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Toward the Photostability Mechanism of Intramolecular Hydrogen Bond Systems. The Photophysics of 1′-Hydroxy-2′-acetonaphthone

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Abstract: The photophysical behavior of 1′-hydroxy-2′-acetonaphthone in dry cyclohexane, methanol, and dimethyl sulfoxide was studied. The compound was found to exhibit a single fluorescence band (both at room temperature and at 77 K) that was scarcely dependent on the solvent used as well as an anomalously small Stokes shift (ca. 6000 cm^{-1}) for an excited-state intramolecular proton-transfer mechanism and a fluorescence spectrum similar to the mirror image of its absorption spectrum. The compound was also found to exhibit a single fluorescence band both in gas phase at 368 K and in crystal phase at 298 K. Despite the fact that the compound seemingly undergoes a proton phototransfer, it is no more photostable than 2-(2′-hydroxy-5′-methylphenyl)benzotriazole itself, which is regarded as the archetype of photostability. This finding sheds some light on the mechanism whereby substances containing an intramolecular hydrogen bond acquire their photostability.

Introduction

The excited-state intramolecular proton-transfer mechanism (ESIPT) which takes place via an intramolecular hydrogen bond (IMHB), originally hypothesized by Weller[1] to account for the photophysical behavior of methyl salicylate (MS), has been used to explain such interesting and seemingly disparate processes as stimulated light photogeneration[2–4] and light photoprotection,[5–7] both of which require the substances involved to be highly photostable.

Photophysical studies on compounds following an ESIPT mechanism have frequently been hindered by the concurrence of several molecular forms[8–10] in the ground state of the compound concerned. Thus, MS occurs not only in its predominant form I, which photogenerates the keto form Iz via an ESIPT mechanism with a typically unstructured room temperature emission and a large Stokes shift (11 073 cm^{-1}), but also in form II, which also contains an IMHB but does not follow an ESIPT mechanism, and form III, which contains no IMHB and is usually referred to as the "open" form. The presence of this last form is markedly dependent on the properties of the solvent used and is believed to be related to the photodegradability of the compound.

In this work we studied 1′-hydroxy-2′-acetonaphthone (HAN12), which possesses a number of peculiar features that makes it a major photophysical model. In fact, it includes an IMHB (form IV) that endows it with the structural features required to be a photostable substance,[5] it cannot occur in form V (the equivalent of structure II), and the peri effect of the hydrogen atom at position 8 relative to the hydroxyl group must destabilize the open form VI (the equivalent of structure III) in order to reduce its weight.[3,4]

Scheme I

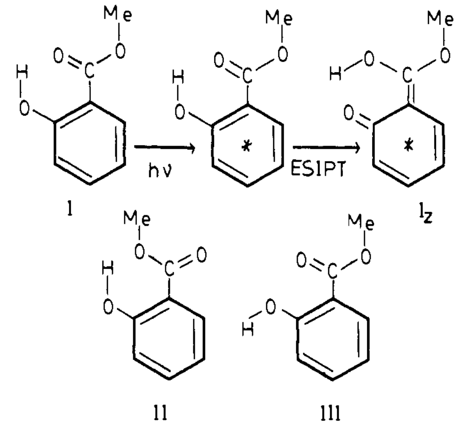
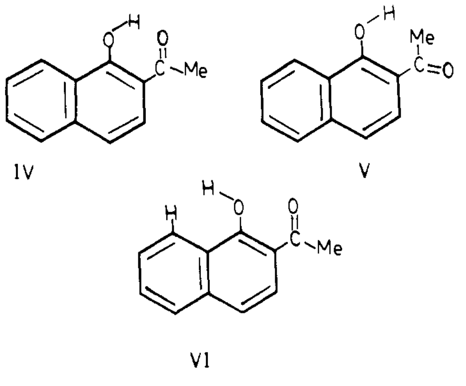


Chart I



Oki et al.[11] ascribed the deviant behavior of the chelate ring in methyl 1-hydroxy-2-naphthoate (MHN12) with respect to methyl 2-hydroxy-3-naphthoate (MHN23) to *pseudo*aromatic properties. Also, Woolfe and Thistlethwaite,[8] who studied the photophysics of phenyl 1-hydroxy-2-naphthoate—very similar to HAN12—, ascribed the lack of a long wavelength emission band in this compound to the lack of a proton transfer. However,

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occurrence of this compound in several fluorescent forms makes the system so complex that it precludes any dynamical study.

