Tautomerism of 1-Hydroxy-2-pyridone and 1-Hydroxypyridine-2-thione in the Excited Triplet State

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Both the title compounds show dual phosphorescence depending on the excitation wavelength and the nature of the solvents at 77 K. 1-Hydroxy-2-pyridone (HP) gives dual emission only in a nonpolar matrix, whereas dual emission of 1-hydroxypyridine-2-thione (HPT) was observed even in polar and hydrogen-bonding solvents as well as in a nonpolar matrix. From a comparison with the phosphorescence behaviour of 2-ethoxypyridine 1-oxide and 2-ethylthiopyridine 1-oxide, which have structures corresponding to the enol and enethiol isomers of the tautomeric HP and HPT, respectively, it is concluded that tautomerization taking place in the excited triplet state is responsible for the dual phosphorescence of the title compounds. Further supporting evidence for this conclusion is obtained from the measurements of the phosphorescence lifetimes and phosphorescence excitation spectra. HPT is much more subject to tautomerization to its enethiol isomer form than HP. This is explained on the basis of the fact that the thiocarbonyl group is more polar and more polarizable than the carbonyl group.

Despite widespread investigations of the ground-state behaviours of cyclic hydroxamic acids, there have been only a few studies on the excited-state behaviour of these compounds.[1] Thus, we have embarked on a systematic study of the excited-state properties of 1-hydroxy-2-pyridone (HP) and related compounds, analogues of aspergillic acid with antibacterial properties,[2] to scrutinize the photophysical and photochemical processes of these hydroxamic acids.

Studies of heteroaromatic tautomerism are important not only for a comprehensive understanding of the reaction mechanism of tautomeric heterocycles but also for the correct interpretation of biochemical processes involving these compounds.[3] The tautomeric equilibrium of HP and its sulphur analogue, 1-hydroxypyridine-2-thione (HPT), in the ground state has been well studied and shown to lie practically completely in favour of the keto and thione forms, respectively, by i.r. and u.v. spectrometric[4] as well as photoelectron spectroscopic measurements,[5] whereas little attention has been paid to the tautomerism of HP and HPT in excited states. We have recently reported that HP tautomerizes to its enol isomer, 2-hydroxypyridine 1-oxide, in the excited triplet state.[6] Since thiones have been known to display anomalous excited-state behaviour,[7] we are interested in examining the triplet-state properties of HPT with a thiocarbonyl group in the molecule as an extension of our investigations on the tautomeric equilibrium of cyclic hydroxamic acids in the triplet state. In this paper we discuss the dual phosphorescence of HP and HPT in glassy matrices, with our attention focusing primarily on the tautomerism of these two compounds.

Results and Discussion

Dual Phosphorescence of HP.—HP in an alcohol glass exhibits an excitation wavelength-independent phosphorescence spectrum with a maximum at 464 nm whose behaviour is identical with that of 1-ethoxy-2-pyridone (EP), which has a structure corresponding to the keto isomer of the tautomeric HP, as shown in Figure 1 [curves (a) and (b)]. The phosphorescence excitation spectra of HP were determined by monitoring the emission at various wavelengths and agreed well with the first absorption band of HP existing in the keto form, which is a maximum at 304 nm in the same solvent (methanol–ethanol 1 : 1 v/v) at room temperature. On the other hand, the phosphorescence of 2-ethoxypyridine 1-oxide (EPO), whose structure corresponds to that of the enol isomer of HP, has an emission maximum at *ca.* 440 nm which is much weaker in intensity compared with those of HP and EP, thus providing no evidence

