THE ROTATORY DISPERSION OF BENZIL

By S. Chandrasekhar

(*Memoir No. 51 of the Raman Research Institute, Bangalore*)

Received May 5, 1954

(Communicated by Sir C. V. Raman, F.R.S., N.L.)

1. Introduction

Benzil ($C_6H_5.CO.CO.C_6H_5$) is a yellow solid which crystallises in the form of hexagonal prisms belonging to the space-groups D_3^4 and the enantiomorphous D_3^6. The structure of benzil has not been fully determined; but it is known that the unit cell contains three skew molecules disposed spirally about the principal axis and in such a way that the benzene rings are more nearly parallel than perpendicular to the axis. The substance is optically active in the crystalline state. This has been measured by Des Cloizeaux (1870), who finds the rotatory power for λ 5893 Å to be slightly greater than that of quartz.

The refractive dispersion and birefringence of benzil have been studied in detail by E. E. Jelley (1941) and W. M. D. Bryant (1943). The optical behaviour of this crystal exhibits certain interesting features. For λ 5893 Å, the crystal is uniaxial and *positive*, the birefringence being slightly greater than that of quartz. As we proceed towards the violet, the birefringence progressively decreases, till at λ 4205 Å the crystal is optically *isotropic*. Beyond that wavelength, the birefringence reverses sign, the crystal then becoming uniaxial and *negative*.

These optical properties are evidently related to the absorption spectrum of the substance. The ultraviolet absorption spectrum of benzil dissolved in organic solvents has been studied by several workers. It will suffice here to quote the data given in the International Critical Tables (1930). The benzil solution has a comparatively weak absorption which extends from 4500 Å onwards into the shorter wavelength side of the spectrum, with a maximum lying at about 3900 Å. This absorption is the cause of the characteristic yellow colour of the substance. There is a much more intense absorption at 2500 Å and another still more intense farther out in the extreme ultraviolet.

The present investigation was taken up with a view to determine the rotatory dispersion of benzil over a wide range of wavelengths and to correlate it with its absorption spectrum. Measurements have been possible from

about 9000 Å in the infrared upto about 3600 Å in the ultraviolet right through an absorption band. Some interesting results have emerged which will be described in the course of the paper. In some earlier papers published in these *Proceedings* (Chandrasekhar, 1952, 1953), we have already examined the rotatory dispersion of quartz, sodium chlorate and cinnabar. We shall now proceed to consider the case of benzil.

2. PREPARATION OF THE CRYSTALS

The commercially available chemical was first purified by repeated crystallisation by evaporation of a solution of the substance in alcohol or ether. The crystals thus obtained are generally in the form of needles and hence not very suitable for the present study. Since the melting point of benzil is only 95° C., bigger crystals could be grown from the melt without much difficulty. The purified substance was taken in a glass tube tapered at the bottom and melted in an electric furnace. The furnace was so constructed that a steady current through its heater coil established a temperature gradient down its length, the lower portion being a few degrees cooler. The tube was slowly lowered at the rate of a few millimetres per hour by means of a clockwork arrangement. The tapered bottom facilitates the crystallisation to start from a point. Crystals of about 0·5 to 1 cm. length were obtained after a few trials. The optic axes of these crystals, which were ascertained by observation through a pair of polaroids, generally coincided with the direction of the temperature gradient. After several crystallisations, a few clear transparent specimens were selected for the present study. Amongst these, both right and left rotating crystals were present.

The crystals are extremely soft and brittle so that great care had to be exercised in cutting and polishing them. They were ground by means of very fine carborundum and polished with rouge spread on wet chamois leather. When extremely thin specimens less than 0·03 mm. thick had to be prepared, the crystal, properly cut, was first stuck on by means of a very thin layer of canada balsam (whose rotatory power is negligible) to a glass plate to prevent its fracture and then slowly rubbed down to the required thickness. Very fine carborundum and in the later stages rouge itself was found to be suitable for the grinding.

