Photophysics of 1-Azacarbazole Dimers: A Reappraisal

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A systematic study of 1-azacarbazole (1AZC) dissolved in 2-methylbutane (2MB) at gradually decreasing temperatures from room temperature to 77 K revealed the chromophore to exhibit four fluorescence emissions: a structured fluorescence in the UV region that is due to the 1-azacarbazole monomer, a structureless emission centered at 500 nm and assigned to the centrosymmetric dimer formed by double hydrogen bonding, an also structureless emission centered at ca. 400 nm and due to a noncentrosymmetric doubly hydrogen bonded dimer, and a fourth, structured emission at 357 and 375 nm due to a card-pack dimer. Evidence obtained from dilute solutions of 1-azacarbazole is for the first time assigned to a card-pack dimer, consistent with the photophysical behavior of carbazole in the same medium. Previously established photophysical evidence for such an interesting compound, which has been used as a model for studying light-induced double proton transfer mutational mechanisms, is completed or discussed here. The evidence obtained in this work reveals that 1AZC at a 10^{-4} M solution in 2MB does not exhibit doubly hydrogen bonded centrosymmetric dimer emission as the temperature decreases from room temperature up to 113 K (with a corresponding exponential increase of the solvent viscosity). At this temperature and below, however, the doubly hydrogen bonded centrosymmetric dimer emission appears. This evidence and others implemented in this work contradict the assumption of Waluk et al. that the appearance of the doubly hydrogen bonded centrosymmetric dimer is hindered by an increased viscosity of the medium.

Introduction

In 1969, Kasha et al.[1] found the unusual green fluorescence of 7-azaindole dimer (7AI) to be produced by a tautomeric form of the dimer generated via an excited-state double proton transfer (ESDPT) mechanism (see Scheme 1). Despite the biochemical implications of this finding, it was not until 1980 that another molecular structure was shown, by El-Bayoumi et al.,[2] to follow this mechanism. These authors found a 6×10^{-4} M solution of 1-azacarbazole (1AZC) in 3-methylpentane (3MP) to exhibit a fluorescence emission centered at 510 nm; however, they detected no such emission in a more dilute dilution (2×10^{-5} M).

El-Bayoumi et al.[2] found the previous 6×10^{-4} M solution of 1ACZ in 3MP to give two structureless fluorescence bands centered at 374 (F_1) and 510 nm (F_2), which they assigned to a dimer of the compound. In fact, they assigned the former band to emission from the normal electronically excited dimer of 1AZC and the latter to a tautomer of the dimer produced by double proton transfer from the first π,π^* excited electronic state; see Scheme 1. In addition, they found the relative strength of the two fluorescence emissions in a 6×10^{-4} M solution of 1AZC to depend very strongly on the excitation wavelength and solution temperature.

The ESDPT processes for 7AI and 1AZC have been used as models for light-induced mutational mechanisms in DNA.[4−6] In 1982, Sepiol and Wild,[7] based on the fact that the base pairs interacting via hydrogen bonds in DNA involve different bases (i.e., that the pairs are in fact heterodimeric in nature), very aptly examined the feasibility of an ESDPT process in a heterodimer consisting of an 1AZC molecule and a 7AI molecule, and concluded that excitation of the resulting heterodimers produced a fluorescence emission centered at 510 nm, so they should be able to engage in an ESDPT process.

A few years later, Waluk et al.[8−10] studied the luminescent properties of 1AZC at variable temperatures in solutions containing a concentration of 10^{-4} M or higher of the compound in 3MP, methylcyclohexane/isopentane, or liquid paraffin, and also in the solid phase (as a powder, thin film, or small crystals). Based on their results, they reached two interesting conclusions:

(a) In the crystal phase, where 1AZC molecules formed centrosymmetric dimers[4] via double hydrogen bonds, the ESDPT process occurred with no apparent energy barrier and the fluorescence of the tautomer was detected throughout the temperature range studied (293−1.5 K).

(b) Whereas the ESDPT process in 7AI dimer is temperature-controlled, that in 1AZC appears to be viscosity-controlled. Thus, lowering the solution temperature increases the solvent viscosity and a temperature is reached where the tautomer fluorescence F_2 ceases to be detected since, according to Waluk et al., formation of the tautomer is suppressed by the high solvent viscosity at that temperature level. In other words, above a given solution viscosity level, the formation of doubly hydrogen bonded centrosymmetric structures is hindered and the ESDPT mechanism is no longer efficient as a result.

