Benzoyl-1-butene was collected by preparative GC (10% SE-30 column at 160 °C) from a sample of 1 g of **1**-Br in 250 mL of benzene irradiated in an immersion well with a Pyrex-filtered 450-W mercury arc. Its spectroscopic properties were identical with those from an independently prepared sample (addition of phenylmagnesium bromide to 4-cyano-1-butene): IR (neat 1685, 1455, 1220, 1010, 920, 750, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (m, 2 H), 3.00 (t, 2 H), 4.8–5.3 (m, 2 H), 5.5–6.3 (m, 1 H), 7.2–8.0 (m, 5 H); MS *m/e* 160, 105, 77.

Identification of Photoproducts from 3 and 4. 1,4-Dimethyl-4-benzoyl-4-cyclohexene (**5**) was collected from an irradiated solution of **3** and shown to have identical spectroscopic characteristics to the synthetic precursor to **3**. Injection of unirradiated benzene solutions of **3** onto a 3% QF-1 column at 150 °C resulted in two peaks on the GC trace, in a 1:3 ratio. The lesser one corresponded to **5**. After 12 h irradiation of the solution, the second peak had totally disappeared and was therefore assigned to **3**. Only three product peaks appeared: one corresponding to **5**, one corresponding to benzaldehyde, and a small new one with a retention time slightly shorter than that of **3**. IR analysis of this solution showed a moderately intense absorption at 3500 cm^{-1}, suggesting the presence of the expected cyclobutanol. The benzene was removed and replaced with CCl_4. Addition of Br_2 resulted in the precipitation of an orange solid which melted at 79 °C. Addition of Br_2 to authentic **5** resulted in a dibromide with a melting point at 83 °C. This dibromide did not yield **5** during GC analysis. Treatment with zinc dust of the dibromide prepared from irradiated **3** yielded **5**, as judged by GC analysis. A solution of **3** in benzene-d_6 containing 0.05 M pyridine was placed in a NMR tube, degassed, and sealed. Irradiation for 4 h at 313 nm produced a white precipitate; NMR analysis of the solution showed vinylic resonance at δ 5.2 identical with that of authentic **5**.

Irradiation of 4-Benzoylbutyl Tosylate. Benzene solutions 0.1 M in ketone were irradiated as usual. GC analysis of unirradiated solution showed only a large peak with the characteristic retention time of 4-benzoyl-1-butene. Analysis of irradiated solution also showed a large peak corresponding to acetophenone.

Irradiation of ε-Iodohexanophenone. A degassed benzene solution 0.17 M in ketone and 0.5 M in pyridine was irradiated at 313 nm. A white precipitate formed. GC analysis showed four photoproducts, the three most volatile having relative peak areas of 14:2:1. They were collected by GC analysis. The largest was acetophenone, as determined by its characteristic retention time and NMR spectrum. The second had identical GC retention time and ^1H NMR as an authentic sample of 5-benzoyl-1-pentene:[13] δ 1.5–2.4 (m, 4 H), 2.92 (t, 2 H), 4.8–5.1 (m, 2 H), 5.3–6.0 (m, 1 H), 7.1–7.4 (m, 3 H), 7.7–7.9 (m, 2 H). The 14:2 area ratio of the two major products, when corrected for a 8:12 carbon ratio, corresponds to a 10:1 mole ratio. The other products were not identified.

Quantitative Studies. Generally, samples were irradiated in 13 × 100 mm Pyrex tubes which had previously been degassed and sealed. Sample tubes were always irradiated in parallel with valerophenone[14] or benzophenone–1,3-pentadiene[17] actinometers on a rotating "merry-go-round".[54] The 313-nm region of a 450-W Hanovia mercury arc was isolated with an alkaline chromate filter solution[48] and the 365-nm region with a Corning No. 7-83 filter combination. Product and reactant concentrations were determined by GC analysis on $^1/_8$ in. columns with FID detectors. Responses were calibrated relative to alkane internal standards present in known concentration from 0.002 to 0.02 M. Varian 600 and 1200 gas chromatographs were used with Infatronics digital integrators. NMR spectra were recorded on Varian T-60 and CFT-20 spectrometers and mass spectra on a Perkin-Elmer-Hitachi RU-6.

Solutions of **1** were prepared containing *n*-hexadecane and *n*-heptadecane, which served as internal standards for GC monitoring of acetophenone and **2**, respectively. A 12 ft column containing 10.4% QF-1 and 2.2% Carbowax 20M in 60–80 mesh Chromosorb W was used at 120–130 °C. Acetophenone appearance from valerophenone actinometers and from attempts to quench butyrophenone with alkyl halides was monitored relative to 0.004 M tetradecane. Disappearance of **1**-Cl and **1**-Br was monitored relative to octadecane or eicosane as internal standard on a 6-column containing 5% SE-30 on Chromosorb G. Product yields from ring-substituted **1**-Cl were determined on a 6 ft column containing 3% QF-1 on Chromosorb G at 145 °C, relative to 0.003 M hexadecane. Analyses of 3 and **4** used the same column, with tetradecane as standard for benzaldehyde appearance and pyridine disappearance, hexadecane for **5** appearance, and nonadecane for cyclic alcohol from **3**. Pentadiene isomerization was monitored at 50 °C on a 25 ft column containing 25% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P.

