

Charge transfer complexes between 4,4'-disubstituted diphenyldiacetylenes: experimental and theoretical study

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Received 30 March 2000; revised 21 July 2000; accepted 22 August 2000

Abstract

Novel charge transfer (CT) complexes containing donor and acceptor derivatives of diphenyldiacetylene have been synthesised and characterised. The structure of CT complexes was modelled at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory. It was found that the complex formation is mainly due to dipole–dipole interaction between side groups of diacetylene molecules and there was no significant charge transfer between donor and acceptor in the ground state. On the other hand, optical excitation of CT complexes leads to strong charge transfer from donor to acceptor molecule as followed from the modelling using time-dependent density functional theory (DFT) method. Diacetylene molecules adopt strongly bent configuration in CT complexes which is prohibitive for solid-state topochemical polymerisation of diacetylenes © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Charge transfer; Density functional theory; Diacetylenes

1. Introduction

It is well known that the solid-state polymerisation of diacetylenes (DAs) is sensitive to structural factor [1] and unfavourable crystalline structure precluded the so-called topochemical polymerisation [2]. Co-crystallisation of two DAs might create a favourable packing for the topochemical polymerisation even though they do not undergo topochemical polymerisation separately. Thus, almost inactive 1,6-bis-(*m*-trifluoromethylphenylsulfonate)hexa-2,4-diyne participated in solid-state polymerisation when co-crystallised with 1,6-bis(toluenesulfonate)hexa-2,4-diyne [3]. Some of the DAs with carbazole and

anthracene substituents can be polymerised as mixed crystals by γ -irradiation whereas they do not undergo polymerisation by γ -irradiation as pure compounds.

There have been reported efforts to prepare and polymerise charge transfer (CT) complexes containing DAs. Enkelman [4] reported CT complexes between DAs, containing either anthryl or carbazolyl groups and acceptors. Schofield and Schultz tried to polymerise CT complexes between acceptors such as tetracyanoquinodimethane, tetracyanoethylene, trinitrofluorenone, etc and 1,6-bis(3-pyrenoxy)-2,4-hexadiyne but failed [5]. To our knowledge, none of the CT complexes has been polymerised topochemically to date. The explanation of this phenomenon is: either unfavourable molecular packing in CT complexes or specific electronic interactions hampering the solid-state polymerisation. The goal of this work is to synthesise model DA containing CT

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in 50 ml acetone, and catalyst (CuCl (0.05 g) and N,N,N',N'-tetramethylenediamine (TMDA) (0.1 ml)) was added to the reaction mixture. The reaction mixture was stirred at room temperature overnight under oxygen flow. The solid precipitate was filtered off and crystallised from ethanol. Yields were 60–80%.

4,4'-diaminodiphenyldiacetylene (**7**) was prepared by the reduction of compound **4** by SnCl₂.

Compound **4** (10 mmol) were added to solution of SnCl₂ (100 mmol) in the mixture of conc. HCl (20 ml) and acetic acid (40 ml). The reaction mixture was stirred for 5 h at 60°C. The salt precipitated on cooling was filtered off, dissolved in minimal amount of water and solid Na₂CO₃ was added to the solution until pH = 10. The diamine was extracted with benzene and crystallised from ethanol; yield 58%.

2.1. Preparation of CT complexes

Diacetylene acceptor (1 mmol) (**4** or **5**) dissolved in hot toluene (10 ml) was mixed with equimolar amounts of diacetylene donor molecules dissolved in 10 ml of hot toluene and the solution was cooled down to 0°C. The precipitated crystals of CT complex were filtered off, dried in vacuum and analysed. The elemental analysis data for all the synthesised compound are listed in Table 1. The synthetic route to **CT-1** and **CT-2** complexes is shown in Scheme 1.