3. THE ULTRAVIOLET TRANSMISSION SPECTRUM

The earlier investigations on the ultraviolet absorption spectrum of benzil appear to be restricted to solutions of the substance in organic solvents. It was therefore thought worthwhile to make at least a qualitative study of the transmission spectrum of crystalline benzil. A tungsten filament lamp

served as a convenient continuous source of light. Transmission photographs were taken with a Hilger medium quartz spectrograph for varying thicknesses of the crystal ranging from about 1 cm. to about 0·02 mm. These have been reproduced in Fig. 1, Plate XXI. For each thickness of the crystal three exposures have been given, increasing from a few seconds to 10 minutes. Proceeding upwards, the successive groups of three exposures each were taken with specimens of thicknesses roughly 1 cm., 1 mm., 0·1 mm., 0·05 mm. and 0·02 mm. respectively. The exposure just below the wavelength scale is that of the lamp itself. It will be noticed that as the thickness is reduced, the limit of transmission shifts in a step-like fashion. One can also see the notable diminution in the intensity beyond 4000 Å even in the thinner specimens. This marks the presence of an absorption band in that region of the spectrum which extends upto 4800 Å for thicker crystals. But, even with the thinnest crystals, there is an almost sharp cut off beyond 3400 Å. This is evidently the beginning of the very intense absorption lying farther out in the ultraviolet.

Fig. 2, Plate XXI reproduces photographs taken with a tungsten lamp and a mercury arc respectively, which demonstrate the pleochroism exhibited by benzil. A crystal about 0·05 mm. thick, cut parallel to the optic axis was used for this purpose. In both Figs. 2 (*a*) and 2 (*b*), the upper exposure is the transmission for light polarised with the electric vector perpendicular to the optic axis, *i.e.*, for the ordinary ray, while the lower one is the transmission for the electric vector parallel to the optic axis or the extraordinary ray. An inspection of Fig. 2 (*a*) will make it clear that in the region of 4000 Å there is greater absorption for the ordinary ray than for the extraordinary ray, whereas the reverse is the case at about 3600 Å. This is even more obvious in Fig. 2 (*b*) where the transmissions for λ 4046 Å and λ 3665 Å are clearly oppositely polarised. Broadly speaking, we may state that the effective absorption maximum for the ordinary ray is at a slightly longer wavelength than that for the extraordinary ray. As we shall see later, this fact will be useful in explaining the refractive dispersion and birefringence of benzil over the range of wavelengths for which data is available.

Ganguly and Choudhury (1953) have studied the polarisation of the fluorescence of crystalline benzil. They find that, irrespective of whether the incident light is polarised or not, the fluorescent light is partially polarised, the vibrations $\perp$ to the optic axis being stronger than the $\parallel$ vibrations. It is interesting to find that a somewhat similar result has been obtained in our absorption studies, the $\perp$ component being more absorbed than the $\parallel$ component. These results are evidently related to the molecular orienta-

tions in the crystal, but as the structure of the molecule itself has not been definitely established it would be premature at this stage to discuss this aspect of the problem.

The transmission spectrum of benzil dissolved in benzene was also photographed, though this has not been reproduced here. Upto the wavelength studied (3400 Å), both the crystal and the solution exhibit very similar features, except that the positions of the absorptions of the solution are slightly shifted towards longer wavelengths as compared to those of the crystal. A cursory examination of the transmission of light by benzil vapour revealed that its absorption spectrum is not very much different from that of the crystal or the solution.

4. MEASUREMENT OF THE ROTATORY DISPERSION

The polarimeter consisted of two nicols, one of which was mounted on a divided circle and served as the analyser. By a suitable system of lenses, light from a mercury arc was made to pass through the polarimeter and the crystal and focus on the widened slit of a spectrograph. Photographs of the spectrum were taken with different settings of the analyser, the time of exposure for the successive photographs being made exactly the same varying from a few minutes to half an hour depending on the region of the spectrum which was being studied. By finding out the exposures of equal intensity on either side of the minimum, the position of extinction could be determined for each wavelength to within a fraction of a degree.

