Preliminary Note

Solvent effects upon the phosphorescent triplet states of cyanopyridine and pyridinecarboxaldehyde

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(Received April 6, 1978)

The interest in the pyridine molecule stems from its being the simplest monoazine derivative of benzene. Attempts to characterize the nature of the lowest triplet state have remained an active area of research since the initial work by Hoover and Kasha on pyridines and substituted pyridines [1]. Although pyridine itself does not exhibit phosphorescence from the lowest excited triplet state, many of the substituted pyridines do in fact show radiative properties and have been the subject of study by several workers. Some notable examples of such substituted pyridines which have been studied are aminopyridine [2], monomethylpyridine, dimethylpyridine and trimethylpyridine [3], hydroxypyridine [4], cyanopyridine (CNP) [5] and pyridinecarboxaldehyde (PCA) [6].

Goodman [7] has suggested that the intervening $^3n,\pi^*$ state in azabenzenes should lie between the $^1\pi,\pi^*$ and the phosphorescent $^3\pi,\pi^*$ states. Recent studies seem to indicate that the energy of such a $^3n,\pi^*$ state is dependent upon solvent interactions with the non-bonding orbital. In some cases an inversion of the triplet levels can occur such that the $^3n,\pi^*$ and $^3\pi,\pi^*$ states interchange simply by change of solvent [8].

In this communication we report a study involving the pyridines CNP and PCA which are substituted at the 2, 3 and 4 positions. These guest molecules were substituted into host matrices of *p*-xylene, *p*-dichlorobenzene (DCB) and *p*-dibromobenzene (DBB). The study involves the technique of phosphorescence microwave double resonance (PMDR) which has been shown to be a powerful method in the characterization of the nature of the phosphorescent triplet state.

The PMDR method relies on the different populations usually achieved among the triplet sublevels in the phosphorescent triplet state with continuous optical pumping. Upon sweeping the resonance energies of the triplet sublevels, the perturbation of the population will cause a phosphorescence intensity change. The analysis of the recovery dynamics in reaching steady state conditions can yield information regarding the phosphorescence decay rates, while the resonance energies directly yield the zero field splittings (zfs)

TABLE 1

Zfs frequencies and total phosphorescence rate constants for cyanopyridines in several hosts

Guest		Host		
		p-Xylene	p-Dichlorobenzene	p-Dibromobenzene
2-Cyanopyridine	Transitions	—	4233	5327
	(MHz ± 10 MHz)	3539	3384	3585
		—	—	1713
	k_1 (s^{-1} ± 10%)	12	1.8	100
	k_2 (s^{-1} ± 10%)	1.1	2.2	57
	k_3 (s^{-1} ± 10%)	0.23	0.30	15
3-Cyanopyridine	Transitions	—	4468	4516
	(MHz ± 10 MHz)	3460	3394	3346
		1638	1078	1116
	k_1 (s^{-1} ± 10%)	20	3.7	62
	k_2 (s^{-1} ± 10%)	1.2	2.5	56
	k_3 (s^{-1} ± 10%)	0.54	0.36	27
4-Cyanopyridine	Transitions	5780	5720	5917
	(MHz ± 10 MHz)	4040	4040	3801
		—	—	2162
	k_1 (s^{-1} ± 10%)	20	190	17
	k_2 (s^{-1} ± 10%)	3.8	230	2.8
	k_3 (s^{-1} ± 10%)	0.36	4.8	0.43

due to electron spin–spin dipolar interaction. Both the phosphorescence decay rates and the zfs can be correlated to the nature of the triplet state [9].

The isomers of CNP and PCA were purchased commercially, subjected to multiple vacuum distillations and stored under an inert atmosphere at 0 °C. p-Xylene (Phillips Research grade) was found to be free of impurity emission and was used without further purification. DCB and DBB were re-crystallized several times and zone refined for over 300 passes. Single crystals of the hosts were grown with guests at about 1 mol.% concentrations in a standard Bridgman furnace.

The zfs and total phosphorescence decay rate constants as measured by the PMDR method are shown in Table 1. In all cases CNP exhibited zfs which are characteristic of $^3\pi, \pi^*$ states, although in 4-CNP the zfs were about 20% greater than in 2-CNP and 3-CNP. In 4-CNP the phosphorescence decay rate constants are generally significantly larger than in 2-CNP and 3-CNP, except for 4-CNP in DBB. These results seem to suggest that in 4-CNP some mixing of the $^3\pi, \pi^*$ state with a nearby $^3n, \pi^*$ state might exist, rather than a complete reversal of the energies of the two excited states. As postulated by Hoover and Kasha, the energies of the $^3A_1(\pi,\pi^*)$ and $^3B_1(n,\pi^*)$ states of 4-CNP are about 100 cm^{-1} apart [1]. The possibility of

