

SHORT COMMUNICATIONS

The Photoinduced Rotational Isomerization of Benzil in a Mixture of Water and Ethanol

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The benzil molecule has been considered to take a nonplanar configuration in which the central carbonyl-carbonyl bond is strongly twisted.¹⁾ Therefore, the two benzoyl parts are almost not in conjugation with each other and, consequently, benzil shows an electronic spectrum very similar to that of benzaldehyde.

Now, we wish to report on the photoinduced spectral changes of benzil in several liquid solutions. In a cyclohexane solution and in an ethanol solution the absorption spectra indicated only decompositions upon ultraviolet irradiation by means of a low-pressure mercury lamp. In a mixture of water and ethanol, however, benzil was found to show characteristic spectral changes with the irradiation. Obviously, water molecules play an essential role in this photoinduced change. As is shown in Fig. 1, the intensity of the 262 m μ band of the nonplanar species gradually decreases with the irradiation time, and at the same time an absorption band appears at 314 m μ . In this case, the isosbestic points were observed for the first several seconds of irradiation, but further irradiation shifted the absorption curves and caused them to deviate from the isosbestic points. The shift is probably due to the beginning of decomposition.

Moreover, in the initial stage of irradiation the photoproduct species absorbing at 314 m μ can be reversed to the original nonplanar benzil by heating at 83°C for 50 min in a dark room, as is indicated by curve IV in Fig. 1.

From the experimental results obtained above, the photoproduct species can be inferred to be a configurational isomer which possesses a nearly planar configuration, for the product shows a relatively longer wavelength band than that of the

nonplanar species. As to the role of the water molecule, the hydrogen-bonding formation between two carbonyl groups and a water molecule can be considered plausible. The hydrogen-bonding energies may contribute to the stabilization of the nearly planar isomer of the benzil molecule, which is illustrated in Fig. 2. A detailed investigation is now in progress.

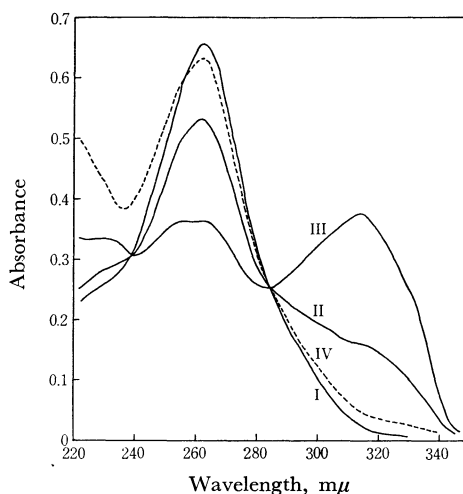


Fig. 1. The spectral changes of benzil in the mixture of water and ethanol (1:1).

- I: 0 sec irradiation
 II: 3 sec irradiation
 III: 8 sec irradiation
 IV: heat 83°C, 50 min after irradiation.

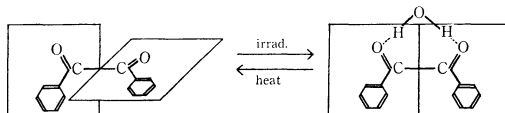


Fig. 2. Nonplanar and planar hydrogen-bonded isomers of benzil.

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