$$\mathrm{ZnTPP} + \mathrm{L{:}} \rightleftharpoons \mathrm{L{:}ZnTPP} \qquad (6)$$

cases cannot be assigned merely to "noncoordinating" vs "coordinating" solvents since there are at least six AD and AHD solvents in common to the regressions in both eq 4 and eq 5. Clearly, solvent dipolarity has an important role in each instance of the solvent shifting the Soret peak even though the size of that shift is smaller for NiPPDME. On the other hand, for NiPPDME in the presence of strong EPD solvents (i.e., piperidine) in which nickel assumes a higher C.N., the Soret band shows a large red shift not unlike ZnTPP with ligands of comparable basicity.[9] Just as Nappa and Valentine observed for ZnTPP,[8] the Soret band for NiPPDME undergoes a greater solvent shift than does the α band.[15]

From the Gouterman four-orbital model,[20] it is the porphyrin a_{1u}, $a_{2u} \rightarrow e_g$ electronic transition associated with the Soret band which is ultimately responsive to the changes in solvent. In the case of ZnTPP undergoing axial ligation (eq 6) the 4-fold C.N. for the ground-state Zn(II) expands exclusively to a five-coordinate complex.[21] Thus, the magnitude of the Soret red shift is a measure of the extent to which negative charge is transferred within the complex from the basic atom in the ligand through the metal (Zn) into the porphyrin ring.[8]

Since the electronegativity of Ni is a little greater than that for Zn, the magnitude of the Soret peak shift would be expected to be larger for Zn than for Ni in identical porphyrin structures.[20] Shelnutt and Ortiz have assigned this influence of metal substitution to a shift in energy for the porphyrin a_{2u} level while the a_{1u} level remains fixed.[22] The findings of Spellane et al. indicate that there is a greater resemblance in the orbital spacings between a given metal protoporphyrin and its metal porphyrin than to those spacings in the metal TPP species.[23]

In the related C.N. 5 case of vanadyl tetraphenylporphyrin (VOTPP) investigated by Su et al.[24] the resonance Raman V–O stretching frequency is responsive to th solvent-induced polarization of the V–O bond. This enhancement of the V–O stretching mode appears to arise from its resonance with the corresponding Soret electronic transition for the porphyrin. Although the empirical decrease in the V–O stretching frequency relates linearly to an increase in Gutmann acceptor number (AN) of the solvent, the data set is bisected into the separate AD and HB classes of solvents;[24] and like the DN numbers, correlations with the AN scale have been shown to lead to ambiguities in the assignment of solvent effects upon electronic spectral shifts. On the other hand, the application of the Kamlet–Taft relationship (eq 1) to the data of Su et al.[24] now yields the improved regression in eq 7. Again, within the precision of the experimental data,[24] no $d\delta$ term is needed. From the s/a ratio of 0.64/1.0 in eq 7, it is clear that hydrogen bonding to the oxygen in VOTPP makes a major contribution to the shift in the V–O stretching frequency for *both* weak and strong hydrogen-bond donor solvents (i.e., weak HBD like CH_3CN, CH_2Cl_2, CH_3NO_2, $CHCl_3$; strong HBD like the alkanols). At the same time the only remaining solvent influence upon the V–O stretching band at 1007 cm^{-1} is a dipole–dipole orientational effect by the ARA, AD, AHD, and HB member solvents.[24]

$$\bar{\nu}\ (\mathrm{cm}^{-1}) = 1006.3\ (\pm 0.1) - 9.38\ (\pm 0.05)\pi^* - 14.6\ (\pm 0.06)\alpha \qquad (7)$$

$$(\bar{\nu}(\mathrm{calcd})\ \mathrm{SD} = \pm 0.5\ \mathrm{cm}^{-1};\ r = 0.988;\ n = 11)$$

In this respect the orientational effects of dipolarity and hydrogen bonding appear to be the principal solvent influences upon the solvent dependency of the Soret shift for those C.N. 4 and C.N. 5 metalloporphyrins where competitive ligation is absent.

Registry No. NiPPDME, 15304-70-8; Zn(TPP), 14074-80-7.

---

(20) Gouterman, M. et al. *J. Chem. Phys.* **1973**, *59*, 676.

(21) Kadish, K.; Shiue, L.; Rhodes, R.; Bottomley, L. *Inorg. Chem.* **1981**, *20*, 1274.

(22) Shelnutt, J.; Ortiz, V. *J. Phys. Chem.* **1985**, *89*, 4733.

(23) Spellane, P.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. *Inorg. Chem.* **1980**, *19*, 386.

(24) Su, Y.; Czernuszewicz, R.; Miller, L.; Spiro, T. *J. Am. Chem. Soc.* **1988**, *110*, 4150.

Dual Fluorescence of 4-(Dialkylamino)pyrimidines. Twisted Intramolecular Charge Transfer State Formation Favored by Hydrogen Bond or by Coordination to the Metal Ion

Jerzy Herbich,* Zbigniew R. Grabowski,*

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

Hanna Wójtowicz, and Krzysztof Golankiewicz

Chemistry Department, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
(Received: June 28, 1988; In Final Form: October 14, 1988)

4-(*N*,*N*-Dimethylamino)pyrimidine (4-DMAP) does not exhibit any markedly dual luminescence even in highly polar (aprotic) solvents, unless the ortho substituent deviates the amino group from coplanarity with the ring. Protic solvents or complexation with Zn^{2+} cause the long-wave fluorescence to appear distinctly. Contrary to 4-DMAP, 4-(*N*,*N*-diethylamino)pyrimidine (4-DEAP) reveals dual luminescence in sufficiently polar (aprotic) environment. In alcoholic solutions the intensity of the fluorescence is drastically reduced. Fluorescence properties of this group of compounds fit well to the TICT model. The importance of nonradiative deactivation increases with the proton-donating ability of the solvent.

Introduction

Electron donor (D)–acceptor (A) molecules linked by a single bond have been widely used for studying structural requirements and kinetics of intramolecular electron transfer processes. Dual fluorescence of a number of dialkylaniline derivatives and high polarity of the lowest excited states of several compounds with mutually orthogonal donor and acceptor orbitals (as well as thermodynamics and kinetics of the excited-state process) have been explained in terms of the twisted intramolecular charge transfer (TICT) state model.[1-4]

---

(1) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.

