Intermolecular Excited State Double Proton Transfer in Dipyridocarbazole:Alcohol Complexes

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Addition of alcohols to solutions of dipyrido[2,3-*a*:3′,2′-*i*]carbazole leads to fluorescence quenching and to the appearance of a new, strongly red-shifted fluorescence band. This new band is interpreted in terms of excited state double proton transfer in dipyridocarbazole:alcohol complexes. This conclusion is supported by the results of transient picosecond absorption studies and the calculations performed for the intitial and tautomeric forms. Two different precursors of the tautomer are identified: in one of them, the reaction occurs through a barrier, while in the other, phototautomerization proceeds even at low temperatures.

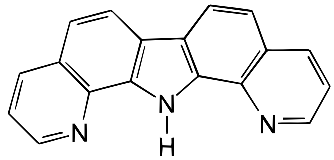
I. Introduction

Various azaaromatic systems that possess both hydrogen-bonding acceptor and donor groups are able to form complexes with hydrogen-bonding solvents. In many cases, the excited state properties of such intermolecular hydrogen-bonded species are totally different from those of nonbonded molecules in nonpolar or polar aprotic solvents.[1] For instance, a second fluorescence band is observed, which exhibits a large Stokes shift. For 7-azaindole,[2−23] 1-azacarbazole,[24,25] hydroxyquinolines,[26−35] and 3-hydroxyflavone,[36−40] the origin of the strongly red-shifted emission has been attributed to a phototautomer created as a result of transfer of protons occurring in the excited singlet state. For other molecules, which do not exhibit dual emission in alcohols, excited state proton transfer has been postulated on the basis of observed strong fluorescence quenching. The quenching process involves cooperative movement of protons leading to increased internal coversion or to a formation of a nonfluorescent tautomer. Such a mechanism was proposed for indoloquinoxalines,[41] 2-(2′-pyridyl)benzimidazole,[42−44] and 2-(2′-pyridyl)indoles.[45−47]

Various mechanisms of the excited state proton transfer have been proposed, with such parameters as solvent polarity or acidity being the controlling factor. In many cases, the rate of intermolecular phototautomerization was found to be strongly dependent on solvent viscosity. This observation has been explained as being due to the fact that prior to the proton translocation in the excited state, a solvent reorientation is required in order to attain a favorable geometry for proton transfer.[8−10,16,17,47] Therefore, the reaction is usually observed at normal temperatures and low solvent viscosities. Lowering of temperature stops the excited state tautomerization process in alcohol complexes. It is interesting to note that the hydrogen-bonded dimers of 7-azaindole and 1-azacarbazole, which also exhibit excited state double proton transfer, reveal this process even at low temperatures.[48] In other words, the kinetics of the reaction is crucially dependent on the details of the proton trajectory.

In this work, we present experimental and theoretical results for dipyrido[2,3-*a*:3′,2′-*i*]carbazole (**DPC**, see Chart 1), a molecule capable of acting both as a hydrogen-bonding donor and acceptor. Dual emission, detected in alcohol solutions, has been interpreted as an indication of excited state intermolecular double proton transfer. A remarkable observation is that the tautomeric fluorescence persists even at low temperatures in rigid alcohol glasses. This shows a presence of ground state complexes with appropriate geometry for the rapid excited state reaction.

CHART 1: Dipyrido[2,3-*a*:3′,2′-*i*]carbazole (DPC)



II. Experiment and Calculations

The precursor of **DPC**, 3,4-dihydrodipyrido[2,3-*a*:3′,2′-*i*]-carbazole, was prepared from 5,6,7,8-tetrahydro-8-quinolone and 8-hydrazinoquinoline as described previously.[49] All reagents and solvents were commercial grade and used without further purification. Nuclear magnetic resonance spectra were obtained on a General Electric QE-300 spectrometer at 300 MHz for ^{1}H, and chemical shifts are reported in parts per million downfield from Me_4Si.[50] Infrared spectra were obtained on a Perkin Elmer 1330 spectrophotometer. Elemental analysis was performed by Canadian Microanalytical Service, Ltd., Delta, B.C.

Dipyrido[2,3-*a*:3′,2′-*i*]carbazole (DPC). A mixture of 3,4-dihydrodipyrido[2,3-*a*:3′,2′-*i*]carbazole (0.45 g, 1.66 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.54 g, 2.38 mmol) in tetrahydrofuran (250 mL) was stirred at room temp for 1 h. The reaction mixture was made basic with 10% aqueous NaOH and extracted (3×) with dichloromethane. The organic layers were washed with water and dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent afforded 435 mg (98%) of dipyrido[2,3-*a*:3′,2′-*i*]carbazole, mp 214−15 °C: ^{1}H NMR ($CDCl_3$) d 11.35 (bs, 1H, NH), 8.97 (d, 2H, $J = 4.0$ Hz, H_2), 8.34 (d, 2H, $J = 8.1$ Hz, H_4), 8.27 (d, 2H, $J = 8.5$ Hz, H_5 or H_6), 7.67 (d, 2H, $J = 8.5$ Hz, H_5 or H_6), 7.51 (d of d, 2H, $J = 4.3$, 8.1 Hz, H_3); IR (KBr) 3155, 3045, 1590, 1420, 1380, 910, 830, 800 cm^{-1}. Anal. Calcd for $C_{18}H_{11}N_3$: C, 80.26; H, 4.12; N, 15.62. Found: C, 80.03; H, 4.27; N, 15.61.