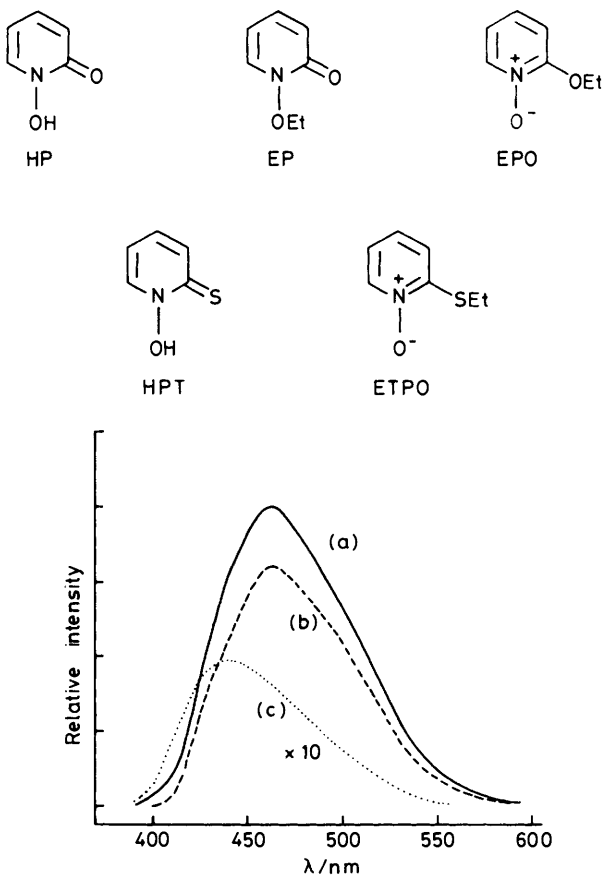


Figure 1. Phosphorescence spectra of HP (a), EP (b), and EPO (c) in methanol–ethanol (1 : 1 v/v) at 77 K. Excitation wavelengths (nm): (a) 307; (b) 307; (c) 307; [HP], [EP], and [EPO] 1.5—2.0 × 10^{-4} M

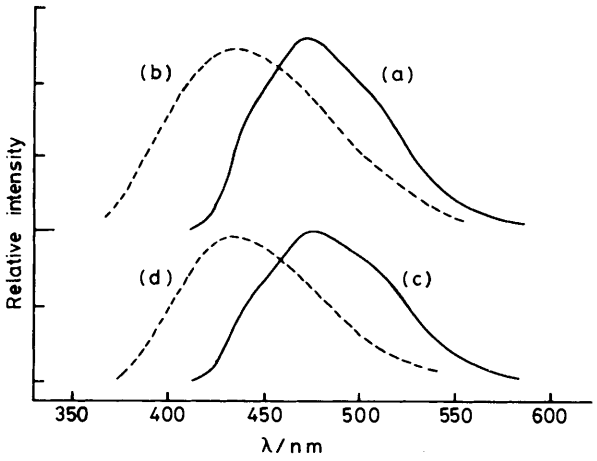


Figure 2. Phosphorescence spectra of HP (a), (b), EP (c), and EPO (d) in methylcyclohexane at 77 K. Excitation wavelengths (nm): (a) 310; (b) 279; (c) 310; (d) 279; [HP], [EP], and [EPO] 1.5—2.0 × 10^{-4} M

keto isomer enol isomer

for the existence of the tautomeric equilibrium of HP in the triplet state in an alcohol glass. We have also observed an excitation wavelength-independent phosphorescence of HP at 467 nm in n-butyronitrile at 77 K. In addition, the excitation spectrum for this phosphorescence corresponds to the first absorption band of HP with a maximum at 310 nm in n-butyronitrile, indicating no occurrence of the tautomerization to the enol isomer in an n-butyronitrile glass.