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Supplementary Material Available: Final positional and thermal parameters (Tables IV and V), bond distances and angles (Table VI), and structure factors with standard deviations (Table VII) for **3** (10 pages). Ordering information is given on any current masthead page.

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Excited-State Prototropism in Esters of *o*-Hydroxy-2-Naphthoic Acids

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Contribution from the Physical Chemistry Department, University of Melbourne, Parkville, Victoria, Australia. *Received October 14, 1980*

Abstract: The photophysical behavior of methyl 3-hydroxy-2-naphthoate (I) and phenyl 1-hydroxy-2-naphthoate (II) have been investigated. The former compound exhibits two emission bands. The longer wavelength band is characteristic of the excited-state zwitterion formed by rapid excited-state intramolecular proton transfer. The normally Stokes-shifted emissions of both I and II exhibit a nonexponential fluorescence decay. This is interpreted in terms of more than one excited state (originating from excitation of distinct ground-state conformers) emitting within the fluorescence band. The behavior of these compounds is compared to that of methyl salicylate.

Recently it has been suggested that the explanations of Sandros[1] and Klöpffer and Naundorf[2] for the photophysical behavior of methyl salicylate should be extended.[3] Fluorescence quenching measurements on the short wavelength emission band have indicated that there are two distinct contributions to this band. The interpretation was in terms of two "slowly" interconverting ground-state conformers, which upon excitation gave rise to emission in the short wavelength band. The suggested conformers are ones in which the phenolic proton is H bonded to the "ether" oxygen atom of the ester group (Figure 1a), and a nonintramolecularly H bonded, or "open-ring" conformer (Figure 1b). The

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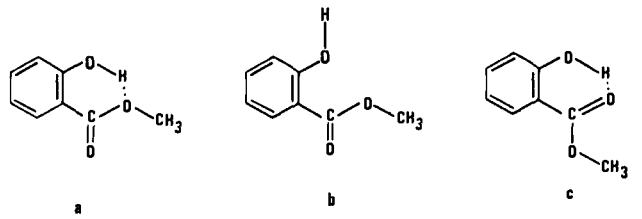
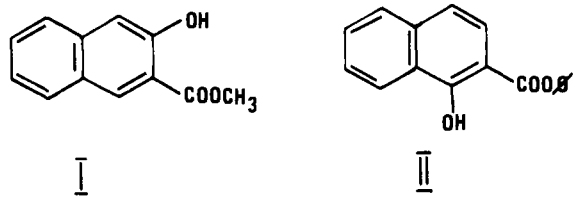


Figure 1. Ground-state conformers of methyl salicylate: (a) "ether bonded", (b) "open-ring", and (c) "closed-ring".

latter has been termed the trans conformer and is stabilized in hydroxylic solvents by solute–solvent H bonding. Preliminary fluorescence decay measurements using single-photon counting appear to verify the results of the quenching experiments. In a third conformer (Figure 1c), in which the phenolic proton is H bonded to the carbonyl oxygen, intramolecular proton transfer occurs upon excitation, giving rise to a zwitterion which emits at 450 nm. This is referred to as the cis conformer.

While salicylic acid and its derivatives have been extensively studied,[1-6] the *o*-hydroxynaphthoic acids and their derivatives have received scant attention.[5] As structural analogues of the salicylic acid derivatives, these compounds should be capable of forming intramolecular H bonds and exhibiting excited-state prototropism. In this paper we shall discuss two hydroxynaphthoic acid esters: methyl 3-hydroxy-2-naphthoate (I) and phenyl 1-hydroxy-2-naphthoate (II).



We are unable to study the 350-nm emission band of methyl salicylate with our streak camera system as our input optics have a transmission cutoff at ca. 400 nm. The emission spectra of I and II lie almost entirely above 400 nm, allowing a complete study of their normally Stokes-shifted emission bands. The observation of a nonexponential fluorescence decay for these bands in both I and II strengthens the earlier assumption of a dual contribution to the 350-nm band of methyl salicylate. The lowest energy absorption band of I lies at considerably longer wavelengths than that of the corresponding methoxy methyl ester. Bergmann et al.[7] have proposed that this is due to the presence of an intramolecular H bond between the hydroxylic proton and the carbonyl group in I. The methoxy compound is incapable of forming any intramolecular H bonds. Similar observations for methyl salicylate and methyl *o*-methoxybenzoate have been interpreted in an identical fashion.[7] A similar red shift of the absorption spectrum of methyl 1-hydroxy-2-naphthoate is not observed. Oki et al.[8] have interpreted the spectra on the basis of pseudoaromaticity of the fused chelate ring formed by intramolecular H bonding. This interpretation suggests that no red shift should be observed in this latter case.