The solvents used for absorption and emission studies, *n*-hexane, benzene, ethyl ether, methanol, ethanol, *n*-propanol,

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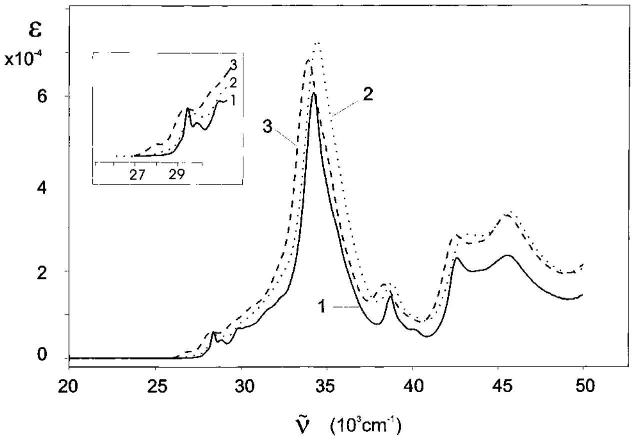

Figure 1. Room temperature absorption spectra of **DPC** in various solvents: *n*-hexane (1), butyronitrile (2), and *n*-propanol (3).

n-butanol, pyridine, and dimethyl sulfoxide (DMSO) were of fluorescence grade (Merck). Butyronitrile (Merck, for synthesis) was purified as described previously.[45]

Electronic absorption spectra were run on a Shimadzu UV 3100 spectrophotometer, equipped with a temperature-controlled sample chamber. Emission was measured on a Jasny spectrofluorimeter[51] and corrected for the spectral sensitivity of the instrument. Fluorescence quantum yields were measured with quinine sulfate ($\phi = 0.51$) used as a standard.[52]

Fluorescence lifetimes were measured using the sampling method (MSG 350 S nitrogen laser as the excitation source, boxcar BCI 280 on the detection side). The solutions were deaerated to avoid fluorescence quenching by oxygen. In some cases, the single-photon-counting technique was applied, using either BESSY (Berliner electron synchrotron) or a PTI setup (a nanosecond lamp coupled to two detection systems, Strobe-Master and TCSPC).

Transient absorption spectra were measured by means of a home-built picosecond spectrometer, described in detail previously.[53] Pulses of 25 ps fwhm from a mode-locked Nd^{3+}/YAG laser (EKSMA/EKSPLA) were amplified, and the third harmonic (355 nm) was used to excite the sample. The picosecond continuum, used as a probe, was generated in D_2O by the beam of fundamental frequency, delayed with respect to the excitation beam. The transmitted pulses were spectrally resolved and detected by photodiode array polychromators.

Excited state energies were computed using the INDO/S method,[54] with 200 singly excited configurations taken into account in the CI procedure. For both normal and tautomeric forms of **DPC**, ground state geometry optimizations were performed by molecular mechanics (MMX force field, PC-MODEL). The resulting geometry was used in the input for the calculations of excited state properties.

III. Results and Discussion

Room temperature absorption spectra of **DPC** are presented in Figure 1. A red shift of all transitions is observed upon increasing the solvent polarity. A distinct band appears at the red-energy side. Figure 2 shows the absorption changes observed upon adding small amounts of *n*-butanol ($c < 10^{-2}$ M) to the *n*-hexane solution. The presence of isosbestic points indicates the equilibrium between two ground state species. It is natural to assign one of them to the alcohol complex of **DBC** and the other to the uncomplexed molecule. The equilibrium constant, K, for a reaction involving n alcohol molecules

$$B + nA = BA_n \qquad K = [BA_n]/([B][A]^n) \qquad (1)$$

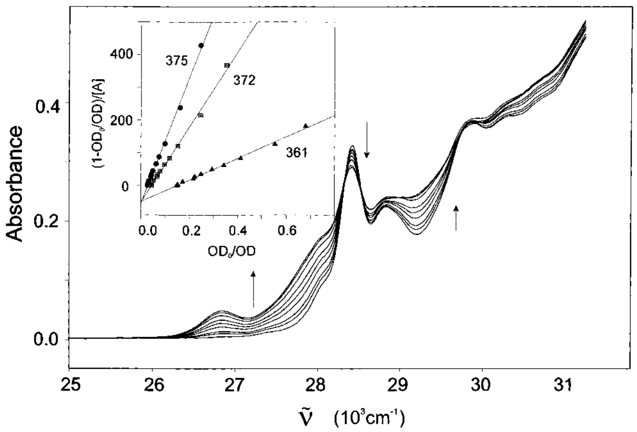

Figure 2. Absorption changes observed upon adding *n*-butanol to a 10^{-5} M solution of **DPC** in *n*-hexane at 293 K. The alcohol concentration is low enough so that only the butanol monomers are present. The concentrations of butanol were 0, 8.8×10^{-4}, 1.76×10^{-3}, 3.51×10^{-3}, 7.02×10^{-3}, 1.05×10^{-2}, 1.40×10^{-2}, and 1.76×10^{-2} M. The arrow indicates increasing alcohol concentration. Inset: Determination of the equilibrium constant of DPC:*n*-butanol complex formation using eq 3 from the optical density values measured at three different wavelengths.

may be expressed as

$$K = (OD - OD_0)/\{(OD_\infty - OD)\cdot[A]^n\} \qquad (2)$$

where OD_0 and OD_∞ denote the optical density measured when only the uncomplexed or complexed forms are present and OD is the optical density measured at an alcohol concentration [A]. From the plot of $\ln[(OD - OD_0)/[(OD_\infty - OD)]$ vs $\ln[A]$ one may obtain n, the number of alcohol molecules in a complex. The values extracted from such plots varied between 0.75 and 0.85, pointing to the 1:1 stoichiometry. The fact that these values are slightly smaller than 1 may be due to the errors produced by working with low concentrations. On the other hand, increasing the alcohol concentration would lead to problems related to formation of alcohol aggregates and, therefore, was deliberately avoided.