2.2. Theoretical methods

All geometry optimisations were carried out with Jaguar 3.5 version package [8]. The obtained geometry was used to run frequency and TD-DFT calculations using GAUSSIAN 98 revision A.7 program [9]. Due to the importance of dispersion interactions in the formation of CT complexes between polarisable organic molecules it is indispensable to use the model explicitly taking into account the electron correlation. Because of the size of CT complexes the only practical correlated methods are DFT ones which are computationally less demanding compared to convenient post Hartree–Fock models. Among the DFT methods, hybrid functionals perform the best especially when significant irregularity of electron density distribution is involved as is the case of CT complexes. Becke three-parameter hybrid (B3) [10]

exchange functional in combination with Lee–Yang–Parr (LYP) [11] correlation functional (B3LYP) was used for all calculations in combination with 6-31G(d) basis set. This model was tested first on benzene–N₂ molecular complex. According to the experimental data [12–14] this complex has C₂ symmetry with N₂ parallel to the benzene plane and equilibrium distance of 3.5 Å between molecules with dissociation energy of 0.85–0.99 kcal/mol. The B3LYP/6-31G(d) model gave an equilibrium distance of 3.59 Å for this complex and a binding energy of 0.6 kcal/mol, taking into account ZPE correction. Therefore B3LYP/6-31G(d) model performs reasonably well and was used for all calculations.

3. Results and discussion

Coloured precipitates were formed on cooling only for the solutions of compounds of either **4** and **6** or **4** and **7** indicative of the formation of CT complexes. In other cases only the physical mixtures of the compounds were isolated which was confirmed by IR spectra and DSC. The CT complexes of compounds **4** and **6** (**CT-1**) and compounds **4** and **7** (**CT-2**) were orange and dark red powders, respectively. CT complexes only existed in the solid state immediately dissociating in solution. UV absorption spectra of the CT complexes were taken on polycrystalline films deposited onto quartz plates from solution. They showed broad CT bands with maxima at 810, 465 and 590 nm. IR spectra of CT complexes differed strongly from simple superposition of spectra of individual compounds. **CT-1** shows changes in two regions, 3150–2800 and 900–800 cm⁻¹. The former is related to C–H stretches of both benzene rings and methoxy groups, and the latter is due to bending modes of *p*-substituted benzene rings. In the case of **CT-2** complex the major changes were observed in the region of N–H and C–H stretches (3300–2800 cm⁻¹). Elemental analysis data showed that both **CT-1** and **CT-2** are formed in a 1:1 molar ratio.

According to DSC data compound **4** does not melt until 305°C where decomposition occurs. The DSC curve of compound **6** shows four peaks; the first three of these being endotherms. The first one observed at 101°C in the solid state can be ascribed to a crystal–crystal transition which is usual among

Table 2
Some of the experimental and theoretical IR frequencies (in cm^{-1}) for **CT-1** and **CT-2** molecules

CT-1		CT-2	
Calculated ^a	Experimental	Calculated ^a	Experimental
3110	3110	3445	3480
3081	3080	3289	3399
2893	2840	3055	3100
2890		3027	3010
2950	2966	2221	2210
		2214	2200
857	855		
		2146	2150
843	830		
		2131	2130
		1292	1360

^a Scaled frequencies. Scale factor is 0.9613 [21].

diacetylenes [15]. The second, at 146°C is because of melting into the nematic state. The third transition occurred at 188°C is attributed to isotropisation. It has been observed with a microscope with crossed polars at 146°C that the solid melted into a bire-

fringent liquid with typical nematic structure, and at 188°C the birefringence disappeared and the melt became optically isotropic. The exotherm starting at 242°C is attributed to the thermal decomposition of compound **6**. According to TGA data weight loss started at 200°C and reached 30% at 300°C . In the DSC thermogram of **CT-2** only the melting transition at 244°C and an exotherm peaking at 280°C due to the thermal decomposition of the complex that followed from TGA data, was observed: weight loss started at 200°C and reached 35% at 300°C . The UV or electron beam irradiation of CT complexes did not produce any polymer either.

As it can be seen from those data neither **CT-1** nor **CT-2** polymerised in the solid state. To gain a better understanding of the nature of CT complexes their geometries were fully optimised at the B3LYP/6-31G(d) level of theory. Frequency jobs were run at optimised geometry to reach theoretical IR frequencies and thermochemistry data. Since IR spectra are very sensitive to the geometry of molecules especially in the region below 1500 cm^{-1} the comparison between experimental and theoretical IR spectra is a good test for the reliability of the model chosen for the

