CHEMISTRY LETTERS, pp. 683-686, 1980.

THE TRIPLET GEOMETRY OF BENZIL

Hiroyasu INOUE, Tsunehisa MORI, and Tadamitsu SAKURAI
Department of Applied Chemistry, Faculty of Technology, Kanagawa University,
Kanagawa-ku, Yokohama 221

Benzil shows dual phosphorescence in an ethylene glycol glass at 77 K. The short-lived phosphorescence at 504 nm is assigned to near-planar transoid geometry. Evidence indicates that the long-lived one appearing three maxima at 402 nm, 427 nm, and 460 nm is due to medium imposed near-planar cisoid geometry.

The geometries of the benzil ground and excited states have been accepted extensive attention. In the ground state a near-skewed geometry is found in the benzil crystal where the carbonyls make a dihedral angle of 111 .[1)] Several descriptions are available concerning the triplet geometry of benzil, it is found to be near-planar transoid conformation.[2-6)] Recently, Singer et al[7,8)] noted that the role of photorotamerism in benzil in low temperature glasses has been complicated by sustrate crystallization and matrix imposed geometric restrains. Previously, Hammond et al[9)] suggested the existence of the cisoid triplet along with the transoid triplet as for β-naphthil.

In this paper we examine the photorotamerism of benzil in an ethylene glycol glass at 77 K. Ethylene glycol was chosen as a medium, because in it benzil underwent the unusual photoreaction.[10)]

Phosphorescence spectra were recorded on a Shimadzu RF-500 spectrofluorimeter at liquid nitrogen temperature. Excitation wavelength is 330 nm.

The phosphorescence of benzil in a benzene glass is a structureless band with a maximum at 517 nm. However, in an ethylene glycol glass phosphorescence spectrum shows four maxima at 402 nm, 427 nm, 460 nm, and 504 nm (Fig. 1). As shown in Fig. 1, the relative intensities of the maxima change drastically when the rate of rotation of the sector is varied. With fast chopping rate the maximum of the phosphorescence appears at 504 nm, while three maxima appear at 402 nm, 427 nm,

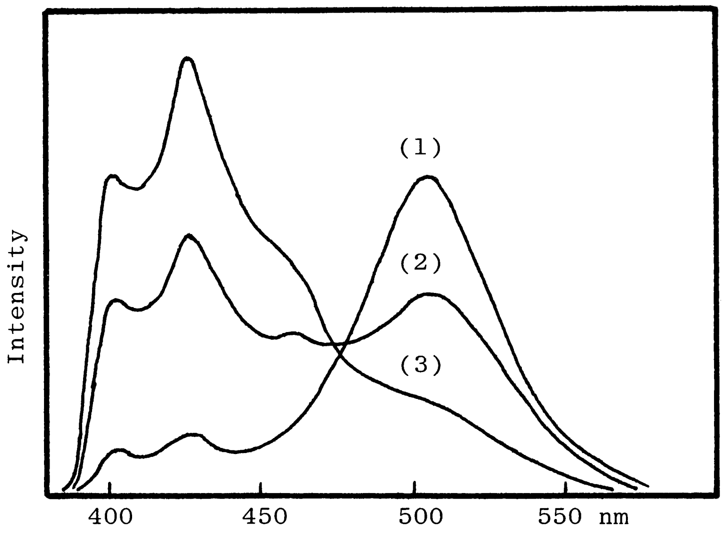


Fig. 1. Phosphorescence spectra of benzil in a ethylene glycol glass at 77 K with fast (1), medium (2), and slow (3) chopping rate. [Benzil]=1.03×10^{-3} M

