July, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 1951—1955 (1990) 1951

Proton-Transferred Ion Pairs of *p*-Hydroxybenzaldehyde and *p*-Hydroxyacetophenone in Ethers at Low Temperature

Hiroyasu INOUE,* Tadamitsu SAKURAI, Toshihiko HOSHI,† and Jun OKUBO†
Department of Applied Chemistry, Faculty of Technology, Kanagawa University, Kanagawa-ku, Yokohama 221
†Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Tokyo 157

(Received December 21, 1989)

The self-associations of *p*-hydroxybenzaldehyde (HBA) and *p*-hydroxyacetophenone (HAP) have been studied from measurements of phosphorescence and the excitation spectra at 77 K. At appropriately high concentrations of HBA and HAP in ethereal matrices, such as 1,4-dioxane, these compounds exhibit dual phosphorescences around 430 and 470 nm with excitation at 290 and 330 nm, respectively. The shorter-wavelength emission is due to monomeric species of the substrates. The longer-wavelength emission can be interpreted as being due to ion pairs, in which the proton of the hydroxyl group of the substrate molecule is transferred intermolecularly to the formyl group of another substrate molecule. The phosphorescence excitation spectra show that the ion pairs are formed in the ground states of the phenolic compounds, being in equilibrium with the monomeric species at 77 K. The ion pair formation is strongly dependent on the medium.

It has been known that some organic acids are associated with bases to give ion pairs as well as hydrogen-bonded complexes.[1–4] In particular, phenols, naphthols, and their related compounds behave as a hydrogen or a proton donor in these molecular interactions.[5–8] In the cases of molecules having both hydrogen-donating and -accepting group at the ortho-position, intramolecular proton transfers have been observed.[9–12] Intermolecular and intramolecular proton-transfer interactions in the ground and excited states are attractive subjects in connection with acid-base equilibria, characteristics of excited and emissive states, quenching processes, and photochemical reactivities.

The formation of an ion pair may be characterized by its unique absorption, emission, and excitation spectra. In most of the hitherto-reported papers describing intermolecular proton transfer, substrate concentrations were appropriately low enough to avoid self-associations. Previously, *p*-hydroxybenzaldehyde (HBA) was found to form a hydrogen-bonded dimer in the ground state at appropriately high concentrations in methanol.[13] However, the absorption spectra of HBA at room temperature provide no evidence for the existence of ion pairs in various solvents. On the other hand, Baba[14] has reported that at 77 K the HBA-triethylamine system involves a proton-transferred ion pair as well as a simple hydrogen-bonded complex.

In this work intermolecular self-interactions for HBA and *p*-hydroxyacetophenone (HAP) were studied as proved from phosphorescence and its excitation spectra measured at 77 K for various substrate concentrations in several ethereal matrices.

Experimental

HBA and HAP were obtained from Wako Pure Chemical Industries Ltd. and were purified by recrystallization from aqueous ethanol and vacuum sublimation. *p*-Methoxybenzaldehyde (Wako) was subjected to repeated fractional crystallizations. 1,4-Dioxane and tetrahydrofuran (Wako) were spectrograde and used without further purification. Other solvents and amines were used after distillation.

Ultraviolet absorption spectra were measured with a Shimadzu UV-210A spectrophotometer. Phosphorescence and excitation spectra were recorded on a Shimadzu RF-500 spectrofluorimeter equipped with a cylindrical rotating sector at 77 K using a 3.5 mm diameter quartz tube cell. The observed phosphorescence and excitation spectra were uncorrected. The infrared spectra were taken with a Hitachi 270-30 infrared spectrometer using a 1 mm KRS-5 cell.