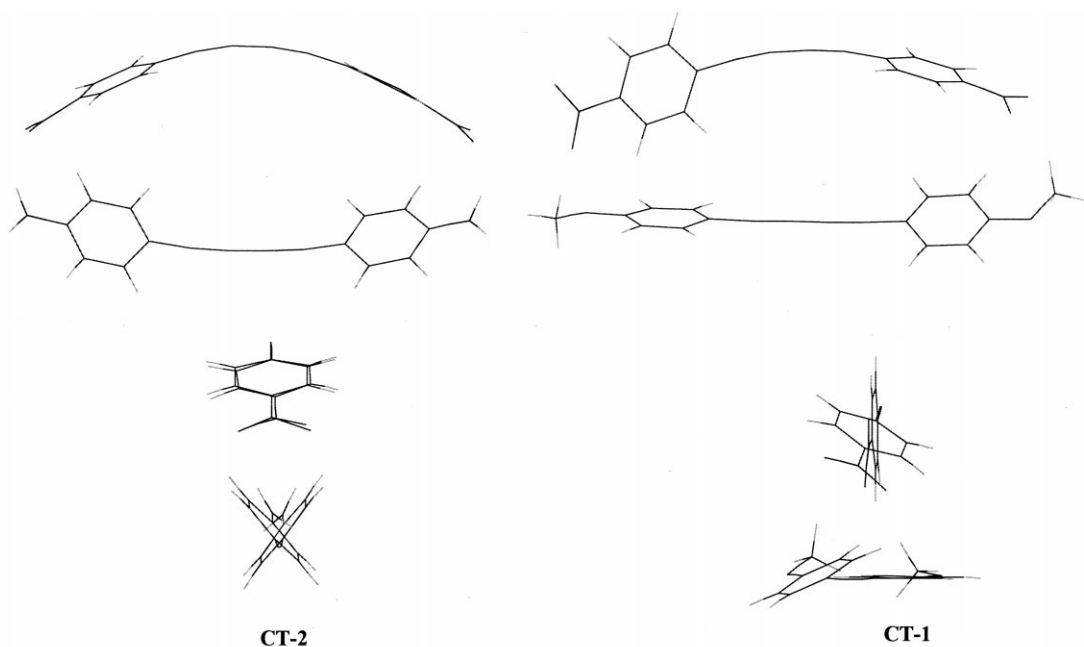


Fig. 1. General view of optimised geometry at B3LYP/6-31G(d) level for charge transfer complexes **CT-1** and **CT-2**.

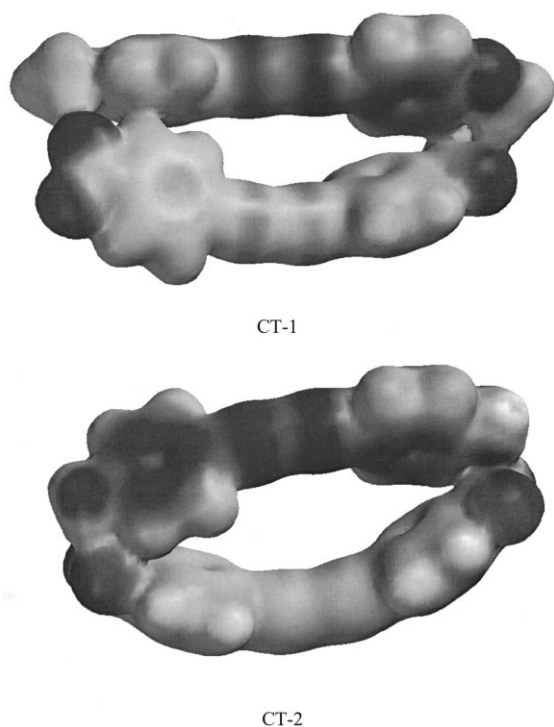


Fig. 2. Molecular electrostatic potential mapped into total charge density surface. Dark, negative; light, positive values.

study. Table 2 shows the most intense observed and theoretical IR frequencies of CT complexes absent in both donor and acceptor molecules but which appear in the spectra of their complex. The assignment of peaks in IR spectra has been made on the basis of calculated intensities and normal modes corresponding to each frequency. As can be seen from Table 2 all the peaks are predicted by B3LYP/6-31G(d) model with reasonably good accuracy suggesting that the structure of CT complexes are reproduced fairly well by chosen model.