(2) Grabowski, Z. R.; Dobkowski, J. *Pure Appl. Chem.* **1983**, *55*, 245.

(3) Grabowski, Z. R. *Acta Phys. Polon.* **1987**, *A71*, 743.

0022-3654/89/2093-3439$01.50/0 © 1989 American Chemical Society

The photophysics and acid–base equilibria of 4-(*N*,*N*-dimethylamino)pyrimidine (4-DMAP, I) and of its *o*-methyl derivative (II), with a steric hindrance to coplanarity between the ring and $N(CH_3)_2$ group, have been previously investigated by Wierzchowski and his co-workers.[5,6] They have demonstrated that the primary excited state of II converts to a highly polar fluorescent state, as evidenced by the huge Stokes shift of about 14 500 cm^{-1} in acetonitrile and by the large dipole moment change upon excitation (about 11 D). Dual luminescence was observed for 4-DMAP in sufficiently polar solvents. It has been concluded that the excited-state solvent-induced rotation of the donor ($-NMe_2$ group) and acceptor (pyrimidine) moieties to a mutually perpendicular conformation is responsible for the observed effects.[5]

It can be inferred from the reported results that the dual luminescence of 4-DMAP is due to emission from both substrate and product of the intramolecular electron transfer. The TICT state formation is thermodynamically possible: the exothermicity of the charge separation, ΔG_0, was evaluated from the equation[2,7]

$$\Delta G_0 = E_{1/2}^{\mathrm{ox}}(\mathrm{D}) - E_{1/2}^{\mathrm{red}}(\mathrm{A}) - E_{00}(\text{4-DMAP}) - \frac{e^2}{r\epsilon} = -0.6\ \mathrm{eV} \quad (1)$$

where $E_{1/2}^{\mathrm{ox}}(\mathrm{D})$ and $E_{1/2}^{\mathrm{red}}(\mathrm{A})$ are polarographic half-wave potentials of the one-electron oxidation of the donor ($E_{1/2}^{\mathrm{ox}}(\mathrm{NMe_3})$ = 1.05 vs SCE) and reduction of the acceptor ($E_{1/2}^{\mathrm{red}}$(pyrimidine) = −2.34 V) in CH_3CN[2]; E_{00}(4-DMAP) is the electronic energy of the primary excited singlet state of 4-DMAP (3.85 eV is the mean value of fluorescence and absorption maxima in CH_3CN (Figure 1)), and the last term corresponds to the Coulombic stabilization energy in a singly bonded radical-ion pair (TICT state).

It is also possible to evaluate[2] the energy of the TICT fluorescence ($hc\tilde{\nu}_{\mathrm{max}}^{\mathrm{f}}$) of I and II:

$$hc\tilde{\nu}_{\mathrm{max}}^{\mathrm{f}} = -E_{1/2}^{\mathrm{red}}(\mathrm{A}) + E_{1/2}^{\mathrm{ox}}(\mathrm{D}) + T\Delta S_0 - \frac{e^2}{r\epsilon} - E_{\mathrm{dest}} \quad (2)$$

where ΔS_0 is the standard entropy change in the charge-separation (ion-formation) process; E_{dest} is the energy difference between the Franck–Condon ground state and the solvent-equilibrated (but in the perpendicular conformation of the solute) ground state. All terms except $E_{1/2}^{\mathrm{red}}(\mathrm{A})$ should be roughly constant for a series of $(CH_3)_2N$ derivatives of various (but similar) acceptors. Thus, $hc\tilde{\nu}_{\mathrm{max}}^{\mathrm{f}}$ can be evaluated from the linear correlation between the TICT fluorescence maxima with the redox potential, $E_{1/2}^{\mathrm{red}}(\mathrm{A})$. The value estimated for II, 20 000 cm^{-1}, is close indeed to the fluorescence maximum of II observed in CH_3CN, 21 000 cm^{-1} (Figure 2).

The aim of this paper is to find out the nature of the long-wave fluorescence of 4-DMAP. Contrary to the previous study,[5] we do not find any distinct long-wave emission band of 4-DMAP in aprotic solvents. The results indicate the excited-state intramolecular electron transfer to be favored by hydrogen (or metal ion) bonding to the pyrimidine nitrogen atom. The findings seem to give further insight into the much discussed and often controversial evidence on the TICT states. 4-DMAP is also the simplest molecule known as yet exhibiting the double fluorescence related to the TICT-state formation.

Experimental Section

Materials. 4-(Dialkylamino)pyrimidines (I and III) and their twisted model derivatives (II and IV) were synthesized on two different routes with 2-thiouracil or thymine as the starting materials, respectively.

The compounds were identified by their magnetic resonance and mass spectra. ^1H NMR spectra were recorded with a JEOL FX 90 (90-MHz) spectrometer in dimethyl sulfoxide (DMSO) or $CDCl_3$ solutions using TMS as internal reference. MS were recorded with the IMS-D-100 JEOL mass spectrometer.

Synthesis of 2,4-Dichloro-5-methylpyrimidine. This compound was prepared as in ref 23.

Synthesis of 4-(Dimethylamino)-5-methylpyrimidine. II was obtained via 2-Cl-5-Me-4-DMAP as described.[6] The product was purified on silica gel column (hexane + $CHCl_3$ 1:1 as solvent) and distilled (bp 68 °C at 1 mmHg). Spectral data were as follows: ^1H NMR ($CDCl_3$) δ 8.51 (s, 1, C^2–H), 8.01 (s, 1, C^6–H), 3.10 (s, 6, $N(CH_3)_2$), 2.28 (s, 3, C^5–CH_3).

The spectral position (λ) and the absorption coefficient (ϵ) of the low-energy (1) and dominant (2) absorption maximum in *n*-pentane are as follows: λ_1 = 274 nm (ϵ 4350); λ_2 = 250.5 nm (ϵ 9800). MS: [M^+] 137 (61%).