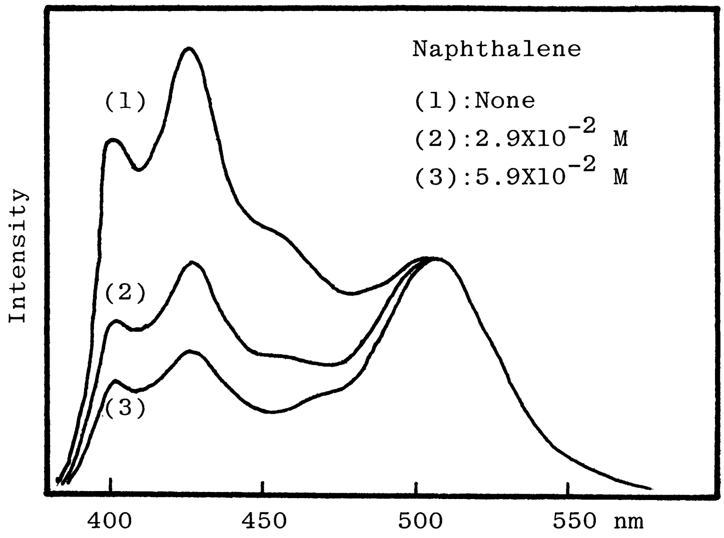


Fig. 2. Quenching for phosphorescence of benzil by naphthalene. [Benzil]=1.03×10^{-3} M

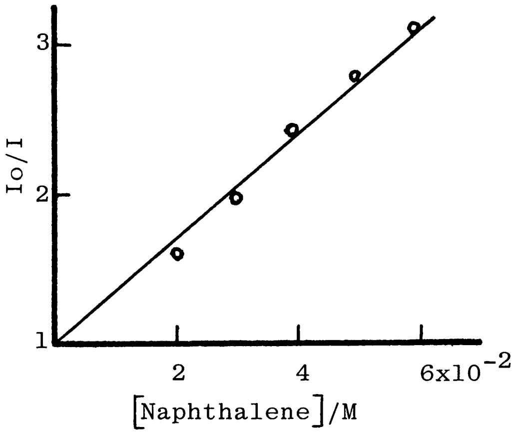


Fig. 3. Stern-Volmer plot of benzil by naphthalene at 427 nm.

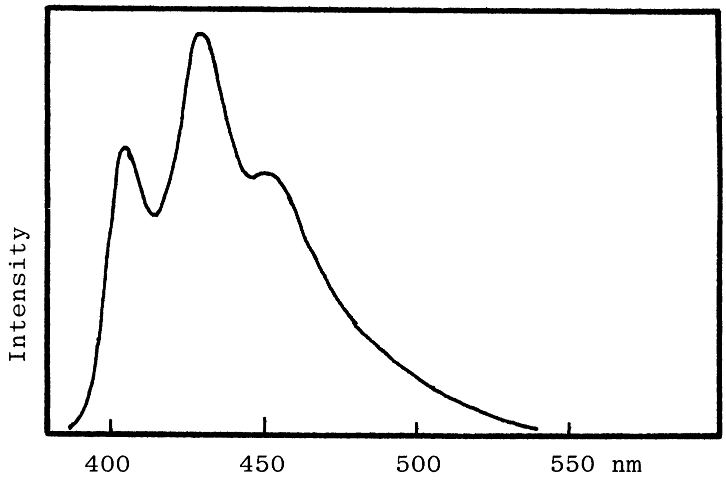


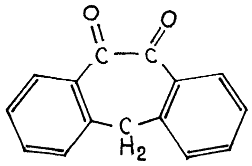
Fig. 4. Phosphorescence spectrum of bridged benzil.

and 460 nm with slow chopping rate. None of the emission arises from the solvent under experimental conditions employed here. Furthermore, the appearance of dual phosphorescence depends upon medium as follows. As well as ethylene glycol, glycerol and ethanol-water mixture are suitable solvents for the dual phosphorescence, but ethylene glycol monomethylether and ethanol are not. Therefore, solvent molecules play an important role in appearance of the short wavelength maxima, and have to possess two or more hydroxylic hydrogen atoms. The result of solvent dependence indicates that the observed maxima are not due to an impurity. Under the experimental conditions employed here, the possible photochemical change of the sample10) was not detected. The delayed fluorescence from benzil in benzene at room temperature is observed at 505 nm.11) However, the fluorescence in ethylene glycol at room temperature has been found at 366 nm.12)

From the maxima at 402 nm and 504 nm, the energies of two phosphorescent triplet states can be estimated approximately to be 71.0 kcal/mol and 56.6 kcal/mol, respectively. Taking into account these values, phosphorescence quenching experiments were performed using fluoranthene (T_1=52.9 kcal/mol) and naphthalene (60.9 kcal/mol).13) In the case of fluoranthene, both the short and long wavelength phosphorescences were quenched equally. On the other hand, naphthalene which has the lowest triplet energy between the estimated energies of benzil quenches only the short wavelength portion of the phosphorescence as shown in Fig. 2. Stern-Volmer plot is presented in Fig. 3.

