	0.0980
	12	6.7108	−444.66389	Singlet	0.0000	0.0000	0.0000	0.0000

*The assigned transition energy is marked with asterisk.

has been transferred from aniline to TCNE in the ground state of the complex. It is also interesting to find from Table 3 that the complex formation between TCNE and aniline is enthalpy favored (−1.34 kcal mol^{-1}) at the HF/3-21G optimization. Formation of the complex therefore results in a more ordered state, possibly due to the freezing of the motional freedom of both the acceptor and donor molecules. Since the formation of such an ensemble involves either entropically or enthalpically driven organization of individual components, the yields of such complex frequently exceed those obtained for analogous covalently linked systems. However, the HF calculations are often misleading to more or less higher energy conformers due to the inherent accuracy in involving

weak interactions such as π-π and CH⋯π interactions [25]. Thus, the B3LYP/6-31G* single-point energy calculations have been performed at the HF/3-21G optimized geometry. According to such calculation, the TCNE-aniline complex is still found to be more stable by –3.80 kcal mol^{-1} than that obtained in HF calculation (Table 3). It should be mentioned at this point that the full optimization at the B3LYP level of calculation was not performed due to the computational limit. Other than B3LYP method in DFT calculation, we have also estimated various ground state parameters by BP, BLYP and EDF1 methods using DFT calculations (Table 4). Enthalpies of formation (ΔH_f^0) value for TCNE/aniline complex was shown to produce highest value as estimated by B3LYP method (Table 3). Highest

Table 7 Excited state, excitation energy, total energy for each state, multiplicity, transition dipole moments (μ) and oscillator strengths (f) of TCNE in gas phase estimated by B3LYP calculation using 6-31G* basis set

Method	Excited state	Excitation energy (eV)	Total energy (eV)	Multiplicity	μ			F
					μ_x	μ_y	μ_z	
B3LYP	1	2.3693	−447.43066	Triplet	0.0000	0.0000	0.0000	0.0000
	2	4.2437	−447.36178	Triplet	0.0000	0.0000	0.0000	0.0000
	3	4.3735	−447.35701	Triplet	0.0000	0.0000	0.0000	0.0000
	4	4.4367	−447.35468	Singlet	0.0000	0.0000	0.0000	0.0001
	5	4.5364	−447.35102	Triplet	0.0000	0.0000	0.0000	0.0000
	6	4.5826	−447.34932	Triplet	0.0000	0.0000	0.0000	0.0000
	7	4.7296	−447.34392	Triplet	0.0000	0.0000	0.0000	0.0000
	8	4.7861	−447.34184	Singlet	0.0000	0.0000	0.0000	0.0000
	9	4.8347*	−447.34006	Singlet	2.2866	0.0000	0.0000	0.6193
	10	4.9675	−447.33518	Singlet	0.0000	0.0000	0.0000	0.0000
	11	5.4049	−447.31910	Singlet	0.0000	−1.0530	0.0000	0.1468
	12	5.4906	−447.31595	Singlet	0.0000	0.0000	0.0000	0.0000

*The assigned transition energy is marked with asterisk.

Table 8 Excited state, excitation energy, total energy for each state, multiplicity, transition dipole moments (μ) and oscillator strengths (f) of TCNE in gas phase by BP, BLYP and EDF1 calculations using 6-31G* basis set

