

Electrical conductivity and luminescence of 9-chloro-10,10'-bis-(dichloromethylene)-(9'H)-10,10'-dihydro-9,9'-bianthryl (CDDB)

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MS received 20 February 1993; revised 14 June 1993

Abstract. The absorption and fluorescence of 9-chloro-10,10'-bis-(dichloromethylene)-(9'H)-10,10'-dihydro-9,9'-bianthryl (CDDB) has been studied in polar and nonpolar solvents and also in microcrystal. In polar solvents CDDB emits from two molecular forms, the normal charge transfer form (locally excited, LE form) and the solvent-induced twisted intramolecular charge transfer (TICT) form. Electrically, CDDB possesses semiconducting property with conductivity approximately $10^{-9} \text{ S cm}^{-1}$ and this conductivity further increases to $10^{-7} \text{ S cm}^{-1}$ on photoexcitation. Intramolecular charge transfer by hopping mechanism is assumed to be the main process for controlling activation energy and electronic conduction.

Keywords. Bichromophoric molecule; dual fluorescence; twisted intramolecular charge transfer; dark and photoelectrical conductivities.

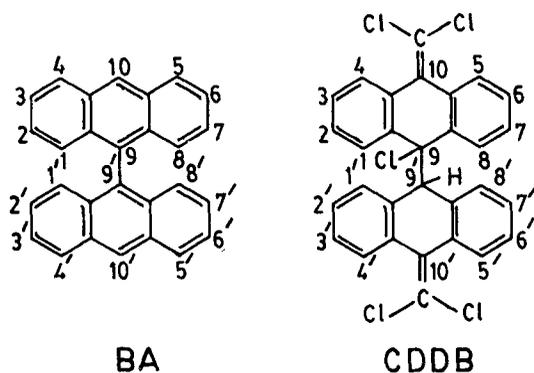
1. Introduction

Bichromophoric organic molecules (Rettig 1986) have gained importance in view of their electrical conductivity and photoluminescence. The electrical charge separation is the basis for numerous present developments in organic conductors and superconductors (Rettig 1986). Some of these bichromophoric organic molecules exhibit luminescence and so they offer a well-suited model to study the mechanisms for charge separation. The internal and environmental effects on photophysical processes give detailed information on their electrical conduction.

In this communication we have investigated the electrical conductivity and luminescence properties of a newly developed bichromophoric molecule, 9-chloro-10,10'-bis-(dichloromethylene)-(9'H)-10,10'-dihydro-9,9'-bianthryl (CDDB). This molecule bears some basic resemblance in structure and properties to 9,9'-bianthryl (BA). Bianthryl undergoes charge separation and symmetry breaking on photoexcitation and forms twisted intramolecular charge transfer (TICT) state (Kahlow *et al* 1987; Kang *et al* 1988). So CDDB like BA is expected to be a good model compound to study photosynthesis (Lueck *et al* 1991) and fast electron transfer mechanism (Toublanc *et al* 1989).

2. Materials and experimental details

CDDB was prepared according to the method of Bowen and Rohatgi (Rohatgi 1952; Bowen and Rohatgi 1953). Pure crystal obtained has a melting point (m.p.) of 105°C. On analysis, the solid gave C, 65.06%; H, 3.04%; and Cl, 31.90%, compared to the theoretical value for $\text{C}_{30}\text{H}_{17}\text{Cl}_5$: C, 64.92%; H, 3.06% and Cl, 32.01%. The analysis was quite in agreement with the published data (Rohatgi 1952; Bowen and Rohatgi



1953) and it was further confirmed from NMR and mass spectra. All the solvents used here were of spectroscopic grade or were purified by standard methods.