In contrast with the behaviour in a polar glassy matrix, HP gives dual phosphorescence depending on excitation wavelength in methylcyclohexane at 77 K as presented in Figure 2. Shorter-wavelength excitation increases the intensity of the short-wavelength emission relative to that of the long-wavelength emission, resulting in a shift of the emission maximum to shorter wavelengths. Figure 2 shows that the short- and long-wavelength phosphorescence spectra are similar in both emission maximum and intensity to those of EPO and EP, respectively, suggesting the existence of a tautomeric equilibrium between the keto isomer, 1-hydroxy-2-pyridone, and the enol isomer, 2-hydroxypyridine 1-oxide, in the triplet state. This possibility of tautomerization is further supported by the finding that the excitation spectra for the short- and long-wavelength phosphorescences nicely correspond with those for the EPO and EP phosphorescence, respectively, as seen from Figure 3. The excitation wavelength-dependent phosphorescence of HP in a methylcyclohexane glass, therefore, can be interpreted as the superposition of the phosphorescence from the keto and enol isomers. From these observations, we conclude that tautomerization to the enol isomer form occurs to an appreciable extent in the triplet state.* The failure to observe the enol isomer spectrophotometrically in the ground state suggests that the ground-state enol isomer is thermodynamically less stable and reverts to the more stable keto isomer. Because of overlapping of intense fluorescence (peak at 365 nm) with weak phosphorescence of the two tautomers in a methylcyclohexane glass, we could not determine the phosphorescence lifetimes.

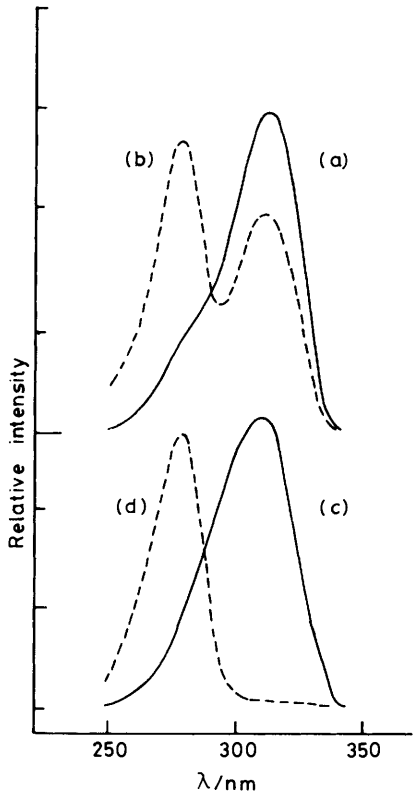
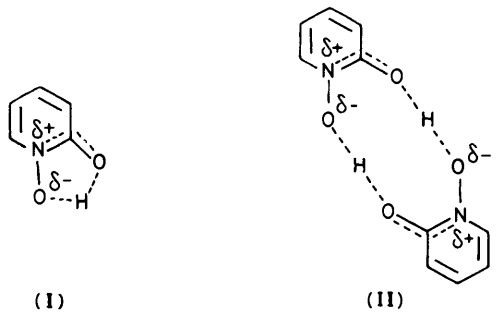


Figure 3. Phosphorescence excitation spectra (not corrected) of HP (a), (b), EP (c), and EPO (d) in methylcyclohexane at 77 K. Emission wavelengths (nm): (a) 525; (b) 435; (c) 477; (d) 435



(I) (II)

There are two conceivable tautomerization processes to give the enol form. One is an intramolecular process (**I**) which was suggested for the tautomeric interconversion of 2-pyridone in the gas phase,[9] and the other an intermolecular process involving a dimer (**II**). Although we have no definitive evidence concerning the mechanism of tautomerization, the observation that HP is strongly hydrogen-bonding intramolecularly as a monomer in nonpolar solvents[4b] suggests that an intramolecular process is very likely. The measurement of the HP

* In this regard, it is worth noting that HP undergoes a solvent dipole-induced rotational isomerization about the N–O bond of the molecule in the excited singlet state at room temperature.[8] The rotational isomerization of HP do not take place in methylcyclohexane either at room temperature or at 77 K. In addition, this rotational isomerization is suppressed to a great extent in a polar glassy matrix at 77 K, indicating that the rotational isomerization in the excited singlet state occurs to a negligible extent under the present experimental conditions for measuring phosphorescence spectra.

