

In search for phototautomerization in solid dipyrido[2,3-*a*:3',2'-*i*]carbazole

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Abstract

Dipyrido[2,3-*a*:3',2'-*i*]carbazole (DPC) is known to undergo excited state double proton transfer in cyclic complexes with alcohols. This process is detected by the appearance of low-energy fluorescence, red-shifted with respect to the “normal” emission. X-ray studies show that DPC forms cyclic, but strongly nonplanar doubly hydrogen-bonded dimers in the crystalline phase. No tautomeric fluorescence could be detected for DPC crystals. However, this emission becomes readily observed for solid DPC samples that have been exposed to water vapor, or prepared on hydroxylic supports, such as wool, filtration paper, or mica. These results suggest possible use of DPC as a probe for detection of humidity and hydroxyl groups. Tautomeric emission was also observed for DPC embedded into a hydroxyl-group-containing polymer, poly(vinyl butyral-*co*-vinyl-alcohol-*co*-vinyl acetate). The ability to form cyclic, doubly hydrogen-bonded dimers and complexes with hydroxyl-group-containing partners is compared in a series of structurally related molecules: DPC, 1H-pyrrolo[3,2-*h*]quinoline, 7-azaindole, 1-azacarbazole. Molecular geometry dictates that the systems with the strongest propensity to form flat dimers should have the weakest tendency for the formation of cyclic solvates, and vice versa.

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1. Introduction

Light-induced transfer of two protons in a dimeric system was first observed more than 30 years ago for concentrated solutions of 7-azaindole (7AI) [1]. Since that time, this photoreaction has been thoroughly studied (for reviews, see [2,3]). Recent years have brought a real explosion of both experimental [4–29] and theoretical [30–45] results concerning the spectroscopy and photophysics of 7AI. However, the mechanism of the phototautomerization process in 7AI dimers remains a subject of strong controversy. On the basis of time-resolved experiments which combined the techniques of supersonic jets, Coulomb explosion, and mass spectroscopy detection, it was proposed that the transfer occurs in a stepwise fashion [4,14–16,23,25,39,45]. The first proton is transferred in about 600 fs, whereas several picoseconds are required for the second proton. Some authors, however, question the interpretation of the Coulomb explo-

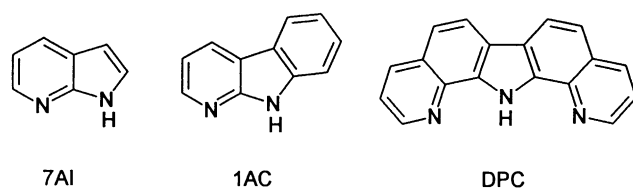
sion experiments and postulate a concerted, simultaneous double proton transfer mechanism [17,22,28].

Interestingly, in solid 7AI tautomerization is not observed. This is due to the fact that 7AI does not form dimers in the crystal phase. The structure consists of basket-like tetramers, in which each molecule is doubly hydrogen-bonded to two other 7AI partners [46].

The experiments in molecular beams revealed the existence of two different dimeric forms of 7AI, of which only one is able to tautomerize [10,47,48]. The structure of the latter was assigned to a planar, cyclic, doubly hydrogen-bonded dimer. The arrangement of the two monomeric units in the other form was less clear. Similar results have been obtained for a structurally similar molecule, 1-azacarbazole (1AC). The evidence for two types of dimers was presented not only for molecular beams [47], but also for solutions [49]. A convincing argument for the structural assignment of the tautomerizing species was provided by X-ray analysis of 1AC. In contrast to 7AI, 1AC was found to form nearly planar, cyclic, doubly hydrogen-bonded dimers [50] (Scheme 1). By showing that the excited state double proton transfer in the

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Scheme 1. 7AI, 1AC, and DPC.

crystalline dimers occurs at temperatures as low as 1.5 K, we pointed out that this process must be either barrierless or must occur by tunneling through a small barrier [51].

