Hydrogen Bonding and Conformational Change of 2,2′-Pyridil in Polyhydric Solvents

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Hydrogen bonding interaction of di-2-pyridyl diketone (2,2′-pyridil) with polyhydric solvents such as ethylene glycol, propane-1,2-diol, glycerol, and water has been studied by means of u.v. absorption spectroscopy. From the drastic change of the $\pi\pi^*$ bands in these solvents compared with those in other solvents in which 2,2′-pyridil takes the skewed structure, it has been suggested that the hydrogen bonding causes geometrical change in 2,2′-pyridil with variation of the carbonyl–carbonyl dihedral angle. Regardless of solvents, the geometry in the lowest triplet state is deduced from the phosphorescence spectra to be the skewed structure.

Di-2-pyridyl diketone (2,2′-pyridil), as well as benzil, is known to take the skewed structure in which the central bond between the two 2-pyridyl planes are twisted nearly at right angles.[1,2] Although rotamerism of α-diketones in electronic excited states has been the subject of extensive investigations,[3-6] the geometrical change in the ground state owing to external factors has been little reported. Absorption and emission spectra were reported for several α-diketones that possess widely differing carbonyl–carbonyl dihedral angles.[7] For benzil, a benzene analogue of 2,2′-pyridil, the energy barrier of the rotation around the central bond is not so high that it can rotate into the near-planar *transoid*-geometry from the skewed structure, when it is doped in a stilbene crystal.[8]

The absorption spectra of α-diketones are known to be affected by the angle between the planes of the carbonyl groups.[9] Therefore, the geometry of the α-diketones in the ground state can be discussed on the basis of the absorption spectral data obtained by conventional methods. In this paper, solvent effects on the absorption spectrum of 2,2′-pyridil are dealt with, taking into account the conformational change occurring through the formation of hydrogen bonds involving the aza nitrogen and the carbonyl oxygen atoms of 2,2′-pyridil with hydrogen-donating solvent molecules.

Results and Discussion

The u.v. absorption spectra of 2,2′-pyridil were measured in various solvents. As typical examples, the spectra in cyclohexane, ethanol, and ethylene glycol are illustrated in Figures 1 and 2. The bands in Figure 1 are due to the π–π^* transitions, and those in Figure 2 are assigned to the n–π^* transitions of the two types.[10] The shorter wavelength $n\pi^*$ band, appearing around 340 nm, has been assigned to the transition involving the aza nitrogen lone pairs, and the longer wavelength band to the transition involving the carbonyl lone pairs.[10] As seen in Figure 2, both the $n\pi^*$ bands are shifted to shorter wavelengths in hydroxylic solvents. In particular, in ethylene glycol the pronounced blue shift of the n(nitrogen lone pair)–π^* band, $\Delta\tilde{\nu}$(ethylene glycol–cyclohexane) = 1 190 cm^{-1}, was observed, and the absorption maximum of the n(carbonyl lone pairs)–π^* band became unclear as a result of the significant blue shift. Moreover, the absorption intensities decreased appreciably in ethylene glycol. These observations can be interpreted in terms of the formation of hydrogen bonds involving the aza nitrogen and carbonyl lone pairs with the hydrogen-donating solvents.

As seen in Figure 1, the $\pi\pi^*$ bands in cyclohexane and ethanol are similar to each other and the observed minor band shift can be regarded as the ordinary solvent effect. However, the $\pi\pi^*$ spectrum in ethylene glycol differs markedly in shape and intensity from those in ethanol and cyclohexane. The solvents in which 2,2′-pyridil shows anomalous $\pi\pi^*$ absorption bands similar to those in ethylene glycol are propane-1,2-diol, glycerol, and water. These solvents are classified as ‘ Solvents A.’ The single molecule in Solvents A has at least two hydrogen atoms which can participate in hydrogen bonding. On the other hand, in other solvents such as hydrocarbons, monohydric alcohols, ethers, and acetonitrile, the $\pi\pi^*$ bands of 2,2′-pyridil correspond well in positions and in intensities to those of 2-acetylpyridine (ratio of intensities, 2,2′-pyridil : 2-acetylpyridine = 2 : 1). These solvents are classified as ‘ Solvents B.’ Since 2-acetylpyridine can be regarded as a model compound for the half-molecule of 2,2′-pyridil, the $\pi\pi^*$ spectra observed in Solvents B indicate that the 2,2′-pyridil molecule takes the skewed structure in which little π-electronic interaction between the two 2-pyridoyl moieties occurs.