Synthesis of 5-Methyl-4-(diethylamino)pyrimidine (IV). The reaction of 15 g of 2,4-dichloro-5-methylpyrimidine + $NHEt_2$ and then hydrogenation and subsequent processing of the products were analogous as in the case of II: bp 79–80 °C at 1 mmHg. Yield 3.5 g (61%); ^1H NMR ($CDCl_3$) δ 8.48 (s, 1, C^2–H), 7.98 (s, 1, C^6–H), 3.51 (q, 4, $N(CH_2)_2$), 2.25 (s, 3, C^5–CH_3), 1.20 (t, 6, N–(C–CH_3)$_2$); UV (*n*-pentane) λ_1 = 278 nm (ϵ 5100), λ_2 = 253 nm (ϵ 12 000); MS, [M^+] 165 (33%).

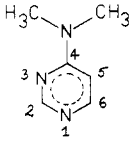
Synthesis of 4-Hydroxypyrimidine. This compound was prepared from 20 g of 2-thiouracil by reduction with Raney nickel in aqueous NH_3 (refluxed 4 h). The filtrate was evaporated, dissolved in 50 mL of EtOH, treated with active charcoal, filtered, and cooled. After recrystallization: yield 9.2 g (61%).

Synthesis of 4-(Dimethylamino)pyrimidine (4-DMAP, I). 4-Chloropyrimidine was obtained similarly to 2,4-dichloropyrimidine and I analogously to II: bp 69–70 °C at 1 mmHg; yield 2.7 g (63%); ^1H NMR ($CDCl_3$) δ 8.59 (s, 1, C^2–H), 8.17 (d, 1, C^6–H), 6.41 (d, 1, C^5–H), 3.11 (s, 6, $N(CH_3)_2$); UV (*n*-pentane) λ_1 = 284 nm (ϵ 2700), λ_2 = 243 nm (ϵ 13 400); MS, [M^+] 123 (100%).

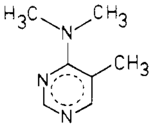
Synthesis of 4-(Diethylamino)pyrimidine (4-DEAP, III). The procedure (4 g of 4-chloropyrimidine + $NHEt_2$) was analogous to that in case of I: bp 75–76 °C at 1 mmHg; yield 2.2 g (42%); ^1H NMR ($CDCl_3$) δ 8.56 (s, 1, C^2–H), 8.12 (d, 1, C^6–H), 6.36 (d, 1, C^5–H), 3.51 (q, 4, N–$(CH_2)_2$), 1.19 (t, 6, N–(C–CH_3)$_2$); UV (*n*-pentane) λ_1 = 284 nm (ϵ 3350), λ_2 = 246 nm (ϵ 18 100); MS, [M^+] 151 (81%).

Synthesis of 4-(Dimethylamino)pyrimidine–Methyl Iodide ($V{\cdot}I^-$). 0.2 g of I + 0.2 g of CH_3I + 1 mL of CH_3OH were refluxed for 2 h. The residue after evaporation was dissolved in acetone and treated with active carbon. Crystals from the cooled filtrate were recrystallized (acetone + hexane, 5:1): white needles, mp 154–155 °C; yield 0.168 g (39%); ^1H NMR (DMSO-d_6) δ 8.84 (s, 1, C^2–H), 8.34 (d, 1, C^6–H), 7.18 (d, 1, C^5–H), 3.86 (s, 3, N^1–CH_3), 3.30 (s, 3, N–CH_3), 3.26 (s, 3, N–CH_3).

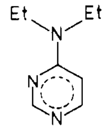
Synthesis of 4-(Diethylamino)-5-methylpyrimidine–Methyl Iodide. $VI{\cdot}I^-$ was obtained as above, from IV. Pale yellow needles: mp 101–102 °C; yield 0.149 g (38%).



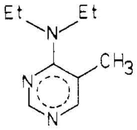
I (4-DMAP)



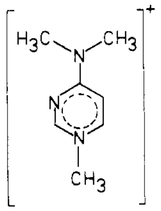
II



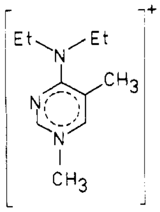
III (4-DEAP)



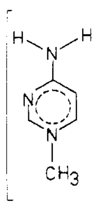
IV



V



VI



VII

---

(4) (a) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971. (b) Lippert, E.; Rettig, W.; Bonačić-Koutecký, V.; Heisel, F.; Miehé, J. A. Photophysics of Internal Twisting. In Advances in Chemical Physics 68; Prigogine, I., Rice, S. A., Eds.; Wiley: New York, 1987; p 1.

(5) (a) Smagowicz, J.; Berens, K.; Wierzchowski, K. In *Excited States of Biological Molecules*; Birks, J. B., Ed.; Wiley: New York, 1976; p 1. (b) Smagowicz, J. Thesis, Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Warsaw 1974.

(6) Proba, Z.; Wierzchowski, K. L. *Acta Biochim. Polon.* **1975**, *22*, 131, and the literature cited therein.

(7) Weller, A. *Z. Phys. Chem.* (*Munich*) **1982**, *133*, 93.

TABLE I: Fluorescence Lifetimes, τ, Stern–Volmer Constants, K_{SV}, and Resulting Rate Constants, k_q, of the F_B Fluorescence Quenching of 4-DMAP by Protic Solvents

solvent	τ/ns	quencher	K_{SV}/M^{-1}	k_q/M^{-1} s^{-1}
CH_3CN	3.7 (±0.3)	H_2O	5000	1.3 (±0.4) × 10^{12}
		CH_3OH	6000	1.6 (±0.4) × 10^{12}
DMF	3.7 (±0.3)	H_2O	1600	4.3 (±0.5) × 10^{11}

Solvents. The alcohols, *n*-butyl chloride and *n*-pentane were of spectroscopic or fluorescence grade. Water was used after four distillations over $KMnO_4$ in a quartz apparatus. The aprotic solvents were carefully dried before use to eliminate any content of water.[8] DMSO and dimethylformamide (DMF) were purified by repeated vacuum distillation over Al_2O_3 or $CuSO_4$, respectively, and over molecular sieves. Acetonitrile and butyronitrile were distilled over $CaCl_2$ and next over P_2O_5. All solvents did not show any traces of luminescence. Zinc perchlorate was dehydrated by multiple dissolutions in DMF with subsequent evaporations of the solvent. The product was checked for the absorption and luminescence.