It thus became apparent that the planarity of the dimer is an important factor for efficient phototautomerization. In order to find out to what degree can the process be hampered by distortion from planarity, we were looking for nonplanar dimeric systems which, however, retain the pattern of cyclic double hydrogen bond. It turned out that such a situation occurs in dipyrido[2,3-*a*:3',2'-*i*]carbazole (DPC), a molecule for which we have detected two-proton photoinduced tautomerization in alcohol complexes [52,53]. In this work, we present the X-ray data for DPC together with the results of photophysical studies, which show that the excited state double proton transfer reaction is hindered in highly nonplanar dimers of DPC. On the other hand, exposure of solid DPC to hydroxylic environment can induce the ability to undergo phototautomerization, which is evident from the appearance of the tautomeric emission.

2. Experimental and computational details

The synthesis and purification of DPC have been described previously [52]. The crystal data are as follows: $C_{18}H_{11}N_3$, orthorhombic, Pbcn $a = 21.711(1)$, $b = 8.178(1)$, $c = 14.702(1)$ Å, $F(000) = 1120$, $Z = 8$, $\mu(\text{Cu K}\alpha) = 6.57 \text{ cm}^{-1}$; 3217 reflections were measured, 2814 unique, $R1 = 0.038$, $wR = 0.135$ (for all data), $S = 1.072$. The data were collected at room temperature by using a KM4 (Kuma Diffraction) diffractometer, graphite monochromated, $\lambda(\text{Cu K}\alpha) = 1.54718$ Å, $\omega - 2\theta$ scan mode. The Lorentz-polarization corrections were applied, but not for absorption. The structure was solved by direct methods (SHELXS-83 [54]) and refined by a full-matrix, least-squares procedure (SHELXL-93 [55]). Hydrogen atoms were located on a difference Fourier map and refined as isotropic.

Various procedures were used for preparation of solid DPC samples for spectral measurements. For temperature dependence studies, microcrystals were placed between two quartz windows used in the closed-cycle Displex 202 (APD-Cryogenics) cryostat. Alternatively, DPC was sublimed onto the quartz window. In another variant, a thin film of solid DPC was obtained by evaporation from diethyl ether solution. Samples of solid DPC were obtained

on various supports: quartz, mica, and graphite plates, filtration paper, wool. The exposure of solid DPC to humidity occurred either under normal conditions (i.e., leaving the sample in the air for extended periods (from hours to days) or was realized by placing the sample above water (at temperatures varying between 293 and 373 K). Different ways of water-containing sample preparation led to different ratios between “normal” and tautomeric fluorescence intensities. However, the spectral location of the emission bands as well as lifetimes remained very similar.

Samples of DPC incorporated into poly(vinyl butyral-*co*-vinyl-alcohol-*co*-vinyl acetate) (PVB) sheets were obtained by evaporating tetrahydrofuran solution of the polymer (Aldrich) containing small amounts of DPC.

Stationary fluorescence measurements were done on an Edinburgh FS 900 CDT spectrometer. The spectra were corrected using the spectral sensitivity curve of the instrument. Fluorescence lifetimes were obtained by means of an Edinburgh FL 900 CDT time-resolved fluorometer, with estimated time resolution of 300 ps.

3. Results and discussion

Fig. 1 presents the fluorescence of solid DPC obtained as a function of the temperature. The spectrum strongly resembles the emission obtained for DPC solutions in nonpolar solvents. With respect to the latter, the vibronic structure is less resolved at 293 K, but becomes quite sharp at low temperatures. The low temperature spectrum of solid DPC is red-shifted with respect to that in *n*-hexane solution by about 1500 cm^{-1} and virtually identical in shape.

Absent in the emission of solid DPC is the red fluorescence, characteristic of a phototautomer, and readily observed in alcohol solutions of DPC, both at 293 and 77 K [52]. This fluorescence corresponds to the product of the excited state double proton transfer reaction occurring in cyclic, doubly hydrogen-bonded 1:1 complexes of DPC with alcohol (Scheme 2).

In a related 1AC molecule, the tautomeric emission has been observed both in alcohols [56] and in the solid state [49,51]. 7AI, in turn, shows the photoreaction in alcohols [1,57–59], but not in the solid state. Lowering of temperature leads to the disappearance of the red band in alcohol solutions of 1AC and 7AI. This is not the case, however, in the solid 1AC, where the tautomeric band was observed even at 1.5 K. This difference has been explained by postulating that in the alcohol solutions of 1AC, the cyclic complex is only formed after excited state solvent relaxation. In the solid, however, the reactive structure, a cyclic, doubly hydrogen-bonded dimer, exists already in the ground state. Indeed, the crystallographic data for 1AC reveal a quasi-planar dimeric structure, with nearly linear $\text{NH}\cdots\text{N}$ hydrogen bonds [50]. The persistence of tautomeric emission even at lowest temperatures proves that the photoreaction in the cyclic 1AC dimers is either barrierless or occurs via tunneling.