Results and Discussion

Phosphorescence Spectra. HBA and HAP show strong phosphorescences in various matrices at 77 K, while showing very weak fluorescence. In methanol and cyclohexane the shapes of the phosphorescence bands are independent of the concentrations, ranging over 10^{-6}—10^{-2} mol dm^{-3} and on the excitation wavelengths. This indicates that there are no marked solute–solute interactions. However, a different situation has arisen in the 1,4-dioxane matrix (Fig. 1) in which the phosphorescence bands of HBA obtained for relatively low and high concentration matrices with varying excitation wavelengths are presented. It can be seen from this figure that HBA shows dual phosphorescences in a dioxane matrix of high concentration (10^{-2} mol dm^{-3}), depending on the excitation wavelength (λ_E); one is obtained with excitation at 295 nm and has an emission peak at 437 nm with two shoulders (this band is referred to as A band, (2) in Fig. 1); the other is obtained with excitation at 337 nm and is a structureless band with a peak at 467 nm (called as B band, (3) in Fig. 1). In the lower concentration matrix (10^{-5} mol dm^{-3}) only the A band ((1) in Fig. 1) is observed, irrespective of the

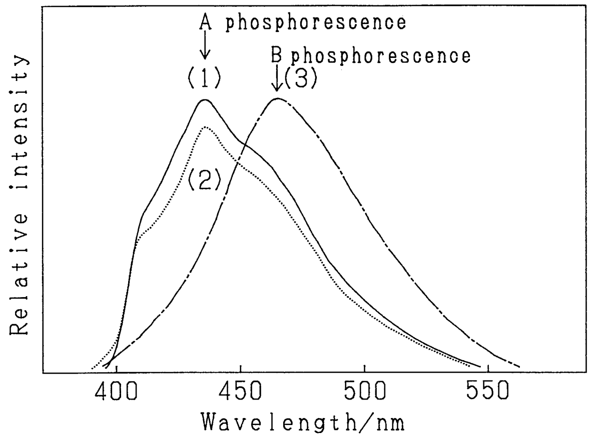


Fig. 1. Phosphorescence spectra of HBA in 1,4-dioxane. Concentration and excitation wavelength: (1) 1.0×10^{-5} mol dm^{-3}, 294 nm, (2) 1.0×10^{-2} mol dm^{-3}, 295 nm, (3) 1.0×10^{-2} mol dm^{-3}, 337 nm.

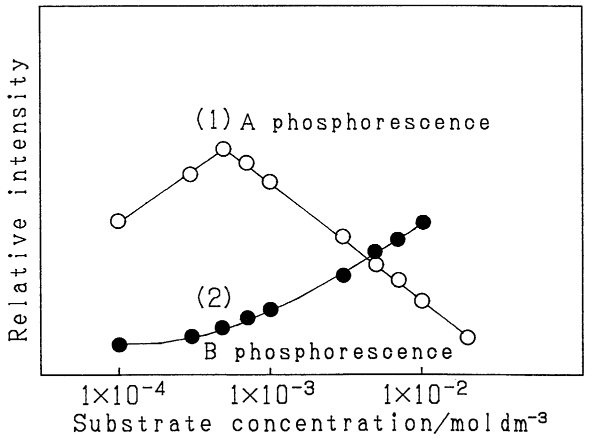


Fig. 2. Substrate concentration dependence of intensities of the A phosphorescence at 434 nm and the B phosphorescence at 460 nm for HBA in dioxane. Excitation wavelength: (1) 300 nm, (2) 358 nm.

Table 1. Dependence of the Intensity Ratio of the A and B Phosphorescence Bands of HBA on Cooling Rate

Cooling rate	Fast[a]	Medium[b]	Slow[c]
I_B/I_A[d]	0.7	1.4	1.9

a), b), c) Final low temperature (77 K) was attained within a few seconds (a), 10 sec (b), and 20 sec (c). d) I_A is the intensity of the A band at 440 nm with excitation at 295 nm. I_B is of the B band at 465 nm with excitation at 344 nm.

excitation wavelength employed. This band well resembles those observed in methanol and cyclohexane.

