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Ground and Excited State Dipole Moments of *N*,*N'*-Bis(4-methoxycarbonylphenyl)piperazine and its Implications†

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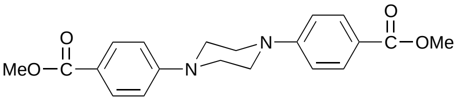
The fluorescence behaviour of the title compound indicates structural changes in the excited state leading to the formation of a highly dipolar species.

In continuation of our studies on electron donor–acceptor molecules[1] likely to exhibit twisted intramolecular charge transfer (TICT) phenomena,[2] we report here the synthesis, crystal structure and fluorescence properties of the title compound **1**, essentially a dimer of 4-dimethylaminomethyl benzoate.[3] The interest on this system is generated from the possibility of application of these materials in molecular electronic devices and a report on a structurally similar system **2** that displays flourescence[4] very similar to the long-wavelength fluorescence band of 4-(*N*,*N*-dimethylamino)benzonitrile (**3**) which is commonly interpreted as an emission from a state (TICT state) in which the dimethylamino moiety is orthogonal to the planar aromatic ring.[2,5] Further, it is interesting to note that even though the excited state dipole moment of **2** is expected to be less than that of the TICT state of **3** (because of partial cancellation of moments in the Acceptor–Donor–Spacer–Donor–Acceptor configuration of the molecule) the measured excited state dipole moment of **2** is reported to be more than that of the TICT state of **3**.[6] In order to find out whether other derivatives of this class show similar behaviour the following work was undertaken.



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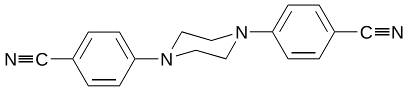

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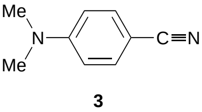

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Experimental

Absorption and fluorescence spectra were recorded on a JASCO 7800 spectrophotometer and a JASCO FP777 spectrofluorimeter respectively. The AM1 calculations were carried out on a personal computer (PC 486) using Hyperchem software. NMR and IR spectra were recorded on a Bruker ACF-200 spectrometer and a JASCO 5300 spectrophotometer respectively. The CHN analysis was performed on a Perkin-Elmer 240C CHN analyser. The fluorescence quantum yield and the lifetimes were measured following procedures outlined in ref. 1(*a*).

Compound **1** was prepared by treating a mixture of piperazine (6.5 mM) and methyl benzoate (13 mM) in dimethyl sulfoxide at 90 °C for 24 h. Addition of water followed by extraction with ethyl acetate yielded a brownish solid on evaporation which on purification by column chromatography and recrystallisation afforded a yellowish solid, mp 225–229 °C, 30% yield. ν_{max} (KBr)/cm^{-1} 2950, 1699, 1601, 1518, 1284, 1182, 1109. δ_H (CDCl$_3$) 7.95 (d, *J* 9 Hz, 4 H), 6.9 (d, *J* 9 Hz, 4 H), 3.85 (s, 6 H), 3.5 (s, 8 H). (Found: C, 19.44; H, 5.55; N, 75.0. $C_{20}H_{22}N_2O_4$ requires C, 19.08; H, 5.37; N, 74.33%). Compound **2** was prepared according to the published procedure.[4]

Crystal Data for **1**.—A crystal of **1** ($C_{20}H_{22}N_2O_4$, M_r = 354.40) was grown from an acetonitrile solution of the compound. Space group $P2_1/n$, cell parameters $a = 9.4015(4)$, $b = 8.1435(4)$, $c = 11.8872(5)$ Å, $\alpha = 90$, $\beta = 102.978(2)$, $\gamma = 90°$. Unit cell volume 886.85 Å^3, $F(100) = 376$, $\mu = 0.093$ mm^{-1}, $D_{calc} = 1.327$ g cm^{-3}. A crystal of dimensions 0.22 × 0.15 × 0.10 mm was mounted on a Siemens SMART charge coupled device detector system single crystal diffractrometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Preliminary unit cell constants were determined with a set of 60 narrow frames (0.3° in Ω) scans. A total of 1500 frames of intensity data were collected with a frame width 0.3° in Ω. The collected frames were integrated using an orientation matrix determined by narrow frame scans. Final cell constants were determined by a global refinement of *xyz* centroids of 1490 reflections. No absorption correction was applied to the data. The integration process yielded 5549 reflections of which 1559 were independent reflections.‡