Fluorescence and Absorption Spectroscopy. Absorption spectra were recorded with the C. Zeiss Specord M40 UV-vis spectrophotometer and the luminescence and excitation spectra by means of the Jasny spectrofluorimeter.[9] For determination of the fluorescence decay time, the sampling technique was used, with excitation provided by the second harmonic from a rhodamine 6G dye laser pumped by the IGT 50 nitrogen laser (pulse duration 0.5 ns). The experimental decay curves were analyzed with a nonlinear least-squares procedure; the χ^2 test and the distribution of residuals served as criteria for the quality of the fit.

INDO/S Calculations. The standard INDO/S method[10] was used for calculating the properties of the lowest excited singlet states of I and II. The CI procedure included all excited configurations lying below 10 eV. The geometry of the ring was assumed either crystallographic[11] or "idealized": r(C–C) = 140 pm, r(C–N) = 135 pm, r(C–H) = 108 pm; the angles, 120°. The amino nitrogen was sp^2-hybridized, and the bond lengths were taken as 137 pm for $r(C{-}NMe_2)$ and 146 pm for $r(N{-}CH_3)$. The choice of geometry was not critical, as the calculated observables only weakly depended on the bond lengths and angles.

Results and Discussion

Absorption and fluorescence spectra (at room temperature) of I–III are shown in Figure 1. The spectra of IV in polar solvents are nearly identical with those of II.

Interesting results are provided by the different photophysics of 4-DMAP in highly polar (aprotic) solvents and in alcohols. On the basis of previous reports,[5] and of the investigations of *p*-(*N*,*N*-dimethylamino)benzonitrile (DMABN),[1-4,12,13] the formation of the TICT state of 4-DMAP in sufficiently polar solvents was expected. This compound exhibits, however, in aprotic polar solvents (CH_3CN, C_3H_7CN, DMSO, and DMF) the short-wave-fluorescence band, its long-wave tail hiding probably a faint second band. The emission is very efficiently quenched by H_2O and CH_3OH (Table I) with a simultaneous appearance of the long-wave emission band (F_A). Anomalously high apparent k_q values (as measured on the F_B band) indicate a static quenching, i.e., the formation of 4-DMAP–alcohol complexes in the ground state (however, the decay time of F_B in CH_3CN and DMF decreases with addition of H_2O, so that it is, in part at least, a dynamic quenching).

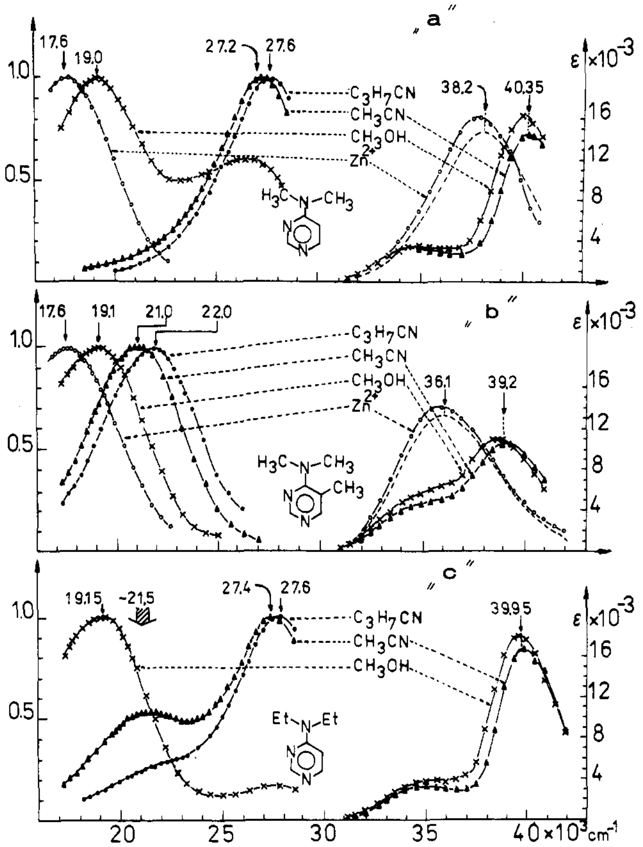


Figure 1. Room temperature absorption and (corrected and normalized) fluorescence spectra of 4-DMAP (a), II (b), and 4-DEAP (c) in selected solvents and of the corresponding protonated cations and 1:1 complexes with Zn^{2+} in CH_3CN. Concentrations of I–III in the range 5 × 10^{-5} to 5 × 10^{-3} M (no dependence on concentration was observed). The spectra in DMSO and DMF are similar to those in CH_3CN or C_3H_7CN. Fluorescence F_A in 1-propanol has a maximum at 19 700 cm^{-1} (I) or 19 800 cm^{-1} (II–IV). Absorption and fluorescence spectra of IV in polar solvents are very similar to those of II (maximum of the dominant absorption band of IV is at 39 000 cm^{-1} in CH_3CN and at 38 650 cm^{-1} in CH_3OH; the fluorescence at 21 200 and 19 250 cm^{-1}, respectively). The emission of IV in *n*-pentane (26 800 cm^{-1}) lies about 2200 cm^{-1} lower than that of II (29 000 cm^{-1}). Absorption spectra of N-methylated cations V and VI (dashed curves) are close to those of the corresponding protonated forms.

Dual luminescence of 4-DMAP was observed in alcoholic solutions. The intensity of this fluorescence seems to be governed by proton-donating ability of the solvent; the quenching increases in the same order: propanol–ethanol–methanol (the emission being not detectable in water) as the parameter α' describing the acidity of these hydrogen-bonding solvents (α' = 0.78, 0.85, 0.98, and 1.10, respectively[14]).

In Figure 1 the spectra of 4-DMAP are compared with those of its twisted *o*-methyl derivative II. One can expect nearly the same energy of the TICT states of I and II (eq 2) (usually the methyl substitution at the ring shifts the $E_{1/2}^{red}(A)$ value by not more than ~0.1 V). Contrary to similar thermodynamics of the excited-state intramolecular electron transfer in both compounds, the kinetics can differ. The steric repulsion preventing a coplanarity in II should reduce the height of the energy barrier to the excited-state process (Figure 3).[1]

The luminescent properties of II are different indeed as compared to those of I. The fluorescence and absorption spectra of II in polar solvents reveal a very large Stokes shift (Figure 1b), similar to the results previously described.[5] A considerable red shift of the fluorescence occurs with increasing solvent polarity,

---

[8] Mann, C. K. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcell Dekker: New York, 1969; Vol. 3, p 57.