For conductivity measurement surface type of cells using aluminium (Al) and gold (Au) coated electrodes on glass slides were used. Electrode distance and film thickness were 0.2–0.3 cm and 0.5×10^{-3} to 10^{-3} cm respectively. The slide was covered by a clean quartz plate with Teflon tape. This surface cell was placed in a copper optical dewar fitted with electric heater to maintain desired ambient temperature. Copper-constantan thermocouple was used to measure the ambient temperature. Current was measured by Keithley electrometer (Model 617 programmable). Desired electric field across the electrode was applied from a high voltage d.c. unit (E.C. India, model HV 4800-D). Using Al and Au electrodes current was measured (dark current) for various voltages and I - V characteristic curves were drawn. At a constant electric field the variation of current and hence conductivity at different ambient temperatures was also obtained and $\ln \sigma$ vs $1/T$ graph plotted. For the measurement of photocurrent the sample was illuminated by UV light at a particular wavelength from a high pressure mercury lamp (200W) using a monochromator. All the experiments were performed in nitrogen atmosphere. Absorption spectra were recorded on a Perkin-Elmer spectrophotometer (Lambda 3A) and the fluorescence spectra on a Spex Fluorolog spectrophotometer (Model FIII A).

3. Results and discussion

3.1 Absorption and fluorescence spectra

The compound CDDB has some basic similarity in structure and properties with BA. Absorption and fluorescence spectra of CDDB in ethanol and cyclohexane and those of BA in ethanol are shown in figure 1. The absorption and fluorescence spectra of CDDB microcrystal are shown in figure 2. The absorption spectrum of BA (Schneider and Lippert 1968) has three distinct bands, viz. 1L_a and 1L_b bands (300 nm ~ 400 nm), 1B_b band (~ 252 nm) and 1C_b band (~ 225 nm). The intense peak positions for CDDB in the shorter wavelength region in cyclohexane and in ethanol are 254 nm and 252 nm respectively, corresponding to the $^1B_b \leftarrow ^1A_1$ transition of anthracene or BA. However, the transitions of CDDB corresponding to the 1L_a and 1L_b regions of anthracene or BA are very very weak ($\epsilon_{340\text{ nm}}^{\text{EtOH}} \approx 400$) compared to 1B_b transition ($\epsilon_{252\text{ nm}}^{\text{EtOH}} \approx 44668$) and not detectable at concentrations below 10^{-3} M. At

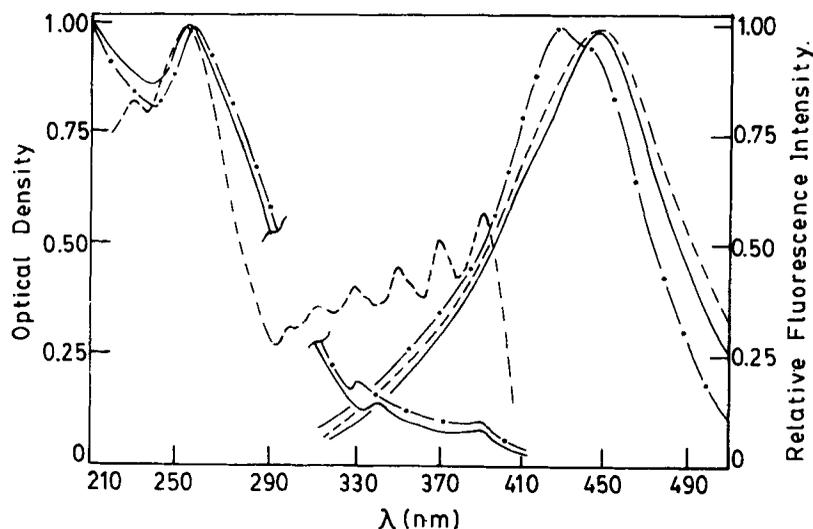


Figure 1. Absorption and fluorescence spectra of bianthryl in ethanol (-----) and those of CDDB in cyclohexane (—●—●—●—) and ethanol (———). The absorption spectrum of bianthryl in ethanol is taken from Schneider and Lippert (1968) and the fluorescence spectrum from Zander and Rettig (1984).