Fig. 1 shows general views of the minimised geometries of the CT-1 and CT-2 complexes. An important observation can be made when analysing the structure of CT complexes. While pure molecules **4**, **6** and **7** are perfectly plane, they adopt a bent shape in the complexes, the bending is especially noticeable for compound **4**. The shape of the CT complexes suggests that only donor and acceptor substituents are involved in the interaction and not the entire conjugated molecule. To test this statement the elec-

tron density distribution of CT complexes has been analysed and compared with that of separated molecules. Fig. 2 represents the molecular electrostatic potential mapped into total charge isosurface at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory. Dark-coloured areas represent negative potential while light regions have positive potential values. As seen from Fig. 2 donor molecules **6** and **7** have positively charged hydrogens while the rest of the atoms bear negative charge. On the other hand, in the acceptor molecule **4** only oxygens have negative electrostatic potential values and the rest of the atoms are positively charged. When analysing the electron density distribution it is seen that oxygen atoms of the nitro group of acceptor **4** interacts with hydrogens of the methoxy group in CT-1 and those of the amino group in CT-2. Thus, the shortest H–O distance in CT-1 between the hydrogen of methoxy and the oxygen of nitro groups is 2.22 Å and similar distance in CT-2 between the H of amino and nitro groups is 2.10 Å. It seems that the nature of these interactions is essentially electrostatic taking into account partial charges of the interacting units. The charge distribution in isolated molecules is almost identical to that of the complexes, suggesting no significant charge transfer in the ground state of these complexes.

Thermochemical analysis of the CT complexes done for 298.15 K showed that formation of both CT-1 and CT-2 is an exothermic process with ΔH of -11.8 and -12.6 kcal/mol, respectively. Slightly more negative ΔH for the CT-2 complex is explained by more positively charged protons of amino group compared with those of methoxy (0.35 and 0.21e, respectively) signifying stronger electrostatic interactions for the CT-2 molecules. In part, this fact also explains shorter H–O distances in the CT-2 molecule, however, in this case also bulky OMe groups might play an important role. Unlike enthalpies, the free Gibbs energies of formation of CT complexes are slightly positive (2.11 and 2.75 kcal/mol for CT-1 and CT-2 molecules, respectively), due to the entropy loss on complex formation. The calculated ΔG correspond to equilibrium constants of 2.8×10^{-2} and 9.7×10^{-3} for CT-1 and CT-2 molecules, respectively. Relatively small values of equilibrium constant suggest complete dissociation of CT complexes in solution which agrees with experimental observations.

Table 3

Calculated wavelengths and oscillator strengths (f) of the lowest singlet excited states of **CT-1** and **CT-2** molecules calculated at the TDB3LYP/6-31G(d) level of theory

Excitation		Coefficients of wavefunction ^a	Wavelength (nm)	f
No.	Transition			
CT-1				
1	HOMO → LUMO	0.70	1015	3.7×10^{-4}
2	HOMO → LUMO + 1	0.70	801	1.8×10^{-3}
3	HOMO-1 → LUMO	0.70	560	0.7×10^{-4}
4	HOMO-1 → LUMO + 1	0.70	502	2.3×10^{-3}
5	HOMO-2 → LUMO	0.70	460	3.2×10^{-4}
6	HOMO-5 → LUMO	0.22	433	7.4×10^{-2}
	HOMO-4 → LUMO	-0.46		
	HOMO-3 → LUMO	0.45		
7	HOMO-5 → LUMO	0.21	418	9.8×10^{-2}
	HOMO-4 → LUMO	0.50		
	HOMO-3 → LUMO	0.36		
CT-2				
1	HOMO → LUMO	0.63	2002	3.0×10^{-2}
	HOMO-1 → LUMO	0.64	1997	1.4×10^{-4}
	HOMO → LUMO + 1	0.18		
2	HOMO-1 → LUMO	-0.20	1234	0.8×10^{-2}
	HOMO → LUMO + 1	0.67		
3	HOMO-1 → LUMO + 1	0.71	1111	1.1×10^{-2}
	HOMO → LUMO	-0.11		
4	HOMO-3 → LUMO + 1	-0.10	573	1.5×10^{-2}
	HOMO-2 → LUMO	0.68		
5	HOMO-3 → LUMO	0.66	560	2.6×10^{-3}
	HOMO-2 → LUMO + 1	-0.18		
	HOMO → LUMO + 2	-0.12		

^a Only coefficients larger than 0.1 are listed.