[9] Jasny, J. *J. Lumin.* **1978**, *17*, 143.

[10] Ridley, J.; Zerner, M. A. *Theor. Chim. Acta* **1973**, *32*, 111.

[11] Wheatley, P. J. Handbook of Molecular Dimensions. In *Physical Methods in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1972.

[12] (a) Rettig, W. *J. Lumin.* **1980**, *26*, 21, and the literature cited therein. (b) Rettig, W.; Wermuth, G. *J. Photochem.* **1985**, *28*, 351. (c) Rettig, W.; Gleiter, R. *J. Phys. Chem.* **1985**, *89*, 4676.

[13] (a) Cazeau-Dubroca, C.; Ait Lyazidi, S.; Nouchi, G.; Peirigua, A.; Cazeau, P. *Nouv. J. Chim.* **1986**, *10*, 337. (b) Pilloud, D.; Suppan, P.; Van Haelst, L. *Chem. Phys. Lett.* **1987**, *137*, 130.

[14] Kamlet, M. J.; Dickinson, C.; Taft, R. W. *Chem. Phys. Lett.* **1981**, *77*, 69.

indicating that the dipole moment is larger in the S_1 than in the S_0 state. The increase in the dipole moment value upon excitation, as determined both from the reported[5] and present data by the Kawski–Bilot solvent-shift method,[15] with the solvent polarity function

$$F(\epsilon,n) = \frac{2n^2+1}{n^2+2}\left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right] \quad (3)$$

is about 10 D (Onsager cavity radius was assumed $a = 3.5$ Å). Interesting results are provided by emission of II in alcohols: the fluorescence in methanol ($F = 0.852$, $\tilde{\nu}_{max}{}^{f} = 19\,100$ cm^{-1}) and in propanol ($F = 0.789$, $\tilde{\nu}_{max}{}^{f} = 19\,800$ cm^{-1}) is considerably red shifted with respect to that in aprotic solvents of similar polarity: acetonitrile ($F = 0.865$, $\tilde{\nu}_{max}{}^{f} = 21\,000$ cm^{-1} and butyronitrile ($F = 0.779$, $\tilde{\nu}_{max}{}^{f} = 22\,000$ cm^{-1}). The shapes and positions of the luminescence of II in alcoholic solutions closely match those of the long-wave fluorescence of I in the corresponding solvents. This hints at a specific solute–solvent interaction and suggests that II, similarly to 4-DMAP, forms the emitting hydrogen-bonded complexes with alcohols. In the hydrogen-bonded complex, the electron affinity of the acceptor is increased, hence the shift (eq 2).

Contrary to I, 4-DEAP reveals a distinct dual luminescence in sufficiently polar (aprotic) solvents. Such effect of the diethylamino donor was not expected, but similar results were obtained by Rettig et al.[12] They have shown for *p*-(*N*,*N*-dialkylamino)benzonitriles[12a] and corresponding esters[12] that the ratio of the long-wave (F_A) to the short-wave (F_B) fluorescence depends on the type of the $-NR_2$ substituent: at room temperature the relative yield of F_A for $-NEt_2$ derivatives is higher as compared to DMABN or *p*-(*N*,*N*-dimethylamino)benzoic acid ester, respectively.

To account for this effect at least two different mechanisms might be postulated:

(i) Different ground-state conformation of I and III: in 4-DEAP the formation of the planar structure is probably somewhat hindered by ortho repulsion due to the free rotation of the ethyl groups (in the gas phase *p*-(*N*,*N*-diethylamino)benzonitrile (DEABN) is probably twisted in the ground state by $\alpha = 21°$ around the $C-NEt_2$ bond, while DMABN is nearly coplanar;[12c] a similar difference is assumed also for the solutions[12a]). The steric repulsion should reduce the height of the energy barrier in the excited state, and thus the formation of a TICT state could be accelerated (Figure 3iii).

(ii) An enhancement of the electron-donating ability of $-NEt_2$, with respect to the $-NMe_2$ donor (the vertical ionization potentials of Me_3N and $MeEt_2N$ are 8.53 and 8.22 eV, respectively[16]). This hypothesis, however, seems less probable in polar solvents because the redox potentials are very similar: for NMe_3 and NEt_3 $E_{1/2}{}^{ox} = 1.05$ and 1.15 V vs SCE,[2,17] while for *N*,*N*-dimethylaniline and *N*,*N*-diethylaniline $E_{1/2}{}^{ox} = 0.65$ and 0.64 V, respectively. Our results also contradict such a mechanism, as only a small change in the spectral position of the dominant absorption band ("L_a type") between $-NMe_2$ and $-NEt_2$ derivatives (I vs III or II vs IV) was observed (Figure 1). Moreover, contrary to the expectation that the higher electron-donating ability of the donor should lower the energy of the TICT state (eq 2), a small but blue shift of $\tilde{\nu}_{max}{}^{f}$ in IV with respect to II appeared in CH_3CN or CH_3OH (Figure 1).

It is noteworthy that the energy of the emitting highly polar state (F_A band) of 4-DEAP is nearly identical with that of its markedly twisted model compound IV in alcoholic solutions (similar to the dimethylamino derivatives I and II or their Zn^{2+} complexes (Figure 1)). This suggests a mutually perpendicular conformation of the donor and acceptor moieties in the relaxed excited charge transfer (TICT) states.

TABLE II: Computed Effective Potentials, *W*, for the Valence Electrons on Two Different Aza Nitrogens and Estimated Corresponding p$K_a{}^{est}$ Values for the Ground State of Pyrimidine (P) and 4-DMAP (I) and (II):

$$pK_a{}^{est} \approx 1.3 + 10[W_{I\ or\ II}(N_i) - W_P], \quad i = 1.3 \quad \text{(ref 19)}$$

compound	protonation center	W/eV	pK_a(est)	p$K_a{}^a$
pyrimidine	N1, N3	−12.02		1.3
I	N1	−11.50	6.5	6.35
	N3	−11.70	4.5	
II[b]	N1	−11.55	6.0	6.64
	N3	−11.65	5.3	

[a] Experimental pK_a values are taken from ref 6 and 18. [b] The calculations were performed for twisted conformation (assumed angle between donor and acceptor moieties $\alpha = 45°$).