Method	Excited state	Excitation energy (eV)	Total energy (eV)	Multiplicity	μ_x	μ_y	μ_z	f
BP	1	2.3426	−447.43681	Triplet	0.0000	0.0000	0.0000	0.0000
	2	3.8042	−447.38309	Triplet	0.0000	0.0000	0.0000	0.0000
	3	3.9760	−447.37678	Singlet	0.0000	0.0000	0.0000	0.0000
	4	4.0404	−447.37441	Triplet	0.0000	0.0000	0.0000	0.0000
	5	4.0746	−447.37316	Triplet	0.0000	0.0000	0.0000	0.0000
	6	4.1299	−447.37113	Triplet	0.0000	0.0000	0.0000	0.0000
	7	4.2144	−447.36802	Triplet	0.0000	0.0000	0.0000	0.0000
	8	4.2758	−447.36576	Singlet	0.0000	0.0000	0.0000	0.0000
	9	4.3861	−447.36171	Singlet	0.0000	0.0000	0.0000	0.0000
	10	4.5509	−447.35565	Singlet	0.0000	0.0000	0.0000	0.0000
	11	4.6612*	−447.35160	Singlet	−2.2475	0.0000	0.0000	0.5769
	12	4.9103	−447.34244	Singlet	0.0000	1.0146	0.0000	0.1238
BLYP	1	2.3484	−447.34128	Triplet	0.0000	0.0000	0.0000	0.0000
	2	3.8060	−447.28772	Triplet	0.0000	0.0000	0.0000	0.0000
	3	3.9671	−447.28179	Singlet	0.0000	0.0000	0.0000	0.0000
	4	4.0373	−447.27921	Triplet	0.0000	0.0000	0.0000	0.0000
	5	4.0888	−447.27732	Triplet	0.0000	0.0000	0.0000	0.0000
	6	4.1630	−447.27459	Triplet	0.0000	0.0000	0.0000	0.0000
	7.	4.2530	−447.27128	Triplet	0.0000	0.0000	0.0000	0.0000
	8	4.2747	−447.27049	Singlet	0.0000	0.0000	0.0000	0.0000
	9	4.4057	−447.26567	Singlet	0.0000	0.0000	0.0000	0.0000
	10	4.5883	−447.25896	Singlet	0.0000	0.0000	0.0000	0.0000
	11	4.6492*	−447.25672	Singlet	2.2451	0.0000	0.0000	0.5741
	12	4.8929	−447.24777	Singlet	0.0000	−1.0096	0.0000	0.1222
EDF1	1	2.3538	−447.52863	Triplet	0.0000	0.0000	0.0000	0.0000
	2	3.8283	−447.47445	Triplet	0.0000	0.0000	0.0000	0.0000
	3	3.9902	−447.46850	Singlet	0.0000	0.0000	0.0000	0.0000
	4	4.0446	−447.46650	Triplet	0.0000	0.0000	0.0000	0.0000
	5	4.0931	−447.46472	Triplet	0.0000	0.0000	0.0000	0.0000
	6	4.1550	−447.46244	Triplet	0.0000	0.0000	0.0000	0.0000
	7	4.2509	−447.45892	Triplet	0.0000	0.0000	0.0000	0.0000
	8	4.2815	−447.45779	Singlet	0.0000	0.0000	0.0000	0.0000
	9	4.3966	−447.45357	Singlet	0.0000	0.0000	0.0000	0.0000
	10	4.5856	−447.44662	Singlet	0.0000	0.0000	0.0000	0.0000
	11	4.6693*	−447.44355	Singlet	2.2514	0.0000	0.0000	0.5799
	12	4.9187	−447.43438	Singlet	0.0000	−1.0184	0.0000	0.1250

*The transition energy is marked with asterisks

occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the TCNE/aniline complex determined applying various DFT methods like BP, BLYP and EDF1, at various electronic states, were tabulated in Table 5.

Determination of CT transition energy in gas phase

Detailed results of configuration interaction singlet (CIS) [26] calculation on TCNE at five different levels of theory are shown in Tables 6, 7 & 8. These calculations were done using 12 states in CIS calculations. The experimental

transition energy of TCNE is 4.592 eV [27]. Tables 6, 7 & 8 also reveal that TDDFT calculations produce very close value of transition energy with the reported experimental value. Transition energies of the TCNE-aniline complex along with total energy of different excited states, ground-to-excited state transition electric dipole moments (μ) and oscillator strengths (f) were computed by restricted configuration interaction singlet (RCIS) method at five different levels of theory (using 12 states in CIS method); results are tabulated in Tables 9 & 10 in which the first six transition energies are shown. The characteristic electronic transitions of aniline have been estimated to belong to UV region and

Table 9 Excited state, excitation energy, total energy for each state, multiplicity, transition dipole moments (μ) and oscillator strengths (f) of TCNE-aniline complex in gas phase obtained by HF, BP and BLYP methods using 6-31G* basis set