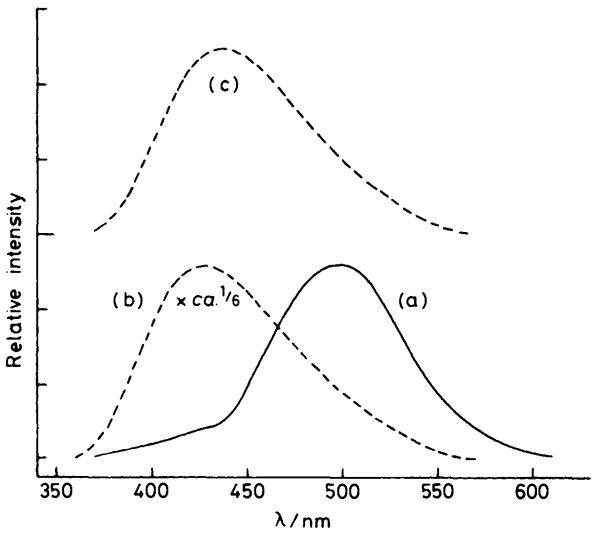


Figure 4. Phosphorescence spectra of HPT (a), (b) and ETPO (c) in methanol–ethanol (1:1 v/v) at 77 K. Excitation wavelengths (nm): (a) 350; (b) 293; (c) 300; [HPT] and [ETPO] 2 × 10^{-4}M. Intensities have been adjusted for the sake of clarity

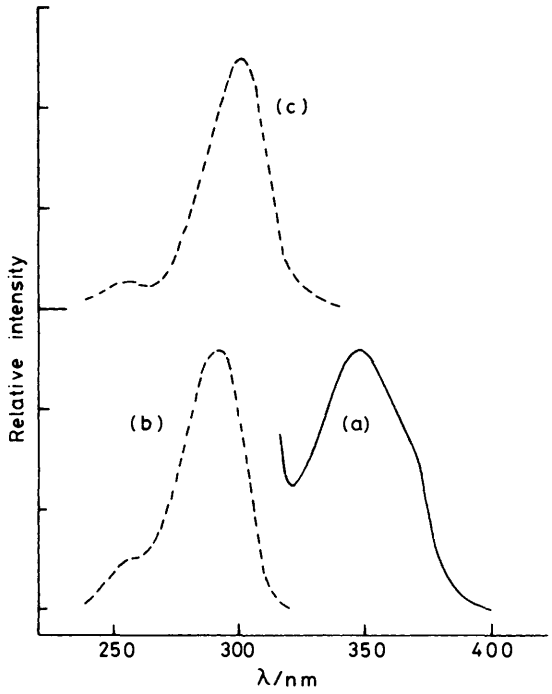


Figure 5. Phosphorescence excitation spectra (not corrected) of HPT (a), (b) and ETPO (c) in methanol–ethanol (1:1 v/v) at 77 K. Emission wavelengths (nm): (a) 498; (b) 429; (c) 438. Intensities have been adjusted for the sake of clarity

phosphorescence at low concentration (10^{-4}M) and at low temperature (77 K) provides further support for this intramolecular process. The facts that polar solvents weaken the intramolecular hydrogen bond of HP, and that intramolecular proton transfer is made unfavourable by the solvation of the carbonyl oxygen atom in the pyridone skeleton *via* hydrogen bonds in protic solvents[10] might be responsible for the failure to observe the tautomerism of HP in a polar and proton-donating matrix.

