Fluorescence and Phosphorescence of 2- and 4-Aminobenzophenone

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Summary The electronic absorption and emission properties of 4-aminobenzophenone, are found to be dependent on temperature and matrix.

THE phosphorescence of 4-aminobenzophenone (I) in isopropyl alcohol and in cyclohexane, at 77° K, has been reported.[1] The lifetimes of the $T_1 \rightarrow S_0$ emission of (I) in polar and non-polar matricies were related to differences in triplet-state configuration (π,π^* and n,π^*) and photoreactivity in these solvents at room temperature. Use of the luminescence of (I) and 2-aminobenzophenone (II) to detect small quantities of these compounds formed on irradiation of benzanilide (III)[2] has revealed several interesting aspects of the emission properties of (I) and (II) (Tables 1—3) which were not reported by Porter and Suppan.[1]

TABLE 1

Absorption maxima of (I) in various solvents

	EtOH	EPA	Cyclohexane	3-Methylpentane	Polystyrene
298° K	3325 Å	3400	3050	3020	3150
77° K	—	3400	—	3470	3250

TABLE 2

Luminescence of (I) and (II) at 77° K in various matrices*

	EtOH	EPA	Cyclohexane	3-methylpentane	Poly styrene	
(I)	4400	4350	4680	4680	none	Fluorescence
	4800	4700	4400	4800	4400	Phosphorescence
(II)	4700			4900		Fluorescence
	none			none		Phosphorescence

* Wavelength of maximum emission in Å.

My data for the phosphorescence of (I) in ethanol and in cyclohexane, at 77° K, are in agreement with those reported.[1] In addition, however, I have observed the following:

(1) A previously unreported fluorescence of (I) and (II) in rigid matricies, at 77° K. No fluorescence was observed at room temperature in fluid solution. These results indicate that intersystem crossing in (I) and (II), at 77° K, is not 100% efficient, as is the case for most ketones.

(2) A bathochromic shift in the long-wavelength charge-transfer (c.t.) transition of (I) in rigid hydrocarbon glasses relative to fluid hydrocarbon solution. I have no well-established rationalization for this observation. Possibilities include (a) aggregation of (I) into clusters at low temperature, (b) association of (I) with traces of water present in the solvent, (c) a change in geometry of (I) which lowers the energy of its c.t. transition. A bathochromic shift of the absorption maximum of all-*trans*-retinal (III) in 3-methylpentane containing a trace of hydrochloric acid has recently been reported by Irving and Leermakers.[3]

(3) The phosphorescence of (I) in glass-forming hydrocarbon solvents differs in wavelength and lifetime from that reported[1] for rigid (crystalline) cyclohexane, and is similar to that observed in polar glasses (EtOH and EPA). This observation is expected on the basis of the change in absorption spectrum of (I) in the hydrocarbons on cooling. A much smaller bathochromic shift of the absorption maximum of (I) is observed in polystyrene film on cooling to 77° K.

(4) The fluorescence of (I) is observed in rigid cyclohexane but not in polystyrene at 77° K. In the former case disposition and solvation of (I) in the crystalline matrix is uncertain. In both cases, the fine structure and lifetime of the phosphorescence of (I) suggest that its triplet state has a considerable degree of (n,π^*) character. The comparison of the room temperature and 77° K data in polystyrene is in accord with my hypothesis that some movement of (I), either translational or intramolecular motion, is required for the observation of a large bathochromic shift of its c.t. transition in hydrocarbon glasses.

TABLE 3

Luminescence yields and lifetimes† of (I) in various matrices*

	EPA‡	EtOH	Cyclohexane	3-methyl pentane	Polystyrene
Φ_F	0·6	0·6	—	0·2	—
t_F (sec.)	—	$4{\cdot}3 \times 10^{-9}$	—	$3{\cdot}7 \times 10^{-9}$	—
Φ_P	0·4	0·2	—	0·03	0·4
t_P (sec.)	—	0·26	0·05	0·22	0·072

* Luminescence quantum yields are accurate to ±30%.

† Fluorescence and phosphorescence lifetimes were measured at the Du Pont Company on instruments constructed by P. C. Hoell.

‡ Diethyl ether : isopentane : ethanol, 5 : 5 : 2.

The dramatic temperature-induced spectral changes observed for (I) emphasize the dangers in relating spectroscopic measurements, in rigid media, at 77° K, to photoreactivity at room temperature in fluid solution.

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[3] C. Irving and P. A. Leermakers, *Photochem. Photobiol.*, 1968, **7**, 665.