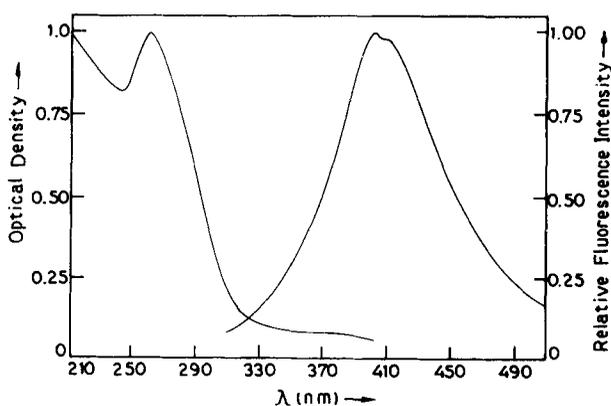


Figure 2. Absorption and fluorescence spectra of CDDB microcrystal.

higher concentration a prominent shoulder at 340 nm and a faint shoulder at 390 nm in ethanol and 328 nm and 388 nm in cyclohexane are two bands corresponding to 1L_a and 1L_b bands of BA or anthracene which are expected to be overlapping with each other. The oscillator strength of CDDB in the longer wavelength region (300 nm ~ 400 nm) was computed (~ 0.02). Bianthryl (Schneider and Lippert 1968) has 1L_a and 1L_b bands in the region similar to that in CDDB. The weak absorption of CDDB in 1L_a and 1L_b regions compared to anthracene or BA is expected due to loss in benzenoid structure in the middle ring of two anthryl moieties. In microcrystal the 1L_a and 1L_b bands of CDDB are also not well resolved; only the intense 1B_b band is detectable at 262 nm. The absorption maxima of CDDB are not solvent dependent except a minor shift of the order of 1 to 3 nm in some cases and the absorptions are also not concentration dependent.

The fluorescence spectrum of CDDB in ethanol is totally diffuse and its peak position of 450 nm almost coincides with that of BA in ethanol (figure 1). The emission peak position of CDDB in cyclohexane is at 429 nm which is red-shifted by 24 nm compared to that of CDDB microcrystal. This shift indicates that there is an intramolecular charge transfer (ICT) in the molecule even in nonpolar solvents like cyclohexane. CDDB is a totally nonsymmetric molecule of point group C_1 . In CDDB one anthryl moiety carrying hydrogen at C_9 , is expected to be slightly negatively charged due to prototropy and the other anthryl moiety carrying chlorine at C_9 will be positively charged due to anionotropy, thereby making the two halves of this molecule electrically of opposite character, which favours the charge transfer process. In polar solvents the red shifts further increased to 22 nm in methanol and 20 nm in ethanol, compared to cyclohexane. This further perturbation in emission in polar solvents is expected due to rotation of the molecule through C_9-C_9' bond along with the intramolecular charge transfer. CDDB has a large change in dipole moment (Chattopadhyay *et al* 1993), about 9 Debye on excitation. So, in polar environment dipole-dipole interaction may help the rotation of C_9-C_9' bond for the formation of twisted intramolecular charge transfer (TICT) state. Such structural changes and dual luminescence have been reported for BA (Hara *et al* 1984; Kahlow *et al* 1987; Nagarajan *et al* 1987; Kang *et al* 1988; Lueck *et al* 1991).

The fluorescence quantum yields (ϕ_f) of CDDB and its actual lifetimes τ_f calculated from single-photon counting technique and the natural radiative lifetimes (τ_e^{abs}) calculated from Strickler-Berg (SB) equation (Strickler and Berg 1962) are tabulated in table 1. The value of τ_e^{abs} in the table is subject to some approximation as the SB equation has been used for the pure spectra extracted from the tail of a highly intense band. From these experimentally determined natural radiative lifetimes, τ_e^{exp} ($= \tau_f/\phi_f$), radiative rate constants k_f ($= 1/\tau_e^{exp}$), and non-radiative rate constants k_{nr} ($= 1/\tau_f - 1/\tau_e^{exp}$) were measured. As mentioned in table 1 for CDDB, τ_e^{abs} is very small compared to τ_f in both the solvents, which is expected due to overlapping of the two transitions ($^1L_a, ^1L_b$) in the lowest energy of absorption. Again τ_e^{exp} is nearly about 8.5 times greater than τ_e^{abs} in cyclohexane and 12.2 times in ethanol, which is an indication for participation of a number of excited states, i.e. S_1^*, S_2^* in the emission and geometry difference between S_1^* and S_0 state (Werner 1976). The difference between τ_e^{exp} and

Table 1. Photophysical characteristics of CDDB in solid state and in solution at 25°C.