The fact that the excitation spectra at F_1 and F_2 were nearly identical led Waluk et al. to conclude that both emissions must be produced by 1AZC dimers.[8−10] However, because the lifetime of F_1 in paraffin at 223 K (11.4 ns) and methylcyclohexane/isopentane at 123 K (14.4 ns) was greater than that of F_2 under identical conditions (viz. 3.3 and 4.8 ns, respectively), they concluded that these two emissions could not be produced by the same dimer since the normal electronically excited dimeric

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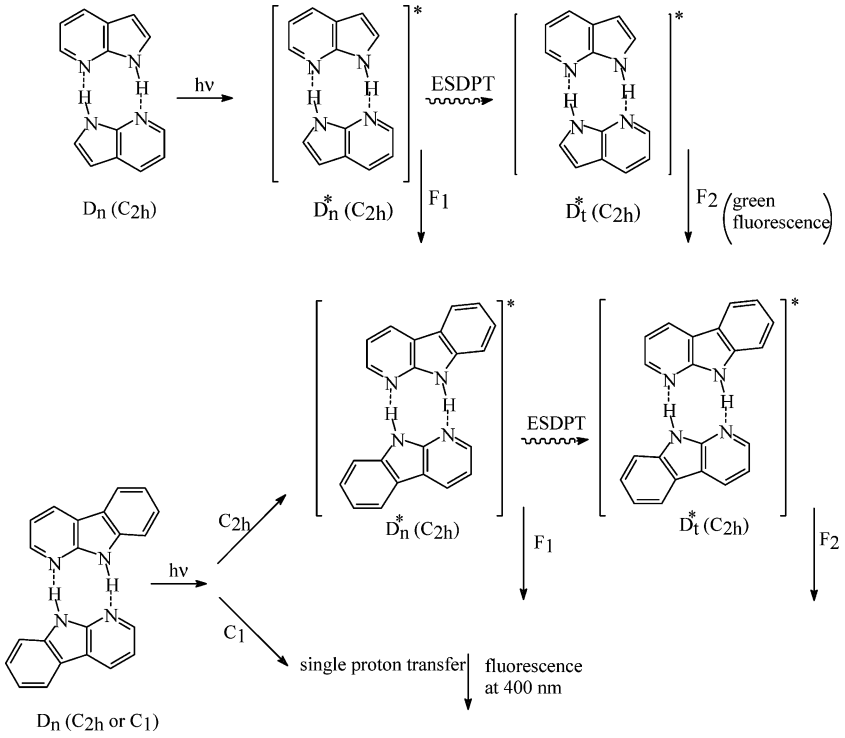
SCHEME 1



form so efficiently produced by the tautomer can never live longer than the tautomer itself.

The close likeness between the excitation spectra for F_1 and F_2 led Waluk et al. to suggest that one of the dimers involved is coplanar (i.e., centrosymmetric) and doubly hydrogen bonded, whereas the other is singly hydrogen bonded but has the planes of the two monomers twisted, their movement toward coplanarity being hindered by an increased viscosity of the medium.

Fluorescence excitation spectra obtained by using the light-induced fluorescence (LIF) and multiphoton ionization (MPI) techniques under supersonic jet conditions led Fuke et al.[12−14] to categorically state that the fluorescence in both the UV region (F_1) and visible region (F_2) of 1AZC are produced by dimeric forms of the compound, the populations of which depend markedly on the stagnation pressure used. Based on the dispersed fluorescence spectrum obtained by exciting the 0−0 component of the first π,π^* excited electronic state, F_2 is a very minor contributor to the spectrum.

If the active sites that facilitate dimerization by double hydrogen bonding in 7AI and 1AZC (viz. a pyrrole or indole nitrogen and a pyridine nitrogen) are so similar, their acid−base properties are enhanced by electronic excitation,[9,15] and the additional benzene ring in 1AZC causes no steric hindrance, then how can the disparate behavior of these two compounds[9] with regard to the ESDPT process be explained in terms of hydrogen bonding interactions? It is also difficult to accept that 7AI dimers adopt a largely planar (centrosymmetric) doubly hydrogen bonded conformation, whereas 1AZC dimers adopt a nonplanar conformation when hydrogen bonding interactions prevail in both compounds.