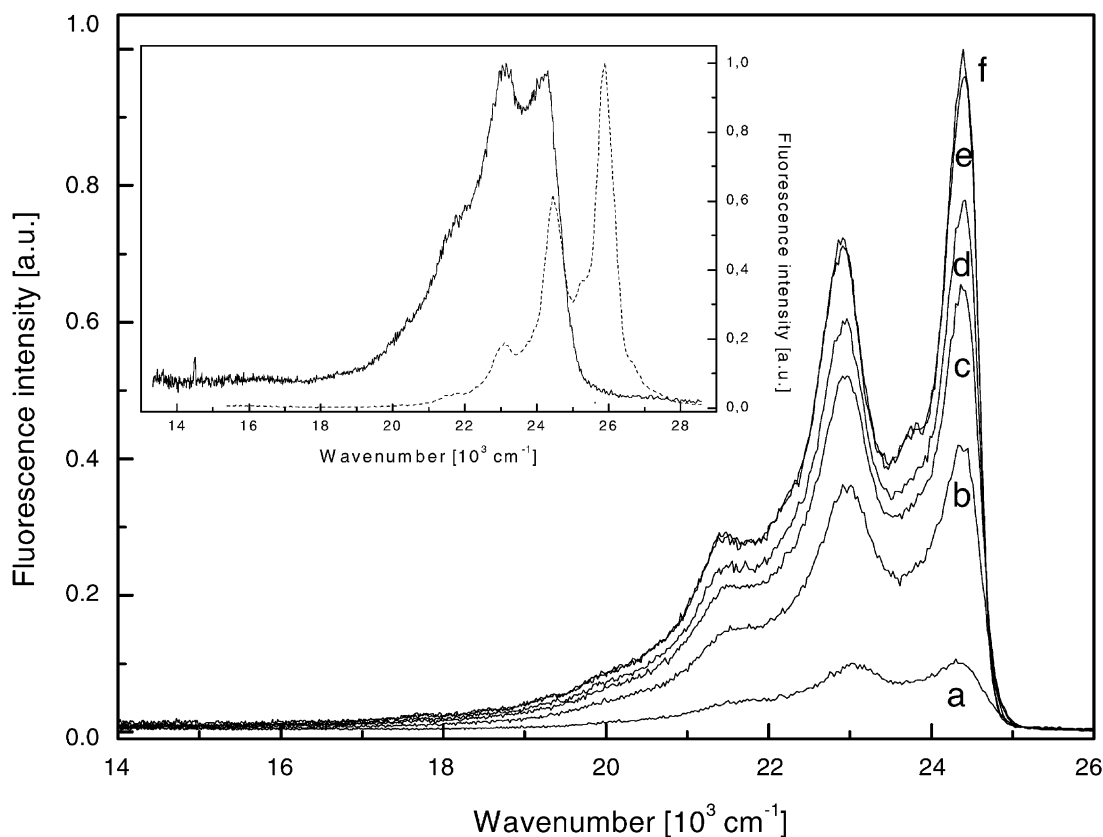


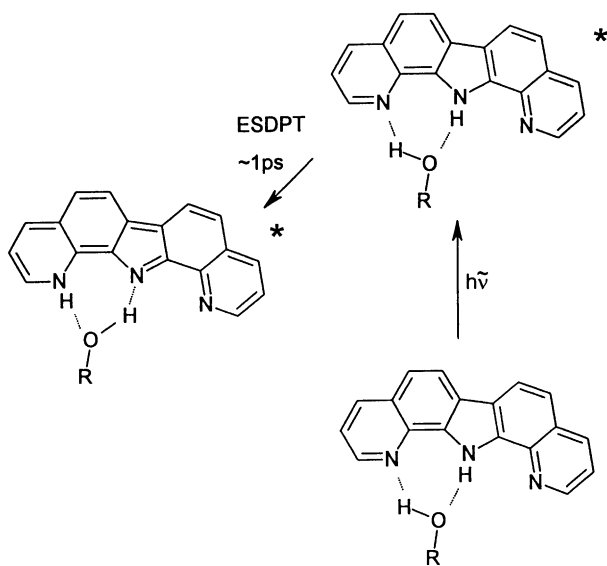
Fig. 1. Fluorescence of solid DPC at different temperatures: 200 K (a), 120 K (b), 90 K (c), 70 K (d), 40 K (e), and 20 K (f). Inset, comparison of room temperature normalized emission spectra of solid DPC (solid line) and of the solution in *n*-hexane (dashed line).