The fluorescence spectrum of I is the subject of some controversy.[5] A fluorescence band at ca. 420 nm, corresponding to a normal Stokes shift of emission, is commonly observed. Naboikin[9] and co-workers also claim to have seen a weak, long wavelength emission (ca. 650 nm) in concentrated solutions. This band has not been observed by Ware et al.[10] nor by Hirota.[11] The fluorescence characteristics of II have not previously been studied, but the closely related methyl 1-hydroxy-2-naphthoate exhibits no anomalous fluorescence.[12] The present work confirms the existence of the long wavelength emission in I and, further, shows that the excited species responsible is not in equilibrium with the emitter(s) of the short wavelength band. Additional evidence of the photophysical differences between I and II, and the relationship of these compounds to the salicylic acid derivatives, is presented.

Experimental Section

Both I and II were obtained from Fluka Chemicals. Methyl 3-hydroxy-2-naphthoate was purified by vacuum sublimation, while phenyl 1-hydroxy-2-naphthoate was recrystallized from methanol. In each case the purity was confirmed by both spectroscopic and melting point determinations.

Methanol was redistilled, and cyclohexane and methylcyclohexane were chromatographically purified by passing through a column of 60–120 mesh silica gel (BDH). These procedures rendered all solvents free from fluorescent impurities. All solutions were prepared immediately prior to use. When fluorescence lifetimes were determined, the solutions were degassed by using five freeze–pump–thaw cycles.

Fluorescence emission and excitation spectra were recorded with a Perkin-Elmer MPF-44A spectrofluorimeter. Excitation spectra were measured by using optically dilute samples to avoid distortions of the spectrum which arise out of the optical geometry of the instrument and saturation effects in the sample. All excitation and emission spectra reported here are uncorrected.

Two methods were employed for the fluorescence decay measurements. The fluorescence decay of II was measured with a laser/streak camera/OMA system similar to that previously described.[13] The solution, contained in a 1-cm quartz cuvette, was excited with a single pulse of the fourth harmonic from a Nd^{3+}–glass laser (λ = 264 nm; τ_p = 6 ps; E = 0.1 mJ). The decay of the resulting fluorescence was measured with an Electrophotonics Photochron II ultrafast streak camera. The input optics of our streak camera are of heavy-flint glass, having a transmission cutoff at ca. 400 nm.

The longer lived fluorescence decay of I required the use of the conventional single-photon-counting technique. An ORTEC/Applied Photophysics Ltd. nanosecond spectrometer was used for these measurements. Samples were excited by the 360-nm emission from an N_2-filled spark-discharge lamp. Fluorescence decay data were analyzed, using nonlinear least-squares curve fitting[14] on a NOVA 2-10 computer. Response function deconvolution of the fluorescence decay data was accomplished with the least-squares iterative convolution method.

Results and Discussion

(i) **Methyl 3-Hydroxy-2-naphthoate in Cyclohexane.** The UV absorption spectrum of I in cyclohexane is very similar to that reported in hexane.[8] The lowest energy absorption band has its maximum at 368 nm with a weak shoulder near 384 nm. The second band shows considerable structure, with maxima at 299, 287, and 276 nm. It is generally accepted that this compound is capable of forming an intramolecular H bond between the hydroxylic proton and the carbonyl oxygen.[7-9] The infrared absorption spectrum provides evidence of the existence of H bonding at the hydroxylic proton.[7] It is believed that such intramolecular H bonding results in the UV absorption spectrum of I lying at lower energies than that of methyl 3-methoxy-2-naphthoate, which is incapable of intramolecular H bonding.[7]

The fluorescence spectrum of I at 1×10^{-5} M in cyclohexane is shown in Figure 2a. Fluorescence spectra must be measured by using very dilute solutions because of the considerable overlap of the absorption and emission spectra. This can result in distortion of the short wavelength region of the fluorescence spectrum by reabsorption of the fluorescence. This effect is apparent at concentrations of 10^{-4} M and above. The emission spectra, at 1×10^{-4} M in cyclohexane, and with excitation wavelengths of 360 and 390 nm, are shown in parts b and c, respectively, of Figure 2. A very weak, long wavelength emission, maximal at 608 nm,

