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Structure and Ionicity of Intramolecular Charge Transfer Zwitterions, $D^{\delta+} - \pi - A^{\delta-}$

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Intramolecular charge transfer (CT) compounds ($D^{\delta+}$-π-$A^{\delta-}$) were synthesized by the reaction between enamine and TCNQ. The CT transition energy ($h\nu_{CT}$) showed the solvent dependence (solvatochromism). The ionicity of these compounds was deduced from the plot of $h\nu_{CT}$ against the solvent polarity. The plot exhibited abnormal behavior.

Keywords: Intramolecular charge transfer ; Zwitterion ; Ionicity ; Molecular structure

INTRODUCTION

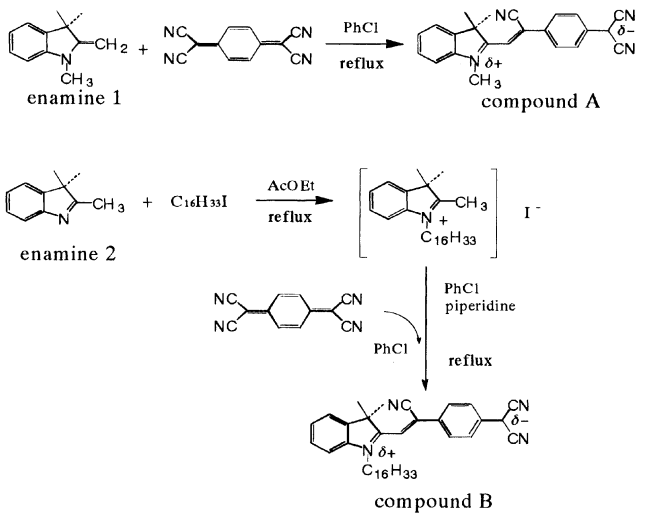
The intramolecular CT compounds have been attracted much interest as

functional dyes for non-linear optics [1], molecular rectifiers and so on. The degree of CT (δ) is an important parameter for determining such functionality. Intramolecular CT compounds are categorized in some groups according to the junction between donor (D) and acceptor (A) parts. Among them, we have investigated D-π-A type ones, in which the D and A parts are connected by a conjugated π system. In this paper, we report the abnormal optical behavior observed in the betaine type compounds denoted as A and B.

EXPERIMENTAL

Synthesis

Compounds A and B were synthesized by the method applied for the analogous compound [1],[2].



scheme 1

Compound A; After the dropwise addition of a solution of enamine 1 (2 mmol) in 5 ml of chlorobenzene into a solution of TCNQ (2 mmol) dissolved in 30 ml of chlorobenzene, the mixture was refluxed for 6 hrs under N_2. The dark green solution was cooled to room temperature and the green precipitates were collected on a glass filter, washed with ether, then hexane. The product was recrystallized from CH_3CN to give green crystals (301 mg, 43%).

Compound B; Into a solution of 1-iodohexadecane (70.0 mmol) in 10 ml of ethylacetate, enamine 2 (74.7 mmol) was added dropwise at room temperature and the mixture was refluxed for 15 hrs under N_2. The solution was cooled to room temperature to give pink precipitates, which were collected on a funnel then washed with hexane (yield 33.24 g, 97.0%). The iodide salt (3.64 mmol) was dissolved into 90 ml of chlorobenzene, into which piperidine (3.29 mmol) was added and the solution was refluxed for 20 min under N_2. The hot solution was added into hot solution of TCNQ (3.02 mmol) in 90 ml of chlorobenzene and the mixture was refluxed for 36.5 hrs under N_2. After concentrated to 10 ml, the mixure was purified by column chromatograpy, and then reprecipitated from hexane to give green powder with golden luster (400 mg, 23.8%).

RESULTS AND DISCUSSION

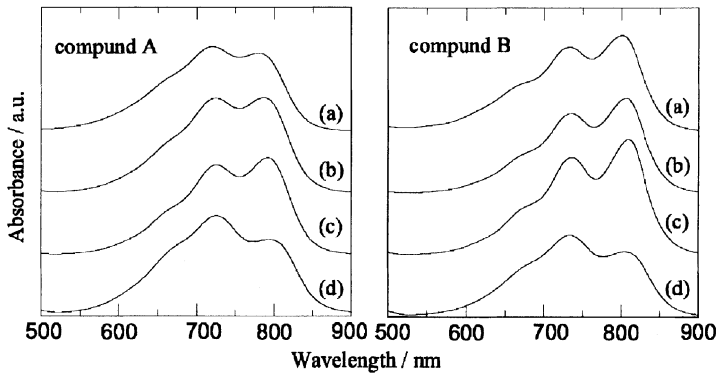


FIGURE 1 Absorption spectra of compounds A and B. The solvents used are ; (a)methanol, (b)acetonitrile, (c)acetone, (d)chlorobenzene.