	$\tilde{\nu}_a^{max}$ (cm^{-1})	$\tilde{\nu}_f^{max}$ (cm^{-1})	ϕ_f	τ_f (ns) ^a	τ_e^{abs} (ns) ^b	τ_e^{exp} (ns)	k_f ($10^7 s^{-1}$) ^c	k_{nr} ($10^7 s^{-1}$) ^d
CDDB microcrystal	38167	24691	—	$\ll 2^e$	—	—	—	—
CDDB in cyclohexane	39370	23310	0.30	9.0	3.5	30.0	3.3	7.7
CDDB in ethanol	39682	22222	0.21	10.8	4.2	51.4	1.9	7.3

^aCalculated from the single-photon counting technique, error ± 0.2 ns.

^bCalculated from Strickler and Berg (1962) equation.

^cEqual to $1/\tau_e^{exp}$

^dEqual to $1/\tau_f - 1/\tau_e^{exp}$

^eOur instrument does not permit measurement below 2 ns.

τ_e^{abs} is due to change in configuration interactions in the singlet excited state (Birk *et al* 1978; Bondarev and Bachilo 1991). The measured lifetimes of CDDB in polar solvents increase with increased polarity whereas quantum yield decreases. k_f also decreases with increase in solvent polarity but k_{nr} does not change appreciably. Usually for molecules with no change in excited geometry, k_{nr} changes as a function of solvent while k_f being intrinsic remains fairly constant. In the present case a reverse in the above trend could probably indicate the presence of a TICT state. The decrease in ϕ_f with increase in polarity is due to transition of the excited CDDB molecule from Franck–Condon state to certain configuration states (Bondarev and Bachilo 1991) which gives dual luminescence. Rettig (1986) reported similar low quantum yield of fluorescence in polar solvents due to TICT state fluorescence along with the normal fluorescence of the molecule. The transition from TICT state to ground state involving two orbitals located on different π -systems which are perpendicular to each other and overlap forbidden is the main cause for their low quantum yield. The torsional angle between the two anthracene molecular planes along the C_9-C_9 bond of bianthryl (Schneider and Lippert 1968, 1970) is at right angle in the ground state, hence the π -electron clouds of the two anthracene chromophores do not interact with each other. It is expected that for CDDB the angle between the two anthracene moieties is not exactly 90° in ground state but an acute angle near to about 90° .

From the comparative study of the emission of CDDB in methanol and in cyclohexane it is expected that in polar solvents CDDB emits from two molecular forms, the normal charge transfer form (locally excited, LE, mentioned by some researchers) and the solvent-induced TICT form. But our measured fluorescence decays both in methanol and cyclohexane show single exponential at room temperature with $\chi^2 = 1.2$. But in methanol one can expect the biexponential decay for CDDB. This indicates that the fluorescence lifetimes of CDDB in both forms are nearly about the same (~ 9 to 10 ns) and not easily separable in the nanosecond time scale. It has been found from the picosecond study that the lifetime of BA for the LE \rightarrow TICT process is very short (about 1 to 4 ps) (Toublanc *et al* 1989) in fluid solvents. The TICT state of BA is formed from the LE state mentioned by Nakashima *et al* (1976), who also observed the single exponential decay both for LE and TICT fluorescence with the lifetimes of the two states being almost equal. Our unpublished results on non-steady state fluorescence will reveal this mechanism.

In conclusion, by drawing a parallel with BA, the possibility of TICT is strongly suggested for the following observations:

- (i) There is no correspondence of the emission spectrum with the longest wavelength absorption spectrum.
- (ii) Figure 1 shows loss of structure and red shift with solvent polarity.
- (iii) The value of τ_f is found to be much higher than that of τ_e^{abs} , even though the application of Strickler–Berg formula is somewhat approximate in this case.
- (iv) k_{nr} remains fairly constant while k_f varies.