Consequently, the results obtained here indicate that the emission in ethylene glycol arises from two different triplets having different radiative lifetimes. This implies that there exists two kind of triplet species. As seen from Fig. 1, the lifetime of the species emitting the short wavelength phosphorescence is longer than the other. Since the structureless broad band at 506 nm in crystal is known to be due to the near-planar transoid triplet,5) the short-lived species (504 nm) is the transoid triplet. As described below, the long-lived species (402 nm, 427 nm, and 460 nm) can be assigned to the cisoid triplet where the carbonyls are nearly planar. It is considered from the solvent dependence described above that the cisoid triplet may be stabilized by the formation of two hydrogen bonds between the carbonyls of benzil and hydroxyl groups of the solvent.

In order to provide decisive evidence for the assignment of the short wavelength phosphorescence, we examined a phosphorescence spectrum of bridged benzil (dibenzo [a, d]cyclohepta [1,4]diene-10,11-dione).[14] This model compound has a rigid near-planar cisoid conformation in the ground and excited states. As shown in Fig. 4, the phosphorescence spectrum of this compound in a methylcyclohexane glass is very similar to the spectrum of benzil observed in an ethylene glycol glass with slow chopping rate (Fig. 1). In the case of bridged benzil, as is to be expected, the rate of rotation of the sector does not affect the spectrum, and no maximum appears around 500 nm.



In conclusion, the short wavelength phosphorescence of benzil can be assigned to the transition from the cisoid triplet to the cisoid ground state.

Absorption spectrum of benzil in ethylene glycol is similar to that in benzene, in which the ground state benzil takes the well known skewed-structure.[15] Excitation spectra for two emission maxima at 427 nm and 504 nm are similar to each other. These facts indicate that two geometrical isomers arise from the electronic excitation.

Study on the relationship between the triplet geometries and photochemical reactivity is now undertaken.

References and Notes

1) C. J. Brown and R. Sadanaga, Acta Crystallogr., 18, 158 (1965).
2) T. R. Evans and P. A. Leermakers, J. Am. Chem. Soc., 89, 4380 (1967).
3) D. J. Morantz and A. J. C. Wright, J. Chem. Phys., 54, 692 (1971).
4) J. F. Arnett and S. P. McGlynn, J. Phys. Chem., 79, 626 (1975).
5) I. Y. Chan and B. N. Nelson, J. Chem. Phys., 62, 4080 (1975).
6) I. Y. Chan and B. A. Heath, J. Chem. Phys., 71, 1070 (1979).
7) T-S. Fang and L. A. Singer, Chem. Phys. Lett., 60, 117 (1978).
8) T-S. Fang, R. E. Brown, and L. A. Singer, J. Chem. Soc.Chem. Comm., (1978) 116.
9) W. G. Herkstroeter, J. Saltiel, and G. S. Hammond, J. Am. Chem. Soc., 85, 482 (1963).
10) H. Inoue, S. Takido, T. Somemiya, and Y. Nomura, Tetrahedron Lett., 1972, 2755.
11) T-S. Fang, R. E. Brown, C. L. Kwan, and L. A. Singer, J. Phys. Chem., 82, 2489 (1978).
12) The geometry in the lowest excited singlet state will be discussed elsewhere.
13) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973).
14) This compound was prepared according to N. J. Leonard, A. J. Kresge, and M. Ōki, J. Am. Chem. Soc., 77, 5078 (1955).
15) C. W. N. Cumper and A. P. Thurston, J. Chem. Soc. Perkin II, (1972) 106.

(Received March 21, 1980)