The reported photophysics of 1AZC dimer in solution is subject to some pitfalls owing to the spectroscopic problems faced in its elucidation. Thus, in order that the dimer species may account for a substantial fraction of the target sample, researchers have used highly concentrated solutions (10^{-4} M or higher) and excited them at wavelengths near the onset of the first band in the absorption spectrum. For example, recording excitation spectra for a 10^{-4} M solution of 1AZC entails using samples with an absorbance in the region of 0.5 at the maximum of the first absorption band and above 2 units in the region from 290 to 300 nm; as a result, the excitation spectra are inevitably contaminated with a strong filtering effect and can hardly be compared with the absorption spectra. This is possibly the reason why none of the previous papers reported an excitation spectrum including the first absorption segment for the compound (viz., the region from 280 to 380 nm). Excitation in the vicinity of the onset of the first absorption band (e.g., ca. 357 nm[9]) introduces optical artifacts in the emission region corresponding to F_1, which peaks at 374 nm according to El-Bayoumi et al.[2]

The previous spectroscopic problems can be partly avoided or minimized by using samples with a low light absorption density (i.e., more dilute solutions), shortening the path length (i.e., using smaller cells) and exciting at much lower wavelengths (e.g., 318 nm). In this work, we examined the absorption, emission, and excitation spectra for 5×10^{-6} and 10^{-4} M solutions of 1AZC in a low-viscosity solvent such as 2-methylbutane (2MB) at temperatures from 293 to 77 K in much the same way as we did with 7AI in previous work.[16] Also, we examined the double hydrogen bonding dimerization process in 1AZC, and the acidity and basicity changes undergone by the compound upon electronic excitation to the first π,π^* singlet state at the DFT/B3LYP/6-31G** level.

Experimental and Theoretical Section

We used 1AZC solutions at concentrations of 5×10^{-6} or 10^{-4} M in Uvasol grade 2MB from Merck, and also 3×10^{-5} M solutions of carbazole (C). The sample temperature ranged from 77 to 293 K, and was controlled via an Oxford DN1704 cryostat equipped with an ITC4 controller interfaced to the spectrophotometers. The cryostat was purged with dried nitrogen (99.99% pure).

UV−visible spectra were recorded on a Cary-5 spectrophotometer, using Suprasil quartz cells of 1 cm light path. Spectroscopic emission measurements of the 10^{-4} M 1AZC

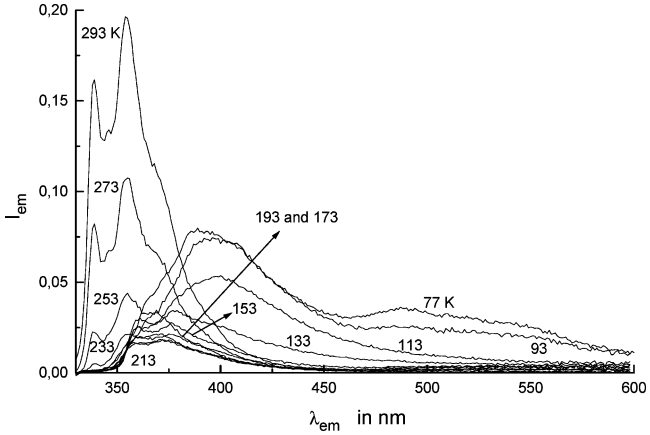


Figure 1. Fluorescence spectra for 10^{-4} M solution of 1ACZ in 2MB on excitation at 318 nm, recording from 293 to 77 K.

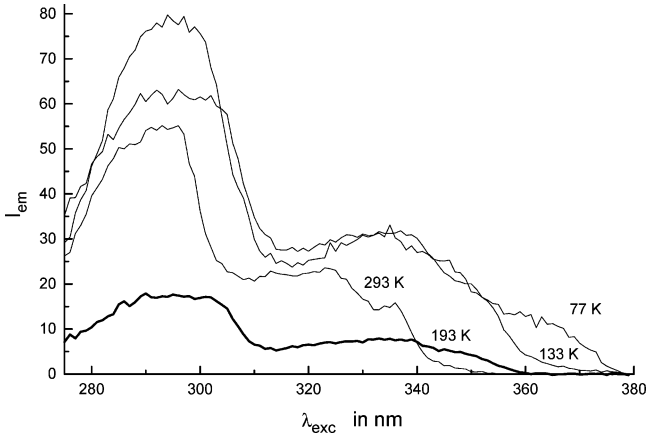


Figure 2. Fluorescence excitation spectra for 10^{-4} M solution of 1ACZ in 2MB on monitoring light at 530 ± 4 nm, and recording at 293, 193, 133 and 77 K.