Dual Phosphorescence of HPT.—The unexpected dual phosphorescence of HPT was obtained depending on excitation wavelength in an alcohol glass at 77 K as illustrated in Figure 4. This phosphorescence behaviour is in contrast with that of HP in the same rigid glassy matrix. While excitation at the first absorption band of HPT gives long-wavelength phosphorescence with a maximum at 498 nm, short-wavelength phosphorescence with a maximum at 429 nm is observed on excitation near the second absorption band. The short-wavelength emission is intense by a factor of *ca.* 6 compared with the long-wavelength one. We have found that no photoproducts derived from HPT are responsible for this dual emission.* HPT which was prepared by an alternate route[2g] also gave dual phosphorescence with the same intensity ratio, suggesting that this duality of emission is not due to impurities. The excitation spectrum of the long-wavelength phosphorescence very closely resembles the first π,π^* absorption band of HPT,† implying that the emitting state is the first triplet state of the pyridinethione form of the tautomeric HPT because HPT has been known to exist predominantly in the thione form in the ground state.[4c] Unfortunately we could not compare the phosphorescence behaviour of HPT with that of 1-ethoxypyridine-2-thione having a structure corresponding to the thione isomer because we have failed to synthesize this compound. On the other hand, a comparison of the short-wavelength phosphorescence and its excitation spectra with those of 2-ethylthiopyridine 1-oxide (ETPO), whose structure corresponds to that of the enethiol isomer of HPT, shows that this short-wavelength emission may originate from the enethiol isomer, 2-mercaptopyridine 1-oxide, formed by tautomerization in the triplet state (Figure 5).

Before we attribute the short-wavelength phosphorescence to the emission from the enethiol isomer form of the tautomeric HPT, the possibility of phosphorescence from the second triplet (T_2) state should be discussed because the excitation spectrum for the short-wavelength emission follows the second absorption band of HPT closely and because emission from upper excited states is of considerable interest and has received much recent attention.[7] If we assume that the short-wavelength phosphorescence comes from the T_2 state, the energy gap of *ca.* 3 200 cm^{-1} between T_1 and T_2 makes it unlikely that this emission originates from the thermally repopulated T_2 state at 77 K,[11] and that a mechanism similar to that for the S_2 fluorescence of azulene and its derivatives[7b] is operative as in the case of benzil and its related compound to which the energy gap hypothesis may be applied.[12] Thus it is very improbable that the short-wavelength emission of HPT is assigned to the T_2 phosphorescence. A relatively intense phosphorescence band of HPT makes the determination of emission lifetime possible although fluorescence interferes with the lifetime measurement of the long-wavelength phosphorescence to some extent. Lifetimes of the short- and long-wavelength phosphorescences were determined to be 30 and 10 ms, respectively, in an alcohol glass at 77 K. The lifetimes are of the same order of magnitude, indicating that the emitting state is of largely π,π^* character because phosphorescence from the $^3(n,\pi^*)$ state of thiones has a lifetime of the order of 0.1—0.01 ms at 77 K.[7c] Therefore, the long- and short-wavelength phosphorescences observed in an alcohol glassy matrix are attributable to those of the thione and enethiol isomers of the tautomeric HPT, respectively.

* The products formed by u.v. irradiation of HPT were isolated and checked for their phosphorescence. The emissions of these photoproducts agreed with neither the long- nor the short-wavelength phosphorescence of HPT.

† HPT exhibits no n,π^* transition in the visible region even at a concentration of 2 × 10^{-2}M.

Absorption and phosphorescence spectral data of HPT[a]

Solvent	λ_{abs}[b]/nm (ε/l mol^{-1} cm^{-1})	λ_{phos}[c]/nm (λ_{ex}/nm)	τ_{phos}[c]/ms	Intensity ratio[d]
Methanol–ethanol (1:1 v/v)	282 (19 000), 347 (6 400)	429 (293), 498 (350)	30, 10	*ca.* 6
Ether–ethanol (1:2 v/v)	283 (21 000), 350 (6 600)	430 (293), 497 (353)	25, 10	*ca.* 5
n-Butyronitrile	282 (21 000), 350 (7 000)	424 (294), 500 (332)	30, 15	*ca.* 8
Methylcyclohexane	291 (19 000), 372 (4 300)	427 (305)	30	

[a] [HPT] 1—3 × 10^{-4}M. [b] At room temperature. [c] At 77 K. [d] Intensity ratio of the short- to long-wavelength phosphorescence.