We recently hypothesized[7] that the photostability of IMHB-containing structures seemingly relies not on the keto form but on precedent forms. Notwithstanding the presence of an IMHB in its structure, if HAN12 can be shown not to occur in keto form (IVz, the equivalent of an Iz structure), then we have a good candidate for investigating the mechanism behind photostability. For this purpose, the photostability of HAN12 and the archetypal compound 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Tinuvin P) against UV light in such an aggressive medium as dimethyl sulfoxide (DMSO) were compared.

Experimental Section

Absorption spectra were recorded at 298.0 ± 0.1 K on a Shimadzu UV-1200 spectrometer furnished with a matched pair of Suprasil cells of 1-cm pathlength. The gas-phase absorption spectrum of 1'-hydroxy-2'-acetonaphthone at 368 K was obtained on a Cary 5 spectrometer by using a matched pair of Suprasil cells of 10-cm pathlength.

Luminescence spectra were acquired at 298 and 77 K by using an SLM 48000S spectrofluorimeter and a cooled wide-band RF housing for the R928 photomultiplier tube employed. Corrected excitation spectra were obtained at a constant excitation intensity that was controlled by means of a rhodamine B quantum counter.

Quantum yields and fluorescence lifetimes were measured at room temperature on freshly prepared samples with optical densities in the excitation region of ca. 0.02 and 0.1 or lower, respectively. MS in cyclohexane (CYH) was used as quantum yield standard ($\phi_f = 0.022$)[10] and refractive indices were appropriately corrected.[12] Fluorescence lifetimes, determined by phase and modulation measurements, were made relative to glycogen scattering solutions[13] by using an SLM 48000S spectrofluorimeter at modulation frequencies between 1 and 250 MHz.

The analysis of experimental multifrequency data is an iteractive process intended to fit an appropriately chosen model to available data by carrying the model's parameters (lifetimes and fractional contributions) in a direction that minimizes deviations between the model and data. Decisions on the suitability of a model rest on examination of the statistics of a fit—a plot of the residual deviations with frequency and the value of the reduced chi-squared, χ^2, a numerical value that reflects the overall goodness of fit. Figure 1 shows the results thus obtained for HAN12 in methanol.

For luminescence measurements at 77 K, samples were held in sealed Suprasil quartz tubes of 3-mm diameter that were placed in the low-temperature SLM accessory. Spectra were recorded by using polarizers in a magic angle arrangement in order to avoid any artifacts potentially arising from polarization effects.

For crystal-phase measurements, HAN12 crystals were grown in absolute EtOH and spectra were also recorded by using polarizers in a magic angle arrangement.

The gas-phase emission spectrum was recorded for a sample obtained by sublimating HAN12 crystals in a closed cell through which a stream of 99.999% pure N_2 was previously circulated.

Room-temperature photostability was determined by using a PTI system consisting of a horizontally mounted water-cooled lamp housing for a 1000-W xenon lamp furnished with an f/4.0 elliptical reflector that concentrated the lamp intensity 4-fold. Light reflected to the sample housing was previously passed through a water-cooled PTI 02-A002 infrared water filter and then through a monochromator by which 330 ± 12 nm light was selected for sample excitation. The photon flux reaching the sample was measured with Aberchrome 540[14] and was found to be 1×10^{16} photons/s. The samples used for photostability measurements had an optical density of 2.0 at 330 nm and were stirred continuously by means of a magnetic stirrer built into the cell. Sample degradation was monitored by UV spectroscopy and was expressed as the ratio of optical densities measured at the different light exposure times and a given wavelength (396 nm for HAN12 and 330 nm for Tinuvin P) to that measured at time zero.