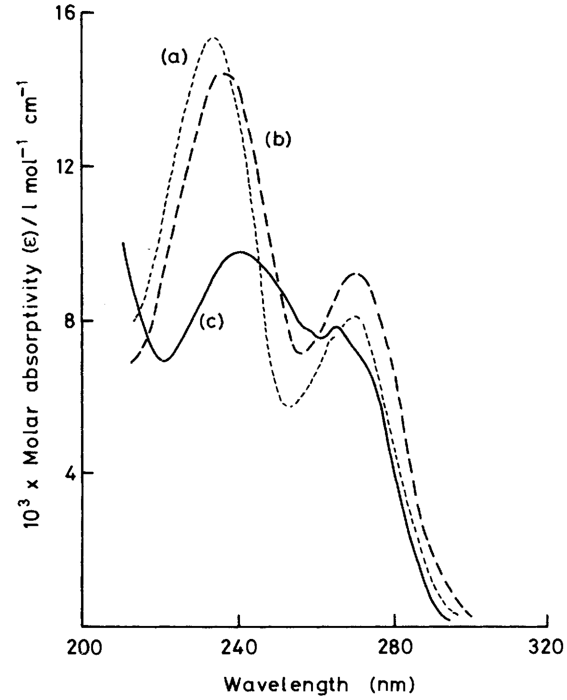


Figure 1. Absorption spectra of 2,2′-pyridil in cyclohexane (a), ethanol (b), and ethylene glycol (c) in the $\pi\pi^*$ region

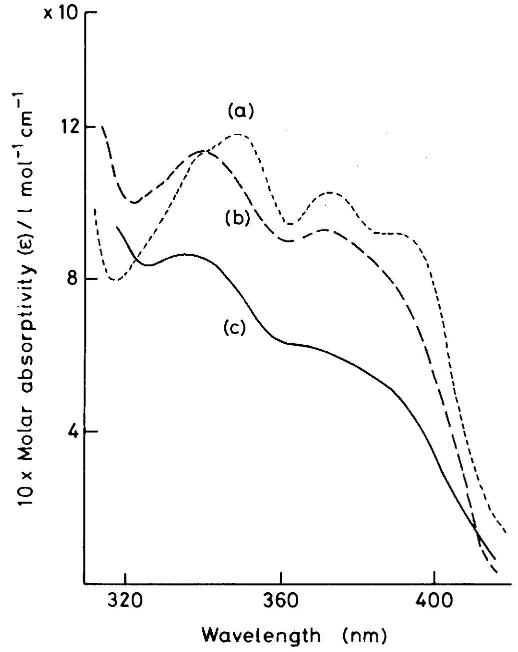
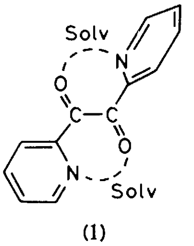


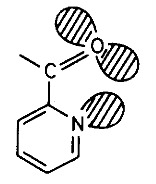
Figure 2. Absorption spectra of 2,2′-pyridil in cyclohexane (a), ethanol (b), and ethylene glycol (c) in the $\pi\pi^*$ region



(I)

In Solvents A, however, the observed spectra strongly suggest that the conformation of the 2,2′-pyridil molecule is affected by the formation of a hydrogen bond with the solvent molecules. The possible conformational change seems to occur by rotation around the central carbonyl–carbonyl bond, deviating from the skewed structure, since the π-electronic system of the 2,2′-pyridil molecule is apparently influenced by the degree of interaction between the 2-pyridoyl moieties. At present, decisive answers cannot be given to the problem of the structure of the hydrogen-bonded complex. Nevertheless, it seems reasonable to suggest that ‘ double hydrogen bonds ’ are formed with the single-solvent molecule, involving two kinds of lone pairs in the different 2-pyridoyl groups as illustrated in (I), because the hydrogen bonding of the single-solvent molecule with the carbonyl and nitrogen lone pairs belonging to the same 2-pyridoyl group is likely to have no effect on rotamerism. In fact, the orbital distribution of the lone pairs in structure (II) is not suitable for the formation of the double hydrogen bonds.