The emission intensities of the A and B bands are plotted with respect to the substrate concentrations in Fig. 2 for HBA. The intensities of the A band increase with increasing concentration of HBA up to about 5×10^{-4} mol dm^{-3}, and then decrease upon further increasing the concentration. On the other hand, the B band appears at HBA concentrations higher than 5×10^{-4} mol dm^{-3} and becomes stronger with a diminution of the A band. These spectral behaviors are also noted for HAP in dioxane; in this case the A- and B-type bands appear at 435 and 475 nm, respectively. The results mentioned above indicate that the A band is due to the monomeric species of the substrate and the B band arises from a solute–solute interaction, a type of self-association. In order to obtain further evidence for the existence of a solute–solute interaction, the phosphorescence spectra were measured for samples whose final low temperature (77 K) was attained at various cooling rates. The results are shown in Table 1, in which the ratios of the A and the B phosphorescence intensities (I_A and I_B) are presented. As can be seen from this table, the ratio I_B/I_A is clearly dependent on the cooling rate, i.e., the ratio becomes larger with a reduction of the rate. This means that an association of solute molecules takes place upon cooling.

Phosphorescence Excitation Spectra. The phosphorescence excitation spectra for the A and B emission bands of HBA are shown in Fig. 3. The excitation spectrum monitored at 415 nm (A band) has a main peak at 293 nm and a weak band at 333 nm (Fig. 3(1)). On the other hand, the 333 nm band becomes the main band, monitored at 465 nm (Fig. 3(3)). The 293 and 333 nm bands are referred to as the A′ and B′ bands, respectively. In spectrum (2) of Fig. 3, the intensities of the A′ and B′ bands are comparable, in which the monitored wavelength (438 nm) is chosen as being intermediate between the A and B emission band positions. As for HAP, the A′ and B′ bands are at 288 and 330 nm, respectively. This spectrum does not agree with the absorption spectrum measured in dioxane at room temperature. That is, although the absorption spectrum has a band at 283 nm, which corresponds to the A′ and, there is no band corresponding to the B′ band. Though the B′ band might be correlated to the nπ* absorption band, the intensity of the B′ band is too strong to be assigned as being due to an nπ* transition. That the B′ band can not be assigned to the nπ* transition is also supported by the fact that the band is not observed in nonpolar hydrocarbons, such as cyclohexane. The phosphorescence excitation spectrum has also been found to depend on the cooling rate of the sample. The B′ band becomes stronger and the A′ one weaker with the decrease in the cooling rate. The observed behavior of the excitation spectra suggests that at least two chemical species exist in the high concentration dioxane matrix of HBA in the ground state at 77 K. One species, giving the A′ absorption band and the A phosphorescence band, can be regarded as being the monomer of the solute molecule. The other, giving

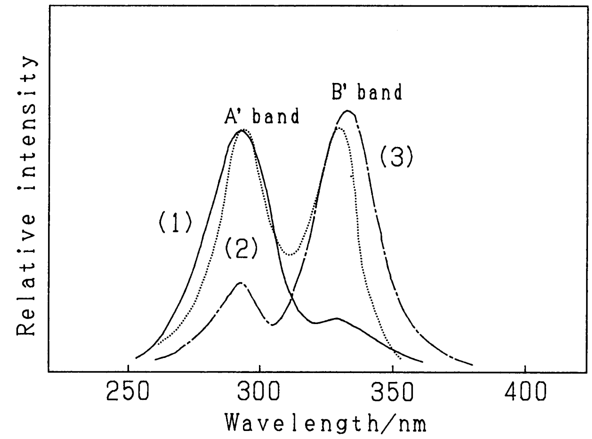


Fig. 3. Phosphorescence excitation spectra of HBA in dioxane. Concentration: 1.0×10^{-3} mol dm^{-3}, Monitored wavelength; (1) 415 nm, (2) 438 nm, (3) 465 nm.

the B′ absorption and B phoshorescence bands, can be regarded as being a solute–solute associated species. In addition, *p*-methoxybenzaldehyde and *p*-methoxyacetophenone, which have no phenolic proton, exhibit only the A phosphorescence bands, even at high concentrations in dioxane matrices, indication that as for the present phenolic and methoxy compounds excimer formations do not occur. Furthermore, the formation of a 1:1 solute–solvent exciplex, such as that found for 4-(dimethylamino)ethyl benzoate in dioxane,[15] can also be ignored in the present systems.