Another interesting result is provided by the difference in 4-DEAP luminescence in alcohols as compared to that in highly polar aprotic solvents. In alcoholic solutions the relative intensity of the short-wave emission is markedly reduced (Figure 1c), probably due to the formation of hydrogen-bonded solute–solvent complexes. Similar to 4-DMAP, the total intensity of the dual luminescence of III in alcohols is governed by the proton-donating ability of the solvent.

Thus, the alcoholic protons quench strongly the luminescence, catalyzing, however, the $B^* \rightarrow A^*$ process, as reflected by the appearance, or by relative enhancement, of the long-wave emission band of 4-DMAP and 4-DEAP. The hydrogen bonding seems to occur at a pyrimidine nitrogen atom (or atoms). In the protonated forms of 4-aminopyrimidines proton is bonded to a ring nitrogen atom.[6,18] Such a view was supported by (i) the marked differences between the absorption spectra of the cations and of pyrimidine, (ii) the bathochromic effect of the methyl groups in the dominant band ("L_a type") of the absorption spectra of 4-amino, 4-*N*-methylamino, and 4-DMAP cations, and (iii) similarity of the absorption spectra of the cations of 4-aminopyrimidine and the 1-methyl derivative VII.[18] The latter observation suggests that the N_1 atom is the center of basicity in the studied compounds. Our INDO/S calculations, performed for a number of selected geometries,[11] confirmed the result. The pK_a values, roughly estimated from the Spanget-Larsen correlation (eq 7 in ref 19a,b) between pK_a and the effective potential *W* for the valence electrons on aza nitrogens, are collected in Table II.

In order to gain insight into the nature of hydrogen-bonded solute–solvent complexes, we tried to repeat the experiments for the corresponding cations and their N-methylated analogues (V, VI). Unfortunately, all these ions did not show at room temperature any trace of luminescence above 13 000 cm^{-1}, which was the low-energy threshold of sensitivity of our spectrofluorimeter. We have concentrated our attention, therefore, on the 1:1 complexes of I and II with Zn^{2+}, expecting them to be good models for the cations with respect to the energies and formation kinetics of the TICT states.

The absorption spectra of these complexes closely resemble those of the corresponding cations (Figure 1a,b). The primary fluorescence (F_B) of 4-DMAP in CH_3CN or in DMF is very efficiently quenched by Zn^{2+} ions (similar to the effects observed in the proton-donating solvents) with a simultaneous increase of the absolute intensity of the low-energy emission band (F_A) and with the marked changes in the absorption spectrum. The observed Stokes shift is very large. The spectral positions of F_A of the Zn complexes of I and II are nearly identical, and both fluorescences lie about 1500 cm^{-1} lower than the corresponding F_A emissions observed in CH_3OH.

INDO/S calculated energies of electronic transitions of 4-DMAP as a function of the angle of twist α between the pyri-

---

(15) Bilot, L.; Kawski, A. *Z. Naturforsch.* **1962**, *17a*, 621.

(16) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311.

(17) Meites, L.; Zuman, P. *Electrochemical Data*; Wiley: New York, 1974; Part 1, Vol. A.

(18) Brown, D. I.; Hoerger, E.; Mason, S. F. *J. Chem. Soc.* **1955**, 4035.

(19) (a) Spanget-Larsen, J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 417. (b) Waluk, J.; Rettig, W.; Spanget-Larsen, J. Manuscript in preparation.

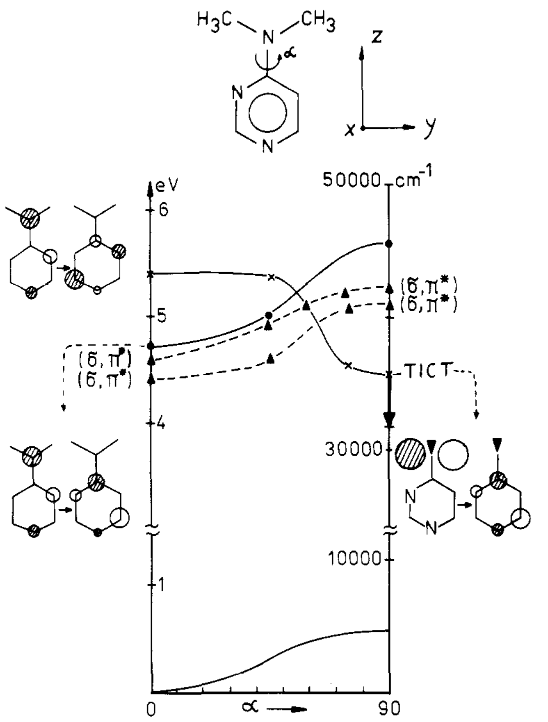


Figure 2. Low-lying electronic states of 4-DMAP as calculated by INDO/S method[10] for selected angles of twist α around the C–NMe_2 bond. For the ground state the rotational barrier height was taken as 0.6 eV,[21] and the computed energies were added to the energy of $S_0(\alpha)$. The orbitals of the dominant configurations are shown for S_3 and S_4 (α = 0°) and for the TICT state (α = 90°); the areas encircled are proportional to the square of the LCAO coefficients and opposite sign of the wave function is indicated by shadowing. The arrow on the right energy scale marks a solvent stabilization of the TICT state in CH_3CN, as estimated according to Amos and Burrows.[22]

midine and dimethylamino moieties are shown in Figure 2.

