

Supporting Information

Fluorescence of 4-(Diisopropylamino)benzotrile (DIABN) Single Crystals from 300 K down to 5 K.

Intramolecular Charge Transfer Disappears below 60 K

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Effective Polarity of DIABN Crystals (Data from refs 11 and 26). The ICT fluorescence of crystalline DIABN at 26 °C has a maximum $\tilde{\nu}^{\max}(\text{ICT})$ at 23200 cm^{-1} , which undergoes a shift to 22000 cm^{-1} just above the melting point of DIABN at 90 °C.¹¹ From a comparison of the $\tilde{\nu}^{\max}(\text{ICT})$ data in solution as a function of solvent polarity (Table S1),²⁶ it appears that $\tilde{\nu}^{\max}(\text{ICT})$ for crystalline DIABN falls between those for ethyl acetate ($\epsilon^{25} = 5.99$) of 22260 cm^{-1} and *n*-propyl acetate ($\epsilon^{25} = 5.52$) of 22380 cm^{-1} (Table S1). It is hence concluded that the effective polarity within the DIABN crystals is equivalent to an ϵ^{25} of around 6,¹¹ similar to that of liquid *N,N*-diethylaniline ($\epsilon^{20} = 5.2$)^{S1,S2}.

Such a polarity estimation is more difficult for molten DIABN at 90 °C, as the other data in Table S1 refer to 25 °C. Generally, increasing the temperature reduces the polarity of a medium, which means that the polarity of molten DIABN will be smaller than the ϵ^{25} of ~7 deduced from the $\tilde{\nu}^{\max}(\text{ICT}) = 21950 \text{ cm}^{-1}$ for DIABN in methyl acetate ($\epsilon^{25} = 6.88$). This small apparent difference with crystalline DIABN is somewhat surprising and could indicate a reduced amount of solvation by neighbouring DIABN molecules in the crystal as well in the melt as compared with solutions.

It should be noted that the $\tilde{\nu}^{\max}(\text{ICT})$ of 23200 cm^{-1} for DIABN single crystals at 27 °C determined from the fluorescence spectrum in Figure 1 is different from that (22300 cm^{-1} , at 26 °C) reported in ref 11. The data from ref 11 and in Table S1 are obtained from fluorescence spectra measured with a setup (see Experimental) different from that employed for Figure 1. It is our general observation that fluorescence spectra in the literature hardly ever are the same, even not for the fluorescence quantum yield standard quinine bisulphate. This no doubt is due to the complexity of the quantum correction procedures for the spectra.

References:

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- (26) Druzhinin, S. I.; Mayer, P.; Stalke, D.; von Bülow, R.; Noltemeyer, M.; Zachariasse, K. A. Intramolecular Charge Transfer with 1-*tert*-Butyl-6-cyano-1,2,3,4-tetrahydroquinoline (NTC6) and Other Aminobenzonitriles. A Comparison of Experimental Vapor Phase Spectra and Crystal Structures with Calculations. *J. Am. Chem. Soc.* **2010**, *132*, 7730-7744.
- (S1) Price, A. H. The Dielectric Relaxation Times of Some Amines, Dimethylthianthrene, Dibenzothiophene, Triphenylphosphine and Triphenylarsine. *J. Phys. Chem.* **1958**, *62*, 773-777.
- (S2) Srivastava, K. K. Dielectric Relaxation Study of Some Pure Liquids. *J. Phys. Chem.* **1970**, *74*, 152-159.

Table S1: ICT Fluorescence Maxima $\tilde{\nu}^{\max}(\text{ICT})$ for 4-(Diisopropylamino)benzonitrile (DIABN) Solutions at 25 °C, Vapor Phase Data Are at 90 °C. Solvent Polarity Data (Dielectric Constants ϵ) Are at 25 °C, See ref 26. For Crystal Data, See ref 11.

medium	ϵ	$\tilde{\nu}^{\max}(\text{ICT})$ [cm⁻¹]
crystal (27 °C)	~6	23200
crystal melt (~90 °C)	~7	22000
vapor		26270
perfluoromethylcyclohexane	1.82	26080
<i>n</i> -hexane	1.88	25730
<i>n</i> -hexadecane	2.05	25570
di(<i>n</i> -pentyl) ether	2.86	24400
di(<i>n</i> -butyl) ether	3.05	24340
di(<i>n</i> -propyl) ether	3.26	24170
diethyl ether	4.24	23530
tetrahydrofuran	7.39	22370
<i>n</i> -butyl acetate	4.95	22680
<i>n</i> -propyl acetate	5.52	22380
ethyl acetate	5.99	22260
methyl acetate	6.88	21950
dichloromethane	8.87	21780
1,2-dichloroethane	10.4	21680
valeronitrile	19.8	21310
butyronitrile	24.2	21100
propionitrile	29.2	20880
acetonitrile (MeCN)	36.7	20490

Fluorescence Decay Times for DIABN Single Crystals as a Function of Temperature from Two Experimental Setups.