samples were made in Suprasil cylindrical cells of 3 mm light path; as a result, the path length to the center of the cell, which governs so-called "filtering effects" on fluorescence, a major influential factor with highly absorbing solutions, was less than 1.5 mm, with the average path length ranging from 0 to 1.5 mm. Spectroscopic emission measurements of the 5×10^{-6} M 1AZC samples were done with a Suprasil quartz cell of 1 cm light path. Corrected fluorescence and excitation spectra were obtained by using a precalibrated Aminco-Bowman AB2 spectrofluorimeter. All 1AZC and C samples were excited at substantially lower wavelengths than that of the onset of the first absorption band (viz., 303 nm for the 5×10^{-6} M solution of 1AZC, 318 nm for the 10^{-4} M solution of the same compound, and 295 nm for the 3×10^{-5} M solution of C), using light from a continuous wave (CW) 140 W xenon lamp to obtain steady-state spectra. The spectral widths used were as follows: 4 and 2 nm in the respective monochromators for the emission spectra; 2 and 4 nm, 2 and 8 nm, or 4 and 16 nm depending on the emission intensity in the monitored region in those for the fluorescence excitation spectra.

All computations were done within the framework of the density functional theory (DFT), using the Gaussian 98 software package.[17] Full geometric optimization of the electronic ground state was done by using the hybrid functional B3LYP[18,19] with the 6-31G** basis set. The optimized geometries for the ground state were used to compute the Franck−Condon (FC) excitation energies for the singlet excited state S_1 (π,π^*) in light of the recently developed time-dependent density functional theory (TDDFT), which has so far provided excellent results.[20−23]

Results and Discussion

Let us start with the fluorescent behavior of a 10^{-4} M solution of 1AZC in 2MB at temperatures from 293 to 77 K, compare the results with those for a more dilute solution (5×10^{-6} M), and, finally, compare the evidence thus derived with the UV−vis absorption spectra for the compound. The conclusions thus drawn are checked against the theoretical results for the acid−base properties of the compound and also with the fluorescent behavior of a solution of carbazole in 2MB. Finally, the fluorescence of 1AZC is explained on the basis of the dimer structure prevailing under the experimental conditions studied.

Spectral Behavior of 1AZC in 2MB. Figure 1 shows the emission spectra for a 10^{-4} M solution of 1AZC in 2MB as obtained by excitation at 318 nm over the temperature range from 293 to 77 K. Note that the spectra are much more complex than those for an equivalent solution of 7-azaindole in 2MB. Thus, as can be seen from Figure 2 in ref 16, the spectra for 7AI include (a) a double fluorescence emission in the UV region at 293−227 K, the intensity of which decreases dramatically as the temperature is lowered, and (b) an emission centered at 480 nm in the visible region that grows with decreasing solution temperature. The former emission was assigned to 7AI monomer and the latter to a doubly hydrogen bonded tautomer of its dimer. Only one fluorescence emission was observed below 227 K; that was assigned to the dimer tautomer and increased in intensity and structure as the solution temperature was lowered.

By contrast, the spectra of Figure 1 here expose four different fluorescent behaviors. One involves a single, structured fluorescence emission with peaks at 339, 346, and 354 nm that decreases dramatically as the temperature is lowered from 292 to 233 K. A new fluorescence peaking at 359 and 375 nm is observed at temperatures from 213 to 153 K, below which one other, structureless fluorescence emission peaking at ca. 400 nm appears that grows in intensity as the temperature is lowered further and becomes the dominant emission at 113 K. Below such a level, where the 2MB matrix is formed, the previous fluorescence is accompanied by a new one peaking at ca. 520 nm.

Figure 2 shows the excitation spectra obtained at 293, 193, and 133 K by monitoring light at 400 nm, and that obtained at 77 K by monitoring light at 530 nm. The four spectra are different enough to conclude that a 10^{-4} M solution of 1AZC in 2MB at the previous temperatures contains different chromophoric structures responsible for the emissions of Figure 1. It should be noted that the excitation spectrum obtained at 293 K (Figure 2) was that with the onset of its first absorption band most clearly falling in the blue region; also, it exhibits structured bands. The first absorption band in the spectrum obtained at 193 K is structureless and has its onset red-shifted with respect to the previous one. Also, the spectra recorded at the lowest temperature are markedly more shifted in their onsets and exhibit a disparate intensity ratio between their first two bands. Two such emissions can in principle be readily assigned; thus, the first emission in the UV region can be assigned to 1AZC monomer and that peaking at 520 nm can be assigned to the tautomeric form of the doubly hydrogen bonded centrosymmetric dimer of the compound. The other two emissions must be produced by 1AZC clusters other than the classical doubly hydrogen bonded centrosymmetric dimers.