In DPC:alcohol complexes, the photoreaction is observed at 77 K in rigid alcohol glasses, which shows that in this case, the reactive complex structure is achieved in the ground state [52,53,60]. Thus, contrary to the case of 7AI and 1AC, no

major solvent rearrangement is required around the excited DPC chromophore. This difference explains much faster phototautomerization rate in DPC complexes, where the reaction takes place in about a picosecond at 293 K [61]. In 7AI, the process is about two orders of magnitude slower [62].

These experimental findings were corroborated by Monte Carlo and molecular dynamics calculations performed for 7AI, 1AC, DPC and related systems [34,63]. Simulations for alcohol and water solvents indicated that for DPC a large fraction of complexes exist in the ground state as “correctly” solvated forms, whereas this is not the case for 1AC and 7AI.

Our present results show that the relative propensity of DPC vs. 1AC to form photoreactive species is reversed in the solid state with respect to the situation in alcohols. The absence of phototautomerization in solid DPC shows the inability of the system to reach the reactive structure, a flat dimer. The reason for this behavior becomes clear upon analyzing the X-ray data, shown in Fig. 2. DPC forms dimeric, doubly hydrogen-bonded units. However, the two moieties are strongly twisted with respect to each other. The dihedral angle between the two planes is $67.53(1)^\circ$. The $\text{NH}\cdots\text{N}$ atoms engaged in hydrogen bonding form an angle of $150.52(1.77)^\circ$; the corresponding N–N distance is $3.055(2)\text{ \AA}$. This structure is quite different from that of the 1AC dimer, in which the two planes are parallel, the



Scheme 2. The scheme of phototautomerization process in the alcohol solvates of DPC.

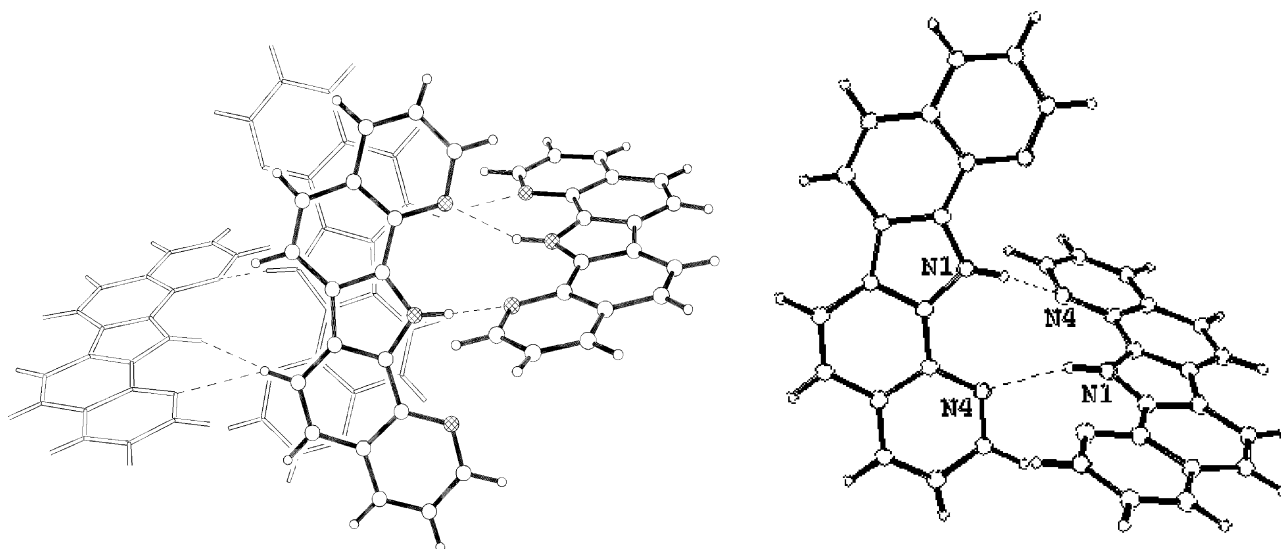


Fig. 2. Fragment of the X-ray structure of DPC. The dimeric unit is shown on the right.