3.2 Dark and photoelectrical conductivities

3.2a *Dark conductivity*: Dark conductivity of CDDB was calculated from I - V characteristic curves which were drawn on the basis of the experimental data obtained in our laboratory using vacuum-deposited Au and Al electrodes. The current was

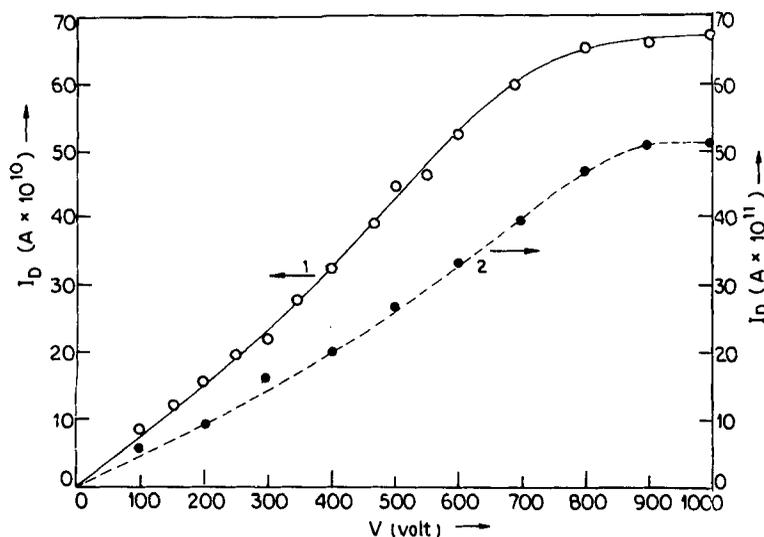


Figure 3. Current, I_D vs voltage V characteristics of CDDB film using gold electrodes (1) and aluminium electrodes (2).

Table 2. Electrical characteristics of CDDB and anthracene.

Sample	Activation energy (eV)	Dark conductivity	σ_D ($S\text{cm}^{-1}$)	Photoconductivity σ_p ($S\text{cm}^{-1}$)	
		using Al electrode	using Au electrode	Initial	Final
Anthracene*	1.93	1.0×10^{-19}	—	—	—
CDDB	1.1–1.2	$(1.48\text{--}1.6) \times 10^{-9}$	$(3.01\text{--}3.08) \times 10^{-9}$	1.22×10^{-7}	10.6×10^{-7}

*Taken from Inokuchi and Akamatu (1961).

found to follow linear nature over a short range of voltage in low-voltage region and otherwise it was nonlinear in nature. The current was generally controlled by carrier concentration. At high voltage the current attained saturation limit as shown in figure 3. The dark conductivity as calculated from I - V curves was found to be of the order of $10^{-9} S\text{cm}^{-1}$. This value was found to be much higher than the value of dark conductivity of the highly conjugated anthracene molecule as shown in table 2.

To find out the electrical effect on conductivity and activation energy, we used Au and Al as electrodes and found a definite change in conductivity of CDDB but no change in activation energy. This clearly suggests that the activation energy is the inherent property of the substance (CDDB) used but the conductivity may be influenced by contact potential, work function and similar other causes (Goodings 1976). The experiment on the thin film of CDDB clearly showed a definite increase in conductivity with a rise in temperature as for inorganic semiconductors (figure 4) and follows the exponential relation given by (1) below:

$$\sigma = \sigma_0 \exp(-E/2kT), \quad (1)$$

where E is the activation energy and σ_0 the conductivity extrapolated at infinite temperature. From this relation it is clear that the conductivity of the sample mainly

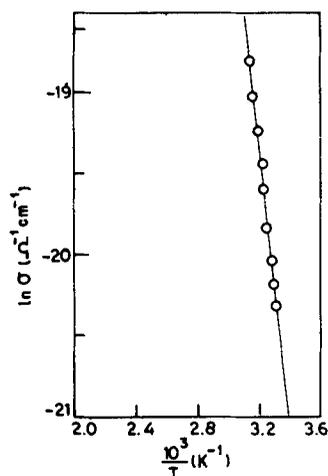


Figure 4. Variation of conductivity with reciprocal temperature for CDDB film.

depends on the activation energy of the molecule. Carrier production and its transportation is mainly controlled by the activation energy (Rosenberg and Bhowmik 1969). The activation energy of the highly conjugated organic molecule anthracene and that of the molecule CDDB can be compared in table 2. It is evident that the higher value of conductivity of CDDB in comparison to the conductivity of the more conjugated molecule anthracene is due to the lower activation energy of CDDB.