Figure 3 shows the emission spectra for a highly dilute (5×10^{-6} M) solution of 1AZC in 2MB. The spectral behavior of this solution is identical with that of the 10^{-4} M solution of the

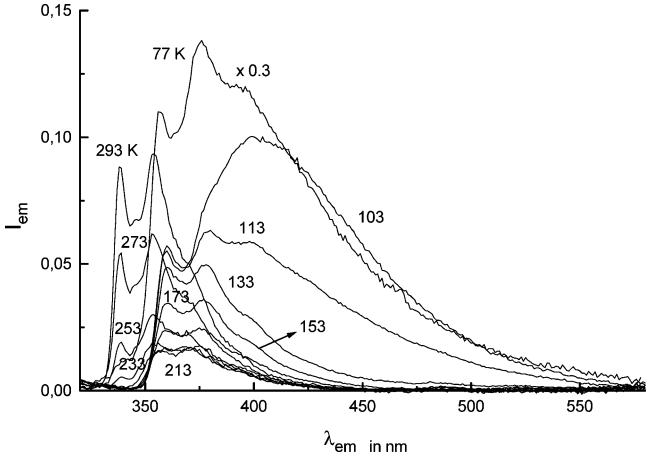


Figure 3. Fluorescence spectra for 5×10^{-6} M solution of 1ACZ in 2MB on excitation at 303 nm, recording from 293 to 103 K.

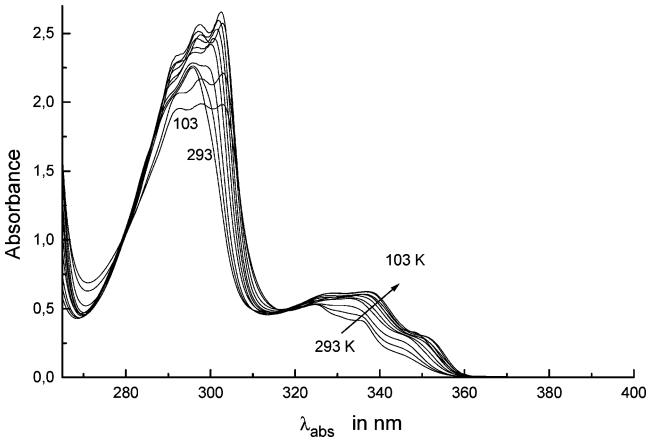


Figure 4. UV−vis absorption spectra for 10^{-4} M solution of 1ACZ in 2MB, recording from 293 to 77 K.

compound, except that the more dilute solution exhibits no appreciable emission at 520 nm (i.e., the more dilute solution does not seem to form, to an appreciable extent, the expected doubly hydrogen bonded centrosymmetric dimers efficiently produced by the dimeric form transferred via an ESDPT mechanism). Also worth noting is the fact that the emissions tentatively assigned to 1AZC clusters are so well-defined for such a highly dilute solution that they must be due to a dimeric form.

Figure 4 shows the UV−vis absorption spectra for a 10^{-4} M solution of 1AZC in 2MB over the temperature range 293−103 K. A comparison of the excitation spectrum obtained at 293 K and the corresponding absorption spectrum reveals that a 10^{-4} M solution of 1AZC in 2MB at 293 K contains not only the monomer, but also some dimer, as the onset of the absorption spectrum is red-shifted with respect to the excitation spectrum. Also, the absorption spectra lose structure and their onset is red-shifted as the temperature is lowered, which is consistent with the excitation spectra at 293 and 193 K (see Figure 2). Especially worth noting are the changes in the excitation spectra as the temperature is lowered further; thus, their onset is gradually red-shifted, some structure is recovered, and, more importantly, the intensity of the second absorption band decreases substantially. This last is especially relevant in photophysical terms as it suggests that any doubly hydrogen bonded centrosymmetric dimers in a 10^{-4} M solution of 1AZC in 2MB at a low temperature are present in minor amounts. The absorption spectra for a 5×10^{-6} M solution of 1AZC in 2MB, not shown, are consistent with those of Figure 4.

Acidity and Basicity of 1AZC. Based on DFT(B3LYP)/6-31G** calculations for the generation of the doubly hydrogen bonded centrosymmetric dimer of 1AZC, 1AZC + 1AZC → $(1AZC)_2$, this equilibrium is a spontaneous process in the gas phase, with $\Delta G^\circ_{298\,K} = -3.43$ kcal/mol versus −3.85 kcal/mol as experimentally determined by El-Bayoumi et al.[2] in 3-methylpentane (3MP). It should be borne in mind that similar computations for the dimerization of 7AI[24] provided a significantly greater $\Delta G^\circ_{298\,K}$ value (viz., −4.42 kcal/mol, which is quite consistent with its experimental counterpart as determined in 3MP by El-Bayoumi et al.,[25] −4.5 kcal/mol, and in cyclohexane by Chou et al.,[26] −4.54 ± 0.15 kcal/mol). Therefore, we can conclude that the formation of the doubly hydrogen bonded centrosymmetric dimer is considerably less likely in 1AZC than it is in 7AI.