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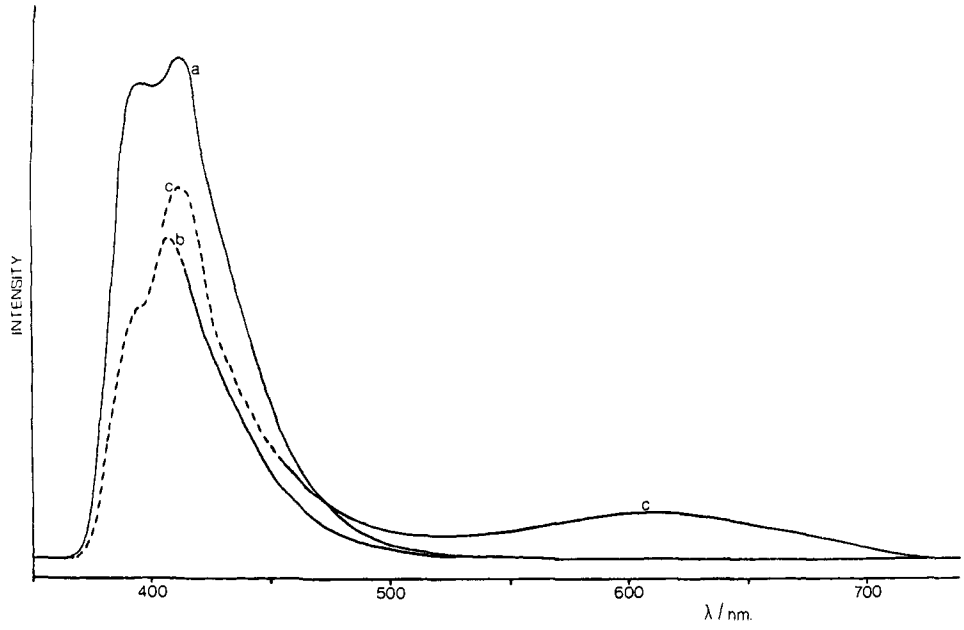
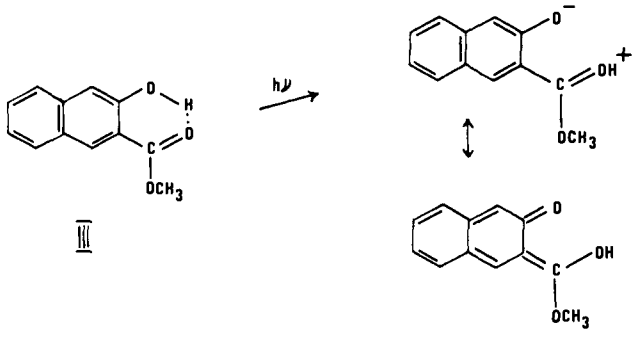


Figure 2. Fluorescence of methyl 3-hydroxy-2-naphthoate in cyclohexane: (a) 1×10^{-5} M, (b) 1×10^{-4} M, $\lambda_{ex} = 360$ nm, (c) 1×10^{-4} M, $\lambda_{ex} = 390$ nm.

can be seen in Figure 2c. This long wavelength emission is more apparent in concentrated solutions. Furthermore, excitation in the long wavelength region of the absorption spectrum enhances the long wavelength band intensity relative to that of the normally Stokes-shifted emission. Naboikin et al.[9] have also observed a weak, long wavelength emission at 650 nm in concentrated solutions with hydrocarbon solvents. We believe that this is the same band that we observed at 608 nm. Improvements in spectrofluorimeter performance since 1959, together with the broadness and weakness of the emission, probably account for the discrepancy. It is unlikely to be attributable to the fact that our spectra are uncorrected.

The fluorescence excitation spectrum of the normally Stokes-shifted and the long wavelength emissions are shown in parts a and b, respectively, of Figure 3. The excitation spectrum of the short wavelength emission has two maxima and lies at shorter wavelengths than the featureless excitation spectrum of the 608-nm emission band. Neither excitation spectrum bears a close relationship to the absorption spectrum, but this is hardly surprising, since the absorption spectrum is a superposition of the spectra of at least two distinct ground-state species, as evidenced by the excitation spectra.

The observation of distinct excitation spectra for the short and long wavelength emission bands is common to several members of the salicylic acid family.[6] The molecules are further unified by the fact that the excitation spectrum of the long wavelength emission lies to the red of that of the short wavelength emission. By analogy with these other molecules we can attribute the long wavelength emission in I to a zwitterion species formed by intramolecular proton transfer in the first excited singlet state. The ground-state precursor of the zwitterion is an intramolecularly H-bonded conformer, III, which is consistent with the interpre-



III

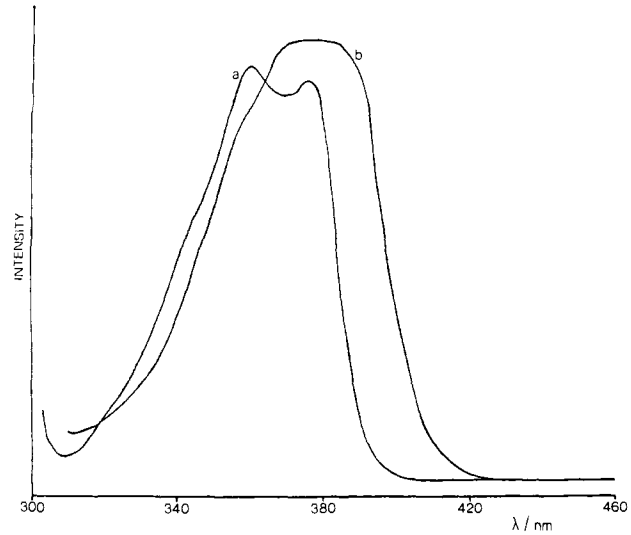


Figure 3. Fluorescence excitation spectra of methyl 3-hydroxy-2-naphthoate in cyclohexane: (a) short wavelength emission and (b) long wavelength emission.

tation of Bergmann et al. that the red shift of the absorption spectrum of I relative to that of the 3-methoxy compound is due to intramolecular H bonding. Naboikin et al. have considered two alternative explanations of the long wavelength fluorescence. They have provided evidence against this band being dimer fluorescence. Our own measurements show both the absorption spectrum band shape to be invariant and Beer's law to be obeyed, over a range of concentrations from 1×10^{-5} to 1×10^{-2} M. Naboikin et al. have also observed the long wavelength emission in a solid polystyrene matrix, arguing against its being excimer fluorescence. We have measured the fluorescence decay of the long wavelength emission of I in cyclohexane and found it to be a single exponential with a lifetime of 60 ± 6 ps. No rise time could be observed, reinforcing the idea that excimers are not responsible for this emission. The shortness of the lifetime is a common feature of many species produced by intramolecular proton transfer and indicates some efficient radiationless process which is not open to, or less probable for, the nonproton-transferred species.

