formed on initial association, Displacement appears to involve formation of a considerably higher energy pentacoordinate species.[2,7]

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Temperature Effects on the Luminescence of Benzophenone in Polymers

Sir:

Benzophenone has been studied extensively both as a triplet-state sensitizer and for its photochemical reactivity. Saltiel and coworkers[1] recently reported that in degassed carbon tetrachloride solutions benzophenone and several other ketones exhibit phosphorescence and delayed thermal fluorescence at 296°K. For benzophenone, approximately 10% of the total emission was attributed to delayed fluorescence. Borisevich and Gruzinskii[2] reported earlier a comparable delayed fluorescence for benzophenone vapor. The possible presence of significant populations of excited singlet-state ketone molecules in equilibrium with triplet-state molecules could be of great significance to the photochemistry of these molecules because reactions previously attributed to ketones in their triplet state might actually occur from the excited singlet state.

Although the results of Saltiel, *et al.*, and Borisevich and Gruzinskii are consistent with their interpretation, it is also possible that the "delayed fluorescence" is actually due to thermally activated energy transfer to a diffusing impurity with an excited state of higher energy and shorter lifetime than benzophenone. Indeed, the phosphorescence lifetime of benzophenone in fluid solvents has been shown to vary with concentration,[2,3] and the spectral distribution of the phosphorescence[1-3] does not agree with the previously published low-temperature phosphorescence spectrum.[4] Because of the importance of delayed thermal fluorescence to the interpretation of the photochemistry of benzophenone (and other ketones), we have investigated the effects of temperature on the luminescence of benzophenone in polymers that prevent molecular diffusion. We have been able to establish that benzophenone does emit delayed thermal fluorescence at 300°K and that the spectrum of this emission is an approximate mirror image of the structured singlet–singlet n, π^* absorption spectrum. The use of polymer matrices has also provided insights into the effects of temperature and matrix on the triplet-state lifetime of benzophenone.

Our experimental techniques are essentially the same as reported previously.[5] Spectroquality carbon tetrachloride (MCB) and zone-refined benzophenone (Princeton Organics PAR Grade) were used as received. The emission spectra were corrected for instrument spectral response with an Aminco spectrophotofluorometer (Model 4-8202) having a corrected spectra attachment (Model 4-8210). All of the emission spectra for polymer samples were recorded with a phosphoroscope to exclude scattered excitation.

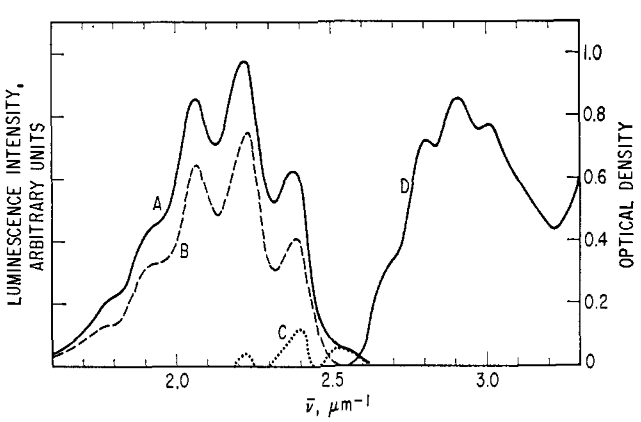

Figure 1. Absorption (curve D) and quanta-corrected delayed luminescence (curves A, B, and C) spectra of benzophenone in polystyrene at 300°K (A and C), 197°K (B), and 77°K (D). Curves A and C are plotted on the same intensity scale. Curve C is the delayed thermal fluorescence spectrum.

Delayed Fluorescence. In agreement with Saltiel, *et al.*,[1] we find that at 300°K the luminescence spectrum of benzophenone in carbon tetrachloride exhibits an extra band on the high-energy side of the phosphorescence, with a peak height roughly $^1/_7$th that of the 0–0 phosphorescence band. In poly(methyl methacrylate), I, poly(α-methylstyrene), II, poly(α,β,β-trifluorostyrene), III, and polystyrene, IV (curve A in Figure 1), at 300°K, we observe the same spectra as in CCl_4, except for a solvent shift. The ratio of the 0–0 phosphorescence band to the 0–3 and 0–4 bands is much larger in our corrected spectra than in the corrected spectra reported by Saltiel, *et al.*,[1] and by Clark, Litt, and Steel.[6] We believe our spectra are the true room-temperature emission spectra because of their agreement (after correction for delayed fluorescence) with the low-temperature spectra in these polymers (curve B in Figure 1) and the agreement of the latter with the previously reported low-temperature phosphorescence spectra.[4] Our observation of the same luminescence spectrum for varying wavelength of excitation (290–360 nm) and for several different rigid polymers rules out the possible contribution of impurities to the spectrum.

The assignment of the band at 2.52 μm^{-1} to delayed fluorescence is reinforced by our observation that it is actually one of several thermally activated emission bands appearing between 2.6 and 2.1 μm^{-1}. The thermally activated component of the emission spectrum (curve C in Figure 1) was obtained: (1) by subtracting from curve A a low-temperature phosphorescence spectrum that was recorded at low resolution to duplicate the band width of curve A and (2) by normalizing the two spectra at 2.07 μm^{-1}, where the relative contribution of the delayed fluorescence is minor. The resulting difference spectrum, which we assign to delayed fluorescence, is in fact an approximate mirror image of the structured singlet–singlet n, π^* absorption spectrum of benzophenone in IV (curve D in Figure 1).