Assuming the formation of a 1:1 complex one can use the relation[55]

$$(1 - OD_0/OD)/[A] = -K + (\epsilon_{11}/\epsilon_P)K(OD_0/OD) \qquad (3)$$

for the determination of the equilibrium constant from the intercept of the plot of $(1 - OD_0/OD)/[A]$ vs (OD_0/OD); ϵ_{11} and ϵ_P denote the extinction coefficients of the complex and of the uncomplexed molecule. It follows from eq 3 that their values are not required for the determination of K. The inset in Figure 2 shows the application of eq 3 to the optical density values measured at various wavelengths. The value of $K = 40 \pm 5$ M^{-1} is obtained for the mixtures of *n*-butanol with *n*-hexane at 293 K. From the van't Hoff plot, the values of $\Delta H = -7.51 \pm 0.05$ kcal/mol and $\Delta S = -17.90 \pm 0.15$ e.u. were obtained. These values are quite similar to those obtained for the alcohol complexes of a structurally similar molecule, 3,3′-dimethylene-2-(2′-pyridyl)indole.[47] It should be stressed that the above results do not exclude formation of complexes with $n > 1$ at higher alcohol concentrations. As it will be shown later, the experiment strongly suggests the presence of at least two different forms of the complexes in bulk alcohols.

Figures 3 and 4 present fluorescence spectra in different solvents and at different temperatures. The values of the fluorescence quantum yields at 293 K are given in Table 1. In alcohols, a large decrease of the fluorescence intensity is

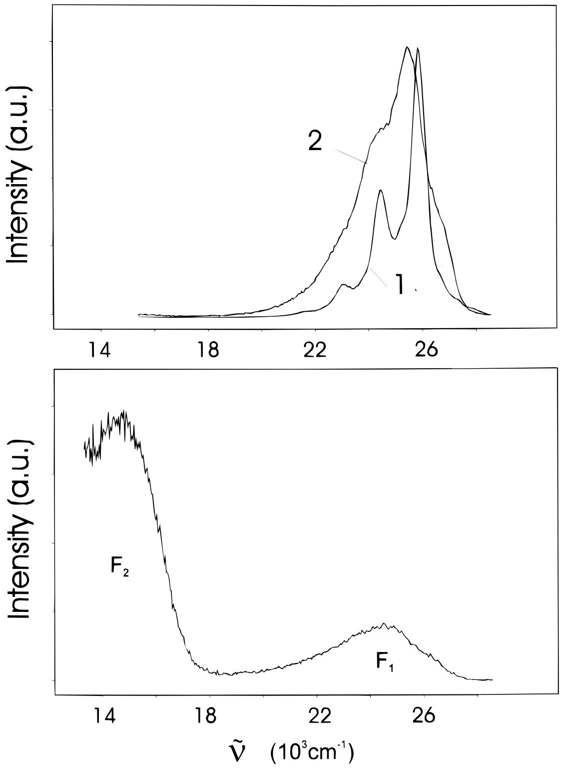

Figure 3. Room temperature fluorescence spectra of **DPC** in various solvents. Top, *n*-hexane (1) and butyronitrile (2); bottom, *n*-propanol.

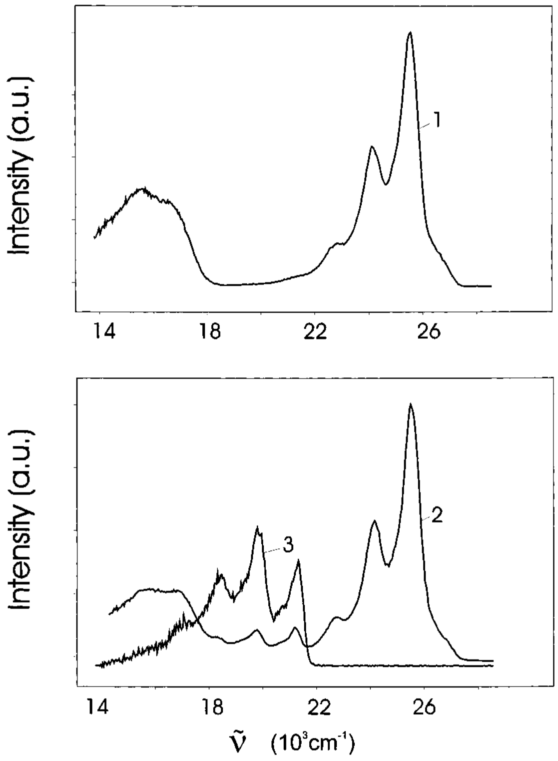

Figure 4. Luminescence of **DPC** in *n*-propanol at 123 K (top, 1) and at 77 K (bottom, 2); 3, phosphorescence at 77 K, separated from fluorescence by using choppers.

observed. Moreover, in addition to the "normal" fluorescence, which we label F_1, another fluorescence band (F_2) appears, characterized by a huge Stokes shift of about 11 000 cm^{-1}. The fluorescence excitation spectra of F_1 and F_2 coincide with each other and with the absorption spectrum (Figure 5).

Room temperature studies in mixed solvents, e.g. adding *n*-butanol ($c < 10^{-2}$ M) to *n*-hexane solutions of **DPC**, reveal both static and dynamic quenching of F_1 fluorescence. This implies that the value of the equilibrium constant for the formation of the complex with alcohols is higher in S_1 than in the ground state. Similar behavior was observed for 2-(2′-pyridyl)indoles.[45]

TABLE 1: The Values of Fluorescence Quantum Yields at 293 K[a]

	F_1	F_2
n-hexane	0.27	
butyronitrile	0.19	
DMSO	0.35	
methanol	0.0002	0.0013
ethanol	0.0004	0.0016
n-propanol	0.0005	0.002
n-butanol	0.0005	0.002
n-butanol-*O*-*d*	0.0009	0.004

[a] The solutions in *n*-hexane, butyronitrile and DMSO were deaerated in order to avoid fluorescence quenching by oxygen.