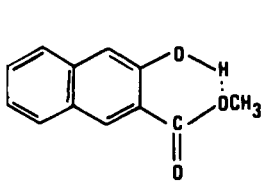
The short wavelength emission band of I in cyclohexane is characterized by a nonexponential and concentration-dependent

fluorescence decay. At all concentrations the fluorescence decay was well fitted by a double exponential decay function shown in eq 1, where τ_1 and τ_2 are the fluorescence lifetimes and f is the

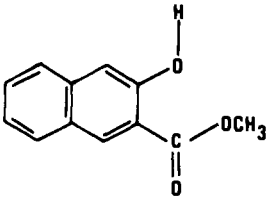
$$I(t) = A[f \exp(-t/\tau_1) + (1-f) \exp(-t/\tau_2)] + B \quad (1)$$

"zero-time" fraction of th emission intensity having lifetime τ_1. At a concentration of 10^{-4} M, $f = 0.78 \pm 0.03$, $\tau_1 = 23.3 \pm 0.2$ ns, and $\tau_2 = 5.1 \pm 0.9$ ns. As the concentration is increased, the longer of the two lifetimes is progressively reduced, but the value of f remains unchanged within experimental error. These observations suggest that there are two distinct contributions to this short wavelength band. We have previously presented quenching evidence for a dual contribution to the short wavelength emission of methyl salicylate. The more direct kinetic evidence obtained here supports the conclusions of the earlier work and suggests a similar explanation in the present case.

Our interpretation is in terms of two interconvertible ground-state conformers. Interconversion is sufficiently slow that it does not occur during the excited-state lifetime. The suggested conformers are ones in which the hydroxylic proton is H bonded to the "ether type" oxygen of the carboxyl group (IV) and an

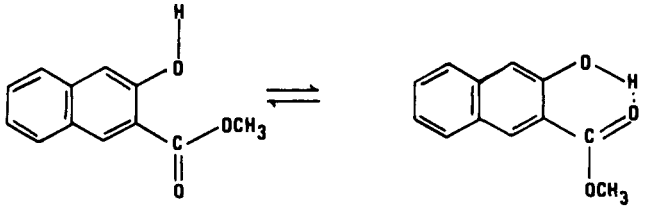


IV



V

"open-ring" form containing no intramolecular H bonds (V). Excited-state prototropism, as postulated earlier to account for the long wavelength emission, depends in part on an increase in basicity, on excitation, of the carbonyl oxygen. No such change in basicity is expected for the ether oxygen. Thus these conformers should show a normal Stokes shift of emission. In a non-H-bonding solvent like cyclohexane, we would expect conformer IV to be more stable than V and hence it should be the predominant species contributing to the short wavelength emission. We can therefore attribute the 23.3-ns lifetime to conformer IV and the 5.1-ns lifetime to V. Additional evidence in support of the existence of conformer IV comes from the absorption spectrum. Naboikin et al. have calculated the enthalpy of the intramolecular H bond in conformer III to be 21 kJ mol^{-1}. If species V were the only precursor of short wavelength emission and we made the reasonable assumption that the entropic contribution to the free energy difference between species V and III was negligible, then a calculation of the equilibrium constant for the reaction yields

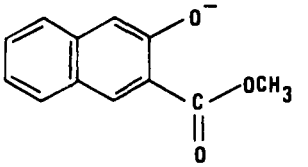


V III

a value of approximately 5×10^3. The equilibrium should therefore lie almost entirely in favor of III. On this basis then, the absorption spectrum would bear a close similarity to the excitation spectrum of the long wavelength emission band. This is clearly not the case, and in order to explain the observations, we require a conformer of more comparable energy to III to be the major precursor of the short wavelength emission. The postulated conformer IV appears to fill the requirements adequately. (McTigue[15] has shown that H bonds involving ether oxygens and carbonyl oxygens are of similar strength for intermolecular H bonding between H_2O and various organic ketones and ethers in CCl_4 solution. These situations approximate those in conformers IV and III sufficiently well for us to propose that the conformers will be of similar energy.) The absorption spectrum is virtually independent of temperature between 293 and 328 K in cyclohexane and between 160 and 280 K in methylcyclohexane. This is consistent with conformers III and IV being energetically similar, with conformer V making up only a very small proportion of the ground-state mixture.