Figure 1 shows the optical absorption spectra of the compounds A and B in different solvents. They exhibit characteristic absorption bands which consist of mainly three peaks at around 750 nm. The chromophors of D and A showed the absorption peaks in the higher energy regions, respectively. The absorption coefficients of the bands shown in figure 1 exhibited no concentration dependence. Hence, these bands are assigned to intramolecular CT transition. To express the intramolecular CT transition energy ($h\nu_{CT}$), we employed the peak position of the central one. The $h\nu_{CT}$ showed the solvent dependence. For compounds A and B, the deviations of $h\nu_{CT}$'s are 131 and 36 cm^{-1} within the solvents used, respectively. From the solvatochromism of the CT band, one can estimate the δ in the ground state of $D^{\delta+}$-π-$A^{\delta-}$. When the $h\nu_{CT}$ shows no solvatochromism, the δ should be close to 0.5.

When the ground state is neutral, the $h\nu_{CT}$ decreases with increasing the polarity of the solvent, vice versa. As the measure of the polarity of solvent, we adoped the E_T value derived by C.Reichardt [3]. The plot of $h\nu_{CT}$ against E_T showed abnormal feature [4] (Figure 2).

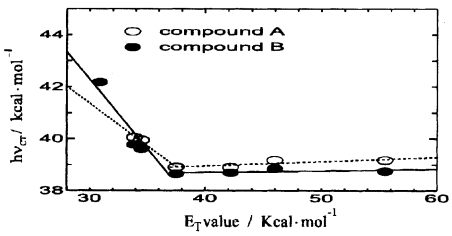


FIGURE 2 The plot of $h\nu_{CT}$ against E_T values of several solvents : methanol (E_T = 55.5), acetonitrile (46.0), acetone (42.2), chlorobenzene (37.5), benzene (34.5), toluene (33.9), hexane (30.9).

In the small E_T region, the ground state seems to be neutral, however, in the big E_T region, the ground state seems to be ionic. This means that the ionicity of the ground state is different between in non-polar solvent and in polar one. To understand this behavior, we concerned the flexibility of our D-π-A molecules. In the 2:1 complex between compound A and TCNQ, two crystallographically independent molecules of compound A have different intramolecular dihedralangles (ϕ) between D and A parts (Figure 3 bottom). Based on each molecular conformation (ϕ = 51.4, 9.8°), the MOPAC calculation gives different intramolecular δ value (0.516, 0.367, respectively). Our interpretation contains the switching of the ground state (neutral and ionic) of D-π-A system according to the

environment. To prove this idea, the synthesis of other D-π-A compounds in this class and the examination of the structure analysis are on the way.

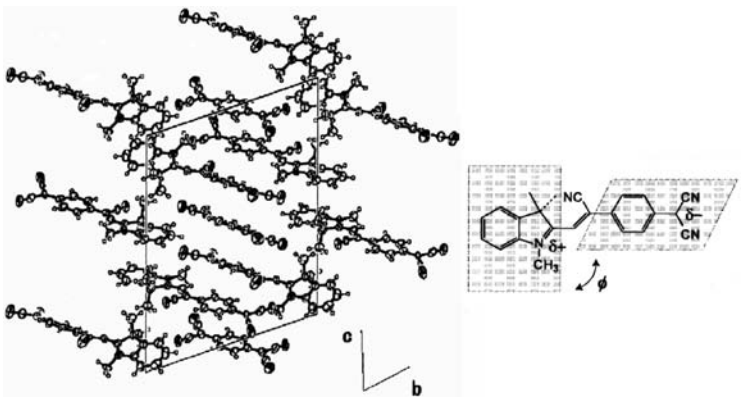


FIGURE 3 Crystal structure of (compound A)$_2$TCNQ.

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