HAN12, 2'-hydroxy-1'-acetonaphthone (HAN21) and 2'-acetonaphthone, 99% pure, were purchased from Aldrich Chemie and used without further purification. Methyl 3-hydroxy-2-naphthoate, over 98% pure, was purchased from Fluka and recrystallized three times in absolute ethanol (Riedel-de Haën, over 99.8% pure) prior to use. CYH and methanol (MeOH) were Merck Uvasol reagents for fluorescence spectroscopy. To the former was added a few sodium threads in order to remove water. Finally, DMSO was a Merck Uvasol chemical for spectroscopy.

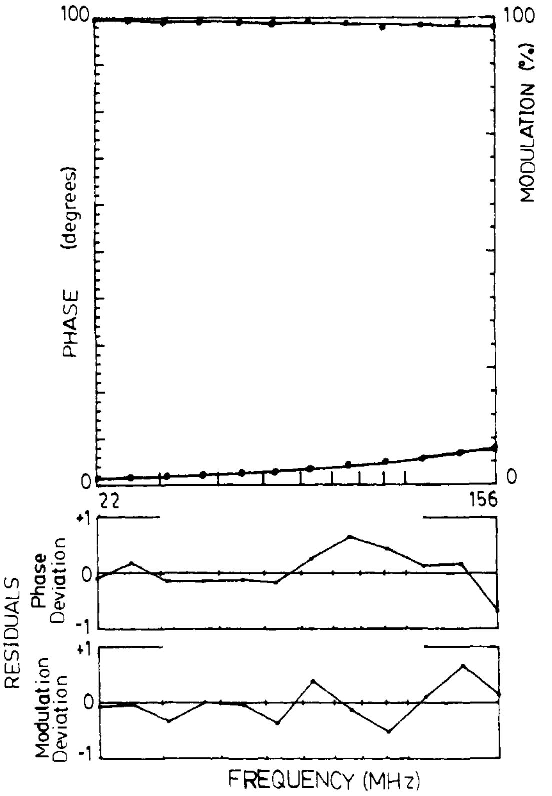

Figure 1. Multifrequency phase and modulation data (solid points) for 1'-hydroxy-2'-acetonaphthone in methanol. The solid curves denote the best single exponential fits to the data.

^{1}H NMR spectra were recorded at 30 °C on a Varian XL-300 spectrometer operating at 300 MHz. Chemical shifts (ppm) were measured in per-deuterated dimethyl sulfoxide (DMSO-d_6) and CCl_4 referred to TMS as internal standard. In CCl_4, the lock signal was obtained by using DMSO-d_6 in a tight-closed capillary as external reference. IR spectra were recorded in DMSO-d_6 and CCl_4 by using a Perkin-Elmer 681 spectrophotometer furnished with cells of 0.1-mm path length.

Results and Discussion

As can be seen from Figure 2a and Table I, the UV spectrum of HAN12 varies very little with the solvent used, whether it is nonpolar (e.g., CYH); highly basic, polar, and nonprotic (DMSO); or polar, protic, and basic (MeOH). We should emphasize that such a highly basic solvent as DMSO does not alter the absorption spectrum of HAN12, which clearly indicates that the hydrogen atom at position 8 hinders development of the open form (VI) even in this type of solvent.[15] Figure 2b shows the UV spectra of HAN21, where no steric hindrance destabilizes the corresponding open form (VII). Its spectral envelope varies clearly with the solvent used (CYH, MeOH, or DMSO), i.e., HAN21 is sensitive to the solvent basicity. These results are consistent with the spectral behavior of HAN12 and HAN21 in isooctane and ethanol reported by Berlmann et al.[16]

Emission bands in the three solvents are also very similar and tend to stabilize as the solvent polarity–polarizability increases. Thus, maxima lie at 473 nm in CYH, 483 nm in MeOH, and 487 nm in DMSO (Figure 3). It should be noted that, contrary to the expectations for room temperature emissions from Iz forms generated via ESIPT mechanisms in this type of compounds,[8,17] the emission in CYH is not entirely unstructured but appears as two shoulders at 450 and 502 nm.

