Perturbation of the Benzil Ground and Excited State Geometries at Low Temperatures in Hydrocarbon Glasses

By Tai-Shan Fang, Ronald E. Brown, and Lawrence A. Singer*

(Department of Chemistry, University of Southern California, Los Angeles, California 90007)

Summary The benzil phosphorescence in methylcyclohexane (MCH) and isopentane (IP) glasses is dominated by emission from the benzil crystal at concentrations $>10^{-4}$ M, below which the phosphorescence from monomeric species is: MCH, λ_{max} 580 nm from T_1-planar$\rightarrow S_0$ planar, and IP, λ_{max} 530 nm from T_1-skewed$\rightarrow S_0$-skewed; excitation spectra show that the absorbing geometry of the absorbing ground state species is planar in MCH but skewed in IP.

In 1950, Leonard and Blout[1] deduced from electronic absorption spectra that the ground state of benzil resembles two independent benzoyl fragments rotating around the central C–C bond. Recent dipole moment measurements ($\mu = 3{\cdot}73$ D in benzene at 25 °C) indicate that the PhCO planes intersect at 98° in a skewed conformation.[2] A near-skewed geometry is found in the benzil crystal where the carbonyls make a dihedral angle of 111° 36′.[3]

In fluid media, benzil and other nonrigid 1,2-dicarbonyls appear to emit from *trans*-planar S_1 and T_1 states of the n,π^* configuration.[4–7] Morantz and Wright[5] suggest that skewed $\rightsquigarrow$ planar relaxation occurs immediately after excitation of benzil and a large Stokes shift is noted in the fluorescence (5650 cm^{-1} in 3-methylpentane at 300 K).[7] In agreement, Arnett and McGlynn[7] have shown that 1,2-dicarbonyls possessing planar or very nearly planar ground state geometries have small Stokes shifts (dimesityl diketone, 400 cm^{-1}).

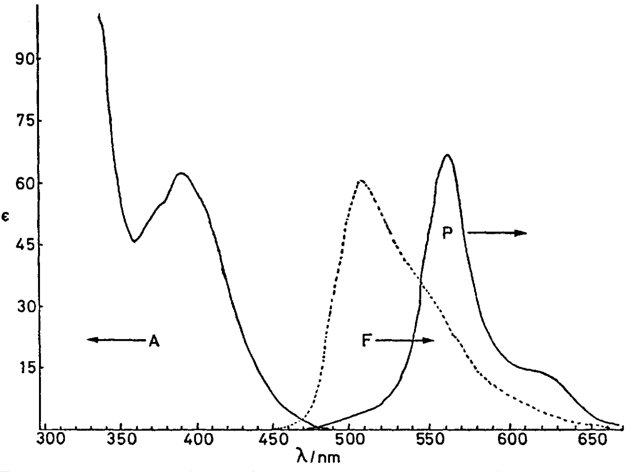

Figure 1. The absorption and normalized emission spectra (fluorescence, . . ; phosphorescence, ———) of benzil in methylcyclohexane at 298 K.

Unfortunately, the similar clarification of the role of photorotamerism in benzil in rigid glasses at low temperature[8] has been retarded by complications such as substrate crystallization[9] and matrix perturbations. We describe herein our observations on the benzil emissions in methylcyclohexane (MCH) and isopentane (IP).

Figure 1 shows the absorption and emission[10] spectra of benzil in MCH at 298 K. The phosphorescence spectrum red-shifts from 560 to 570 nm with slight cooling due to loss of thermal delayed fluorescence[11] which appears as a small high-energy shoulder in the room temperature spectrum (Figure 2). Otherwise, the phosphorescence spectra of dilute benzil solutions in MCH ($\leqslant 5 \times 10^{-4}$ M) do not change down to the glass transition temperature ($T_g = 147$ K). The excitation spectrum† of this single emission between 150 and 298 K corresponds to the absorption spectrum shown in Figure 1. Similar observations are noted in IP ($T_g = 112$ K). Thus, dilute solutions of benzil in MCH and IP show phosphorescences from geometrically relaxed T_1's above the T_g's in agreement with the Morantz and Wright model.[5]

