

SPECTRA OF BENZIL AND ITS MOLECULAR CONFIGURATION†

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In the course of an investigation of photochemistry in solid aromatic carbonyls and their dihydro derivatives, absorption and emission spectra of benzil have been obtained in various media.

The molecular configuration of benzil has been the subject of considerable study,¹⁻⁴ particularly in regard to the possible existence of isomers resulting from twisting about the central carbon-carbon bond. Recently Brown and Sadanaga⁵ obtained the crystal structure of benzil and found that the two planes containing the $C_{ar}-C=O$ atoms made an angle of 68° with each other. Whilst their study shows that the skew configuration is the favoured one under the influence of an equilibrium crystal field, it does not preclude the possible formation of rotational isomers via excited electronic states or in different media.

The molecular symmetry of benzil molecules in the skew configuration is C_2 , the only element of symmetry being that of twofold rotation about an axis z normal to the $C-C$ bond. The lowest energy transition in aromatic diketones is known to involve a singlet n, π^* excited state.⁶ From simple molecular orbital theory it can be shown that two nearly degenerate $\pi^* \leftarrow n$ transitions are allowed for benzil in C_2 symmetry. These are $A \leftarrow A$, polarized along the z molecular axis and $B \leftarrow A$, polarized in the (x, y) plane of the molecule where y lies along the $C-C$ bond axis. Were the molecular configuration planar *cis* or *trans*, only one n, π^* transition would be dipole-allowed.

Benzil crystallizes in the enantiomorphic trigonal space groups D_3^4 and D_3^6 . There are only three molecules in the unit cell so that the molecules lie with their mid-points on the crystallographic twofold axis which is normal to $(11\bar{2}0)$. The z molecular axis is therefore normal to the $[0001]$ or c axis of the crystal. A study of the polarized absorption spectrum of the crystal therefore permits a unique identification of the two n, π^* transitions to be made. If no change in molecular geometry occurs in the excited state, only the $B \leftarrow A$ transition will be allowed in the spectrum polarized parallel to the c crystal axis ($\parallel c$) whereas both transitions will be allowed in the spectrum polarized perpendicular to the c axis ($\perp c$). Absorption spectra of benzil crystals are shown in Figure 1.

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¹ Caldwell, C. C., and Le Fèvre, R. J. W., *Nature*, 1939, **143**, 803.

² Rasmussen, R. S., Tunnicliff, D. D., and Brattain, R. R., *J. Am. chem. Soc.*, 1961, **71**, 1068.

³ Cureton, P. H., Le Fèvre, C. G., and Le Fèvre, R. J. W., *J. chem. Soc.*, 1961, 4447.

⁴ Bernal, I. D., *Nature*, 1963, **200**, 1318.

⁵ Brown, C. J., and Sadanaga, R., *Acta crystallogr.*, 1965, **18**, 158.

⁶ Sidman, J. W., *Chem. Rev.*, 1958, **58**, 689.

The principal feature of these spectra is the occurrence of a broad maximum at 25470 cm^{-1} in the $\perp c$ component before the onset of strong absorption in the $\parallel c$ component. This band is assigned as the origin of the $A \leftarrow A$ z -polarized n, π^* transition whilst the band in the $\perp c$ component at 26320 cm^{-1} accompanied by a band in the $\parallel c$ spectrum at 26410 cm^{-1} is assigned to the $B \leftarrow A$ (x, y) polarized transition. A shoulder at about 27800 cm^{-1} ($\parallel c$) is probably a vibronic band. The interband spacing of about 1400 cm^{-1} is approximately the frequency of an excited state C=O stretch in aromatic carbonyls.⁷ A very weak shoulder appearing at about 25600 cm^{-1} in the $\parallel c$ spectrum might arise from an $A \leftarrow A$ component appearing through crystal-induced mixing with the nearby strong $\pi^* \leftarrow \pi$ transition.

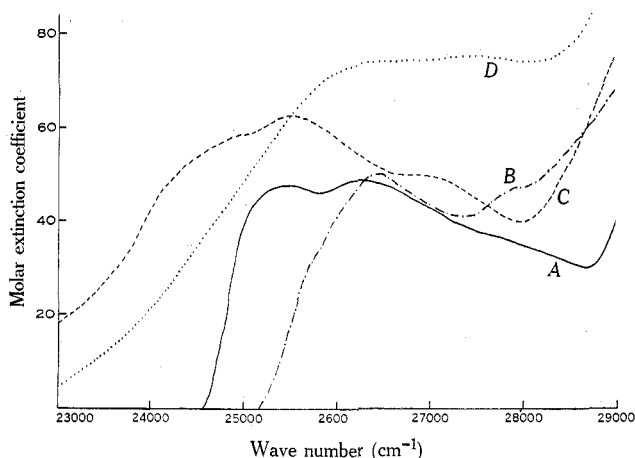


Fig. 1.—Absorption spectra of benzil. A, Polarized spectrum of crystal at 77°K . Electric vector of light vibrating perpendicular to c crystal axis. B, Polarized spectrum of crystal at 77°K . Electric vector of light vibrating parallel to c crystal axis. C, Solution spectrum in n -hexane. D, Solution spectrum in methanol. (For the crystal spectra the ordinate scale is accurate only to $\pm 20\%$.)