As can be seen from Figure 3, a plot of emission $[F(\bar{\nu})/\bar{\nu}^3]$ against absorption $[\epsilon(\bar{\nu})/\bar{\nu}]$ exhibits roughly mirror symmetry.

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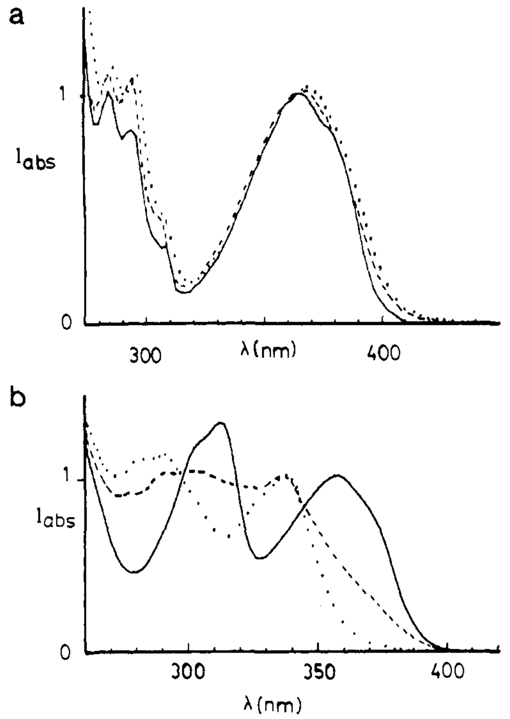
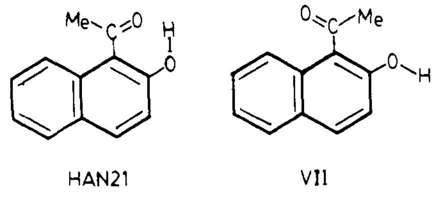


Figure 2. Absorption spectra of 1'-hydroxy-2'-acetonaphthone (a) and 2'-hydroxy-1'-acetonaphthone (b), in DMSO (···), MeOH (- -), and CYH (—). All spectra were recorded at 298 K.

Table I. Absorption, Emission Maxima and Stokes Shift of 1'-Hydroxy-2'-acetonaphthone in Different Studied Solvents

solvent	absorption (nm)	emission (nm)	Stokes shift (cm^{-1})
cyclohexane	366	473	6160
	307		
	295		
	284		
methanol	365	484	6610
	306		
	294		
	285		
DMSO	367	488	6770
	307		
	295		
	285		
GAS	358	458	6100
	301		
	289		
	279		

Chart II



HAN21 VII

Hence the molecular geometries of the absorbing and emitting forms must be very similar.[18,19]

