

# 1P056      **Computational Study of the Hexamethylbenzene-Tetracyanoethylene Charge-Transfer Complexes**

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Intermolecular interactions such as hydrogen bonding interaction, van der Waals interaction, and charge-transfer interaction play an important role in various chemical and biological processes. Weak intermolecular interactions in solution- especially nonbonded ones is very useful and easy to design and or synthesis of self-assembling catenanes, rotaxanes, and other molecular machines. Moreover, the low-frequency spectra of these weak interactions have experienced increasing interest because of their importance for the flexibility and thus the function of many biomolecules. Charge-transfer complexes is one of the typical non-covalently bonded systems, and their intermolecular interactions and dynamical fluctuations as well as molecular structure have been studied for a couple of decades. Charge-transfer complexes consisting of hexamethylbenzene (HMB) and tetracyanoethylene (TCNE) have been extensively studied both experimentally and theoretically. Depending on the chosen concentration of the HMB-TCNE complex one can form both 1:1 donor-acceptor (DA) and 2:1 donor-acceptor-donor (DAD) complexes in solution. The low-frequency spectra of HMB-TCNE complexes have recently been probed by Terahertz radation. However high level computational study of the electronic structure and to predict the absorption spectra of these complexes to compare with the experimental observation is missing.

All the calculations have been carried out using the Gaussian 03 program. The ground-state geometry, normal modes of vibration, dipole moment, and interaction energies of the DA complexes of hexamethylbenzene with tetracyanoethylene have been calculated using the density functional theory (DFT) and the Hatree-Fock (HF) theory. Full geometry optimizations were performed for the monomers and the complex without imposing any constraint and the resultant geometries were confirmed through the frequency calculations to represent the minima on the respective potential energy surface. Binding energy was corrected for the basis set superposition error (BSSE) by counterpoise method. The ground state geometry and the normal modes of vibration of the DAD complex have been calculated at the HF theory.

Harmonic vibrational frequencies were computed in the gas phase for the monomers and the complex at the B3LYP 6-31G(d) level. Since the HMB-TCNE complex is comprised of 40 atoms, it has 114 normal modes, of which 84 are HMB modes and 24 are TCNE modes. The remaining 6 modes may come from the intermonomer vibrations. We have identified these intermonomer modes ranging from 15 to 81  $\text{cm}^{-1}$ . The donor-acceptor vibrational modes whose frequencies are lower than 81  $\text{cm}^{-1}$  are listed in Table I. The calculated frequencies are scaled by a factor of 0.9614. Hayashi *et. al.* also reported the normal mode calculations for the HMB-TCNE complex at HF 3-21G level theory. They have found seven intermolecular modes in the frequency range less than 100  $\text{cm}^{-1}$ , two of which are highly mixed with a HMB C-CH<sub>3</sub> twisting

modes. Among these intermolecular modes they assigned one DA stretching mode at  $59\text{ cm}^{-1}$ . However, in our calculation we observed a mode at  $60.43\text{ cm}^{-1}$  and assigned it as a HMB C-CH<sub>3</sub> twisting and TCNE C-C≡N out-of-plane torsion mode. Since Hayashi *et. al.* have used low level calculation, their results may contain large errors. It is to be noted that we have also performed the calculations at the HF/6-31(G) level. But the results are not satisfactory compared to the reported experimental frequencies, dipole moments, etc. For example, for the HMB-TCNE complex, the HF 6-31G(d) calculates the TCNE C≡N stretching frequency in at  $2334\text{ cm}^{-1}$  whereas the experimental value is  $2222\text{ cm}^{-1}$ . The binding energy of the DA complex were computed at the B3LYP/6-31++G(3df,2p)//B3LYP/6-31G(d) level. The equilibrium binding energy  $\Delta E_c$  were found to be  $-4.40\text{ kcal/mol}$  and  $-3.58\text{ kcal/mol}$  for the BSSE uncorrected and BSSE corrected, respectively. The binding enthalpy  $\Delta H^0$  for the HMB-TCNE complex has been reported to be  $-8.44\text{ kcal/mol}$  in CH<sub>2</sub>Cl<sub>2</sub> and  $-7.75\text{ kcal/mol}$  in CCl<sub>4</sub>. The binding energy is too low compared to the experimental binding enthalpy value. This may be due to the fact that dispersion energy contribution is not considered in the DFT functionals available at present. The dipole moment for DA complex calculated at B3LYP/6-31G(d) level and it is found to be 2.7 debye is pretty close to the experimental value 2.8 debye. The ground state geometry and harmonic vibrational frequencies of the DAD complex were calculated at the HF/3-21G(d) level. For a rigorous treatment of both HMB-TCNE and HMB-TCNE-HMB electron donor-acceptor complexes higher level calculations and analysis are necessary and on going in our laboratory.

Table I: Intermonomer vibrational modes of the HMB -TCNE complex calculated at B3LYP/6-31G(d) level. The harmonic vibrational wavenumbers were scaled by 0.9614

Harmonic vibrational wavenumber (cm <sup>-1</sup> )	IR intensity (km/mol)	Vibrational mode assignment
14.7878	0.0016	HMB-TCNE twisting
48.9290	0.5455	HMB-TCNE sliding
53.9482	0.5351	HMB-TCNE sliding
60.4336	0.2176	HMB C-CH <sub>3</sub> twisting and ring deformation and TCNE C-C≡N out-of-plane torsion
68.5516	2.0568	HMB-TCNE stretching
71.9304	1.8686	HMB-TCNE stretching
80.4164	0.0792	HMB C-CH <sub>3</sub> twisting and ring deformation and TCNE in-plane vibration