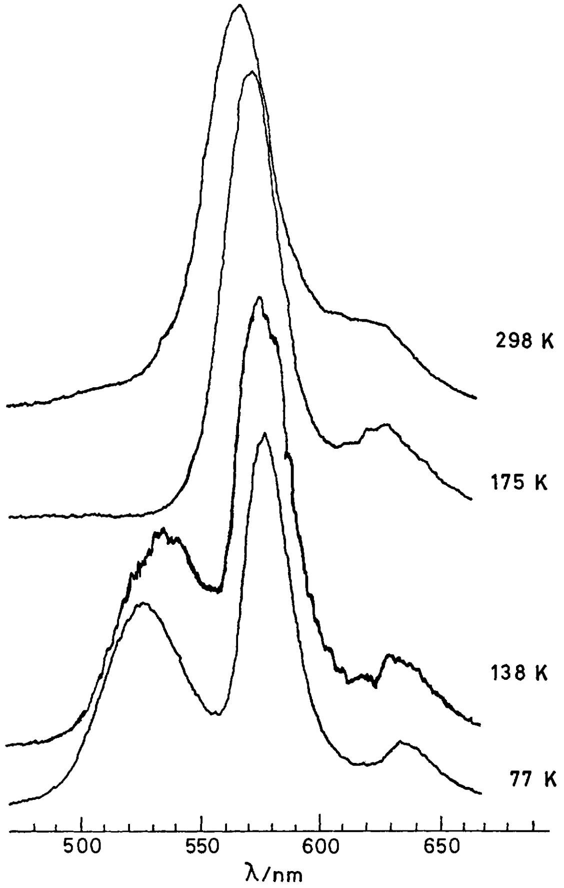

Figure 2. The phosphorescence spectra of 5·0 × 10^{-3} M benzil in liquid (>147 K) and glassy (<147 K) methylcyclohexane. Spectra were recorded using a sampling gate 2 μs wide established 40 μs after nitrogen laser excitation (ref. 10).

---

† Excitation spectra were recorded in photostationary experiments using a conventional American Instrument Co. Spectrofluorimeter. Spectra were corrected for lamp output.

Concentrated solutions of benzil in MCH reveal the onset of a short wavelength emission (λ_{max} *ca.* 530 nm) $\geqslant T_g$ with increasing concentration leading to higher appearance temperatures. A *ca.* 10^{-2} M benzil solution shows this new emission at *ca.* 190 K. The new emission increases relative to the long wavelength emission as the temperature is lowered towards T_g, and below that point little further change is noted.

The short and long wavelength emissions have different lifetimes (*e.g.*, at 77 K: 530, *ca.* 5·0 ms; 570, *ca.* 2·5 ms). Above the T_g, similar excitation spectra are observed for the two emissions but below the T_g, they differ as shown in Figure 3.

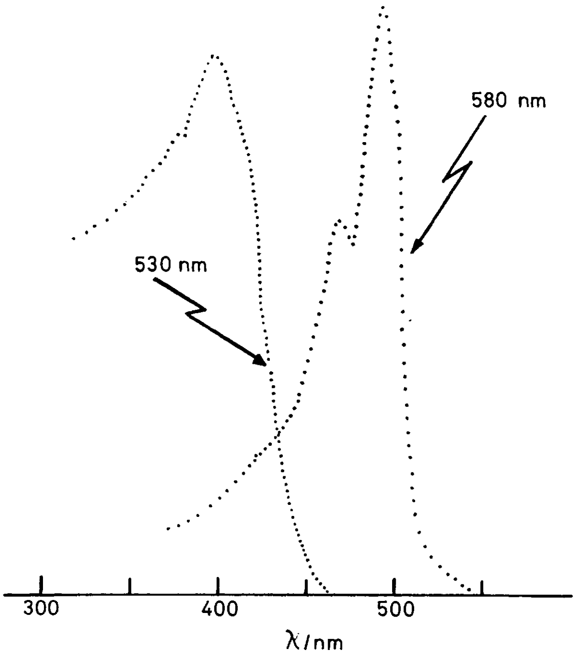

FIGURE 3. Excitation spectra for the short (λ_{max} 530 nm) and long (λ_{max} 580 nm) wavelength phosphorescences from benzil in methylcyclohexane at 77 K. Spectra are corrected for lamp output.

We assign the short wavelength emission to the benzil crystal which has a green (λ_{max} *ca.* 500 nm, emission) phosphorescence and a maximum in its absorption spectrum near 400 nm.[12] Note that the absorption spectrum of the crystal is almost indistinguishable from monomeric benzil dissolved in liquid hydrocarbons.