Absorption Spectra. As a possible solute-solute interaction in the present systems, proton-trasferred ion-pair formation can be considered, since HBA and HPA have both proton donating and accepting groups. In order to determine the structure of the associated species, absorption spectroscopic studies have been carried out. In the cases of the proton-transferred ion- pair formation of aromatic hydroxy compounds in the excited singlet and triplet states with bases such as amines, the excitation spectra for the emissions of the ion pair agree with the absorption spectra of the hydroxy compounds. However, this is not the case for both HBA and HAP systems. As mentioned above, the excitation spectra can be interpreted as being due to the presence of two chemical species in concentrated HBA and HAP solutions at 77 K, i.e., the monomeric and the associated species. This indicates that at 77 K the associated species already exist in the ground electronic states of HBA and HAP. However, no evidence for the existence of the ion pair could be obtained from the absorption spectra at room temperature. Unfortunately, the absorption spectra in dioxane at 77 K could not be measured, because of a lack of transparency of the medium. Hence, for the sake of a comparison with the excitation spectra, the absorption spectra of the phenolate ions of HBA and HAP have been measured at room temperature. The results are shown in Fig. 4. In neutral solutions the absorption bands appear around 280 nm, and in the alkaline solutions around 330 nm. The former and the latter absorption bands correspond well with the A′ and B′ bands in the excitation spectra, respectively. In addition, the phosphorescences of the phenolate ions

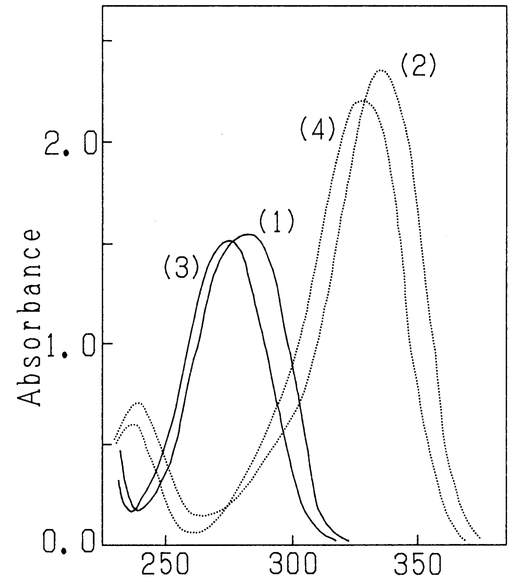


Fig. 4. Absorption spectra of HBA and HAP at room temperature in aqueous dioxane (80 vol%). Concentration: 1.0×10^{-3} mol dm^{-3}, (1) HBA, pH=6.11, (2) HBA, pH=12.00, (3) HAP, pH=6.53, (4) HAP, pH=12.00.

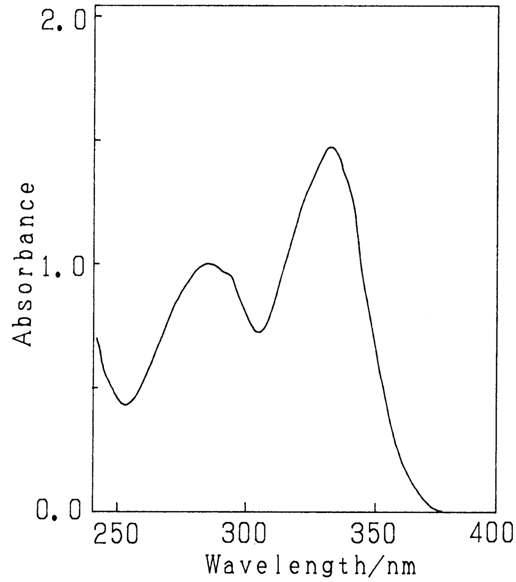
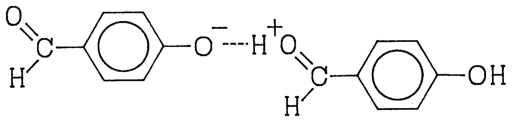


