

Molecular Configuration of Benzil and α -Pyridil

THE molecular configuration of benzil has been the object of considerable interest for some time because of unusual physical characteristics, such as its large optical rotatory power. Caldwell and Le Fevre¹ measured its dipole moment in several solvents and compared it with that of phenanthroquinone, which is planar and contains two *cis* carbonyl groups. From the lower (3.5 D) electric dipole moment of benzil these authors concluded that the molecule must be skew and that the two $C_6H_5-C=O$ halves must lie in two different planes making an angle of $90^\circ-100^\circ$ with each other.

Knaggs and Lonsdale² compared this suggestion with their X-ray diffraction results and found that it was quite reasonable. Furthermore, they concluded that neither a planar *cis* nor a planar *trans* configuration was acceptable for the interpretation of their X-ray data. Finally, Le Fevre *et al.*³ have estimated from dielectric and Kerr constants that the molecule is twisted about the $O=C-C=O$ bond.

In connexion with some work on 2,2'-dipyridyl glyoxal (α -pyridil), we have recorded the infra-red spectrum of benzil and of the foregoing substance. Comparison of our results with that in the literature revealed that previous measurements^{4,5} of the infra-red spectrum of benzil showed a single band in the carbonyl region ($1,700\text{ cm}^{-1}$) and, furthermore, this was used as evidence⁶ for a *trans* structure for benzil, in contrast with the results quoted above. We find two bands in the carbonyl region for both benzil and α -pyridil, as shown in Fig. 1, A and B. The splitting in benzil is about 14 cm^{-1} while in α -pyridil it is 23 cm^{-1} . Our results, together with that of other workers, are presented in Table 1.

The structure of α -pyridil was worked out in detail by Hirokawa and Ashida⁶, who found that the molecule is rotated about the $O=C-C=O$ bond by an angle of approximately 83 degrees. Since such a conformation makes the relevant point group of the molecule C_2 , one should observe two carbonyl bands for this molecule. Fig. 1, B shows that this is the case. By analogy with α -pyridil, two carbonyl bands should be seen for a benzil molecule in the skew configuration discussed here, and this is shown in Fig. 1, A, to be true.

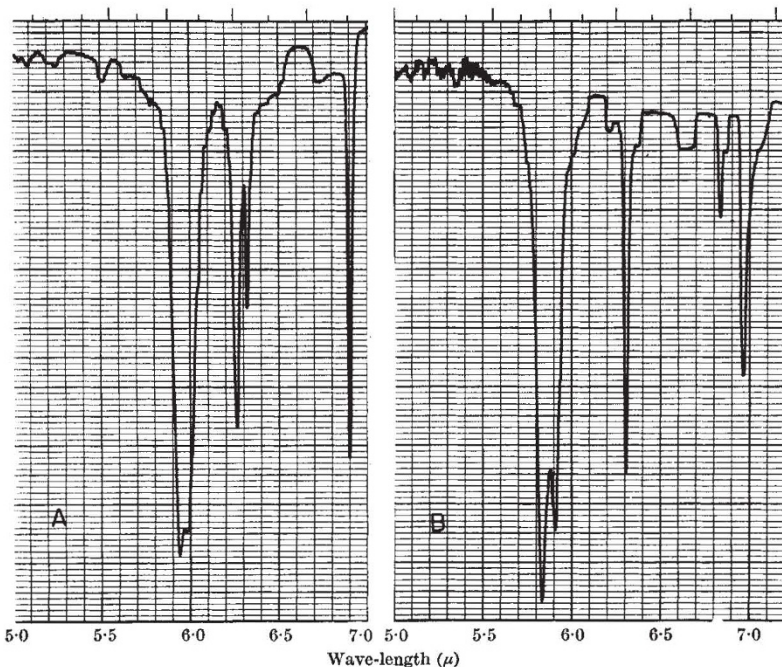


Fig. 1. A, Spectrum of benzil in chloroform; B, spectrum of α -pyridil in chloroform. Both solutions were approximately 0.03 M

Ref.	Benzil	α -Pyridil
This work	$1,686\text{ cm}^{-1}$ (<i>st, sp</i>) $1,672\text{ cm}^{-1}$ (<i>sh</i>)	$1,715\text{ cm}^{-1}$ (<i>st, sp</i>) $1,692\text{ cm}^{-1}$ (<i>st, sp</i>)
4	$1,652\text{ cm}^{-1}$	—
5	$1,681\text{ cm}^{-1}$	—

st, strong; *sp*, sharp; *sh*, shoulder.

The spectra were recorded using a Perkin-Elmer 237 grating spectrophotometer with IRTAN cells. Using an older spectrophotometer and the same solution used to record Fig. 1, A, we were unable to observe the splitting of the carbonyl band in benzil. As a result, the apparent conflict of the infra-red results with the other measurements is due to lack of resolution in the older spectrophotometers.

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¹ Caldwell, C. C., and Le Fevre, R. J. W., *Nature*, **143**, 803 (1939).

² Knaggs, I. E., and Lonsdale, K., *Nature*, **143**, 1023 (1939).

³ Cureton, P. H., Le Fevre, C. G., and Le Fevre, R. J. W., *J. Chem. Soc.*, 4447 (1961).

⁴ Seroco, M., and Liberti, I., *Ricerca Sci.*, **24**, 1687 (1954).

⁵ Rasmussen, R. S., Tunnicliff, D. D., and Brattain, R. R., *J. Amer. Chem. Soc.*, **71**, 1068 (1961).

⁶ Hirokawa, H., and Ashida, T., *Acta Crystal.*, **14**, 77 (1961).

BIOPHYSICS

Viscosity of Deoxyribonucleic Acid Solutions in the 'Sub-melting' Temperature Range

DEOXYRIBONUCLEIC acid (DNA) 'melting' has been mainly investigated using spectroscopic and optical rotation techniques¹. To our knowledge, the viscosity behaviour associated with the 'melting' phenomenon has been examined only in the special cases of synthetic deoxyribopolynucleotides² and phage DNA³. In an investigation of this subject, using DNA preparations from three different sources, it was observed that the change in intrinsic viscosity parallels the change in optical density at $260\text{ m}\mu$, except for the 'sub-melting' temperature range. The peculiar behaviour found in this region is reported here. Briefly, this is characterized by a fall in viscosity which is completely reversed on cooling and seems to be caused by the local melting of deoxyadenylic-thymidylic (dA-T) clusters.

Viscosity was measured using a four-bulb viscometer built according to Eigner⁴. The average velocity gradients associated with each bulb were calculated using Kroepelin's formula⁵: values ranging from 100 to 20 sec^{-1} were found. Three DNA preparations (from calf thymus, chicken erythrocytes and *E. coli*, respectively), obtained essentially according to Kay *et al.*⁶ and displaying intrinsic viscosities close to 70 dl./g. were used at concentrations of $20\text{ }\mu\text{g./ml.}$ in acetate buffer $\mu=0.15$, $\text{pH}=5.6$ (the pH of this buffer did not show any significant change within the explored temperature range). The viscometer was equilibrated at several different temperatures and fresh aliquots from stock DNA solutions were measured at each temperature. Ultra-violet 'melting profiles' were obtained at essentially the same DNA concentration used in the viscosity experiments.

Fig. 1 shows the behaviour of both optical density at $260\text{ m}\mu$ and intrinsic viscosity at zero velocity gradient of calf thymus DNA as a function of temperature. Substantially similar results were obtained