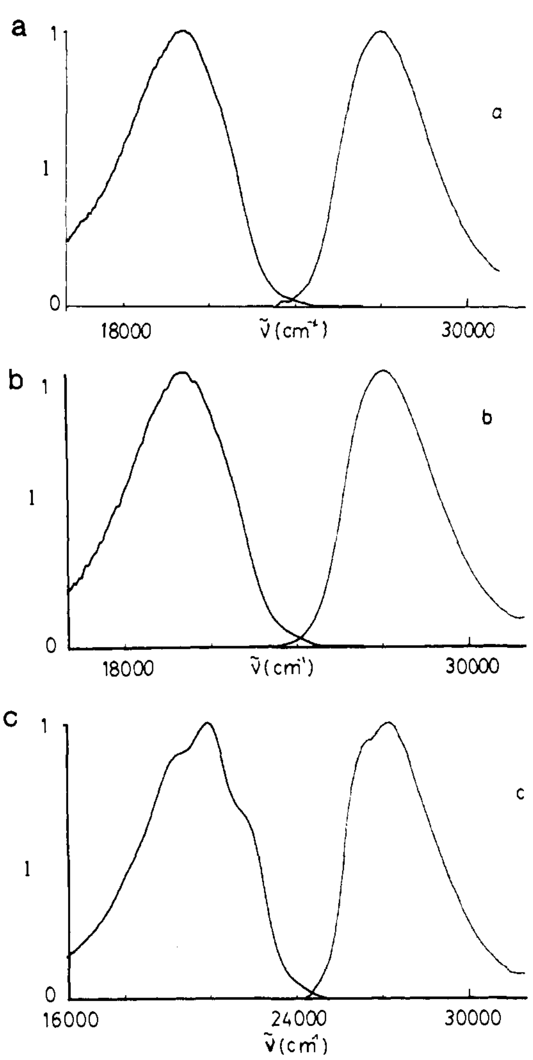


Figure 3. Modified absorption spectra, $\epsilon(\bar{\nu})/\bar{\nu}$, and modified emission spectra, $F(\bar{\nu})/\bar{\nu}^3$, of 1'-hydroxy-2'-acetonaphthone in (a) DMSO, (b) MeOH, and (c) CYH.

Table II. Quantum Yields, Lifetimes, Radiative, and Nonradiative Constants of HAN12 in the Studied Solvents

solvent	$\phi_f{}^a$	τ^b (ps)	$K_f \times 10^{-8}$ (s^{-1})	$K_{nr} \times 10^{-10}$ (s^{-1})
cyclohexane	0.007	69	1.0	1.4
methanol	0.007	148	0.5	0.7
DMSO	0.018	258	0.7	0.4

[a] Excitation wavelengths were at 303 and 309 nm in methyl salicylate and at 303, 309, 364, and 370 nm in HAN12. [b] Excitation wavelength was at 370 nm.

The excitation spectra obtained in the three solvents assayed are faithful replicates of the corresponding absorption spectra. Also, their shape is the same whatever the emission wavelength used, which again shows the occurrence of a single absorbing—and emitting—form in all three solvents.

Table II lists quantum yields and fluorescence lifetimes obtained in the solvents used as well as the calculated radiation and radiationless rate constants.

In order to detect other, much less intense potential fluorescence emissions, we assayed increasing the HAN12 concentration in CYH to 6×10^{-4} M, which revealed no other fluorescence bands such as that of MHN23 at 608 nm.[8,20-22] Also, spectra recorded at 77 K in CYH and DMSO (Figure 4) showed no fluorescence bands other than those observed at room temperature. It should be noted that the shoulder at 450 nm in the room temperature spectrum appeared as maximum in the spectrum recorded at 77

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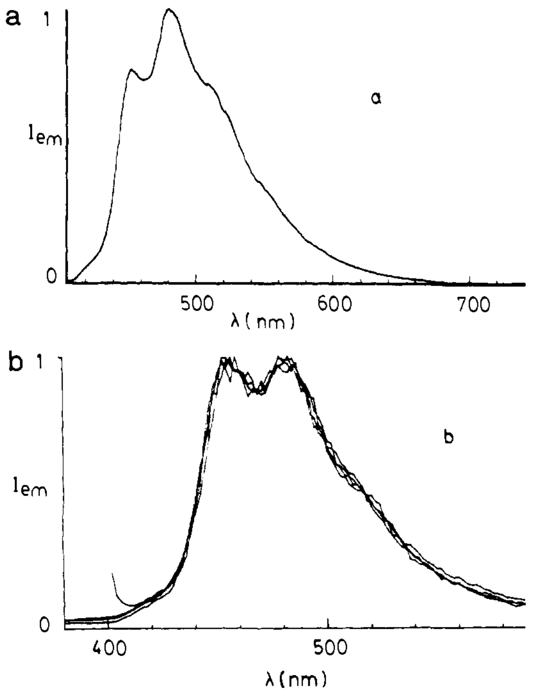

Figure 4. Emission spectra of 1′-hydroxy-2′-acetonaphthone at 77 K in (a) CYH and (b) in DMSO (excitation wavelengths at 310, 330, 350, and 390 nm).