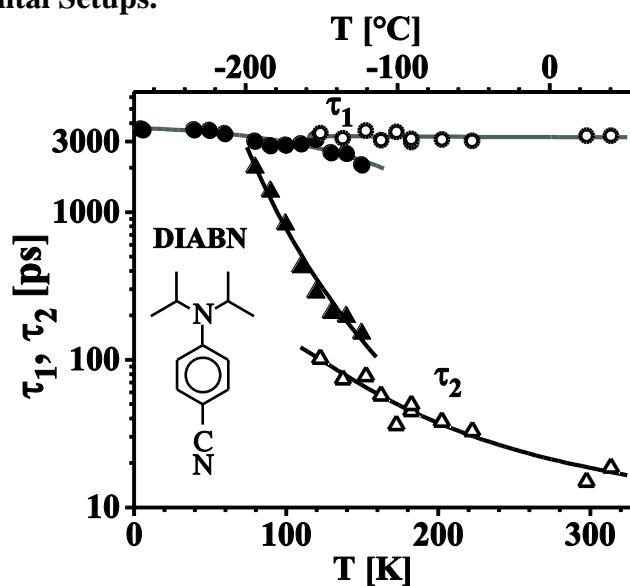


Figure S1. Fluorescence decay times τ_1 and τ_2 of DIABN single crystals as a function of temperature, from two different experimental setups. Black data points SPC1 (ref 27). Open data points SPC2 (refs 29 and 30). See Figures 7 and 10.

Arrhenius Plots for DIABN Single Crystals from Two Experimentals Setups.

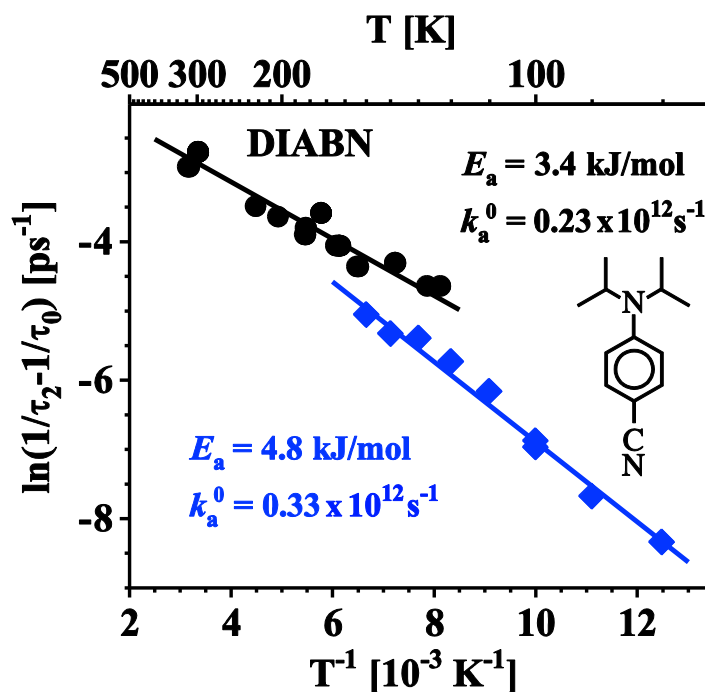


Figure S2. Arrhenius plots of the reciprocal decay time difference ($1/\tau_2 - 1/\tau_0$), see Eq 11, from two different experimental setups. Blue data points SPC1 (ref 27). Black data points SPC2 (refs 29 and 30). See Figures 9 and 12.

Complete References with more than 10 authors:

(6) Druzhinin, S. I.; Galievsky, V. A.; Demeter, A.; Kovalenko, S. A.; Senyushkina, T.; Dubbaka, S. R.; Knochel, P.; Mayer, P.; Grosse, C.; Stalke, D.; Zachariasse, K. A. Two-State Intramolecular Charge Transfer (ICT) with 3,5-Dimethyl-4-(Dimethylamino)benzotrile (MMD) and its Meta Isomer mMMD. Ground-State Amino Twist Not Essential for ICT. *J. Phys. Chem. A* **2015**, *119*, 11820-11836.

(27) Galievsky, V. A.; Druzhinin, S. I.; Demeter, A.; Jiang, Y.-B.; Kovalenko, S. A.; Lustres, L. P.; Venugopal, K.; Ernsting, N. P.; Allonas, X.; Noltemeyer, M.; Machinek, R.; Zachariasse, K. A. *Chem. Phys. Chem.* **2005**, *6*, 2307-2323.