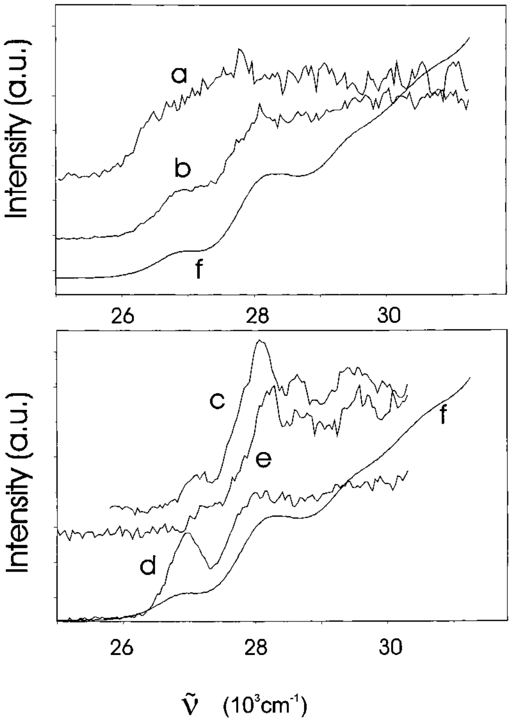

Figure 5. Luminescence excitation spectra of **DPC** in *n*-propanol. Top, 293 K, monitored at 23 800 cm^{-1} (a) and 15 800 cm^{-1} (b). Bottom, excitation spectra at 77 K: fluorescence monitored at 23 800 cm^{-1} (c) and 16 000 cm^{-1} (d), phosphorescence monitored at 19 800 cm^{-1} (e); (f) the absorption spectrum at room temperature.

Lowering of temperature leads to the increase of both F_1 and F_2 emission intensities. The F_1 fluorescence is affected much stronger: its quantum yield in *n*-butanol increases by an order of magnitude between 293 and 183 K (from 0.0005 to 0.005, while the corresponding values for F_2 are 0.002 and 0.007). Moreover, the F_1 emission becomes structured and very similar to the emission observed at 293 K in nonpolar solvents (cf. Figures 3 and 4). It must be noted, however, that the sum of F_1 and F_2 quantum yields in alcohols at low temperature is still much lower than the fluorescence quantum yield at 293 K in nonpolar or polar aprotic solvents (0.012 in *n*-butanol at 183 K vs about 0.3 in room temperature deareated solutions in *n*-hexane, butyronitrile, and DMSO). Deuterium substitution in the hydroxyl group of the alcohol does not change much. In 1-butanol-*O*-*d*, both emissions reveal the same temperature behavior as in the undeuterated alcohol, although the quantum yields are somewhat higher (the F_1 quantum yield increases from

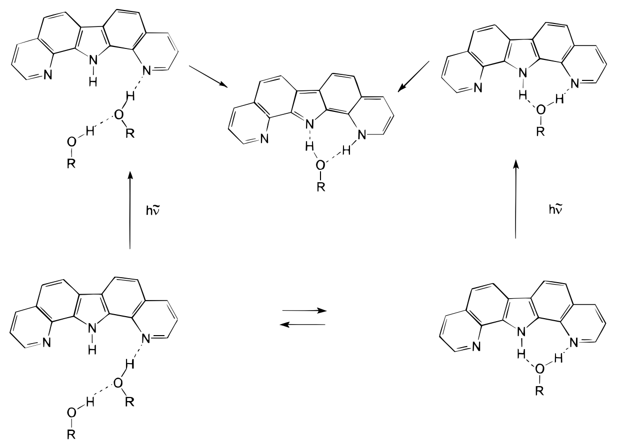

Figure 6. Proposed ground and excited state structure in **DPC**:alcohol complexes.

0.0009 at 293 K to 0.01 at 183 K, the F_2 quantum yield from 0.004 to 0.013).

In rigid alcohol glasses a third emission, phosphorescence, appears, located between the F_1 and F_2 bands. The excitation spectra of phosphorescence and of the F_1 fluorescence are identical. Contrary to the behavior at room temperature, however, the excitation spectra of F_1 and F_2 no longer coincide (Figure 5).

These findings show that at least two different ground state complexes are responsible for the emission pattern in low-temperature alcohol glasses. One of the forms emits the F_1 fluorescence and phosphorescence, whereas the other species gives rise to the F_2 fluorescence. On the other hand, the identity of F_1 and F_2 excitation spectra at room temperature suggests a common precursor of the two emission bands.

In order to interpret the experimental results, we attribute the F_2 emission to a tautomeric species, formed in the excited state after the double proton transfer reaction in the alcohol complex. This would make the **DPC** complexes with alcohol analogous to 7-azaindole and 1-azacarbazole alcohol solvates, in which a dual luminescence was also observed. However, in the latter two molecules, lowering of the temperature leads to a disappearance of the tautomeric emission band and to the recovery of the radiative properties, i.e. to a strong increase of the F_1 fluorescence. This is not the case for **DPC**, in which the F_2 emission is still observed in low-temperature rigid alcohol glasses. It should be then concluded that the **DPC** solvates are "better prepared" for photoinduced tautomerization. It is generally believed that the excited state proton transfer occurs in a cyclic, doubly hydrogen-bonded complex with alcohol (Figure 6). Such a structure can be reached either in the ground state or after excitation. In the case of **DPC**, we may assign the cyclic ground state form to the precursor of the tautomeric fluorescence at low temperatures. The other, "open" form, with only one intermolecular hydrogen bond, would require structural rearrangement prior to tautomerization. Such a rearrangement should obviously be a function of viscosity and temperature, and, therefore, should be blocked at low temperatures.