Table 1 shows the energy results for the protonation and deprotonation of 1AZC in its ground state (ΔE_{prot} and ΔE_{deprot}) and first π,π^* excited singlet state (ΔE^*_{prot} and ΔE^*_{deprot}); the latter were obtained by following the Förster cycle. The table includes the calculations for 7AI for comparison between the two compounds. As expected from the increased polarizability introduced by the additional ring in 1AZC, its basicity (1.7 kcal/mol) and acidity (5.9 kcal/mol) are intrinsically higher than those of 7AI (see Table 1). The differences are maintained in the first excited singlet state, where they amount to 1.4 and −4.1 kcal/mol, respectively.

At this point, we should note that, inasmuch as 1AZC is a pyrrolo-aza-aromatic compound, it should obey the Valle−Kasha−Catalán theorem:[5,27] In a pyrrolo-aza-aromatic molecule with a *pyrrolo* proton donor site and an *aza* (*pyridine*) proton acceptor site, a coincidence or near coincidence of the corresponding cation and anion $S_0 \leftrightarrow S_1$ (π,π^*) transition bands will be manifested as a result of (+) and (−) electrostatic skeletal perturbations on the intact π-electron system. The fluorescence spectra for the protonated and deprotonated forms of 1AZC reported by Waluk et al.[9] confirm that the compound obeys the previous theorem; in fact, as can be seen in Figure 2 of ref 9, they are virtually coincident.

As shown elsewhere,[15] a substance obeying the Valle−Kasha−Catalán theorem must undergo a simultaneous increase in the acidity of its pyrrole site and the basicity of its pyridine site upon electronic excitation to its first excited π,π^* singlet state. In fact, as can be seen from the acidity and basicity data for the ground and first excited singlet states of the compound (Table 1), its basicity and acidity increase dramatically (by 18.4 and 19.5 kcal/mol, respectively) upon electronic excitation; this is consistent with a double proton transfer in the first π,π^* excited state.[15] By experimentally using the Förster cycle, Waluk et al.[9] estimated that the basicity and acidity of 1AZC should increase by 10.2 and 14.7 kcal/mol, respectively. These values are smaller than the respective intrinsic quantities as a result of the polarizability effect of these ring systems on their basicity and acidity, which cancels in solution,[28,29] being excluded.

If the intrinsic acidity and basicity of the sites bearing the two hydrogen bonds in 1AZC dimer are slightly higher than those in 7AI dimer, then the fact that the dimerization energy is lower for 1AZC than for 7AI suggests that the additional ring in the former hinders the formation of the dimer. Some spectroscopic evidence obtained, and the changes in acidity and basicity in 1AZC, suggests that some dimerization mechanism other than hydrogen bonding must also exist, accounting for the UV emission that is red-shifted with respect to the monomer.

Spectral Behavior of Carbazole in 2MB. Figure 5 shows the emission spectra for a 3×10^{-5} M solution of carbazole

TABLE 1: Protonation (ΔE_{prot}) and Deprotonation Energies (ΔE_{deprot}) in the Ground State and the $^1(\pi,\pi^*)$ State for the 1ACZ and 7AI Compounds and Differences from the Values after Electronic Excitation ($\Delta\Delta E_{prot}$ and $\Delta\Delta E_{deprot}$), All in kcal/mol

compd	ΔE_{prot}	ΔE_{deprot}	ΔE^*_{prot}	ΔE^*_{deprot}	$\Delta\Delta E_{prot}$	$\Delta\Delta E_{deprot}$
1ACZ	240.1	362.7	258.2	343.2	18.1	−19.5
7AI	238.4	367.3	256.8	347.3	18.4	−20.0

(C) in 2MB as obtained by excitation at 295 nm over the temperature range 293−113 K. As can be seen, the fluorescence spectrum obtained at 293 K exhibits two sharp peaks at 333 and 347 nm. As the temperature is lowered, the two peaks grow while essentially maintaining their positions and a new peak at ca. 341 nm gradually forms that signals the appearance of an additional fluorescence which prevails below 153 K and increases strongly as the solution temperature is lowered further. The new fluorescence retains the spectral shape of the previous one, with two sharp peaks at 341 and 358 nm; also, the spectral properties of both fluorescence emissions are suggestive of the presence of a card-pack dimer.[30]

Figure 6 shows the UV absorption spectra for a 3×10^{-5} M solution of carbazole in 2MB over the temperature range 293−113 K. Above 213 K, the sample consists almost exclusively of dissolved carbazole monomer and exhibits an absorption band with its 0−0 component at 332 nm. Below 231 K, the compound aggregates and gives an absorption band with its 0−0 component at 338 nm. Figure 7 shows the excitation spectra obtained at 273, 193, and 153 K by monitoring light at 380 nm, based on which the emission with its 0−0 component at 333 nm is due to carbazole clusters. It should be noted that both the monomeric and clustered forms of carbazole exhibit a virtually negligible Stokes shift.