Method	Excited state	Excitation energy (eV)	Total energy (eV)	Multiplicity	μ			f
					μ_x	μ_y	μ_z	
HF	1	2.3504	−730.56958	Triplet	0.0000	0.0000	0.0000	0.0000
	2	3.4992	−730.52737	Triplet	0.0000	0.0000	0.0000	0.0000
	3	3.8096	−730.51596	Triplet	0.0000	0.0000	0.0000	0.0000
	4	3.8847*	−730.51320	Singlet	−0.5645	−0.2606	0.0000	0.0368
	5	4.6351	−730.48562	Triplet	0.0000	0.0000	0.0000	0.0000
	6	5.1850	−730.46541	Singlet	0.0000	0.0000	0.0234	0.0001
BP	1	0.7684	−735.08285	Triplet	0.0000	0.0000	0.0000	0.0000
	2	1.5092*	−735.05562	Singlet	−1.7019	−0.8196	0.0000	0.1319
	3	1.8605	−735.04271	Triplet	0.0000	0.0000	0.0000	0.0000
	4	1.9173	−735.04063	Singlet	0.0000	0.0000	0.0642	0.0002
	5	2.6782	−735.01266	Triplet	0.0000	0.0000	0.0000	0.0000
	6	3.3042	−734.98966	Triplet	0.0000	0.0000	0.0000	0.0000
BLYP	1	0.7744	−734.86008	Triplet	0.0000	0.0000	0.0000	0.0000
	2	1.4860*	−734.83394	Singlet	−1.5466	−1.0222	0.0000	0.1251
	3	1.8472	−734.82066	Triplet	0.0000	0.0000	0.0000	0.0000
	4	1.9011	−734.81868	Singlet	0.0000	0.0000	0.0621	0.0002
	5	2.6839	−734.78991	Triplet	0.0000	0.0000	0.0000	0.0000
	6	3.2896	−734.76765	Triplet	0.0000	0.0000	0.0000	0.0000

*The assigned CT transition energy is marked with asterisk

thus, are not being considered in present calculations (see Appendix A). Looking at the results summarized in Tables 9 & 10, it is found that the $h\nu_{CT}$ value of the TCNE-aniline complex obtained by B3LYP calculation corroborates very closely to the experimentally observed value of 2.097 eV [16]. The results also exhibit that the estimated $h\nu_{CT}$ value obtained from HF method does not correspond well to the experimentally observed CT transition energy. The other methods like BP, BLYP and EDF1 reproduce close values of $h\nu_{CT}$ to the experimental one. However, all of them underestimate the experimental CT transition energy in the range of 0.536 – 0.615 eV. It is to be mentioned here that the CT transition in the present system has been assigned on the basis of properly inspecting the cartesian components of the ground-to-excited state transition electric dipole moments. The optimized geometry of the TCNE-

Table 10 Excited state, excitation energy, total energy for each state, multiplicity, transition dipole moments (μ) and oscillator strengths (f) of TCNE-aniline complex in gas phase obtained by EDF1 and B3LYP methods using 6-31G* basis set

Method	Excited state	Excitation energy (eV)	Total energy (eV)	Multiplicity	μ			F
					μ_x	μ_y	μ_z	
EDF1	1	0.7527	−735.21148	Triplet	0.0000	0.0000	0.0000	0.0000
	2	1.4815*	−735.18470	Singlet	−1.5638	−1.0377	0.0000	0.1281
	3	1.8370	−735.17164	Triplet	0.0000	0.0000	0.0000	0.0000
	4	1.8912	−735.16964	Singlet	0.0000	0.0000	−0.0650	0.0002
	5	2.6912	−735.14024	Triplet	0.0000	0.0000	0.0000	0.0000
	6	3.2824	−735.11852	Triplet	0.0000	0.0000	0.0000	0.0000
B3LYP	1	1.1017	−735.08068	Triplet	0.0000	0.0000	0.0000	0.0000
	2	1.5609*	−735.06380	Singlet	−1.3062	−0.6507	0.0000	0.0814
	3	2.3098	−735.03628	Triplet	0.0000	0.0000	0.0000	0.0000
	4	2.3525	−735.03471	Singlet	0.0000	0.0000	0.0489	0.0001
	5	2.7173	−735.02130	Triplet	0.0000	0.0000	0.0000	0.0000
	6	3.9135	−734.97734	Triplet	0.0000	0.0000	0.0000	0.0000

*The assigned CT transition energy is marked with asterisk

Table 11 Bond length (r), dihedral angle and dipole moment of TCNE-aniline complex in the optimized CT excited state obtained by TDDFT method at the B3LYP level of theory using 6-31G* basis set

