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 Fevre[1] 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°–100° with each other.

Knaggs and Lonsdale[2] 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 cm^{-1}) and, furthermore, this was used as evidence[5] 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 Ashida[6], 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.

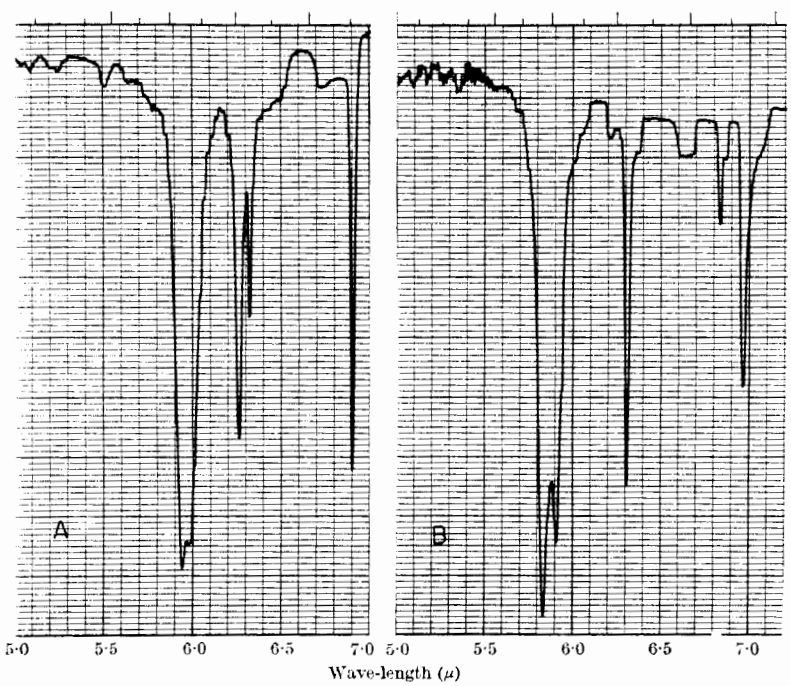

Fig. 1. *A*, Spectrum of benzil in chloroform; *B*, spectrum of α-pyridil in chloroform. Both solutions were approximately 0·03 M

Table 1

Ref.	Benzil	α-Pyridil
This work	1,686 cm^{-1} (*st*, *sp*) 1,672 cm^{-1} (*sh*)	1,715 cm^{-1} (*st*, *sp*) 1,692 cm^{-1} (*st*, *sp*)
4	1,652 cm^{-1}	—
5	1,681 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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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 techniques[1]. To our knowledge, the viscosity behaviour associated with the 'melting' phenomenon has been examined only in the special cases of synthetic deoxyribopolynucleotides[2] and phage DNA[3]. 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 mμ, 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 Eigner[4]. The average velocity gradients associated with each bulb were calculated using Kroepelin's formula[5]: 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 μg./ml. in acetate buffer $\mu = 0{\cdot}15$, $p\mathrm{H} = 5{\cdot}6$ (the *p*H 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 mμ and intrinsic viscosity at zero velocity gradient of calf thymus DNA as a function of temperature. Substantially similar results were obtained

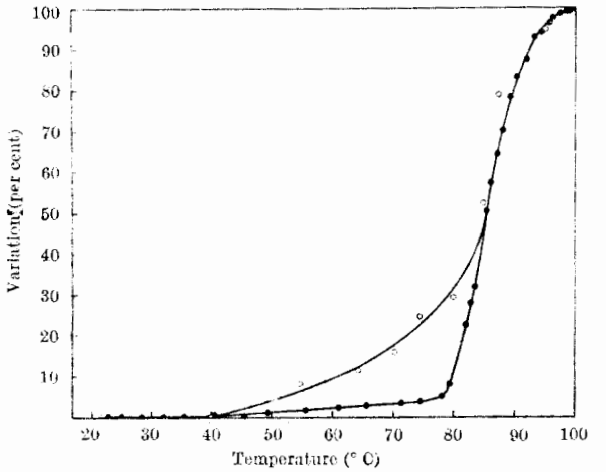

Fig. 1. Viscosity and optical density of calf thymus DNA (sample *B* 18) as a function of temperature. Viscosity decrease (○) and optical density increase (●) are given as percentage of total variation. DNA concentration was about 20 μg/ml. in acetate buffer *p*H = 5·6, μ = 0·15

with the other two samples. It is evident that viscosity undergoes a quite distinct drop in a temperature range where optical density is very slowly increasing in a linear fashion. Results to be published in detail elsewhere indicate that in the temperature range 50°–80° C, DNA hydrolysis occurs according to a 'double hit' mechanism, at a very slow rate and shows a lag-time of more than 40 min. Therefore, the results shown in Fig. 1 (in the range 50°–80° C), which were obtained within 20 min after introducing the solutions in the viscometer, do not need any correction for hydrolysis phenomena. Viscosity results in the temperature range 80°–95° C were corrected for hydrolysis.