(ii) Methyl 3-Hydroxy-2-naphthoate in Methanol. In methanol solution the absorption spectrum of I is very similar to that reported in ethanol.[7] The lowest energy band has its maximum at 364 nm, with a weak shoulder near 379 nm. The fluorescence spectrum at a concentration of 10^{-5} M in methanol is shown in Figure 4a. Again, there is extensive overlap of the absorption and emission spectra, resulting in distortion by reabsorption of fluorescence spectra recorded at higher concentrations. For the long wavelength emission band in methanol to be observed, much higher concentrations than are necessary in cyclohexane are required. In methanol, as in cyclohexane, excitation in the long wavelength region of the absorption spectrum enhances the intensity of the long wavelength emission relative to that of the normally Stokes-shifted band. The emission spectrum of I at 10^{-2} M in methanol, excited at 390 nm, is shown in Figure 4b. Again, the possibility of dimerization can be discounted. We have observed Beer's law to be obeyed and the absorption and excitation spectra to be invariant over a range of concentration from 1×10^{-5} to 1×10^{-2} M. The excitation spectrum of the 420-nm emission band of I is shown in Figure 5. The weakness of the long wavelength emission band has prevented us from obtaining its excitation spectrum without interference from the tail of the short wavelength band. The evidence we have, however, indicates that it lies at considerably longer wavelengths than that of the short wavelength band.

The fluorescence decay of the short wavelength band in methanol is well fitted by eq 1 yielding the following parameters: $f = 0.51 \pm 0.01$; $\tau_1 = 27.4 \pm 0.2$ ns, and $\tau_2 = 5.0 \pm 0.3$ ns. The fluorescence decay of the long wavelength band could not be measured because of its very low intensity. Acidification of the solution to 10^{-3} M in HCl haas not effect on any of the above results, ruling out the possibility of the anionic form VI being responsible for any of the effects noted.



VI

In methanol, we expect the "open-ring" conformer V to be stabilized relative to III and IV by intermolecular H bonding with the solvent. This stabilization is clearly reflected in the decrease in the value of f in the fluorescence decay, while the lifetimes are essentially unchanged. The decrease in the intensity of the long wavelength emission in going from cyclohexane to methanol is probably partly due to a shift in the ground-state equilibria in favor of conformer V and partly due to a decrease in the emission quantum efficiency of the zwitterion species. The blue shift in both the absorption spectrum and the excitation spectrum of the 420-nm emission in going from cyclohexane to methanol is again best interpreted in terms of a shift in the ground-state equilibria toward the "open-ring" conformer. An explanation for the shift in terms of the transition being of an $n \rightarrow \pi^*$ character can be dismissed on the basis of the large value of the extinction coef-

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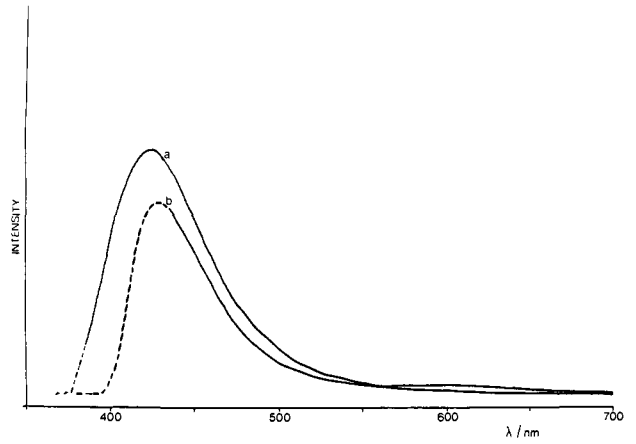


Figure 4. Fluorescence of methyl 3-hydroxy-2-naphthoate in methanol: (a) 1×10^{-5} M and (b) 1×10^{-2} M, λ_{ex} = 390 nm.

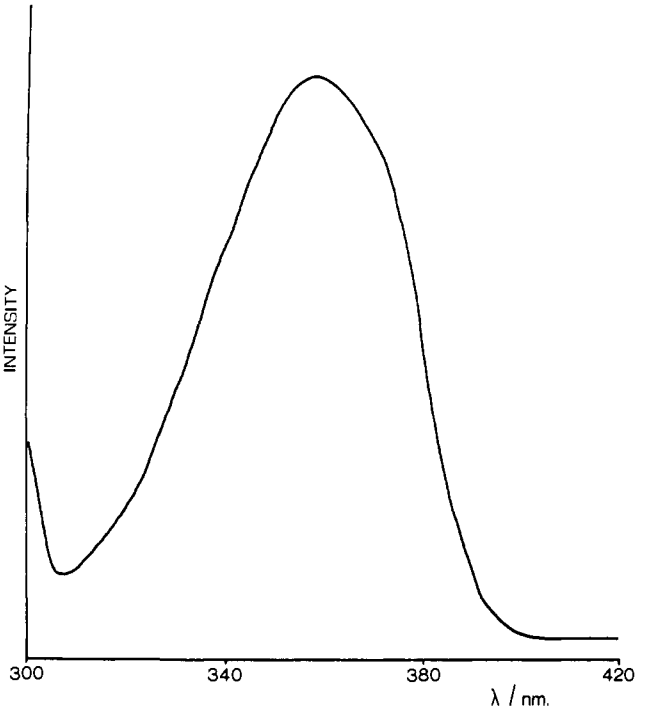


Figure 5. Fluorescence excitation spectrum of methyl 3-hydroxy-2-naphthoate in methanol, λ_{em} = 420 nm.

ficient ($\epsilon \simeq 2.4 \times 10^3$ M^{-1} cm^{-1}).