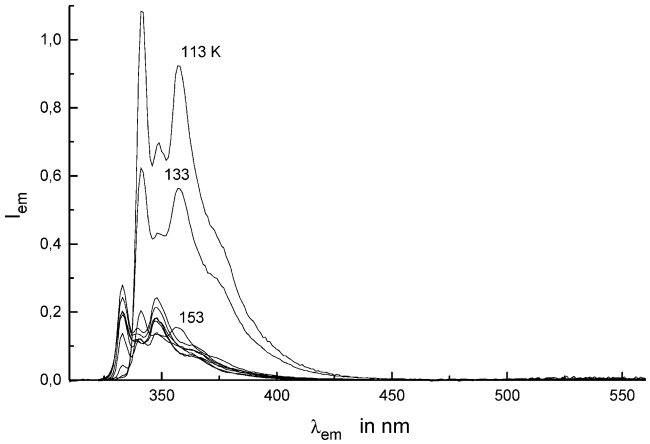


Figure 5. Fluorescence spectra for 3×10^{-5} M solution of C in 2MB on excitation at 295 nm, recording from 293 to 113 K.

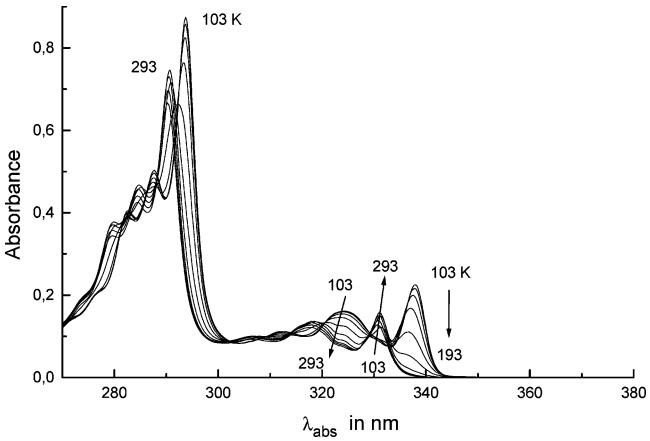


Figure 6. UV−vis absorption spectra for 3×10^{-5} M solution of C in 2MB, recording from 293 to 113 K.

Photophysics of 1AZC. The spectroscopic behavior of 1AZC in an essentially inert solvent such as 2MB is very interesting since, as previously shown, the chromophore produces four different fluorescence emissions at temperatures from 293 to 77 K. As the solution temperature is lowered, a structured fluorescence emission is observed in the UV region that is no doubt due to the monomer; such a band rapidly disappears as the solution temperature is lowered further, which indicates that the sample molecules tend to aggregate. A second fluorescence structurally close to the last molecule, but bathochromically shifted about 10 nm, may be ascribed to the card-pack dimer of the chromophore which does not correspond to the first species generated by another aggregation process. The aggregated species initially does not emit; below a certain temperature, however, it produces the third fluorescence emission of the compound, which is structureless and peaks at ca. 400 nm. As the 2MB matrix solidifies, the sample produces an additional, fourth fluorescence emission that is structureless and centered at ca. 500 nm, and can be assigned to the tautomeric form generated by double proton transfer in the doubly hydrogen bonded centrosymmetric dimer.

The spectral behavior of 1AZC and C in 2MB as the solution temperature is lowered allows one to draw the following conclusions:

(a) Both chromophores aggregate. However, while the 1AZC solution contains aggregated forms at room temperature, C aggregates only below 213 K, where its card-pack dimer starts to be detected. The card-pack dimer of 1AZC is also detected below 213 K.

(b) Consequently, the first 1AZC cluster, which is present at room temperature, must be a hydrogen bonded dimer—most likely, one with a double hydrogen bond involving the acid and basic sites (see Scheme 1).