In phosphate buffer *p*H 7·6, μ = 0·15 (where the melting point is the same as at *p*H 5·6), the difference between the viscosity and optical density curves was less pronounced.

When the temperature was lowered from the 'sub-melting' range down to 25° C (no matter how fast was the drop) a complete recovery of the initial viscosity value was obtained.

The foregoing results suggest that the 'sub-melting' behaviour of viscosity is due to a change in the configuration of DNA molecules. That this change is not related to some trivial aggregation phenomenon mediated by residual protein seems to be suggested by its reversibility. A possible explanation is that it is due to the local melting of dA-T clusters, the existence of which, in runs of up to 9 units, has been shown by Spencer and Chargaff[7]. In connexion with this interpretation it may be recalled that the melting temperature of a synthetic dA-T polymer is about 65° C (ref. 8), well within the range where the 'sub-melting' phenomenon occurs in DNA, and that Greer and Zamenhof[9] found that although guanine is more labile than adenine at high temperatures, depurination almost exclusively affects adenine at temperatures below the 'melting point'.

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Photoconduction of Adenosine in Various Morphological Forms

OPTICALLY clear films can be cast on a substrate when a neutral adenosine aqueous solution is slowly evaporated at about 60° C. Along the perimeter of the film, white needle-shaped crystallites are observed. If the film is exposed afterwards to high humidity, its clear portion will become cloudy. When viewed under the microscope between crossed nicols, this cloudy portion is seen to consist entirely of spherulites as shown in Fig. 1. The infra-red spectra of: (1) potassium bromide pellet of powdered needle-shaped crystallites; (2) non-spherulitic clear film; (3) spherulitic film of adenosine are shown in Fig. 2. From these spectra it is evident that the molecular arrangements of adenosine in these three morphological forms are different. Further work has to be done in order to elucidate the structures of the material in these various forms. In the present work it is intended to report some results on semi- and photo-conduction of the three different morphological forms of adenosine surface cells.

The experimental details for measuring the conduction of organic materials are similar to those reported previously[1]. The temperature dependence of the resistance of adenosine is shown in Fig. 3. Except for the deviation towards the lower temperature end, the resistance follows the well-known equation $R = R_0 \exp(E_d/2kT)$, where R_0 is a constant and E_d is the activation energy for dark conduction. The activation energy of the pellet is 4·52 eV, in agreement with the value reported by Eley and Leslie[2]. The activation energies of the spherulitic and non-spherulitic films are 4·03 and 3·68 eV respectively. The temperature dependence of photocurrent of adenosine shown in Fig. 4 follows the equation $i = i_0 \exp(-E_p/kT)$, where i_0 is a constant and E_p is the activation energy for photoconduction. The values of E_p are about 1·90 eV for the pellet, 1·87 eV for the spherulitic film, and 1·73 eV for the non-spherulitic film.

The activation energies for dark- and photo-conduction of adenosine are much higher than the corresponding values of polyadenylic acid[3] and NaDNA in the dry state[4].

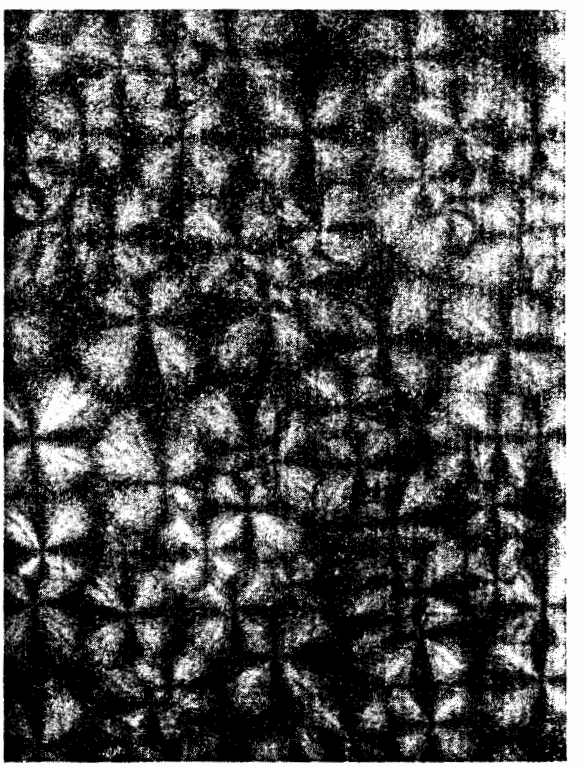

Fig. 1. Adenosine spherulites (crossed nicols × 385)