(iii) **Phenyl 1-Hydroxy-2-naphthoate.** The absorption spectra of II in cyclohexane and methanol are shown in parts a and b, respectively, of Figure 6. The spectrum in cyclohexane is very similar to that reported for methyl 1-hydroxy-2-naphthoate in hexane.[8] The latter compound, unlike its 3-hydroxy isomer, does not exhibit a red shift of its absorption spectrum relative to that of the corresponding *o*-methoxy compound. It is generally thought that such a red shift is characteristic of an intramolecularly H-bonded species. Oki et al., on the basis of the pseudoaromaticity of the fused chelate ring formed by the intramolecular H bonding, have suggested, however, that a red shift may not necessarily be expected in the 1,2 compound. In both cyclohexane and methanol a single emission band, showing a normal Stokes shift and no dependence upon excitation wavelength, is observed. These spectra are shown in Figure 7a,b, while the corresponding excitation spectra are given in Figure 8a,b, respectively. We have found that Beer's law is obeyed, and the absorption, fluorescence, and excitation spectra are invariant over a range of concentration from 1×10^{-3} to 1×10^{-5} M. The possibility of dimerization in these systems can therefore be discounted. The interesting differences between this compound and I are, first, our failure to observe a

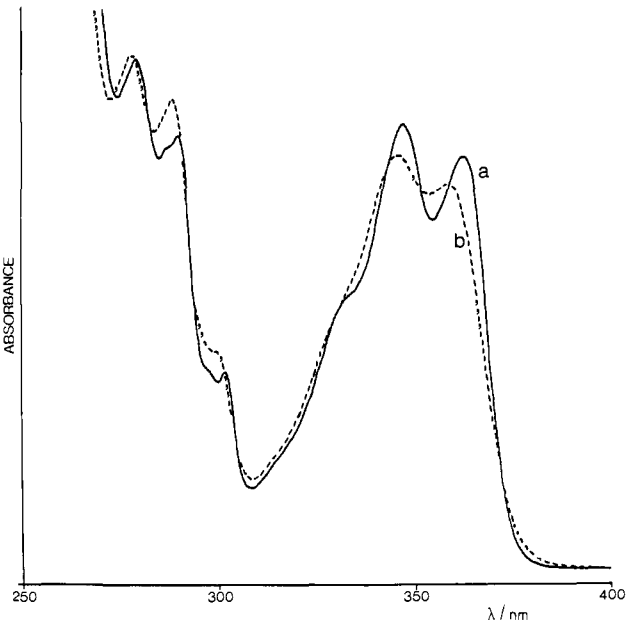


Figure 6. Absorption spectra of phenyl 1-hydroxy-2-naphthoate (a) in cyclohexane and (b) in methanol.

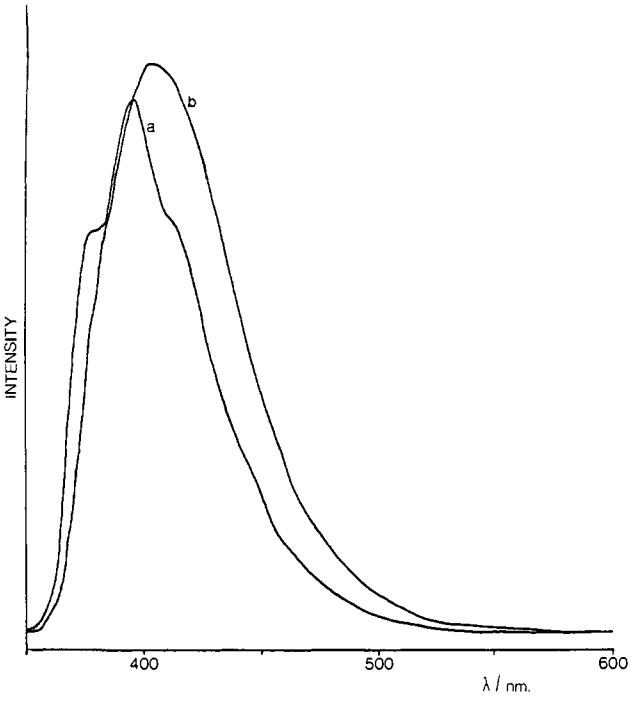


Figure 7. Fluorescence spectra of phenyl 1-hydroxy-2-naphthoate (a) in cyclohexane and (b) in methanol.

long wavelength emission band and, second, the very close relationship between the excitation spectrum of the normally Stokes-shifted emission and the absorption spectrum. The wavelengths of the maxima and the shoulders in the excitation spectra exactly match those found in the absorption spectra for both solvents.