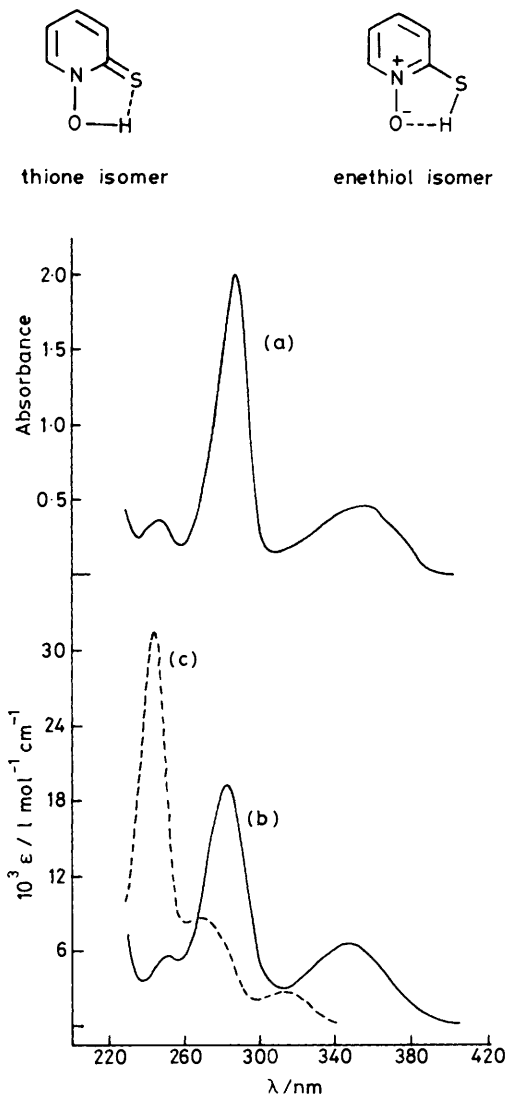


Figure 6. Absorption spectra of HPT (a), (b) and ETPO (c) in methanol–ethanol (1:1 v/v) at different temperatures: (b), (c) room temperature; (a) 100 K; [HPT] 6 × 10^{-5}M

However, there still remains the reasonable possibility of ground-state tautomerization which can explain the observed dual emission of HPT since the excitation spectrum for the enethiol isomer form has been obtained. To shed light on this point, we have measured the absorption spectrum of HPT in an alcohol glass at low temperature (100 K). For comparison the absorption spectrum of ETPO was obtained in the same solvent at room temperature. As shown in Figure 6, one can only find a

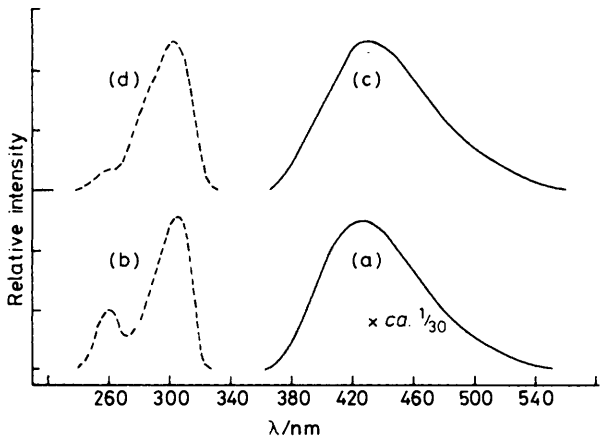
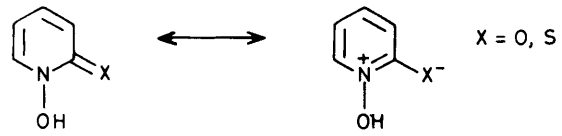