The activation energy E partly depends on the intermolecular potential barrier and partly on constitution (Hansmeier 1974). The large reduction of activation energy of CDDB is mainly due to the peculiar non-symmetric configuration of the molecule which induces a charge transfer process in the molecule. Due to steric hindrance and asymmetry the charge transfer rate is higher in CDDB molecule (Mataga *et al* 1989). One anthryl portion carrying hydrogen at C_9 is expected to be slightly negatively charged and the other anthryl molecule carrying chlorine at C_9 will be oppositely charged. Thus even at room temperature the thermal energy is sufficient to induce intramolecular charge transfer producing necessary amount of charge carrier, hole and electron, on the two chromophores. These holes and electrons jump from one molecule to the other under the influence of the applied external electric field, overcoming the intermolecular potential barrier. Due to lack of conjugation intermolecular potential barrier is higher for such molecules than the conjugated molecules and consequently mobility of charge carrier is expected to be low. Hence, in spite of the creation of charge carrier electrons and holes due to intramolecular charge transfer, the conductivity of CDDB is usually low due to lack of conjugation producing higher intermolecular potential barrier.

3.2b Photoconductivity: CDDB is a photosensitive organic molecule. It shows photoconductivity of the order of $10^{-7} \text{ S cm}^{-1}$ when the film is exposed to the photon of proper wavelength. The photocurrent was found to attain its steady saturation value a long time after the film was exposed to photons (figure 5). Chynoweth and Schneider (1954) attributed this to the formation of space charges. Some workers (Bree *et al* 1955) argued that this was due to contact potential and various other

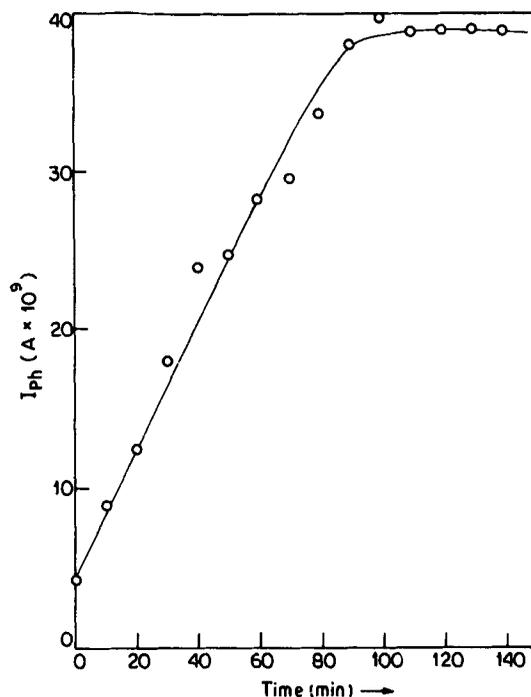


Figure 5. Photocurrent I_{ph} vs time characteristics for CDDB film using aluminium electrodes.

causes. Using good conducting paint such as silver paint for good contact between the electrodes and the sample no measurable improvement in current was observed. So this effect is not due only to the space charge effect or contact potential but it may be due to instrumental lag and various other causes. The experiment was performed by illuminating either of the electrodes in contact with the sample and covering the other by black paper alternately. The photocurrent was found to differ slightly in the two cases but the maximum response was found near to the absorption edge in both the cases. It is natural therefore to expect that the carrier was produced within the molecules in their excited state as otherwise the current would have been identically independent of the direction of the electric field (Kommandeur and Schneider 1957). The photoconductivity as observed in the experiment was found to be 100 times higher than the dark conductivity (table 2). But the mechanism of creation of free carrier and also that of conduction is similar to that mentioned in dark conductivity. The intramolecular charge transfer occurs when the molecules are excited by the photon of proper frequency and thus two chromophores will be oppositely charged creating localized holes and electrons which under the influence of electric field hop from one molecular site to the other. The holes and electrons move in opposite direction overcoming the intermolecular barrier potential.