NH...N atoms arranged in a linear fashion (an angle of 172.89°), and the N–N distance is $2.946(2)$ Å. The structures of 1AC dimer and 7AI tetramer are schematically presented in Fig. 3. The preference of 7AI to form tetramers instead of flat cyclic dimers has been explained by several factors, including better linearity of hydrogen bonds and the stabilizing influence of stacking interactions (these would be less favorable for 1AC, which cannot produce a packed basket structure due to the presence of the additional phenyl ring) [46]. Similar steric arguments may explain the inability of DPC to form flat cyclic dimers. For such structures, the ideal linear arrangement of two parallel NH...N hydrogen bonds can be achieved if the angle between the N–H bond of the pyrrole ring and the bisector of the CNC angle of the pyridine

ring is close to zero. The topology of the monomeric units dictates that for 7AI and 1AC this angle should be around $15\text{--}20^\circ$; the lower value is predicted for 1AC, in excellent agreement with the crystal structure data. On the other hand, in DPC this angle becomes larger than 40° , which makes the flat arrangement highly unfavorable. Another factor acting against planarity is the steric repulsion due to the presence of two extra aromatic rings. It is interesting to note that the latter factor is absent in 1H-pyrrolo[3,2-*h*]quinoline (PQ), a molecule which has the same topology of N atoms as DPC, but is devoid of these rings. The X-ray data for this molecule also show the presence of nonplanar dimers, but the twisting angle is now much smaller than in DPC, 22.6° [64].

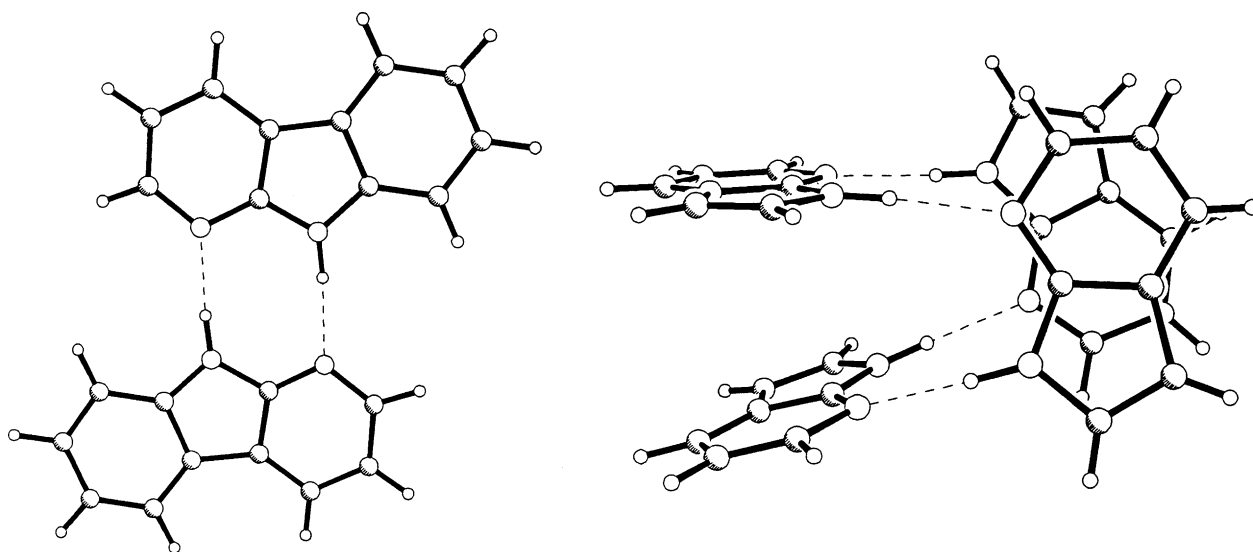


Fig. 3. The structures of 1AC dimer (left) and 7AI tetramer (right).