Parameter	Value
r(C1–C2) (Å)	1.334
r(C1-C5 or C1-C6) (Å)	1.423
r(C2-C4 or C2-C3) (Å)	1.424
r(C4-N4 or C3-N1 or C5-N3 or C6-N2) (Å)	1.138
r(C1-C7) (Å)	3.293
r(C5-N5 or C6-N5) (Å)	3.077
∠(C5,C1,C2,C4) (degree)	0.31
∠(C6,C1,C2,C3) (degree)	−0.31
∠(C1,C2,C3,N1) (degree)	−158.59
∠(C1,C2,C4,N4) (degree)	158.59
∠(N2,C6,C1,C2) (degree)	−170.56
∠(C2,C1,C5,N3) (degree)	170.56
Dipole moment (Debye)	2.630

aniline complex obtained by RCIS method at B3LYP level is shown in Fig. 2. It has also been observed that transition electric dipole moment vector (μ) is negative on going from uncomplexed form of TCNE to its complexed state. The negative sign of μ indicates that ground-to-excited state transition electric dipole moment of TCNE-aniline complex is directed from the aniline to the TCNE moiety. This actuality validates that a substantial amount of electron transfer takes place from the aniline to TCNE during CT transition. The oscillator strength of this CT transition is shown to exhibit higher value compared to the lower energy transitions, which are assigned as internal transitions in TCNE molecule. Some important structural parameters related to CT excited state of the complex, obtained by the
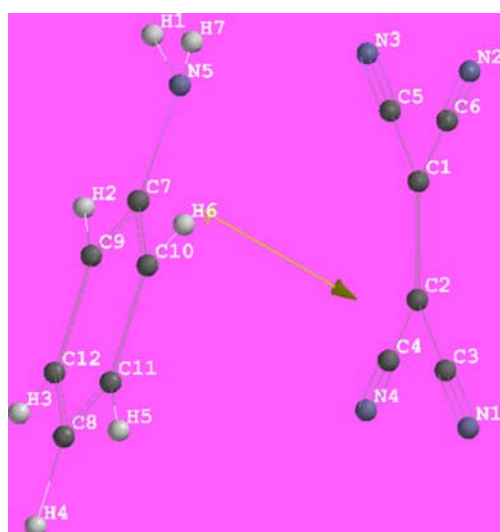
Fig. 2 B3LYP optimized geometry of the CT excited state for TCNE-aniline complex in the gas phase

RCIS/B3LYP method, are provided in Table 11. The most important observation is the increase in the bond length value of carbon and nitrogen atoms of the cyano group of TCNE molecule in TCNE-aniline complex. The closest distance between the carbon atom of cyano group of TCNE and N atom of aniline in TCNE-aniline complex is 3.077Å which is somewhat higher than the C(TCNE)....C(aniline) distance (3.293Å). This is very much in accordance with the optimized geometric structure of the CT state of the TCNE-aniline complex which indicates that other than π-π interaction, n-π interaction also plays vital role behind such transition. However, the fascinating feature of the excited state geometry is shortening of the above mentioned bond distance compared to optimized geometry of the complex in ground state, done by both HF and B3LYP calculations. This strongly suggests that an appreciable amount of interaction takes place between TCNE and aniline in the TCNE-aniline complex at its excited state. This is further supported by greater amount of dipole moment value in the excited state, i.e., 2.63, compared to ground state, e.g., 2.06 as obtained by B3LYP calculation. The CT event in present case can also be realized in a qualitative manner by looking into the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of TCNE-aniline complex in both ground and excited states. The HOMO–LUMO calculations have been done by DFT calculations at B3LYP level of theory. Figures 3 & 4 nicely demonstrated the respective diagram of the molecular orbital spatial distributions of the HOMO and LUMO of the TCNE-aniline complex at different electronic states. Figures 3 & 4 signified that while most of the LUMO, LUMO + 1 and LUMO + 2 states are localized on the TCNE, the predominant part of HOMO and LUMO + 3 states are centered on the aniline moiety. However, the characteristics and the difference in energy levels of highest occupied molecular orbitals and lowest unoccupied molecular orbitals for the TCNE-aniline complex have been affected by the close approach of the TCNE and aniline molecules in the excited state which reinforces the concept of CT transition.