Solution absorption spectra of benzil have been obtained in a wide range of different solvents. In saturated hydrocarbons the spectra are, apart from a solvent shift, qualitatively similar to unpolarized crystal spectra. In hydroxylic solvents, however, there is a strong blue shift in the spectra. Spectra obtained in n -hexane and methanol are shown in Figure 1. In the former solvent a diffuse shoulder at about 24700 cm^{-1} and a broad maximum at 25560 cm^{-1} are attributed to the two non-degenerate n, π^* transitions. In methanol, however, the shoulder disappears and there is an intensification of the first maximum. It is therefore tempting to suppose that hydrogen bonding of solvent molecules to the oxygen atoms of benzil leads to greatly reduced dipole repulsive forces between the two C=O groups allowing the O=C-C=O framework to approach a planar *cis* configuration. In solutions with relatively weak solvent-solute interactions, however, the skew configuration is still preferred. This is in agreement with earlier work^{1,3,4} on benzil solutions in chloroform

⁷ Sidman, J. W., and McClure, D. S., *J. Am. chem. Soc.*, 1955, **77**, 6471.

and carbon tetrachloride. Infrared absorption spectra of benzil in carbon tetrachloride/ethanol solutions of varying composition show the C=O stretching frequency to be split into two bands which are still split even at 50% ethanol content. This splitting is expected for C_2 and planar *cis* C_{2v} symmetry but not for planar *trans* (C_{2h}). A *trans* configuration is also improbable on purely steric grounds on account of hindrance of the oxygen atoms.

Emission spectra (phosphorescence) have been obtained from benzil crystals both at room temperature and at 77°K. Phosphorescence of benzil in various rigid media at 77°K has also been recorded. The lowest triplet state of aromatic ketones is usually n, π^* (refs.^{8,9}) and benzil is no exception to this rule.¹⁰ The crystal phosphorescence spectrum lies in the visible and consists of two broad, distinct maxima separated by about $1530 \pm 50 \text{ cm}^{-1}$. This interval is probably a ground-state Raman-active C=O stretching frequency. The higher energy band in the $\perp c$ polarization lies at 18690 cm^{-1} and is 80–100 cm^{-1} to the red of the $\parallel c$ component and the polarization ratio ($\perp c : \parallel c$) is about 4 or 5 : 1 at 77°K. This suggests that the 3A state lies some 80–100 cm^{-1} below the 3B state and that the intensity of the $\parallel c$ component arises from thermal population (at 77°K) of the latter level. In accordance with this is the observation that the polarization ratio is lower at room temperature but photochemical decomposition becomes troublesome at elevated temperatures, causing a marked broadening and shift in the maxima.

Much sharper bands are observed in emission from rigid solutions. In crystalline *n*-hexane, crystalline benzoin, and methylcyclohexane glass, two fairly sharp maxima separated by $1570 \pm 20 \text{ cm}^{-1}$ are obtained. Again, however, the use of a hydroxylic solvent leads to a marked change in the spectrum. In ether/ethanol (1 : 2) glass the lower energy maximum is greatly diminished in intensity and broadened, the interband separation becomes $1450 \pm 80 \text{ cm}^{-1}$, and there is a 500 cm^{-1} blue shift in the higher energy maximum.

Experimental

Polarized crystal spectra were photographed on a Hilger Littrow quartz spectrograph. Plates were traced on a Joyce-Loebl recording microdensitometer. For absorption studies thin (17μ) crystals were grown from the melt between silica disks separated by mica spacers. Emission studies were made both on thin crystals and on thicker specimens grown from ethanol solution by solvent evaporation. Emission spectra were excited by the 3660 Å group of lines from a filtered high-pressure mercury lamp.

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⁸ Hammond, G. S., and Leermakers, P. A., *J. Am. chem. Soc.*, 1962, **84**, 207.

⁹ Porter, G., and Suppan, P., *Trans. Faraday Soc.*, 1965, **61**, 1664.

¹⁰ Herkstroeter, W. G., Lamola, A. A., and Hammond, G. S., *J. Am. chem. Soc.*, 1964, **86**, 4537.