Figure 7. Phosphorescence and phosphorescence excitation (not corrected) spectra of HPT (a), (b) and ETPO (c), (d) in methylcyclohexane at 77 K. Excitation wavelengths (nm): (a) 305; (c) 303. Emission wavelengths (nm): (b) 427; (d) 430; [HPT] and [ETPO] 2 × 10^{-4}M. Intensities have been adjusted for the sake of clarity

small difference between the room- and low-temperature absorption spectra of HPT, showing that tautomerization to the enethiol isomer occurs to a negligible extent in the ground state at low temperature. This means that the less stable enethiol isomer is generated in a detectable amount by the triplet-state proton transfer (tautomerization) followed by phosphorescent relaxation under photostationary conditions and reverts to the more stable thione isomer when the excitation light was cut off. The excitation spectral behaviour of HP in a methylcyclohexane glass already mentioned can be explained similarly although attempts to measure the low-temperature u.v. spectrum of HP in this nonpolar solvent were unsuccessful owing to the poor transparency of methylcyclohexane glass.

The dual phosphorescence of HPT was obtained also in other polar glassy matrices. The Table summarizes the phosphorescence spectral data including lifetimes and intensity ratios. A comparison of dual emission observed in an alcohol glass with that in other polar glasses indicates that the short- and long-wavelength emissions are assigned to the enethiol and thione isomers in any polar matrix, respectively, and that tautomerization also takes place to a similar extent in other polar solvents at 77 K. Interestingly, HPT in methylcyclohexane at 77 K has only the short-wavelength phosphorescence with no dependence upon excitation wavelength. This emission corresponds well to the short-wavelength phosphorescence observed in an glassy alcohol matrix as illustrated in Figure 7 which includes phosphorescence and phosphorescence excitation spectra of ETPO in a methylcyclohexane glass. There is an appreciable difference in emission intensity between the phosphorescences of HPT and ETPO, whereas the emission maxima of these two spectra are consistent with each other.



(III) (IV)

This difference in emission intensity is larger in methylcyclohexane than in an alcohol. This is accounted for by the finding that the phosphorescence intensity of HPT is not much affected by the polarity and hydrogen-bonding ability of solvents, but a solvent change from an alcohol to methylcyclohexane decreases the emission intensity of ETPO by a factor of *ca.* 5. Because the phosphorescence lifetime in methylcyclohexane is compatible with the short-wavelength phosphorescence lifetime in an alcohol, we conclude that the emission observed in a nonpolar glass originates from the enethiol isomer form generated by tautomerization in the triplet state. Since HPT has been known to be hydrogen-bonded intramolecularly as a monomer in nonpolar solvents,[4b] it is highly probable that the presence of a strong intramolecular hydrogen bond markedly accelerates tautomerization in the triplet state and makes an intramolecular process of tautomerization predominant as in the case of HP.

A comparison of the phosphorescence behaviour of HP with that of HPT reveals that HPT undergoes tautomerization to its enethiol isomer with greater facility than HP in both polar and nonpolar glassy matrices. In addition, the finding that the extent of tautomerization in the triplet state is affected by the polarity and hydrogen-bonding ability of solvents suggests the solvation effect plays a crucial role in determining the ease of tautomerization.*