Among the diols used as solvents, butane-1,3-diol, butane-1,4-diol, and pentane-1,5-diol were found to belong to the B group of solvents, in contrast with the 1,2-diols. This fact may be explained as being due to the difference in spacial suitability for forming the double hydrogen bonds, (I). The two hydroxylic hydrogen atoms of the solvent molecule are required to be close together, corresponding spatially to the separation of the lone pairs of the deformed 2,2′-pyridil molecule.



(II)

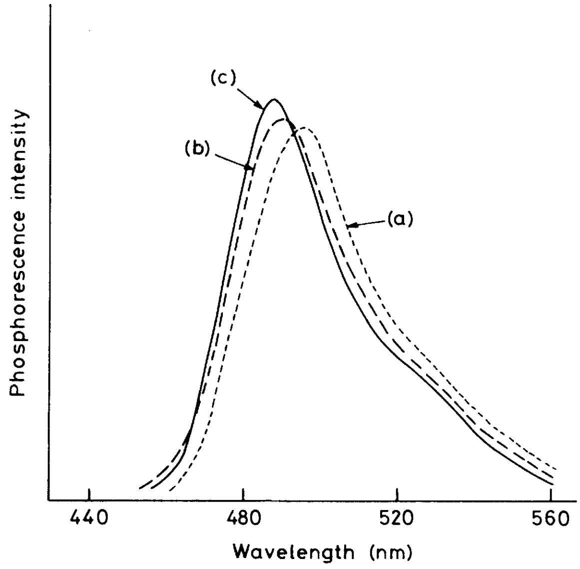


Figure 3. Phosphorescence spectra of 2,2′-pyridil in cyclohexane (a), ethanol (b), and ethylene glycol (c) at 77 K. Concentration = 1.8×10^{-4}M; excitation wavelength = 350 nm

Although 2,2′-pyridil was stable in Solvents B, it was found to change gradually to give pyridine-2-carboxylic acid (2-picolinic acid) in Solvents A (within a few days). The hydrogen bonded complex studied here can be considered to play an essential role in this reaction.

In order to investigate the geometry in the triplet state, the phosphorescence spectra were measured in various solvent matrices at 77 K. As shown in Figure 3, only minor differences were found between Solvents A and B. Therefore, it can be concluded that if the hydrogen bond should be formed, it may not affect the geometry in the triplet state at 77 K, in contrast with the ground state.

Photorotamerism of benzil has been studied widely, and it has been reported that in spite of the solvent, benzil in the triplet state takes the skewed geometry and shows a phosphorescence peak at 530 nm at 77 K, while at higher temperatures it takes the near-planar *transoid* geometry, and shows phosphorescence at 570 nm.^{6,11,12} From a comparison of the positions of the phosphorescence bands for 2,2′-pyridil and benzil, the geometry of 2,2′-pyridil in the triplet state can be considered to be the skewed structure. Recently, we reported phosphorescence results for *cisoid*-benzil and dibenzo[*a*,*d*]-cyclohepta-1,4-diene-10,11-dione, which take a rigid *cisoid*-structure, in ethylene glycol glass at 77 K.^{13} The spectra in Figure 3 are not similar to those of the *cisoid*-benzils, thus indicating that the *cisoid*-geometry can be ruled out for 2,2′-pyridil in the triplet state.

Experimental

2,2′-Pyridil was obtained commercially (Aldrich Chemical Co., Inc.) and was recrystallized from ethanol. 2-Acetylpyridine was obtained from Tokyo Kasei Kogyo Co., Ltd. and was used without further purification.

Absorption spectra were measured at room temperature with a Shimadzu UV-200 spectrophotometer using 1 cm quartz cells. Phosphorescence spectra were recorded on a Shimadzu RF-500 spectrofluorimeter equipped with a rotating sector at 77 K. The solutions of 2,2′-pyridil were prepared immediately before measurements of the spectra.

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