Results and Discussion

The crystal structure of the compound, Fig. 1, is very similar to that of the cyano derivative, **2**.[4] The dipole moment of the molecule in the ground state is zero owing to the antiplanar configuration of the two aromatic moieties. The spectral data of **1** in various solvents are shown in Table 1. The fact that the emitting state is significantly more polar than the ground state is evident from the larger shift of the fluorescence maximum with polarity compared to that of the absorption. Further, a large Stoke's shift between the absorption and fluorescence maximum in any given solvent is indicative of the fact that the emission originates from a low-lying state that is different from the locally excited (LE) state. The solvent polarity dependent shift of the emission maxima and a comparison of the fluorescence data of **1** and **3**[2] indicate that the emission takes place from a highly polar state, which could be either a TICT state[2] or a state involving more pyramidal nitrogen (PICT state).[5] The similarity of the spectral behaviour of **1** and **2** also points to the same conclusion. The measured fluorescence yield (ϕ_f) and lifetime (τ_f) of **1** are indicated in Table 1. With an increase in the polarity of the medium a decrease in ϕ_f and τ_f (which is indicative of an enhancement of the non-radiative rate) is observed.

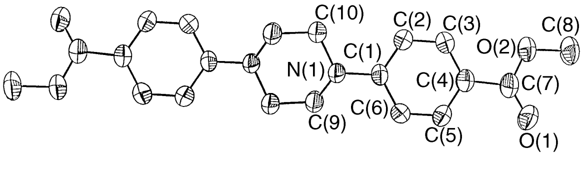

Fig. 1 ORTEP drawing of **1**

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/5.

Table 1 Absorption and fluorescence data of **1** in selected solvents

Solvent	ε^a	λ_{max}^{abs}/nm	λ_{max}^{flu}/nm^b	ϕ_f^c	τ_f/ns^c	$k_{nr}/10^7$ s^{-1}
Toluene	2.38	307.0	394.0	0.24	4.6	16.4
1,4-Dioxane	2.21	307.0	424.5	0.18	5.9	13.8
THF	7.58	307.0	442.0	0.11	4.8	18.3
Ethyl acetate	6.02	307.0	441.5	0.08	3.8	23.6
CH_2Cl_2	8.93	307.0	447.0	0.09	4.2	21.5
Acetonitrile	35.94	308.0	469.5	0.004	0.6	169.4

[a]From ref. 7. [b]λ_{exc} = 305 nm. [c]Measured following procedures given in ref. 1(*a*). [d]The non-radiative rate constants, k_{nr}, were measured using the relation, $k_{nr} = (1-\phi_f)/\tau_f$.

In order to establish the nature of the emitting state (whether LE or TICT) the excited state dipole moment of **1** was estimated from the fluorescence spectral data using the following equation:[5a,8]

$$\bar{\nu}_f = -\frac{2\mu_e^2}{hca^3}\left(f - \frac{1}{2}\bar{f}\right) \qquad (1)$$

where f and $\bar{f}$ are solvent polarity functions defined as $f = (\varepsilon-1)/(2\varepsilon+1), \bar{f} = (n^2-1)/(2n^2+1)$, μ_e is the excited state dipole moment and a is the Onsager cavity radius. ε and n are the dielectric constant and the refractive index of the medium respectively. The use of the above equation for excited state dipole moment measurement instead of the commonly used Lippert–Mataga equation is justified by the fact that the emitting state in the present case cannot be directly populated and it hence resembles more exciplex emitting states.[5a,8] We adopted the following procedure to obtain a reasonable value of the Onsager cavity radius of **1** for the estimation of μ_e using eqn. (1). Since the dipole moment of **2** has been determined by a time-resolved microwave conductivity method that is considered to be accurate,[6] we first analysed the fluorescence spectral data of **2** in terms of eqn. (1) to determine the representative cavity radius for **2**. Such an analysis (using μ_e = 16 D) leads to a cavity radius of 6.94 Å that corresponds closely to the distance between one of the piperazine ring nitrogen atoms and the nearest terminal nitrogen atom of the cyano group (6.82 Å) of the fully optimised (AM1) ground state of **2**. Therefore, μ_e of **1** is estimated using the distance between the ring nitrogen to the terminal carbon atom of the OMe group. From the plot based on eqn. (1), μ_e of **1** is obtained as 18.9 D. Thus the excited state dipole moment of **1** is quite similar to that of **2**. Even though this value may not be very accurate, it clearly suggests that the emitting state of **1** is more polar than the TICT or PICT state of **3**. The ground state dipole moment of **1**, as evident from the crystal structure or AM1 calculated (0.64 D) ground state, is close to zero, indicating cancellation of the dipole moments of the two halves of the molecule. Obviously, if the chair form of the piperazine ring is retained in the excited state a dipole moment larger than that of the TICT state of **3** cannot be explained. The structural restraints in the present system do not allow the dialkylamino group to twist, as commonly observed for this class of system. Even if it is assumed that one of the methoxycarbonylphenyl moieties twists relative to the rest of the molecule, the resulting dipole moment of **1** in the excited state would be less than that of **3** because of partial cancellation of dipole moment. Therefore, a structural change of the piperazine ring (most likely transformation from a chair to a boat) takes place in the excited state.

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