We may thus propose that the phototautomerization of **DPC**:alcohol complexes occurs at low temperatures upon excitation of cyclic, doubly hydrogen-bonded forms. At room temperature, however, even the noncyclic forms may be able to overcome the reaction barrier for the excited state tautomerization. If the energy barrier involves breaking the hydrogen bonds to other alcohol molecules, phototautomerization should be easier in mixed nonpolar/alcohol solutions, with alcohol concentration sufficient to complex all **DPC** molecules, but at the same time low enough to prevent formation of alcohol aggregates. The analysis of the F_1/F_2 intensity ratio in mixtures containing small amounts of alcohols in nonpolar solvents does indeed show that the F_1 fraction is much larger in bulk alcohol. In a solution of **DPC** in *n*-hexane, containing 10^{-2} M of *n*-butanol, only traces of F_1 could be observed.

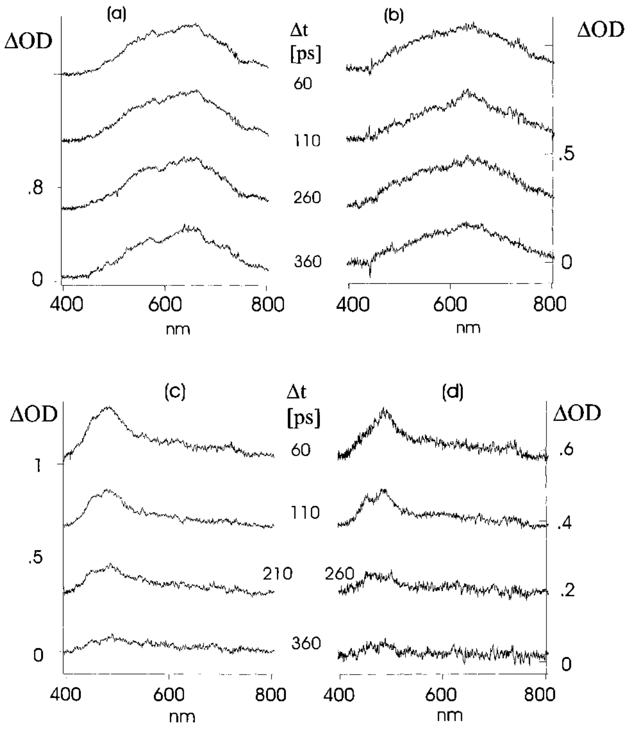

Figure 7. Picosecond transient absorption spectra of **DPC** in *n*-hexane (a), acetonitrile (b), methanol (c), and *n*-butanol (d).

Time-Resolved Measurements. Comparison of picosecond transient absorption spectra performed in nonpolar, polar aprotic, and protic solvents confirms the differences observed by stationary fluorescence measurements. In aprotic solvents, both polar and nonpolar, a broad absorption is observed, peaking around 660 nm (Figure 7a,b). Its intensity is practically constant within the delay of 1 ns. The transient absorption spectra taken in alcohols look completely different (Figure 7c,d). The maximum has now been shifted to 480 nm. The spectrum decays rapidly, in about 300 ps. It is natural to assign the 480 nm band to the tautomeric species and the 660 band to the normal form. It should be noted that the tautomeric band is observed immediately after excitation, which, given our time-resolution, means that it arises in 30 ps or faster. Only weak traces of the band assigned to the initially excited form can be observed, even at short delays.

Fluorescence decay times in room temperature *n*-butanol solutions revealed very similar decay times, about 250 ps for F_1 and F_2 bands, in agreement with the decay of the transient absorption spectra in alcohols. Assuming that only one ground state form is present and thus all the excited population decays in 250 ps would lead to an extremely small value for the radiative constant: $k_r = 0.0005/(250 \text{ ps}) = 2 \times 10^6 \text{ s}^{-1}$. If, on the other hand, one allows for the existence of two forms, of which one decays much faster than the other, then practically only the slowly decaying form contributes to the measured quantum yield: $\phi(F_1) \approx f \cdot k_r \cdot \tau_{slow}(F_1)$; f is the fraction of the slowly decaying species. It is natural to associate it with the noncyclic complex. For $k_r \cong 5 \times 10^7 \text{ s}^{-1}$ (the value measured for DMSO), we estimate $f = 0.04$. This result is in a good agreement with the fact that the F_1 fluorescence quantum yield at low temperature in alcohols is about 30 times lower than in aprotic polar solvents, from which we obtain $f \approx 0.03$.

TABLE 2. Electronic Transition Energies of DPC and Its Tautomer Calculated by INDO/S

	normal form		tautomer	
	E (10^3 cm^{-1})	symm.	E (10^3 cm^{-1})	symm.
1	29.0 (0.004)[a]	A_1	16.6 (0.034)	A′
2	31.2 (0.08)	B_2	18.7 (0.38)	A′
3	31.5 (0.014)	B_1	26.6 (0.18)	A′
4	31.5 (0.000)	A_2	30.1 (0.64)	A′
5	31.7 (0.027)	B_2	30.4 (0.003)	A″
6	34.3 (0.11)	A_1	31.3 (0.61)	A′
7	34.8 (2.04)	B_2	31.5 (0.009)	A″
8	39.5 (0.21)	A_1	31.7 (0.37)	A′
9	39.9 (0.35)	A_1	32.2 (0.10)	A′
10	40.1 (0.030)	B_2	36.4 (0.28)	A′

[a] Oscillator strengths in parentheses.

TABLE 3: Computed Location of $S_n \leftarrow S_1$ Transient Absorption Bands of DPC and Its Tautomer[a]

normal form			tautomer		
n	E (10^3 cm^{-1})	μ^b (D)	n	E (10^3 cm^{-1})	μ^b (D)
10	11.2 (0.12)	4.19	8	15.1 (0.10)	4.37
15	15.2 (0.20)	3.98	9	15.6 (0.10)	3.40
16	15.7 (0.15)	4.38	10	19.3 (0.10)	4.07
25	20.8 (0.29)	2.46	13	21.6 (0.10)	4.43
33	23.6 (0.11)	3.03	16	24.1 (0.11)	8.70

[a] Only transitions with oscillator strength larger than 0.10 are given. [b] Calculated dipole moment value.