K. The spectra obtained at this latter temperature in CYH showed no phosphorescence either, whereas those obtained under the same conditions in DMSO exhibit some, though very weak in any case.

Finally, the emission of an HAN12 crystal grown in absolute EtOH on excitation at 350 nm was measured. The spectrum obtained was similar to that recorded at 77 K and included no emission band in the 520–700 nm that could be assigned to the keto form (Figure 5a). On the other hand, excitation of an MHN23 crystal gave rise to a strong band centered at 630 nm (Figure 5b). Also, as can be seen from Figure 6, which shows the gas-phase absorption (λ_{max} = 358 nm) and emission spectra (λ_{max} = 458 nm) obtained for HAN12 at 368 K,[23] the latter is subject to a Stokes shift of 6100 cm^{-1}. Neither crystal-phase nor gas-phase experiments revealed the occurrence of any emission bands near 600 nm.

In assigning the fluorescent molecular form we must first establish the molecular structure of the compound concerned in its ground state. The C=O stretching band of HAN12 in CCl_4 appears at 1632 cm^{-1} compared to 1687 cm^{-1} for 2′-acetonaphthone. According to Zadorozhnji,[24] a 55-cm^{-1} shift indicates the presence of a strong intramolecular hydrogen bond (ca. 8 kcal/mol). On the other hand, the chemical shift of the hydroxyl group appears as a sharp signal at 13.91 ppm with respect to TMS, which is also consistent with the presence of a very strong intramolecular hydrogen bond (ca. 9 kcal/mol according to Schaefer[25]). From these results it follows that HAN12 occurs

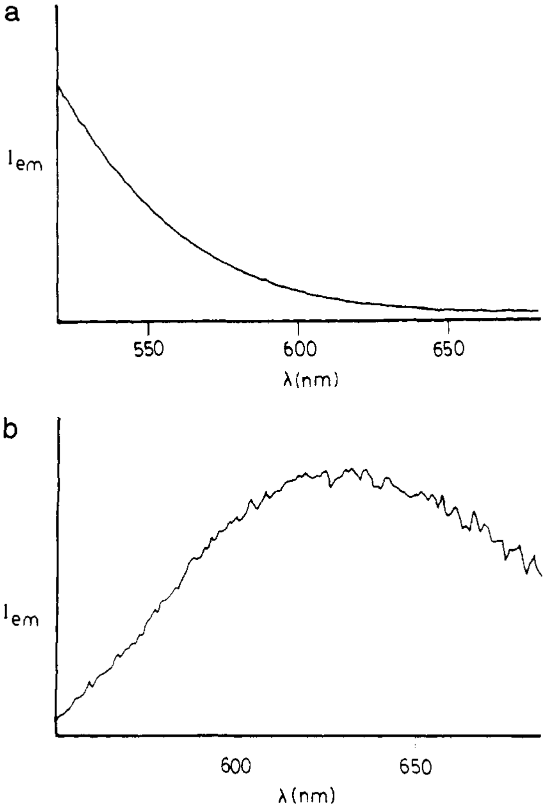

Figure 5. Emission spectra of 1′-hydroxy-2′-acetonaphthone (a) amd methyl 2-hydroxy-3-naphthoate (b) in crystal phase on excitation at 350 nm.