Crystallization of benzil also readily occurs in liquid IP at concentrations $>10^{-4}$ M. For example, at $2{\cdot}5 \times 10^{-4}$ M, the crystal emission appears at *ca.* 140 K.

Dilute solutions of benzil in MCH below the T_g show a single phosphorescence band (λ_{max} *ca.* 580 nm). The excitation spectrum of this emission differs markedly from that above T_g with a maximum noted near 490 nm (Figure 3). We assign this spectrum to excitation of a planar ground state benzil.[‡] This excitation spectrum is invariant with irradiation time which rules out photopumping by the sequence S_0 (skewed) $\longrightarrow$ S_1 (skewed) $\rightsquigarrow\rightsquigarrow$ T_1(planar) $\longrightarrow S_0$ (planar), where S_0 (planar) is matrix trapped. We conclude that the MCH matrix imposes a planar, or near planar, geometry on the monomeric benzil ground state.

In an IP glass ($<$112 K), only the short wavelength emission is noted with solutions ranging from $5{\cdot}0 \times 10^{-3}$ to $5{\cdot}0 \times 10^{-6}$ M. The excitation spectrum of this emission is independent of concentration and corresponds to the absorption spectrum of a skewed benzil. Above the T_g, solutions $<10^{-4}$ M in benzil show only the long wavelength emission (T_1-planar) while more concentrated solutions reveal mixed crystal and monomeric phosphorescences. If, as is likely, the IP glasses with 10^{-5}—10^{-6} M benzil contain only monomeric benzil structures, then the skewed $\rightsquigarrow$ planar relaxation in the excited states is inhibited in this glass.

These observations indicate that geometric perturbations of ground and excited state structures by hydrocarbon matrices can vary from glass to glass with occasional dramatic consequences as in benzil. Also, care must be exercised to avoid complications from substrate crystallization at the temperatures required to form the hydrocarbon glasses.

We gratefully acknowledge the financial support of the U.S. Army Research office

(*Received*, 21*st October* 1977; *Com.* 1099.)

[‡] Two models for the planar ground state structure in benzil are dimesityl diketone (ref. 7) and benzil doped in a stilbene crystal (ref. 12). The excitation spectrum of the 580 nm emission shown in Figure 3 is similar to the reported absorption spectra for the above models in both spectral distribution and vibrational structure.

[1] N. J. Leonard and E. R. Blout, *J. Amer. Chem. Soc.*, 1950, **72**, 484.

[2] C. W. N. Cumper and A. P. Thurston, *J.C.S. Perkin II*, 1972, 106.

[3] C. J. Brown and R. Sadanaga, *Acta Cryst.*, 1965, **18**, 158.

[4] T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1967, **89**, 4380.

[5] D. J. Morantz and A. J. Wright, *J. Chem. Phys.*, 1970, **53**, 1622; 1971, **54**, 692.

[6] J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, *J. Amer. Chem. Soc.*, 1974, **96**, 4385.

[7] J. F. Arnett and S. P. McGlynn, *J. Phys. Chem.*, 1975, **79**, 626.

[8] W. G. Herkstroeter, J. Saltiel, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1963, **85**, 482.

[9] M. Almgren, *Photochem. and Photobiol.*, 1969, **9**, 1.

[10] Emission spectra were obtained by selective sampling of the photomultiplier signal using a Princeton Applied Research Model 160 Boxcar Integrator following nitrogen laser excitation (337 nm, *ca.* 10 ns pulse width) of samples degassed and sealed in Pyrex 1 cm^2 cuvettes: see R. E. Brown, K. D. Legg, M. W. Wolf, L. A. Singer, and J. H. Parks, *Analyt. Chem.*, 1974, **46**, 1690 for further details.

[11] Because the S_1 and T_1 are $n\pi^*$ in configuration, the energy splitting between them is small enough for the thermal activation $S_1 \rightsquigarrow T_1$ to occur at room temperature. From the temperature dependence of the $\Phi_{\Delta_f}/\Phi_{\Delta_p}$, we estimate $\Delta E(S_1 - T_1) = 5{\cdot}7 \pm 0{\cdot}4$ kcal mol^{-1}: T. S. Fang, R. E. Brown, and L. A. Singer, unpublished results.

[12] S. Ch. Bera, R. Mukherjee, and M. Chowdhury, *Indian J. Pure Appl. Chem.*, 1969, **7**, 345; *J. Chem. Phys.*, 1969, **51**, 754.