While there is no significant charge transfer from donor to acceptor molecule in the ground state as follows from calculation, both complexes show broad structureless absorption in the visible region related, as can be expected, to the photoelectron transfer from donor to acceptor molecules. To gain better understanding of the nature of the long wave absorption maxima in CT complexes, time-dependent functional theory (TDDFT) was used to model the excited states of **CT-1** and **CT-2** molecules. TDDFT is a first principles theory which usually provides an accuracy for excitation energies exceeding that of CI singles method and often comparable in accuracy to other more advanced ab initio approaches [16–20]. B3LYP hybrid functional in combination with 6-31G(d) basis set was used for this study. The geometry of CT complexes was that obtained at the

B3LYP/6-31G(d) level of theory. Table 3 shows calculated wavelengths and oscillator strengths of the lowest singlet excited states of **CT-1** and **CT-2** molecules calculated at the TD-B3LYP/6-31G(d) level of theory. Analysing the data of Table 3, it can be concluded from the oscillator strengths and the positions of the peaks that the observed maxima in the visible region of **CT-1** and **CT-2** molecules corresponds to transitions 6,7 and 4,5, respectively. First two transitions found for **CT-1** and first three for **CT-2** lie in the near-IR region. **CT-1** shows a weak broad absorption in the near-IR peaking at 843 nm which can be assigned to the predicted HOMO to LUMO + 1 transition (801 nm) while the other predicted bands in the near-IR are out of reach of common IR and UV spectrometers. All other transitions in the visible region are very weak and lie

well beyond the region of observed peaks making the assignment a relatively easy task. In the case of **CT-1**, two closely located transitions of similar intensity (at 433 and 418 nm) can be identified with a broad observed absorption with maximum at 465 nm while in the case of **CT-2** the observed peak at 590 nm can be associated with two close transitions; one which is more intense at 573 nm, and another much less intense at 560 nm.

When analysing the orbitals involved in transitions it is seen that excitation of molecules leads to the electron transfer from the donor to the acceptor. Thus, in the case of **CT-1** molecules an electron is excited from HOMO-5, HOMO-4 and HOMO-3 to the LUMO. HOMO-5 is located at sp carbons of donor **6**, HOMO-4 belongs to phenyl rings of the donor and HOMO-3 is located at the sp carbons of the acceptor **4**. The LUMO of **CT-1** molecule is localised mainly at the nitro groups of **4**. Therefore, the absorption band in **CT-1** can be described as a mixed inter–intra-molecular electron transfer from triple bonds of molecules **4** and **6** and phenyl rings of donor **6** to the electronegative nitro groups of acceptor **4**.

The most important transition in **CT-2** involves the excitation of an electron from HOMO-3 to LUMO + 1 and from HOMO-2 to LUMO. HOMO-3 and HOMO-2 belong to diamine **7** and they are located at the nitrogens and sp carbons of the diamine, while the LUMO is located generally at the nitro groups and the benzene ring. In this case the optical excitation resulted in pure intermolecular electron transfer from nitrogens and triple bonds of the donor to the nitro and phenyl groups of the acceptor.

4. Conclusions

Novel CT complexes containing donor and acceptor diphenyldiacetylene molecules were synthesised and characterised. None of the complexes underwent topochemical polymerisation in the solid state. Their structure and electronic and optical properties were modelled using the DFT approach. Electrostatic interactions between negatively charged oxygen of the nitro groups and positively charged protons of the amino and methoxy groups are responsible for

the complex formation involving no significant charge transfer as follows from analysis of geometry and electronic density distributions in CT complexes. The optical excitation, however, leads to intermolecular charge transfer from the triple bonds of the donor to the nitro groups of the acceptor.

The restrictions imposed by topochemical polymerisation on crystalline structure of DAs are very severe. The adjacent DA molecules should be strictly parallel to one another while in **CT-1** and **CT-2** complexes individual molecules adopt a bent conformation impeding topochemical polymerisation of the DA groups. This phenomenon seems to be general feature of CT complexes and explains why none of the CT complexes containing DA molecules prepared to date underwent topochemical polymerisation in the solid state.

Acknowledgements

This work was supported by a grant from CONA-CyT under contract 32560-E.

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