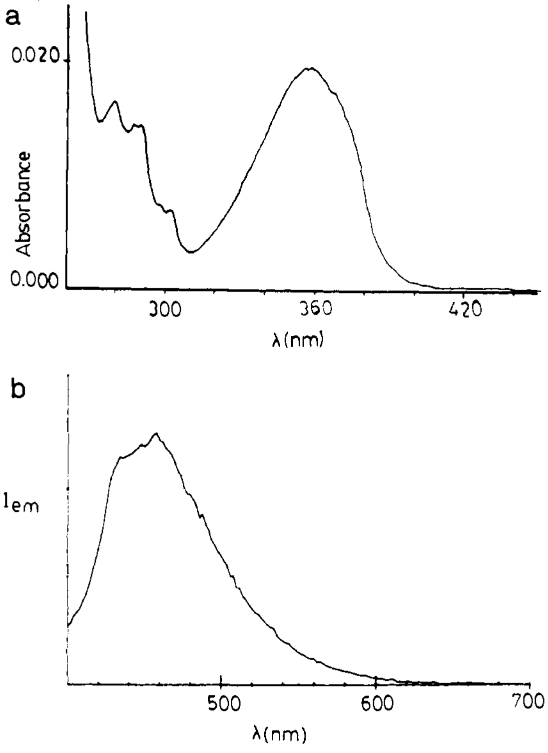

Figure 6. Gas-phase absorption and emission spectra of 1′-hydroxy-2′-acetonaphthone at 368 K. The emission spectrum was obtained on excitation at 360 nm.

in form IV in inert solvents. This compound possesses the same molecular structure in DMSO-d_6 since its C=O stretching band appears at 1630 cm^{-1} (1685 cm^{-1} for 2′-acetophenone) and the chemical shift of the hydroxyl group is reflected in a sharp signal at 14.05 ppm.

The molecular stability with which such a strong intramolecular

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(22) The fluorescence assigned to the keto form of MHN23 was detected at a concentration of 10^{-5} M in cyclohexane on excitation at both 360 and 390 nm. The fluorescence band was quite broad, unstructured, and centered at 630 nm. Its Stokes shift was 10 300 cm^{-1} and the corresponding excitation spectrum coincide in shape with the first absorption band of the compound. From such an emission fluorescence band we obtained ϕ_f = 0.0007, which, together with τ_f = 60 ps (previously measured by Woolfe and Thistlethwaite[8]), allowed us to estimate K_f = 1.1 × 10^7 s^{-1}, i.e., a radiation constant smaller than that of HAN12 by about one order of magnitude (see Table II).

(23) The bathochromic shift undergone by this substance on passing from a gas phase at 368 K to a CYH solution at 298 K is indicative of the polarizability of this chromophore as it cannot arise from a thermochromic effect since the absorption of HAN12 in methyl cyclohexane is not altered on raising the temperature from 298 to 368 K.

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Table III. Ground and Excited State pK Values

molecule	*a*	p*K* (S_0)	p*K* (S_1) *b*	p*K* (S_1) *c*	ref
methyl 2-naphthyl ketone	P	−6.16	5.27	1.5	26
	P	−6.3	2.9	2.3	27
1-naphthol	D	9.23	2.0	2.5	28
	D	9.20	2.1	<1.8	29
	D	9.60	0.7		30
	D	10.0		2.68	31
2-naphthol	D	9.46	2.5	2.81	28
	D	9.45	3.0	2.85	32
	D		3.07		30

[a] Protonation (P) and deprotonation (D). [b] Föster cycle calculations. [c] Fluorescence intensity measurements.

hydrogen bond (ca. 8 kcal/mol) endows form IV obviously reinforced the aforementioned peri effect of the hydrogen atom at position 8, thereby making the open form of HAN12 even more unlikely.

In summary, the UV, IR, NMR, and UV emission data obtained allow one to conclude that HAN12 occurs as molecular structure IV. It is widely accepted that an ESIPT mechanism via an IMHB is controlled by the acid–base properties of the groups involved in the bond. It was thus believed of interest to compare the behavior of 1′-2′ and 2′-3′ groups in compounds MHN12 and MHN23. Clearly, the change in the basic strength of the carbonyl group, which lies at the same position in both compounds, will have no influence on the transition from the ground to the excited state. Also, based on the results given in Table III, the acidity of the hydroxyl group in 1-naphthol and 2-naphthol does not seem to discriminate between the two in relation to an ESIPT mechanism.