Moreover, it is interesting to note that no rise time of F_2 was observed. This can be understood if the majority of the tautomeric species is created in a time much faster than 250 ps and the latter component contributes only a small fraction to the rise of F_2.

Quantum Chemical Calculations. In order to determine whether our assignment of the emission and transient absorption bands can be confirmed by theory, we have performed INDO/S calculations of electronic absorption originating in both S_0 and S_1 states of the normal and tautomeric forms of **DPC**. The results are presented in Tables 2 and 3. The transitions from the ground state to S_1 and S_2 are predicted to lie close to each other, have orthogonal polarizations, and differ in the dipole moment values of the final states (2.81 and 4.83 D for S_1 and S_2, respectively). Our experimental data suggest that the calculated ordering corresponds to the spectra in nonpolar solvents, while in polar solvents the stronger stabilization of the transition with a larger dipole moment is sufficient to bring its energy below that of the other state. This is reflected in the increase of the radiative constants of S_1 depopulation along with solvent polarity. For *n*-hexane, butyronitrile, and DMSO, the fluorescence lifetimes at 293 K are 14.0, 9.2, and 6.7 ns, respectively, which, combined with the quantum yield values (Table 1), produces $k_r = (1.9, 3.3, \text{and } 5.5) \times 10^7$ s^{-1} for these three solvents. A more direct proof is provided by the anisotropy of fluorescence excitation. The anisotropy of the F_1 emission in *n*-propanol at 123 K remains highly positive ($r \approx 0.30$) upon scanning the excitation from the origin of absorption throughout the strongest absorption peak at 34 000 cm^{-1}. There is no doubt that this peak corresponds to the strongest calculated transition, S_7 (see Table 2). Thus, the anisotropy clearly shows that the the transition moment of the F_1 emission is parallel to that of the transition at 34 000 cm^{-1} and corresponds to the long-axis polarization.

For the normal and tautomeric forms of **DPC**, the computed energies of the lowest energy singlet transitions differ by 12 000 cm^{-1}. This difference may be compared with the experimentally observed difference of 10 000 cm^{-1} between the maxima of F_1 and F_2 bands.

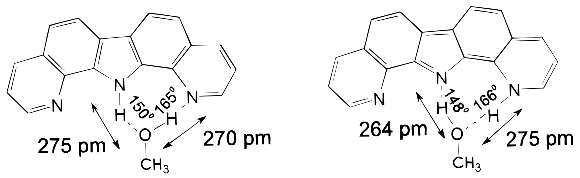

Figure 8. Calculated structures of 1:1 **DPC**/methanol complexes in the normal and tautomeric forms.

For $S_n \leftarrow S_1$ absorption, the calculations predict several transitions lying in the detection range of our instrument. The strong transient absorption of the normal form is predicted between 15 000 and 16 000 cm^{-1}, in good agreement with experiment. For the tautomer the situation is less clear, since the calculations predict transient absorption in approximately the same region. One should note, however, that the two forms should have very different dipole moments in the states engaged in absorption (*cf.* Table 3). For the normal form, the same values, around 4 D, are calculated for S_1 and S_n levels; in the tautomer, the dipole moment in S_1 should be significantly larger (the calculations give 6.84 D). Thus, a blue shift in polar solvents should be expected for the transient absorption of the tautomeric form, whereas in the initial form, the transient absorption should not be shifted upon passing from a nonpolar to a polar solvent. This is indeed observed: the transient absorption spectra in *n*-hexane and butyronitrile are very similar (Figure 7a,b).

The above calculations were performed without inclusion of alcohol molecules. We have also tried to optimize the ground state geometry of **DPC**/methanol complexes. For 1:1 stoichiometry, molecular dynamics calculations yield a cyclic, doubly hydrogen-bonded structure; the same is true for the tautomeric form (Figure 8). All the atoms involved in proton transfer form a planar seven-membered ring. The two distances between the nitrogen atoms and the alcohol oxygen are quite similar. The OHN angles are close to 180°. What seems most important is that these values change only slightly upon passing from the normal into the tautomeric form. Thus, no large structural rearrangement should accompany the phototautomerization, which may explain the lack, or a small value, of the barrier for the reaction.

The calculated heat of formation of 1:1 cyclic complexes was 15.1 kcal/mol. The tautomeric form was predicted to have the ground state energy higher by 23.6 kcal/mol. Taking into account the experimental difference of 10 000 cm^{-1} between the maxima of F_1 and F_2 emissions and neglecting the solvent shifts lead to the estimation that in the excited state the tautomer lies about 5 kcal/mol below the initially excited normal form.

Inclusion of the second methanol molecule led to structures of comparable energies but different geometries (Figure 9). In one of them, the cyclic hydrogen bond with one alcohol molecule was practically unchanged with respect to that of a 1:1 solvate, while the second molecule of methanol was attached via the hydroxyl proton to the “free” nitrogen atom of **DPC**. In the other type of the complex, two alcohol molecules were attached to **DPC** in an equivalent fashion, forming two pairs of cyclic hydrogen bonds. However, the H-bonded rings were no longer planar, and the N−O distances were significantly longer. It may be interesting to note that the average energy per hydrogen bond in the former species was 26.9/3 = 9 kcal/mol, a value larger than 15.1/2 = 7.6 kcal/mol, obtained for a 1:1 complex.