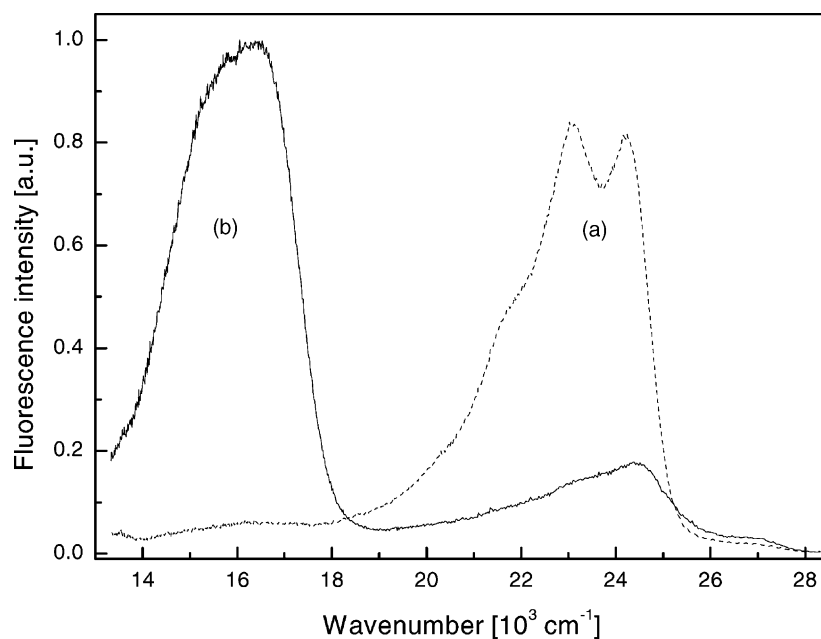


Fig. 4. Room temperature fluorescence spectra of DPC sublimed on a quartz plate before (a) and after (b) saturation with water vapor.

Contrary to the situation in dimers, in cyclic 1:1 complexes with water or alcohol, the arrangement of nitrogen atoms similar to that of DPC and PQ becomes more favorable than that of 1AC or 7AI. The hydroxylic partner simultaneously acts as a hydrogen bonding donor and acceptor. For steric reasons, this is much easier to achieve in the former class of molecules, because in the latter, the ensuing hydrogen bonds would be strongly nonlinear.

In view of high propensity of DPC to form cyclic complexes with alcohols in solution, we checked whether such

structures can also be formed in the solid phase. Indeed, samples of solid DPC exposed to water vapor revealed the tautomeric fluorescence, a clear indication of the presence of cyclic species (Fig. 4). The intensity ratio of the red vs. the blue band increased with exposure time, or when the sample was vigorously saturated, e.g., by holding it above boiling water. The decay time of the red fluorescence at 293 K was about 1.1 ± 0.2 ns, much more than 250 ps, the value obtained for the tautomeric fluorescence in *n*-butanol [52]. The influence of the rigidity of the environment on the

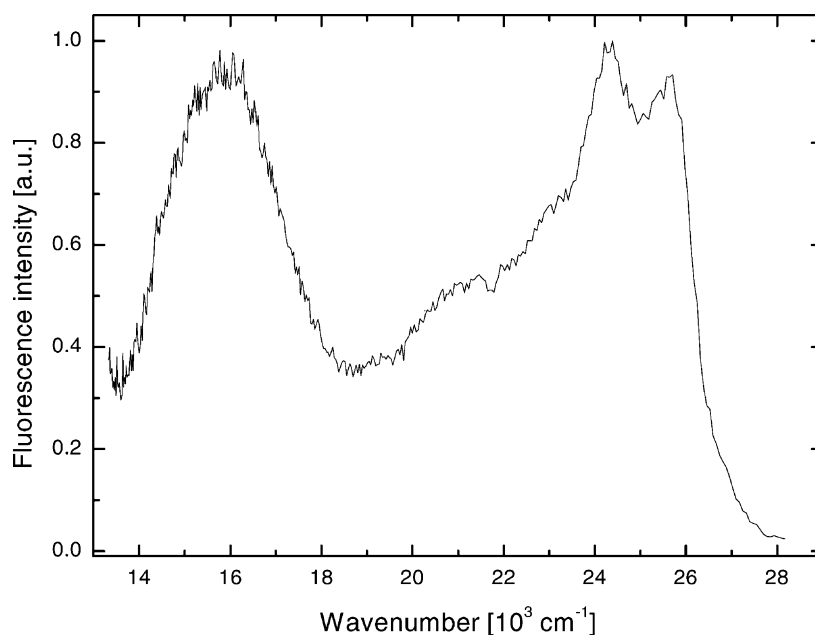


Fig. 5. Room temperature fluorescence spectra of DPC embedded in PVB.