On the other hand, the Stokes shift (6100 cm^{-1} in CYH) of the compound in all the solvents assayed (see Table I) is unusual: (a) it is normally of ca. 11 000 cm^{-1} for molecules following an ESIPT mechanism (e.g., methyl salicylate, methyl 3′-hydroxy-2′-naphthoate, and 2-hydroxyacetophenone, the Stokes shifts of which in CYH are 10 440,[17a] 10 300,[22] and 11 070[17a] cm^{-1}, respectively); (b) it is also inconsistent with the less than 2900 cm^{-1} obtained for an enol form involved in an IMHB (viz. form II of MS[33]).

Hunsberger,[34] Melchior,[35] and Oki[11] ascribed the disparate behavior of 1′-2′ and 2′-3′ naphthalenes bearing a proton-releasing substituent (e.g., –OH) and carbonyl proton-acceptors to the greater double-bond character of the 1′-2′ linkage compared to the 2′-3′ one, which may result in energy alterations hindering a proton transfer. This is supported by the finding of Gillispie et al.[36] that, while 8-hydroxybenzanthrone (8-HBA) follows an ESIPT mechanism, 6-hydroxybenzanthrone (6-HBA) does not.

The Stokes shift obtained, the structured emission obtained in CYH and in gas phase and a situation close to mirror symmetry allow us to conclude that HAN12 emits from an incomplete keto form,[37] which, together with the failure of the different experiments to show the formation of such a form, permit us to assume that, most probably, it is not that such a form does not emit, but that it does not occur in this system. Hence it makes a good candidate for checking whether the compound loses its photostability if the keto form IVz does not develop. For comparison, Figure 7 illustrates the photodegradable behavior of HAN12 and Tinuvin P irradiated with identical light at 330 nm. The behavior of HAN12 is exceptional: the compound is significantly more photostable that in Tinuvin P. This supports our previous hypothesis that the photostability of IMHB-containing structures does not rely on the photophysics of their keto forms.

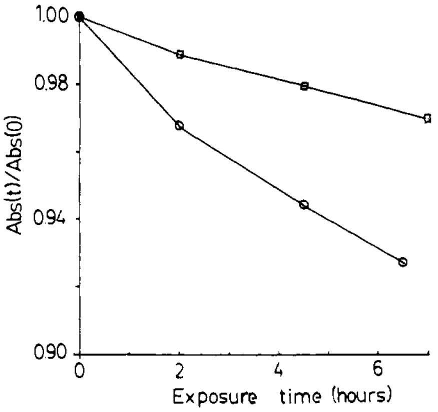
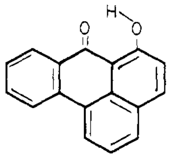
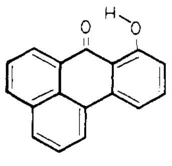


Figure 7. Changes in absorbance as a function of ultraviolet exposure for DMSO solutions of 1′-hydroxy-2′-acetonaphthone (squares) and Tinuvin P (circles) at 298 K.

Chart III



6 HBA



8 HBA

Conclusions

The results obtained in this work reveal the occurrence of a single molecular absorbing and fluorescent form of HAN12, both at room temperature and at 77 K. The peri steric effect of the hydrogen atom at position 8 very effectively hinders development of the open form, both in the ground and in the excited state, which substantially simplifies the photophysical study of 1′-hydroxy-2′-acetonaphthone.

The photostability experiments carried out at an excitation wavelength of 330 nm on 1′-hydroxy-2′-acetonaphthone and Tinuvin P showed the former to be more photostable and not to exist in an open form—at least in the solvents assayed—or in any keto forms. Consequently, the photostability of IMHB-containing compounds in their molecular structures does not rely on their keto forms, even though the presence of such forms must endow the compounds concern with additional photostability via the gap energy law.

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(37) (a) Substitution of the phenolic proton of HAN12 by a deuterium atom results in no change in the emission quantum yield. (b) The theoretical proton transfer curves obtained according to ref 7 confirm that, while the minimum energy of the $1(\pi,\pi^*)^1$ state in 1′-hydroxy-2′-acetophenone corresponds to an O–H distance of 1.32 Å, it appears at only 1.20 Å in 1′-hydroxy-2′-acetonaphthone.