TABLE 2

Phosphorescence origin, zfs and total phosphorescence decay constants for pyridine-carboxaldehydes in several host matrices

Guest	Host		
	p-Xylene	p-Dichlorobenzene	p-Dibromobenzene
2-Pyridinecarboxaldehyde			
0,0 (cm^{-1})	24 270	24 925	24 760
Transitions	6537	9130	9290
(MHz ± 10 MHz)	4234	8668	6185
	—	—	—
k_1 (s^{-1} ± 10%)	80	1800	1600
k_2 (s^{-1} ± 10%)	22	120	60
k_3 (s^{-1} ± 10%)	3.2	24	60
3-Pyridinecarboxaldehyde			
0,0 (cm^{-1})	24 250	25 000	24 810
Transitions	6907	6350	12 120
(MHz ± 10 MHz)	5933	4322	11 558
	—	—	—
k_1 (s^{-1} ± 10%)	1750	1500	1800
k_2 (s^{-1} ± 10%)	31	41	100
k_3 (s^{-1} ± 10%)	215	68	60
4-Pyridinecarboxaldehyde			
0,0 (cm^{-1})		24 290	24 300
Transitions		6869	4579
(MHz ± 10 MHz)		—	—
k_1 (s^{-1} ± 10%)		2000	2300
k_2 (s^{-1} ± 10%)		130	27
k_3 (s^{-1} ± 10%)		44	110

state mixing with such separation energies is not uncommon and in fact is the basis for the explanation given for the unusually large zfs observed in substituted benzaldehydes [9]. This type of mixing, which is allowed, occurs particularly when two states of close promixity couple via out-of-plane vibrations which results in enhanced radiationless processes.

The results of the study of PCA in the three hosts are shown in Table 2. The trend in the 0,0 band energies of 2-PCA, 3-PCA and 4-PCA is consistent with that obtained by other workers [6]. The phosphorescence spectra taken at 1.4 K show a definite progression due to the carbonyl vibration which occurs at about 1700 cm^{-1}. (It should be noted that our results contradict those reported by Padhye and Jahagirdar [6] in which the $^3n,\pi^*$ phosphorescence of PCA was attributed to the pyridine nitrogen.) In many cases the progression is so intense that it extends through the third harmonic. For 4-PCA, vibrations arising from ring modes are observed, although the carbonyl progression is an order of magnitude more intense. In the 2-substituted and 3-substituted isomers the magnitude of the zfs and the

total phosphorescence decay rate constants imply that there is a predominance of the $^3n,\pi^*$ state with no mixing by the $^3\pi,\pi^*$ state and that the phosphorescence intensity originates from the carbonyl n,π^* state. As stated above, an analysis of the phosphorescence spectra of the isomers of PCA shows that in a given host the out-of-plane ring modes are predominantly more intense in 4-PCA than in 2-PCA and 3-PCA. Additionally, the smaller total rate constants and zfs in 4-PCA due to the mixing of the states by pseudo Jahn–Teller interactions all support the idea that the nature of the lowest $^3n,\pi^*$ triplet state in 4-PCA may be largely mixed by the $^3\pi,\pi^*$ state. In fact, since the zfs of 4-PCA very nearly approach those of 4-CNP, the substitutional effect at the 4 position might cause the $^3\pi,\pi^*$ state to red shift, which would result in an even larger interaction with the phosphorescent $^3n,\pi^*$ state.

Although the zfs are nearly alike in 4-PCA and in 4-CNP the total phosphorescence decay rate constants are an order of magnitude larger in the 4-PCA. In addition, for 4-PCA the rate constants appear to be insensitive to the influence of external heavy atoms (*cf.* Tables 1 and 2). The large variation in 2-PCA and 3-PCA as a function of the various hosts seems to be consistent with that observed in the substituted benzaldehydes [9]. The slightly larger zfs for PCA in the DBB host can be attributed to an external spin–orbit contribution to the zfs. However, it should be noted that the actual magnitude of the spin–orbit effect on the zfs still remains uncertain in the light of recent findings in a study involving $^3n,\pi^*$ states of cyclo-alkanones in halogenated and non-halogenated solvents [10].

In summary, the nature of the phosphorescent triplet state of 2-CNP, 3-CNP and 4-CNP is π,π^* and is relatively independent of the solvent type. In PCA, however, the lowest triplet state which resides on the carbonyl group is strongly n,π^*, particularly with the 2 and 3 isomers. For 4-PCA vibronic coupling mixes the lowest $^3n,\pi^*$ state with the intervening π,π^* triplet state.

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