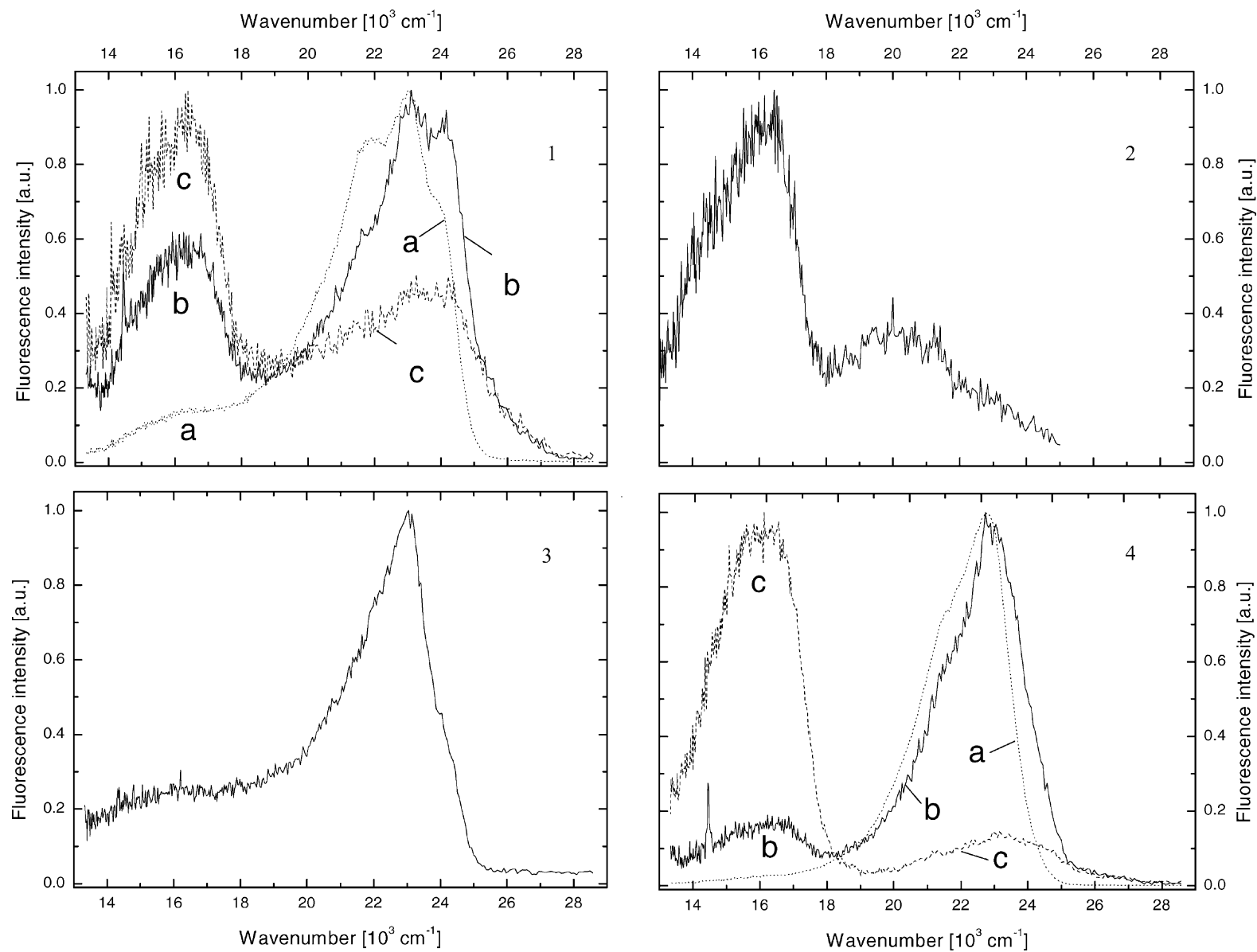


Fig. 6. Room temperature fluorescence spectra of DPC on hydroxylic supports. (1) Filtration paper: freshly sublimed sample (a), after 24 h in air (b), and after exposure to hot water vapor (c). (2) Wool, crystallized from diethyl ether solution. (3) Mica, freshly sublimed sample. These spectra are compared with those obtained on graphite (4), freshly sublimed sample (a), after 9 days in ambient atmosphere (b), and after exposure to hot water vapor (c).

tautomeric fluorescence lifetime could also be seen from the results obtained for samples of DPC embedded into PVB films (Fig. 5). These samples also exhibited the tautomeric fluorescence of which the decay was 1.3 ± 0.2 ns, a value practically identical to that measured for solid DPC. Two components were found in the decay of the blue emission, 9.9 and 1.8 ns. The former value is close to 9.2 ns, the decay time obtained for butyronitrile solution. None of these two components could be observed as risetime in the kinetic profile of the tautomeric band, which shows that the blue and red emissions are not kinetically coupled. The two lifetimes of the blue emission may come from DPC molecules experiencing different microenvironments in the polymer. Lifetime measurements in various solvents indeed show that the decay is very sensitive to the nature of the solvent: 6.0 ns is obtained for DMSO, whereas in *n*-hexane, the decay is much longer, 14.0 ns (both values were obtained in deaerated solutions).

In the solid samples, the decay of the main component in the blue emission was very short, ≤ 0.2 ns. In some samples, a component decaying in about 1.5 ns could also be recovered, pointing to the existence of various emitting species. This is consistent with the observation that the shape of the blue emission changes slightly during saturation of the sample with water. Most probably, both dimeric and “incorrectly” solvated DPC molecules contribute to the blue fluorescence.

The red emission was also observed for DPC samples obtained on supports that contained hydroxyl groups, such as filtration paper, wool fibers, or mica plates (Fig. 6). The relative intensities of the blue and red emissions varied from sample to sample, and even for various locations of the exciting beam across the same sample, but the overall spectral characteristics of the two bands