From the above results, it is quite clear that orbital interaction energy arises mainly from charge transfer between occupied and unoccupied orbitals. This result suggests that corroboration between relative orientation of the acceptor and donor molecules in the TCNE-aniline CT complex can be well rationalized through examination of the molecular electrostatic potential maps (MEPs) at ground and excited states. The MEPs of the TCNE, aniline and their complexes have been calculated at the B3LYP/6-31G level of theory and the optimized geometries are shown in Fig. 5. The MEP plot for TCNE (Fig. 5a) shows that the positive electrostatic potential (shown in blue) corresponds to the center regions of the

Fig. 3 Spatial orientation diagrams for the molecular orbital distribution for the TCNE-aniline complex in different electronic states done by DFT calculations using B3LYP/6-31G* method: HOMO, LUMO, HOMO − 1, LUMO + 1, HOMO − 2, LUMO + 2, HOMO − 3 and LUMO + 3 done by B3LYP/6-31G* method
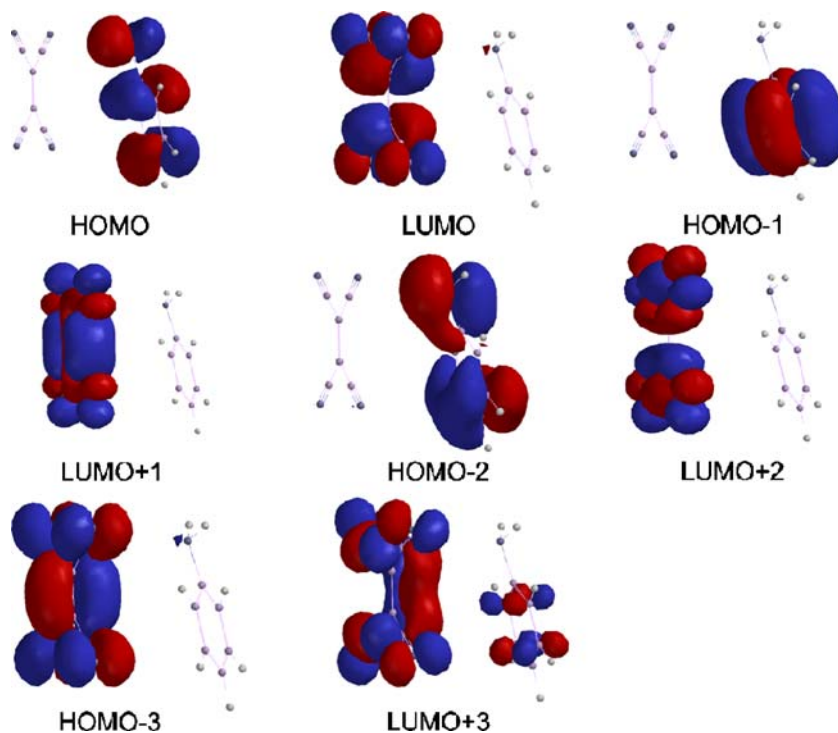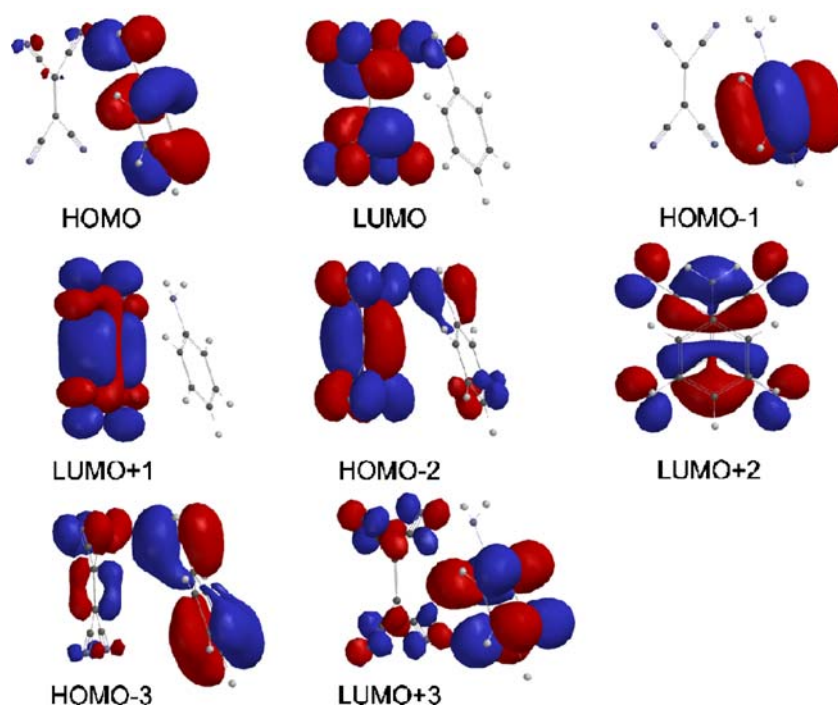
Fig. 4 TDDFT calculations for determination of spatial orientation diagrams for the molecular orbital distribution for the TCNE-aniline complex in different electronic states: HOMO, LUMO, HOMO − 1, LUMO + 1, HOMO − 2, LUMO + 2, HOMO − 3 and LUMO + 3
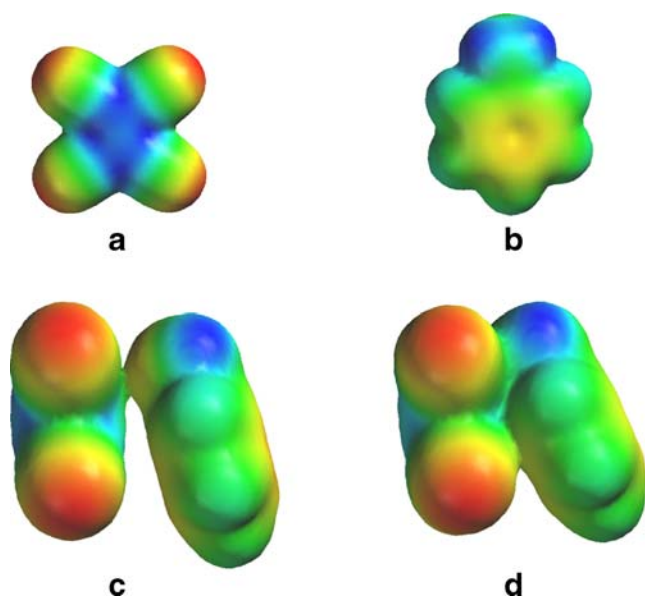
Fig. 5 MEPs of (a) uncomplexed TCNE, (b) free aniline along with TCNE-aniline complex at (c) ground and (d) excited states, respectively, done by DFT/B3LYP calculations using 6-31G*