One possible interpretation of these data is that there exists no ground-state conformer having an intramolecular H bond between the hydroxylic proton and the carbonyl oxygen (VII). There is no a priori reason to deny the existence of conformer VII, and, in fact, infrared evidence for the related ketone 2-acetyl-1-naphthol indicates the presence of an intramolecular H bond.[7] Moreover, our observation of a nonexponential decay for the

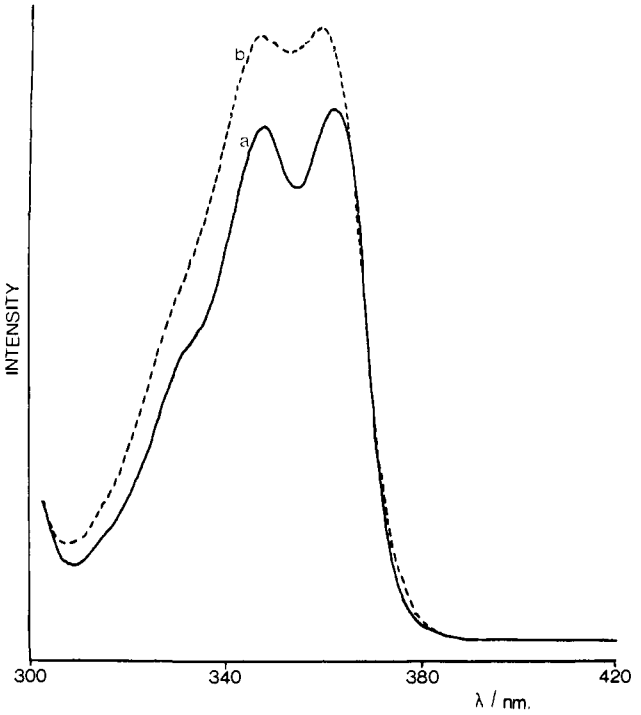
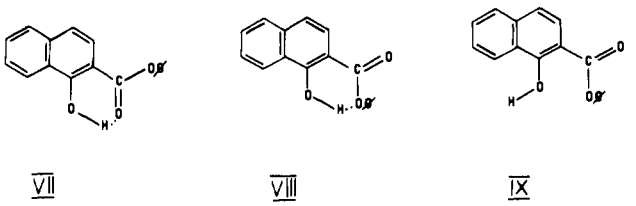


Figure 8. Fluorescence excitation spectra of phenyl 1-hydroxy-2-naphthoate (a) in cyclohexane and (b) in methanol.

400-nm fluorescence points to more than one contribution to this emission. It would therefore appear that at least one intramolecularly H-bonded species exists.

An alternative explanation for the lack of zwitterion fluorescence in II is that the change of acid–base properties upon excitation is inadequate to cause proton transfer in the way postulated for I. If this were the case, then when conformer VII was excited, it might be expected to emit with a normal Stokes shift in the same wavelength region as other conformers in which no proton transfer occurs. The invariance of the emission spectra with excitation wavelength, together with the close relationship of the absorption and excitation spectra, indicates that all the ground-state conformers have very similar absorption spectra and, when excited, exhibit very similar fluorescences. It might be argued that excitation of conformer VII results in proton transfer forming a nonfluorescent or undetectably weak fluorescent zwitterion. This possibility is difficult to discount, but examination of fluorescence decays may provide some clues. The decays are clearly nonexponential, and we have been unable to fit them satisfactorily to eq 1. This inability to fit is particularly apparent for II in methanol. The complex decays observed may be due to the



VII VIII IX

emission resulting from excitation of three distinct ground-state conformers, VII, VIII, and IX.

The quality of streak camera data is inadequate to allow a meaningful fit of a triple exponential decay function. Despite the uncertainties that remain, the data clearly indicate that in II, as in I, the emission in the region of 400 nm contains more than one contribution. On balance, the postulate that all three conformers, VII, VIII and IX, exist in the ground state but that proton transfer fails to occur in VII on excitation seems the more plausible.

Conclusion

The results reported here verify the existence of a long wavelength emission band for I and the self-quenching of the short wavelength band. The 608-nm emission has been attributed to a zwitterion, resulting from excited-state intramolecular proton transfer. The lack of a long wavelength emission band in II has been tentatively interpreted in terms of the failure of such proton transfer. In both I and II, as in methyl salicylate, there is evidence of a multiple contribution to the short wavelength emission band.

In both I and methyl salicylate, two emission bands are observed, one having an abnormally large Stokes shift. The relative intensities of these bands are both solvent and excitation wavelength dependent, the long wavelength band being favored by non-H-bonding solvents and longer excitation wavelengths. In both cases, the results have been interpreted in terms of three distinct ground-state conformers, one of which is capable of undergoing excited-state intramolecular proton transfer to form the zwitterionic species.

The main difference between I and methyl salicylate is that the long wavelength fluorescence band is always less intense than the short wavelength band in I. This is the case regardless of solvent and excitation wavelength. That this is not so for methyl salicylate can probably be attributed to a lower quantum efficiency of the zwitterion in I.

In conclusion, we can state that I behaves in a very similar fashion to methyl salicylate, while II shows some notable differences. The reasons for these differences are yet to be elucidated.

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