IV. Summary

The experimental and computational results led us to propose that excited alcohol complexes of dipyrido[2,3-*a*:3′,2′-*i*]carba-

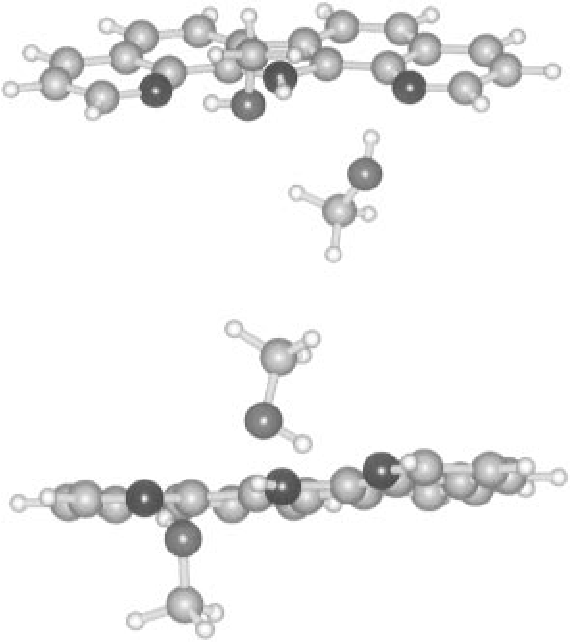

Figure 9. Calculated structures of 1:2 **DPC**/methanol complexes.

zole undergo a rapid excited state tautomerization involving a double proton transfer. This makes **DPC** similar to several structures investigated earlier. However, an important difference is also observed: contrary to the previously studied systems, phototautomerization in **DPC** does not disappear at low temperatures. This shows the existence of complexes with a ground state structure well "prepared" for the excited state reaction. In structurally similar methylene-bridged 2-(2′-pyridyl)indoles, the radiative properties in alcohols are fully recovered in rigid glasses at low temperatures.[47] It is known that the energetics of hydrogen bonding, especially in the cyclic case, is very sensitive to minute geometric details. However, our molecular mechanics calculations performed for 1:1 cyclic complexes of 2-(2′-pyridyl)indoles with alcohols yielded practically the same structures and energies as obtained for **DPC**. We therefore consider the source of different behavior to be the fact that the former molecules have only one pyridine-type nitrogen atom, while **DPC** has two. This may lead, as suggested by calculations, to the strengthening of the cyclic hydrogen bonds upon formation of the other, linear one with another alcohol molecule. Another possibility is the formation of two pairs of cyclic hydrogen bonds. A strong argument for the crucial role of the second pyridine-type nitrogen atom comes from the results obtained for pyrido[2,3-*a*]carbazole, a molecule closely related to **DPC** but lacking one pyridyl ring. At room temperature, fluorescence of this molecule is strongly quenched in alcohols. However, lowering of temperature leads to a huge increase of the quantum yield (from 0.0005 at 293 K to 0.28 at 123 K in *n*-propanol). This behavior is similar to that of 2-(2′-pyridyl)-indoles but very different from **DPC**. The detailed studies of the photophysics of pyrido[2,3-*a*]carbazole will be presented in a separate work.

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References and Notes

(1) Kasha, M. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2379. *Acta Phys. Pol.* **1987**, *A71*, 717. Arnaut, L. G.; Formosinho, S. J. *J. Photochem. Photobiol. A* **1993**, *75*, 1. Formosinho, S. J.; Arnaut, L. G. *Ibid.* **1993**, *75*, 21. Ormson, S. M.; Brown, R. G. *Prog. React. Kinet*. **1994**, *19*, 45. Le Gourrierec, D.; Ormson, S. M.; Brown, R. G. *Ibid*. **1994**, *19*, 211.

(2) Ingham, K. D.; El-Bayoumi, M. A. *J. Am. Chem. Soc.* **1974**, *96*, 1674.

(3) Avouris, P.; Yang, L. L.; El-Bayoumi, M. A. *Photochem. Photobiol.* **1976**, *24*, 211.

(4) Collins, S. *J. Phys. Chem.* **1983**, *87*, 3202.

(5) Fuke, K.; Yoshiuchi, H.; Kaya, K.; Achiba, Y.; Sato, K.; Kimura, K. *Chem. Phys. Lett.* **1984**, *108*, 179. Fuke, K.; Yoshiuchi, H.; Kaya, K. *J. Phys. Chem.* **1984**, *88*, 5840.

(6) Bulska, H.; Grabowska, A.; Pakuła, B.; Sepioł, J.; Waluk, J.; Wild, U. P. *J. Lumin.* **1984**, *29*, 65.

(7) Konijnenberg, J.; Huizer, A. H.; Varma, C. A. G. O. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1163.

(8) Herbich, J.; Sepioł, J.; Waluk, J. *J. Mol. Struct.* **1984**, *114*, 329.

(9) McMorrow, D.; Aartsma, T. J. *Chem. Phys. Lett.* **1986**, *125*, 581.

(10) Moog, R. S.; Bovino, S. C.; Simon, J. D. *J. Phys. Chem.* **1988**, *92*, 6545.

(11) Matsui, K.; Matsuzuka, T.; Fujita, H. *J. Phys. Chem.* **1989**, *93*, 4991.

(12) Kim, S. K.; Bernstein, E. R. *J. Phys. Chem.* **1990**, *94*, 3531.

(13) Moog, R. S.; Maroncelli, M. *J. Phys. Chem.* **1991**, *95*, 10359.

(14) Négrerie, M.; Gai, F.; Bellefeuille, S. M.; Petrich, J. W. *J. Phys. Chem.* **1991**, *95*, 8663.

(15) Gai, F.; Chen,Y.; Petrich, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 8343.

(16) Chou, P.-T.; Martinez, M. L.; Cooper, W. C.; Collins, S. T.; McMorrow, D. P.; Kasha, M. *J. Phys. Chem.* **1992**, *96*, 5203.