ethylene carbon atoms. Along the C≡N bond, region of negative (shown in red) and positive electrostatic potentials are noticeable in the lobe of nitrogen and carbon atoms of cyano group, respectively. For the aniline molecule, the negative potential is mainly associated with the nitrogen atom and the center of the benzene ring, due to the presence of π-electrons (Fig. 5b). However, Fig. 5c clearly demonstrates while in the ground state, there is a feeble electrostatic interaction between TCNE and aniline, it is much more pronounced in the excited state of the complex (Fig. 5d). It has been observed that other than the N atom of the –NH_2 group, the π-electrons of the ethylene carbon atoms becomes stacked with the π-electrons of the benzene ring of aniline molecule. This result is consistent with the fact that TCNE is generally accepted as a good

electron acceptor in forming EDA and CT complexes with various electron donors [28].

Values of various bond moments for the TCNE-aniline complex have been calculated by DFT calculation in both ground and excited states. Two typical bond moments data for such complex calculated by DFT/B3LYP and TDDFT/B3LYP methods, have been given in Tables 12 and 13, respectively. However, according to quantum mechanics, only the highest non-zero 'pole' is independent of the chosen origin. This means that for ions, only the monopole (overall charge) is independent of the origin. For most neutral molecules or complexes, the dipole is independent of origin. Thus, for neutal complex that have a zero dipole moment by symmetry, the quadrupole moment is the highest, non-zero 'pole'. In the present case the various bond moments shown in Tables 12 and 13 give a good view of separation and distribution of charges within the complex molecule which is accounted by the CT phenomena at excited state [29].