Fig. 5. Absorption spectrum of HBA (10^{-4} mol dm^{-3}) in a mixture of ethanol and methanol (1:1) containing triethylamine (10^{-2} mol dm^{-3}).

of HBA and HAP are very similar to those of the corresponding ion pairs (the B phosphorescence). Furthermore, the absorption spectrum of the HBA–triethylamine system in an alcoholic solution well resembles the excitation spectrnm of HBA, as shown in Fig. 5. According to Baba,[14] at 77 K HBA and triethylamine form the proton-transferred ion pair, the phosphorescence band of which is very similar to the present B phosphorescence. Consequently, it is concluded that HBA and HAP in the ground states form proton-transferred ion pairs in an appropriately high concentration of dioxane matrix, as shown below.



It can be shown that the present solute–solute interaction does not lead to the formation of the trimer or higher aggregates. When a sufficiently dilute solution of HBA or HAP in dioxane (ca. 10^{-4} mol dm^{-3}), from which the B phoshorescence is not detected apparently, is added into the concentrated solution of *p*-methoxybenzaldehyde or *p*-methoxyacetophenone (ca. 10^{-2} mol dm^{-3}), B phosphorescence apparently appears. This emission can be attributed to ion-pair formation between the phenolic and methoxy compounds; such an ion pair has no ability to join the additional phenolic compounds because of their low concentrations.

Solvent Dependence of the Ion Pair Formation. The ion-pair formation of HBA and HAP could not occur in some polar media, e.g., mono and polyhydric alcohols, *N*,*N*-dimethylformamide, dimethyl sulfoxide, as well as nonpolar media. Therefore, the solvent polarities seem not to be a critical factor for ion-pair formation. We have thus examined the effectiveness of some ethers as a suitable solvent for ion-pair formation.

In a tetrahydrofuran (THF) matrix, both HBA and HAP exhibit only the A phosphorescences, regardless of the concentrations and excitation wavelengths. In contrast to these emission spectra, the excitation spectra were found to depend on these factors (Fig. 6) for HBA. The dilute matrix gives the A′ band, whereas the concentrated matrix the B′ band. This is also the case for HAP. The features of the excitation spectra in THF well resemble those in dioxane. This means that in THF an ion pair is formed in the ground state; it then dissociates into monomers in the phosphorescent triplet state or in the excited singlet state prior to the occurence of $S_1 \rightarrow T_1$ intersystem crossing. Analogous behavior has been found when diisopropyl ether and acetaldehyde diethyl acetal are used as a media.

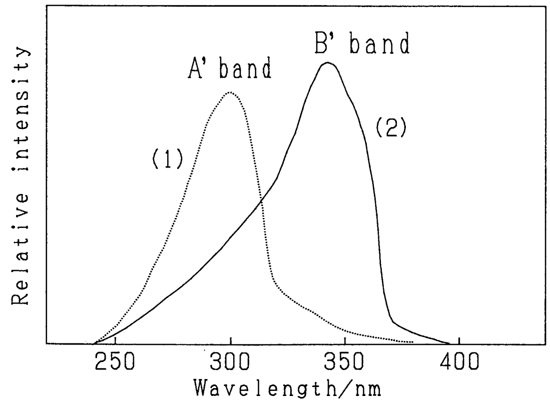


Fig. 6. Phosphorescence excitation spectra of HBA in tetrahydrofuran. (1) Concentration: 1.0×10^{-4} mol dm^{-3}, Monitored at 400 nm, (2) Concentration: 1.0×10^{-2} mol dm^{-3}, Monitored at 455 nm.