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Phosphorescence Lifetimes. The triplet state lifetime τ_p of benzophenone in liquid hydrocarbon solvents can generally be related to the rate constant for photoreduction.[6,7] In benzene, however, τ_p is anomalously short (5.4 μsec at 304°C).[6] This anomalous solvent effect has been attributed to (1) diffusion-controlled quenching by photochemically generated transient impurities,[8] (2) a rapid reversible photoreduction,[7] and (3) the reversible formation of an adduct diradical.[1,9] By using a matrix such as III that has phenyl rings that presumably can interact with the benzophenone solute in the same manner that benzene does, yet prevents molecular diffusion over a wide temperature range, it should be possible to evaluate the above mechanisms.

We observe a relatively long lifetime (1.0 msec) for the phosphorescence of benzophenone in III at 300°K, which by itself suggests that the first mechanism above is important in fluid benzene. In addition, we find that τ_p for benzophenone in benzene increases significantly upon cooling the solvent below its melting point. However, we also observe relatively large values of τ_p at 300°K for benzophenone in I (1.0 msec),[10] II (0.7 msec), and IV (0.65 msec), even though these polymers have alkyl hydrogen atoms available for abstraction from the polymer chain. Apparently, there is a steric requirement for the hydrogen abstraction that is restricted by the polymer matrix. Melhuish has shown directly, using flash spectroscopy, that I hinders the photoreduction of benzophenone.[11] Thus, our data indicate that if the second or third mechanism listed above is important there must be a strong steric requirement for the interaction between the carbonyl group and the benzene ring that is hindered in rigid polymer matrices but not in fluid benzene.

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The Structure of Cancentrine: A Novel Dimeric Benzylisoquinoline Alkaloid

Sir:

We report here the structure of cancentrine (F_{22}), the yellow alkaloid of *Dicentra canadensis* (Goldie) Walp.[1,2] The composition of cancentrine, **1**, its *O*-methyl ether, **2** (from **1** by the Rodionov method[3]), and its *O*-acetate, **3**, were established by high-resolution mass spectrometry.[4] The following physical properties were recorded: **1**, mp 238°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 3450 and 1665 cm^{-1} hydroxyl and carbonyl, respectively; $\lambda_{\max}^{\mathrm{EtOH}}$ 213, 230 (sh), 268, 291 (sh), 330 (sh), and 435 mμ; log $\epsilon_{\max}$ 4.80, 4.63, 4.32, 4.22, 3.62, and 3.82, respectively. The 100-MHz pmr spectrum of cancentrine has signals corresponding to three aromatic methoxyl groups and one *N*-methyl group but no *C*-methyl or methylenedioxy groups. The presence of one basic and one nonbasic nitrogen in cancentrine was deduced from the analysis of its hydrochloride and from paper electrophoresis and the presence of one phenolic hydroxyl group from an examination and comparison of the ir, uv, and pmr spectra of **1**, **2**, and **3**. The *N*-methyl group was shown to be both the basic center of the alkaloid and part of a modified morphine[5] unit by means of physical and chemical methods.

Cancentrine methiodide undergoes Hofmann degradation to the methine **4**[4] (mp 230°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 3450 and 1660 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 227, 270, and 435 mμ; log $\epsilon_{\max}$ 4.61, 4.38, and 3.75, respectively), which upon hydrogenation (H_2–Pt) and methylation (diazomethane) gave the dihydromethine-*O*-methyl ether **5**[4] (mp 189°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1660 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 208, 230 (sh), 270, 330 (sh), and 433 mμ; log $\epsilon_{\max}$ 4.57, 4.37, 4.28, 3.61, and 3.77, respectively). The hydrobromide of **5** forms golden yellow orthorhombic crystals from methanol and these were used for an X-ray single-crystal structure analysis.[6]

There were four molecules per unit cell (space group $P2_1\,2_1\,2_1$) with dimensions of a = 10.639 (2), b = 12.036 (4), and c = 26.979 (7) Å. The observed density was 1.366 g/cm^3 and the calculated value 1.379 g/cm^3. The reflections with $2\theta > 135°$ for Cu Kα radiation were measured using the stationary-crystal–stationary-counter method. The 2475 reflections with I (counts) $> B$ (background counts) $+ 3\sqrt{B}$ were considered observed and used in the analysis. The 1034 reflections below the above level were considered unobserved.

The structure was solved by locating the Br–Br vectors in the sharpened Patterson function and the light atoms in successive Fourier syntheses. The structure was refined by least-squares methods to an R, the usual residual, of 0.13 using individual isotropic thermal parameters, and to an R of 0.072 using anisotropic thermal parameters. No attempt was made to locate the hydrogen atoms, nor is the absolute configuration implied in structure **5**.

The three C–N bonds about nitrogen in the *N,N*-dimethyl group average 1.502 ± 0.010 Å which is close to the value for a C–N single bond. However the N–C_{25} distance of 1.346 ± 0.011 Å is significantly shorter than a single bond and indicates definite double bond character. The bonds N–C_{25}–C_{24}–C_7–O all have distances consistent with a conjugated system (*cis-s-trans-β*-amino enone), which, being part of a dibenzoxapine, is believed to be responsible for the long-wavelength absorption in the visible region[7] observed in the alkaloid and its derivatives.

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