All physical and chemical evidence[13] indicates that the thiocarbonyl group is inherently more polar and more polarizable than the carbonyl group. This means that the dipolar formula (**IV**) contributes more to the thiocarbonyl group than to the carbonyl group. The larger acidity of HPT (pK_a 4.6, lit.,[4c] 4.67) than that of HP (pK_a 6.0, lit.,[4b] 6.0) is consistent with a more highly ionized bond in the thione case. It is reasonable to assume that the tautomerization of HPT takes place to greater extent owing to the greater contribution of (**IV**) to HPT than to HP. On the other hand, the solvation of the carbonyl oxygen and thiocarbonyl sulphur atoms of (**III**) and (**IV**) in polar and hydrogen-bonding solvents should inhibit the tautomerization of HP and HPT to a great extent. One might expect that this solvation effect is reflected in the difference in the extent to which tautomerization occurs in polar and nonpolar solvents although the tendency that HPT tautomerizes to a larger extent may not be altered in both solvents. These considerations of the ground-state properties of HP and HPT can nicely explain the difference in the extent of tautomerization in the triplet state between HP and HPT, implying that the ease of tautomerization of these two molecules in the triplet state depends not only on the ground-state properties but also on the solvation in the ground state. The fact that the tautomerization of HP and HPT occurs to a negligible extent in the ground state demonstrates that the enol and enethiol isomers tend to be stabilized not in the ground state but in the triplet state.

* While dielectric constants of organic solvents increase slightly with decreasing temperature, the extent to which dielectric constants increase is greater in polar solvents than in nonpolar ones. Thus it is likely that there is not much difference in polarity of solvents at room temperature and at 77 K.

Experimental

EPO was prepared from 2-ethoxypyridine,[14] then recrystallized from ether–dioxane, m.p. 70—72 °C (lit.,[14] 71—73 °C). EP was prepared by treatment of EPO with ethyl iodide in ethanol and purified by distillation at reduced pressure affording a light tan oil whose spectral data were consistent with those reported by Dinan and Tieckelmann.[15] HP was synthesized by the method of Newbold and Spring,[14] then recrystallized from dioxane–benzene and sublimed under vacuum, m.p. 149—150 °C (lit.,[14] 149—151 °C). The synthesis of HPT was accomplished by treatment of the adduct, formed from the reaction between 2-bromopyridine 1-oxide and thiourea, with aqueous sodium carbonate.[2g] The crude HPT was purified by repeated recrystallization from aqueous ethanol, m.p. 71.0—72.5 °C (lit.,[2g] 68—70 °C). The structures of these compounds prepared were also established by their i.r. and n.m.r. spectra. ETPO was prepared by the reaction of 2-bromopyridine 1-oxide with ethanethiol according to the analogous method to that of Shaw *et al.*[2g] Repeated recrystallization from ethyl acetate gave needles, m.p. 104—105 °C (Found: C, 53.7; H, 5.8; N, 8.65; S, 20.3. C_7H_9NOS requires C, 54.2; H, 5.8; N, 9.0; S, 20.6%); δ_H (100 MHz; $CDCl_3$) 8.17 (1 H, d, *J* 7 Hz), 7.40—6.92 (3 H, m), 2.91 (2 H, q, *J* 7 Hz), and 1.42 (3 H, t, *J* 7 Hz).

All solvents were checked for their luminescence and showed no significant emission. All solvents in which phosphorescence spectra were recorded became clear glassy matrices at 77 K.

U.v. absorption spectra at room temperature were measured with a Shimadzu UV-210A spectrophotometer. The low-temperature u.v. spectrum was obtained using a Shimadzu UV-360 spectrophotometer. The sample cooling was achieved by employing a home-made liquid nitrogen cryostat with the sample solution contained in a 1 cm square quartz cell. Phosphorescence and phosphorescence excitation spectra were taken on a Shimadzu RF-500 spectrophotofluorimeter (3.5 mm diameter quartz tube) with a cylindrical rotating sector which chops the excitation beam at 77 K. Phosphorescence lifetimes were determined on a Shimadzu RF-502 spectrophotofluorimeter equipped with a rotating sector at 77 K. For the acquisition of phosphorescence decay curves, a mechanical shutter was used to cut off the excitation light. The decay signals were fed to a transient memory (Kawasaki Electronica PMR-120) equipped with a recorder output. Because a period of 10 ms was required for cutting off the excitation light, the decay curve after 10 ms was utilized to determine the phosphorescence lifetime.

Acidity constants (pK_a) were spectrophotometrically estimated in Britton–Robinson buffer at 25 °C.

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