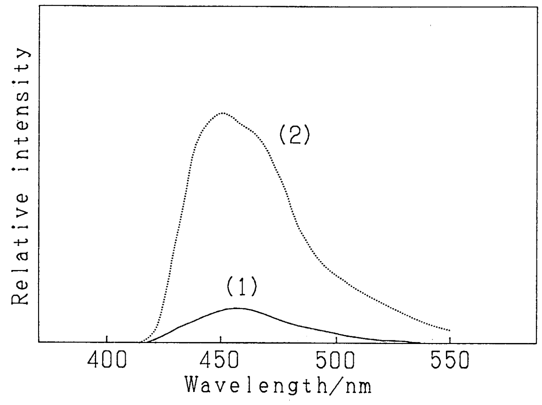
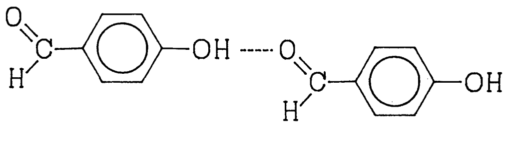


Fig. 7. Phosphorescence spectra of HBA in 1,3-dioxolane. Concentration: 1.0×10^{-4} mol dm^{-3}, Excitation wavelength: (1) 290 nm, (2) 330 nm.

In a 1,3-dioxolane matrix, ion pairs are formed even at concentrations as low as 10^{-4} mol dm^{-3}, as can be seen from Fig. 7. HBA in 1,3-dioxolane exhibits only one phosphorescence band at 451 nm (the B band), irrespective of the excitation wavelengths, i.e., 290 nm (the A′ band) and 330 nm (the B′ band); this indicates the absence of a monomeric species, even in a dilute matrix. This can also be confirmed by the excitation spectrum; that is, no A′ band appears, even though the B′ band is detected by monitoring at any wavelength in the emission band region.

As described above, although there is some differences in the behavior, proton-transferred ion pairs of HBA and HAP are formed in all ethers employed here at low temperature. In view of the observed solvent dependence it can be suggested that a peculiar intermolecular interaction between HBA (or HAP) and ether molecules takes place; thus, the resulting interacting species plays an essential role in ion-pair formation. In this connection, we have recently found that xanthone dimerizes through orbital interactions together with dipole–dipole interactions, and that the dimer has been proposed to take the sandwich like structure facing the carbonyl group and the ethereal oxygen atom.[17)] As for 1,4-dioxane, Suppan et al.[18,19)] noted that its behavior in absorption solvatochromic shifts was anomalous and proposed that in the vicinity of polar solute molecules 1,4-dioxane takes the polar boat form through dipole–dielectric stabilization. As described above, HBA and HAP can form ion pairs with respective partners, *p*-methoxy compounds, even when the *p*-hydroxy compounds are dilute, provided that the concentrations of the methoxy compounds are sufficiently high. From a consideration of this fact, possible hydrogen bonding between the phenols and ethers, -OH···O, can be regarded as not being contributory factor to ion-pair formation. At any rate, further detailed investigations from various points of view need to be performed before the nature of the interactions between the HBA or HAP molecule and ethereal molecules can be clarified.

Hydrogen Bonding. Hydrogen bonding complexation at 77 K should be concerned in view of an earlier report in which the hydrogen-bonded dimer of HBA was found in a concentrated methanol solution at room temperature from measrements of the nπ* absorption band.[13)] Here, it is a question whether the hydrogen-bonded dimer, such as follows, exists at 77 K



or not. It was earlier found from the NMR sectra that phenol did not undergo any intermolecular association in strong polar solvents, such as dimethyl sulfoxide.[20)] On the other hand, several hydroxybenzaldehydes are known to form inter- or intramolecular hydrogen bonds in the solid state.[21)] At room temperature, evidence for solute–solute hydrogen bonding has been derived from the OH stretching vibrational bands in the IR spectra of HBA and HAP in a mixture of carbon tetrachloride and chloroform (7:3). Therefore, equilibrium is established between the monomer and the hydrogen-bonded dimer in both HBA and HAP at room temperature.