remained much the same, as well as the lifetime of the tautomeric fluorescence (1.1 ± 0.2) ns. Naturally, the excited population contains molecules that are in contact with the surface, as well as those that are not. What seems important is that for samples prepared on hydroxylic supports, the red emission is observed without exposure to water vapor. Thus, it corresponds to the photoreaction occurring in molecules doubly hydrogen-bonded to the surface. On a hydrophobic surface, such as graphite, the red emission only appears after saturating the sample with water vapor.

4. Summary and conclusions

Excited state properties of dimers of DPC in the solid state are completely different from those of a related molecular system, dimeric IAC. The reason is a different structure of the two dimers: strongly nonplanar arrangement of the monomeric moieties in the former vs. near coplanarity in the latter. Simple considerations based on molecular geometry can account for the preferential formation of flat dimers in IAC. The same arguments lead to a conclusion that the

tendency for cyclic solvation with alcohol or water will be stronger for molecules that form nonplanar dimers, e.g., DPC or PQ. These predictions are confirmed experimentally. Our results nicely complement the works of Chou and coworkers [5,6,18,26], who demonstrated that the stability of 7AI cyclic complexes with protic partners strongly depends on the geometry of the latter. Thus, the phototautomerization efficiency may be tuned by choosing an appropriate partner. In our case, it is the chromophore that is being tuned up.

A question that remains to be answered relates to the maximum distortion from planarity in a cyclic dimer that still does not preclude phototautomerization. An obvious candidate for experimental studies is the molecule of PQ, which in the solid phase forms nonplanar, doubly hydrogen-bonded dimers, but with the twisting angle much smaller from that of DPC.

Finally it should be pointed out that the sensitivity of DPC fluorescence to hydroxylic partners suggests a possible use of this molecule, e.g., as a probe of hydrophilic/hydrophobic character of a surface. Our initial results in this direction, comparing the emission patterns obtained on freshly prepared graphite and mica plates are encouraging.

Acknowledgements

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