Conclusions

The geometric and electronic structures of the TCNE-aniline complex have been investigated by applying HF and DFT calculations in gas phase. The complex formation is found to be enthalpy favored. However, the relative stability of the complex vary somewhat in HF and DFT calculations, signifying that HF method lacks the inherent accuracy in estimating the weak interactions like π-π and CH···π interactions. By applying the *ab intio* and TDDFT methods, it was possible to determine the CT transition energy of the TCNE–aniline complex. Theoretical value obtained at the HF level does not agree well with the experimental finding. However, the B3LYP and BP levels of theory reproduce the experimental value closely, the former being better in the case of TCNE-aniline CT

Table 12 Values of various bond moments for TCNE-aniline complex calculated by DFT/B3LYP calculation using 6-31G* basis set

Dipole moment (Debye)	X	−1.3854	Y	−1.5207	Z	0.0000
Quadrupole moments (Debye Ang)	XX	−95.4417	XY	5.3403	YY	−96.6678
Octapole moments (Debye Ang^2)	XZ	0.0000	YZ	0.0000	ZZ	−108.7952
	XXX	5.2850	XXY	28.5012	XYY	−33.0796
	YYY	−47.2675	XXZ	0.0000	XYZ	0.0000
	YYZ	0.0000	XZZ	51.3151	YZZ	−15.2610
	ZZZ	0.0000				
Hexadecapole moments (Debye Ang^3)	XXXX	−3064.3616	XXXY	−15.5915	XXYY	720.1346
	XYYY	38.6749	YYYY	−1264.4753	XXXZ	0.0000
	XXYZ	0.0000	XYYZ	0.0000	YYYZ	0.0000
	XXZZ	−748.4828	XYZZ	27.5814	YYZZ	−498.5987
	XZZZ	0.0000	YZZZ	0.0000	ZZZZ	−1282.1154

Table 13 Values of various bond moments for TCNE-aniline complex calculated by TDDFT/B3LYP calculation using 6-31G* basis set

Dipole moment (Debye)	X	−1.3897	Y	−2.2335	Z	0.0000
Quadrupole moments (Debye Ang)	XX	−96.3040	XY	2.5956	YY	−95.7340
	XZ	0.0000	YZ	0.0000	ZZ	−110.1857
Octapole moments (Debye Ang^2)	XXX	−16.0623	XXY	31.3773	XYY	−3.9768
	YYY	−51.4338	XXZ	0.0000	XYZ	0.0000
	YYZ	0.0000	XZZ	−42.5907	YZZ	−21.0677
	ZZZ	0.0000				
Hexadecapole moments (Debye Ang^3)	XXXX	−2126.7837	XXXY	−24.9676	XXYY	−574.9357
	XYYY	−10.7765	YYYY	−1173.2941	XXXZ	0.0000
	XXYZ	0.0000	XYYZ	0.0000	YYYZ	0.0000
	XXZZ	−598.4660	XYZZ	29.9160	YYZZ	−477.8815
	XZZZ	0.0000	YZZZ	0.0000	ZZZZ	−1290.7228

complex. Frontier molecular orbital calculations reveal electron transport phenomenon in TCNE-aniline CT complex.

Appendix A

Table 14 Summary of results obtained from TDDFT/TDA calculations at B3LYP level of theory for aniline

Name of the state	Multiplicity	Excitation Energy (eV)	Total Energy (eV)	f	Transition moment	Amplitude
1	Triplet	3.9757	−287.4518	0.0000	X: 0.0000 Y: 0.0000 Z: 0.0000	0.9920
2	Triplet	4.0500	−287.4491	0.0000	X: 0.0000 Y: 0.0000 Z: 0.0000	V1=0.3836 V2=0.9074
3	Triplet	4.7388	−287.4237	0.0000	X: 0.0000 Y: 0.0000 Z: 0.0000	V1=0.9133 V2=−0.3979
4	Singlet	5.0230	−287.4133	0.0472	X: 0.6194 Y: 0.0000 Z: 0.0000	V1=−0.4023 V2=0.9096
5	Triplet	5.7285	−287.3874	0.0000	X: 0.0000 Y: 0.0000 Z: 0.0000	0.9879
6	Singlet	6.1336	−287.3725	0.1661	X: 0.0000 Y: 0.0000 Z: −1.0514	0.8693
7	Singlet	6.3886	−287.3631	0.0007	X: 0.0000 Y: 0.0000 Z: 0.0000	0.9958
8	Singlet	7.1254	−287.3360	0.1395	X: −0.8938 Y: 0.0000 Z: 0.0000	V1=−0.6076 V2=−0.7234 V3=−0.2841

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