Two low-lying (σ,π^*) states (in a planar conformation the S_1 and S_2 states) carry low oscillator strength f, the transitions being purely x-axis polarized in a planar form, whereas in the twisted conformations they are always polarized perpendicular to the long axis z. The transitions $S_3 \leftrightarrow S_0$ and $S_4 \leftrightarrow S_0$ are of higher f values (in the planar conformation f = 0.18 and 0.30, respectively), nearly z polarized. With increasing α, one of these states is stabilized by 0.9 eV, while the other one goes up in energy by 1 eV. By comparing the absorption spectra of planar 4-DMAP and of the twisted II (see Experimental Section), we conclude that it is the S_4 ("L_a") state which is strongly stabilized by twisting. Apart from the σ,π^* states, anyway less reliable as to their positions, the scheme of terms resembles that of DMABN.[1,20]

For the perpendicular conformation (α = 90°) this lowest excited singlet state is well represented as arising from the HOMO → LUMO excitation (CI coefficient 0.95). The molecular orbitals engaged in the transition correspond to the intramolecular charge transfer character of this state (TICT).

Conclusions

The photophysical properties of 4-(dialkylamino)pyrimidines fit well to the TICT model involving mutually perpendicular conformation of electron donor and acceptor moieties which evidently stabilizes the full electron transfer.[1,3]

The correlation of states (Figure 2) leads to an energy barrier on the excited state relaxation path to the TICT state (Figure 3). The peculiarity of the pyrimidine derivatives is that the potential barrier in I seems to be high enough to prevent any efficient formation of the TICT within the lifetime of the excited state and thus to leave practically only one fluorescence band, F_B, even in highly polar (but aprotic) solvents (Figure 3i). Contrary to that, the compounds II and IV (with a steric hindrance to coplanarity) seem to have a very small, if any, barrier to the excited-state relaxation to the TICT state in polar environment (Figure 3iv). IV emits even in alkane solvents the strongly red-shifted fluorescence that stems from a TICT state (see caption to Figure 1).

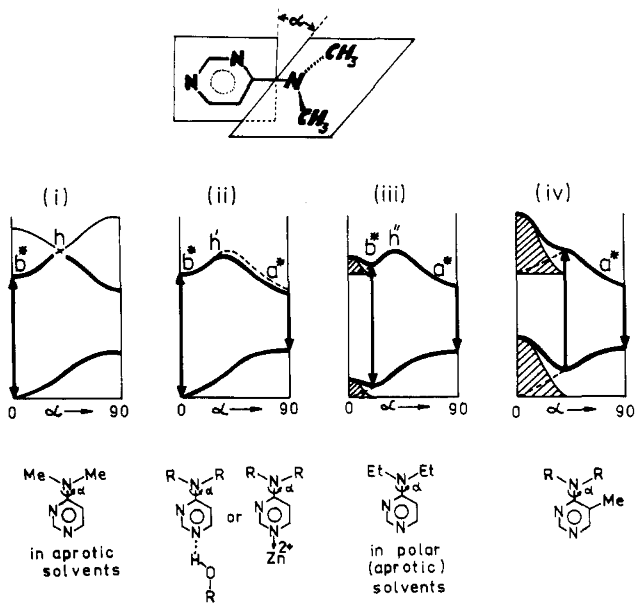


Figure 3. Schematic kinetic model, in form of a cross section of the energy hypersurfaces along the reaction path (represented here by the twist angle α) for TICT-state formation. (i) The excited-state energy barrier of a sufficient height, h, prevents the TICT-state formation. Roughly the case of I in aprotic polar solvents: only the primary fluorescence F_B is observed. (ii) Rise in the electron affinity of the acceptor (pyrimidine ring) lowers the final level of a*, reducing also the barrier h to h'. The case of the hydrogen- (or Zn^{2+}-) bonded complexes: TICT emission appears, strongly red-shifted. (iii) Small steric repulsion (the shadowed component of the potential energy in both the ground and excited state) lowers the height of the barrier ($h \to h''$). The case of III in aprotic polar solvents: the TICT emission appears. (iv) h is much reduced or canceled by large steric interactions. The case of II and IV: no fluorescence F_B appears; only the TICT emission is observed.

In 4-DEAP, probably the small steric interactions lower the height of the energy barrier and cause the long-wave fluorescence to appear clearly (Figure 3iii). The TICT model predicts that the ground-state barrier to internal rotation (0.6 eV in 4-DMAP[21]) and the excited-state relaxation both contribute to the large shift of the TICT (F_A) with respect to the primary emission (F_B).[1]

The hydrogen-bonded pyrimidine ring has markedly stronger acceptor properties than pyrimidine itself (the reduction peak potential of N-methylated pyrimidine (close to $E_{1/2}^{red}(A)$) is −1.06 V vs SCE[17]). With the increasing electron affinity and with corresponding lowering of the energy of the TICT state (eq 2), the barrier may be lowered as well. Both thermodynamic and kinetic factors favor the excited-state reaction in all studied compounds (Figure 3ii), in spite of the strong quenching of the fluorescence.

The 1:1 complexes of I and II with Zn^{2+} are close analogues to hydrogen-bonded or protonated forms with respect to the TICT energies and formation kinetics. The energies and huge Stokes shift of the emission agree well with the TICT-state model.

The energy of the emitting strongly polar state of 4-DMAP and 4-DEAP is nearly identical with that of their respective markedly twisted o-methyl derivatives, II and IV, as expected for the mutually perpendicular conformation of the donor and acceptor moieties in the relaxed excited states.

---

[20] Lipiński, J.; Chojnacki, H.; Grabowski, Z. R.; Rotkiewicz, K. *Chem. Phys. Lett.* **1980**, *70*, 449.

[21] Almog, J.; Meyer, A. Y.; Shanan-Atidi, H. *J. Chem. Soc., Perkin Trans. 2* 1972, 451.

[22] Amos, A. T.; Burrows, B. L. *Adv. Quantum Chem.* **1973**, *7*, 289.

[23] Bhat, C. C.; Munson, H. R. In *Synthetic Procedure in Nucleic Acid Chemistry*; Zorbach, W. W., Tipson, R. S., Eds.; Wiley: New York, 1968; p 84.

Experimental results are nicely supported by INDO/S CI calculations for I (Figure 2), which reveal the lowest excited singlet state in perpendicular conformation to be indeed an intramolecular charge transfer state.