The photons required for the excitation of CDDB molecule generally possess higher energy than thermal energy at ordinary room temperature. So, for this photosensitive molecule CDDB, it is expected that when a thin layer of the sample is exposed to light of proper frequency, a large number of molecules of CDDB are raised to the excited states creating a larger number of holes and electrons. Thus the free carriers, holes and electrons, created by photons, being much higher than that created by

ordinary thermal energy, enhance the magnitude of photoconductivity over that of dark conductivity. This justifies the observed effect.

4. Conclusion

9-Chloro-10,10'-bis-(dichloromethylene)-(9'H)-10,10'-dihydro-9,9'-bianthryl (CDDB) is one of the main products of the photochemical reaction between anthracene and carbon tetrachloride. This molecule (CDDB) is separated and purified to analytical level. CDDB in solution has the structured absorption spectrum in the same region as that of 9,9'-bianthryl or anthracene. The only difference is that the intensity in the long wavelength (300 nm ~ 400 nm) region is very weak compared to that of the two parent molecules. The absorption transitions of CDDB are abbreviated as ${}^1B_b \leftarrow {}^1A_1$, ${}^1L_a \leftarrow {}^1A_1$ and ${}^1L_b \leftarrow {}^1A_1$. In microcrystal, CDDB has no structural feature in the long wavelength region. The fluorescence of CDDB is slightly structured in cyclohexane and red-shifted by 24 nm compared to microcrystal but in a polar solvent like ethanol or methanol it is further red-shifted by ~ 45 nm compared to that in microcrystal. With increase in solvent polarity the fluorescence quantum yield (ϕ_f) and fluorescence rate constant (k_f) decrease and at the same time fluorescence lifetime (τ_f) increases. It is expected that CDDB exists in two different molecular forms one of which is stable in nonpolar solvent and the other in polar solvent. The normal excited form (locally excited) of CDDB is expected to exist in low-polarity solvent due to charge transfer or electron transfer process from one moiety to other but at higher polarity further rotation of $C_9-C_{9'}$ bond is expected due to solvent induction. Hence there exists another new form called twisted intramolecular charge transfer (TICT) form. CDDB is a totally non-symmetric molecule of point group C_1 . On comparison with geometry of bianthryl it may be considered that the two π -electronic systems of CDDB are oriented almost perpendicular to each other in the ground state (S_0) due to steric hindrance. But in the excited state (S_1) some oblique structure is expected and rotation of $C_9-C_{9'}$ bond is also possible in polar solvent.

Electrically CDDB behaves as a semiconductor with a conductivity of $\sim 10^{-9} \text{ S cm}^{-1}$. This conductivity further increases to $10^{-7} \text{ S cm}^{-1}$ on photoexcitation. The increase in conductivity of CDDB compared to anthracene is solely due to the decrease in the activation energy. The experimentally measured activation energy of CDDB is 1.1–1.2 eV, which is lower than that of anthracene (1.93 eV). CDDB is a less conjugated molecule than anthracene, so intermolecular potential barrier is expected to be higher here than in similar conjugated molecules and consequently mobility of charge carrier is expected to be low. In CDDB one anthryl portion carrying hydrogen at C_9 is expected to be slightly negatively charged due to prototropy and the other anthryl moiety carrying chlorine at C_9 will be positively charged due to anionotropy, thus making the two halves of the molecule electrically of opposite character. Intramolecular charge transfer by hopping mechanism is assumed to be the main process for controlling the activation energy and electronic conduction.

Acknowledgement

We wish to thank Dr S C Bera, Jadavpur University, for instrumental help. We are indebted to Profs K K Rohatgi–Mukherjee and A Banerjee, Chemistry Department, Jadavpur University, for their helpful discussions.

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