(17) Chapman, C. F.; Maroncelli, M. *J. Phys. Chem*. **1992**, *96*, 8430.

(18) Négrerie, M.; Gai, F.; Lambry, J.-C.; Martin, J.-L.; Petrich, J. W. *J. Phys. Chem.* **1993**, *97*, 5046.

(19) Rich, R. L.; Chen, Y.; Neven, D.; Négrerie, M.; Gai, F.; Petrich, J. W. *J. Phys. Chem.* **1993**, *97*, 1781.

(20) Chen, Y.; Rich, R. L.; Gai, F.; Petrich, J. W. *J. Phys. Chem.* **1993**, *97*, 1770.

(21) Chen, Y.; Gai, F.; Petrich, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 10158; *Chem. Phys. Lett*, **1994**, *222*, 329.

(22) Gai, F.; Rich, R. L.; Petrich, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 735.

(23) Chang, C.-P.; Wen-Chi, H.; Meng-Shin, K.; Chou, P.-T.; Clements, H. *J. Phys. Chem.* **1994**, *98*, 8801. Chou, P.-T.; Wei, C. Y.; Chang, C.-P.; Meng-Shin, K. *Ibid.* **1995**, *99*, 11994.

(24) Chang, C.; Shabestary, N.; El-Bayoumi, M. A. *Chem. Phys. Lett.* **1980**, *75*, 107.

(25) Waluk, J.; Komorowski, S. J.; Herbich, J. *J. Phys. Chem.* **1986**, *90*, 3868.

(26) Mason, S. F.; Philip, J.; Smith, B. E. *J. Chem. Soc. A* **1968**, 3051.

(27) Thistlethwaite, P. J. *Chem. Phys. Lett.* **1983**, *96*, 509.

(28) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 4828.

(29) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1984**, *106*, 850.

(30) Konijnenberg, J.; Ekelmans, G. B.; Huizer, A. H.; Varma, C. A. G. O. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 39. Jalink, C. J.; Van Ingen, W. M.; Huizer, A. H.; Varma, C. A. G. O. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1103.

(31) Kang, W. K.; Cho, J. S.; Lee, M.; Kim, D. H.; Ryoo, R.; Jung, K. H.; Jang, D.-J. *Bull. Korean Chem. Soc.* **1992**, *13*, 140.

(32) Lavin, A.; Collins, S. *Chem. Phys. Lett.* **1993**, 204, 96; *Chem. Phys. Lett.* **1993**, *207*, 513; *J. Phys. Chem.* **1993**, *97*, 13615.

(33) Chou, P. T.; Martinez, S. S. *Chem. Phys. Lett.* **1995**, *235*, 463.

(34) Douhal, A.; Sastre, R. *Chem. Phys. Lett.* **1994**, 219, 91.

(35) Lahmani, F.; Douhal, A.; Breheret, E.; Zehnacker-Rentien, A. *Chem. Phys. Lett.* **1994**, 220, 235.

(36) Strandjord, A. J. G.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 2355.

(37) Brucker, G. A.; Kelley, D. F. *J. Phys. Chem.* **1987**, *91*, 2856.

(38) Schwartz, B. J.; Peteanu, L. A.; Harris, C. B. *J. Phys. Chem.* **1992**, *96*, 3591.

(39) Woolfe, G. J.; Thistlethwaite, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 6916.

(40) McMorrow, D.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 2235.

(41) Waluk, J.; Komorowski, S. J. *J. Mol. Struct.* **1986**, *142*, 159; *Chem. Phys. Lett.* **1987**, *133*, 368.

(42) Kondo, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3027.

(43) Brown, R. G.; Entwistle, N.; Hepworth, J. D.; Hodgson, K. W.; May, B. *J. Phys. Chem.* **1982**, *86*, 2418.

(44) Rodriguez Prieto, M. F.; Mosquera, M.; Novo, M. *J. Phys. Chem.* **1990**, *94*, 8536.

(45) Herbich, J.; Rettig, W.; Thummel, R. P.; Waluk, J. *Chem. Phys. Lett*. **1992**, *195*, 556.

(46) Herbich, J.; Waluk, J.; Thummel, R. P.; Hung, C. J. *J. Photochem. Photobiol. A* **1994**, *80*, 157.

(47) Herbich, J.; Hung, C. J.; Thummel, R. P.; Waluk, J. *J. Am. Chem. Soc.* **1996,** *118*, 3508.

(48) Hetherington, W. M., III; Micheels, R. M.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979**, *66*, 230. Waluk, J.; Herbich, J.; Oelkrug, D.; Uhl, S. *J. Phys. Chem.* **1986**, *90*, 3866.

(49) Hegde, V.; Hung, C.-Y.; Madhukar, P.; Cunningham, R.; Höpfner, T.; Thummel, R. P. *J. Am. Chem. Soc*. **1993**, *115*, 872.

(50) For NMR purposes the protons are numbered by assigning one to a pyridine nitrogen and then proceeding around the outer periphery of the molecule numbering each sequential nonbridgehead position.

(51) Jasny, J. *J. Lumin.* **1978**, *17* 149.

(52) Velapoldi, R. A. *National Bureau of Standards 378*; Proceedings of the Conference NBS: Gaithersburg, MD, 1972; p 231.

(53) Dobkowski, J.; Grabowski, Z. R.; Jasny, J.; Zieliński, Z. *Acta Phys. Pol*. *A* **1995**, *88*, 445.

(54) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973,** *32*, 111.

(55) Miyasaka, H.; Tabata, A.; Kamada, K.; Mataga, N. *J. Am. Chem. Soc*. **1993**, *115*, 7335; Miyasaka, H.; Tabata, A.; Ojima, S.; Ikeda, N.; Mataga, N. *J. Phys. Chem.* **1993**, *97*, 8222.