Because these dimers of 1AZC fail to emit the expected fluorescence for the tautomer in the 500 nm region, they cannot be centrosymmetric—otherwise, they would follow an ESDPT mechanism and emit at that wavelength. The fact that the doubly hydrogen bonded dimers exhibit a structureless emission in the region of 400 nm resembles the photophysical behavior of doubly hydrogen bonded heterodimers of 7AI in 2MB resulting

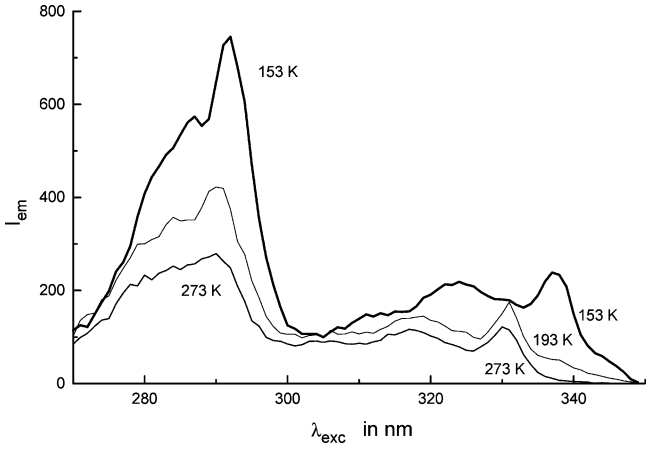


Figure 7. Fluorescence excitation spectra for 3×10^{-5} M solution of C in 2MB on monitoring light at 380 ± 2 nm, and recording at 273, 193, and 153 K.

from deuteration in 7AIh:7AId dimer,[31] substitution in 3Me7AI:7AI dimer,[32] or symmetry in C_1 heterodimers generated by unconcerted twisting of the methyl groups in 3Me7AI:3Me7AI.[33]

The fact that the doubly hydrogen bonded dimer of 1AZC in a 2MB solution gives no emission in the 500 nm region until the 2MB matrix forms is absolutely inconsistent with the photophysical behavior of 7AI dimer in 2MB, the fluorescence of which increases as the solution temperature is lowered from room temperature to 77 K. The resulting loss of centrosymmetry in 1AZC dimer in 2MB must in principle be ascribed to flapping in its additional benzene ring breaking the centrosymmetry of the molecule, which does not occur in 7AI dimer under identical conditions.

Available experimental evidence for 7AI and 1AZC dimers allows one to conclude that excitation of the doubly hydrogen bonded centrosymmetric form causes it to efficiently follow an ESDPT mechanism subject to virtually no energy barrier and hence to emit no fluorescence. Based on the foregoing, it seems inaccurate to assign the fluorescence detected by Waluk et al.[8] in the 26 000 cm^{-1} region to F_1 for the dimer following the ESDPT mechanism (see Figure 1 in ref 8).

In the light of the above-described spectral evidence, one can draw the following conclusions:

(a) The emission at ca. 374 nm detected by El-Bayoumi et al.[2] in a 6×10^{-4} M solution of 1AZC in 3MP cannot be assigned to F_1 or the dimer following the ESDPT mechanism and must be a structured fluorescence.

(b) The assignment by Waluk et al.[9] of the luminescence of a 10^{-4} M solution of 1AZC in paraffin at 77 K illustrated in Figure 4 to the doubly hydrogen bonded dimer is also inaccurate as it belongs to the card-pack dimer.

(c) Consequently, the model of Waluk et al.,[9] based on which ESDPT in 1AZC dimer is viscosity-controlled, should be revised in light of the spectral changes in the compound as the temperature of a solution in 2MB is lowered from 293 to 77 K.

Conclusions

Contrary to previous assumptions, the centrosymmetric dimer of 1AZC in 2MB is produced by the minor species formed as the temperature in a hydrocarbon solvent is lowered; consequently, the emission from the tautomeric form can only be detected in the 2MB matrix. Two other dimers are extensively formed as the solution temperature is lowered: one is a doubly hydrogen bonded, noncentrosymmetric form which exhibits structureless emission in the 400 nm region in highly viscous solvents, and the other is a card-pack dimer which produces structured emission in the UV region.

Based on the excitation spectra obtained in this work, exciting the sample in the 370 nm region (i.e., at strongly red-shifted wavelengths with respect to previous studies) should allow centrosymmetric dimers to be selected. However, we must conclude that the so widely used photophysical approach fails to expose some essential features of the photophysics of these chromophores (e.g., the presence of a card-pack in 1AZC).

The assumption of Waluk et al. that a viscosity threshold exists above which a doubly hydrogen bonded centrosymmetric dimer can no longer be formed is absolutely inconsistent with the evidence obtained in 2MB in this work.

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