In contrast to such behavior at room temperature, a different situation has arisen regarding the phoshorescence behavior at low temperature. No evidence for the occurrence of simple hydrogen bonding between the substrate molecules has been obtained from the phosphorescence spectra at 77 K. A comparison was made between the phosphorescence of HBA in dioxane (A band in Fig. 1) and of *p*-methoxybenzaldehyde. Both spectra agree well with each other with respect to the positions and shapes. Such agreement was also noted between HAP and *p*-methoxyacetophenone. Consequently, it can be considered that equilibria are established between the monomeric species and the ion pairs in ethereal matrices of HBA and HAP at 77 K.

References

1) C. H. Rochester, in "The Chemistry of Hydroxyl Group," Part 1, Chap. 7, Interscience, London (1971).

2) H-. D. Becker, in "The Chemistry of Hydroxyl Group," Interscience, London (1971), Part 2, Chap. 16.

3) R. Stewart, "The Proton: Applications to Organic Chemistry," Academic Press Inc., Orland (1985).

4) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker Inc., New York (1970), p. 293.

5) N. Mataga and Y. Kaifu, *Mol. Phys.*, **7**, 137 (1963).

6) H. Beers, K. H. Grellman, M. Gurr, and A. Weller, *Discuss. Faraday Soc.*, **39**, 183 (1965).

7) A. Matsuzaki, S. Nagakura, and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **47**, 1152 (1974).

8) W. R. Laws and L. Brand, *J. Phys. Chem.*, **83**, 795 (1979).

9) A. Weller, *Naturwiss.*, **7**, 125 (1955).

10) A. Weller, *Z. Elektrochem.*, **60**, 1144 (1956).

11) W. R. Ware, P. R. Shukla, P. J. Sullivan, and R. V. Bremphis, *J. Chem. Phys.*, **55**, 4048 (1971).

12) S. Nagakura, H. Hirota, M. Sumitani, and K. Yoshihara, *J. Am. Chem. Soc.*, **105**, 4220 (1983).

13) H. Inoue and Y. Kato, *Nippon Kagaku Zasshi*, **92**, 772 (1971).

14) H. Baba, *J. Chem. Phys.*, **49**, 1763 (1968).

15) (a) R. J. Visser and C. A. G. O. Varma, *J. Chem. Soc., Faraday Trans. 2*, **76**, 453 (1980). (b) R. J. Visser, C. A. G. O. Varma, J. Konijnenberg, and Ph. Bergwerf, *J. Chem. Soc., Faraday Trans. 2*, **79**, 347 (1983). (c) R. J. Visser, J. Konijnenberg, P. C. M. Weisenborn, and C. A. G. O. Varma. *J. Mol. Struct.*, **114**, 105 (1984). (d) R. J. Visser, P. C. M. Weisenborn, C. A. G. O. Varma, M. P. de Haas, and J. M. Warman, *Chem. Phys. Lett.*, **104**, 38 (1984).

16) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London (1965).

17) T. Hoshi, J. Okubo, Y. Sakaguchi, M. Kobayashi, and H. Inoue, *Ber. Bunsen-Ges. Phys. Chem.*, **93**, 800(1989).

18) M. B. Ledger and P. Suppan, *Spectrochim. Acta*, **23A**, 3007 (1967).

19) P. Suppan, *J. Photochem.*, **18**, 289 (1982).

20) J. G. Traynham and G. A. Knesel, *J. Org. Chem.*, **31**, 3350 (1966).

21) F. Imashiro, S. Maeda, K. Takegoshi, T. Terao, and A. Saika, *Chem. Phys. Lett.*, **99**, 189 (1983).