Last but not least, we found an obscure, as yet, nonradiative channel of increasing importance with growing proton donating ability of the solvents and resulting in the lack of fluorescence of the N-protonated and N-methylated cations (the TICT fluorescence maximum of V evaluated from the far extrapolated linear correlation of $\tilde{\nu}_{\text{max}}{}^{\text{f}}$ vs $E_{1/2}{}^{\text{red}}(\text{A})$ is about 13 500 cm^{-1}, which should be detectable with our spectrofluorimeter).

Acknowledgment. We express our thanks to Dr. J. Waluk for his kind help in INDO/S calculations and for stimulating discussion. We are also indebted to Mr. J. Karpiuk for the determination of the lifetimes. We are really indebted to one of the referees for his keen and stimulating remarks. The work is done within the Polish research programs CPBP 01.19. and RP II.13.

Registry No. I, 31401-45-3; II, 56864-93-8; III, 24260-21-7; IV, 28942-78-1; $\text{V}\cdot\text{I}^-$, 2228-31-1; $\text{VI}\cdot\text{I}^-$, 118714-48-0.

The 320-nm Electronic Spectrum of Carbazole in a Jet by Two-Photon Ionization

D. M. Lubman, Liang Li, and T. M. Dunn*

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055 *(Received: July 1, 1988; In Final Form: November 3, 1988)*

The electronic absorption spectrum of carbazole vapor has been obtained by using one-color resonant two-photon ionization (1CR2PI) methods in an argon-driven jet. The spectrum has been analyzed from the 0_0^0 band (at 30 824 cm^{-1}) to $\sim$1350 cm^{-1} higher energy. The analysis confirms the system origin found by Bombach et al. and makes assignments of the various vibronic origins. The 1CR2PI spectrum is compared with those obtained by LIF in a jet as well as spectra from low-temperature solid-state absorption and fluorescence studies where the carbazole molecule is a guest in a fluorene host lattice. The problems of assigning the vibronic transitions obtained from all the above spectra and those obtained by 2CR2PI spectroscopy are discussed.

Introduction

The electronic absorption spectrum of carbazole ($C_{12}H_9N$) has been studied previously in both absorption[1] and fluorescence[2] diluted in a fluorene matrix at $\sim$10–15 K, in a jet by 1C (one color) R2PI techniques[3] and by LIF of jet-cooled vapor.[4,5] These last studies[4,5] were quite extensive but their spectrum has a different origin than reported here. Thus, the origin was cited[4] as being at 30 694 cm^{-1} whereas we find no band at that frequency. Bombach et al.[3] show the origin of the carbazole molecule at the same frequency as that found in the present study but since their study was concerned with carbazole–hydrate clusters, they did not give a vibronic analysis of the parent system. Their results[3] show that the parent spectrum and its polyhydrates have different vibronic structures and the details of the vibronic structure found in the present work are also different from that given by Auty et al.[4]

Experimental Section

The experimental arrangement is similar to that used in previous work.[6] It consists of a time-of-flight (TOF) mass spectrometer (R.M. Jordan Co.) mounted vertically in a stainless steel six-port cross and pumped by a 6-in. diffusion pump. The acceleration region of the TOF device is enclosed by a liquid N_2 cooled cryoshield and the flight tube is differentially pumped by a 4-in. diffusion pump. A pulsed supersonic molecular beam expands into the acceleration region of the TOFMS and a laser beam which is perpendicular to both the supersonic jet and the flight tube ionizes the sample.

The supersonic jet is produced using a novel hot pulsed valve design which is described elsewhere.[7] This valve is capable of operating up to 550 °C with a 330-μs pulse width. In the case of carbazole, an oven temperature of 150 °C was used in order to generate sufficient vapor pressure to obtain a strong R2PI signal. The reservoir pressure was $\sim 10^{-5}$ Torr when the pulsed nozzle operated at a 10-Hz repetition rate. The orifice was 800 μm and the jet was interrogated 16 cm downstream in order to be in the "free-flow" region.

It is important to correctly adjust the time delay between the nozzle pulse and the ionizing laser pulse in order to avoid spectral interference from potential van der Waals complexes. In this work, the time delay has been adjusted so that the ionizing laser beam intersects with the front portion of the gas pulse. Under this circumstance, we have found that the formation of van der Waals complexes is minimized. We saw no Ar–carbazole clusters in the mass spectrum.

Another characteristic feature of van der Waals complexes in jet spectroscopy is that they show several peaks at a lower energy than the bare (parent) molecular spectrum. We found no features below the origin frequency (30 824 cm^{-1}) of carbazole. Finally, we found no changes in the spectrum when the carrier gas was changed to carbon dioxide which confirms the absence of peaks due to van der Waals molecules in our spectrum.

The laser source consists of the output of a Quanta Ray PDL-1A dye laser pumped by a DCR-3 Nd:YAG laser. Tunable UV radiation is generated by frequency doubling the output of the dye in a phase matched KD*P crystal. This is performed using the Quanta Ray WEX-1 wavelength extension device. The near-UV radiation which has an energy of $\sim$0.1–0.3 mJ at 10 Hz is then collimated with a telescope (positive lens, 30 cm focal length; negative lens 10 cm focal length) to a beam $\sim$2 mm in diameter. A Quanta Ray CDM-1 control display module is used to control the stepping motor which tunes the grating in the dye cavity.

---

* To whom all correspondence should be directed.

(1) Bree, A.; Zwarich, R. *J. Chem. Phys.* **1968**, *49*, 3355.
(2) Bree, A.; Zwarich, R. *J. Chem. Phys.* **1968**, *49*, 3344.
(3) Bombach, R.; Honegger, E.; Leutwyler, S. *Chem. Phys. Lett.* **1985**, *118*, 449.
(4) Auty, A. R.; Jones, A. C.; Phillips, D. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1219.
(5) Auty, A. R.; Jones, A. C.; Phillips, D. *Chem. Phys.* **1986**, *103*, 163.
(6) Tembreull, R.; Lubman, D. M. *Anal. Chem.* **1987**, *59*, 1082.
(7) Li, L.; Lubman, D. M. *Rev. Sci. Instrum.*, in press.
(8) Kurahashi, M.; Fukuyo, M.; Shimada, A.; Furusaki, A.; Nitta, I. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2564 (together with a private communication to the authors footnoted in ref 1).

0022-3654/89/2093-3444$01.50/0