For the range between λ 5893 Å and λ 4916 Å, a specimen of thickness 7·95 mm. (measured by the micrometer caliper) was used. The thickness had to be reduced to about 1 mm. before λ 4358 Å (Hg) was feebly transmitted and measurement was then possible for that wavelength. The next step was to try and penetrate the absorption band and to pursue the measurements upto at least 3600 Å". For this a crystal cut perpendicular to the optic axis of thickness less than 0·03 mm. had to be used. The specimen was prepared in the manner already described. It was thinned down till the λ 4046 Å line was faintly visible after passage through it. In these circumstances, it was found that the transmission extended upto about 3600 Å, so that the measurement of the rotatory power could be extended upto that wavelength.

Similarly, measurements were carried out into the infra-red region of the spectrum upto about 9000 Å. The mercury arc was a good source of light but specially sensitized photographic plates (Kodak IRER) were necessary.

The thickness of the largest crystal was measured by means of a micrometer caliper and those of the other two were estimated in terms of this thickness by a comparison of the values of the rotations for certain common wavelengths. The accuracy of measurement with the first two specimens is quite high, as the value of the total rotations for these thicknesses is large. But with the thinnest specimen the total rotation is hardly a few degrees and this could be determined only to within about 0·1°, so that the accuracy of measurement is considerably less. The values of the total rotations obtained with the three specimens for the different wavelengths together with the mean estimated value of the rotatory power are given in Table I. Throughout, the wavelength (λ) is expressed in microns (μ) and the rotatory power in degrees per millimetre.

TABLE I

λ (in μ)	Total Rotation measured in degrees			Mean Value of Rotatory Power
	Specimen I Thickness measured 7·95 mm.	Specimen II Thickness estimated 1·08 mm.	Specimen III Thickness estimated 0·0281 mm.	
·3590			4·2	149
·3655			4·08	145
·3704			3·70	132
·3785			3·20	114
·3906			2·70	96
·3980			2·20	78
·4046			1·50	53
·4078			1·35	48
·4358		48·4	1·25	44·8
·4916	330·63	44·9	1·14	41·6
·5461	245·38	33·9	0·89	31·4
·5780	212·13	28·9	0·78	26·7
·5893	202·13	27·15		25·3
·6234		23·4		21·7
·6908		18·4		17·0
·7082		16·4		15·2
·7729		13·4		12·4
·8180		12·4		11·5
·8756		10·4		9·6

The rotatory power for λ 5893 Å as determined by Des Cloizeaux is $25° \pm 0·3°$. This value is in good agreement with that obtained in the present work.

It has been shown earlier by the present author that the rotatory dispersion of quartz and cinnabar are represented much better by a formula of the type

$$\rho = \frac{k\lambda^2}{(\lambda^2 - \lambda_0^2)^2} \tag{1}$$

than by a formula of the Drude type. Benzil is in many respects very similar to the two crystals mentioned above. For instance, it crystallises in the same space-group to which quartz and cinnabar belong and also, like the latter, its optical activity, is present only in the crystalline state. Hence we may expect that the rotatory dispersion of benzil to be represented well by a similar formula. The following formula fits the experimental data fairly well:

$$\rho = \frac{6{\cdot}27\,\lambda^2}{[\lambda^2 - (0{\cdot}24)^2]^2} \tag{2}$$

It has been found necessary to assume a characteristic absorption wavelength at 2400 Å in order to fit the data accurately. The absorption spectrum of crystalline benzil has not been studied in the ultraviolet, but one can see that this assumed wavelength roughly corresponds to the actual absorption observed at about 2500 Å in the benzil solution. The small shift of about 100 Å may be expected to be a genuine one from what we have seen earlier regarding the differences in the transmission spectrum of the solution and the crystal. The absorption band at 3900 Å has been neglected altogether as it is a comparatively weak one and as we shall see later contributes only a little to the rotatory power. Further, an exact knowledge of the intensity and shape of the absorption is necessary before we can attempt at fitting a formula which is valid right through the band. There has been no necessity to include a term involving the extreme ultraviolet absorption in this formula, whereas this term contributes considerably to refraction. The values calculated from the formula have been drawn as a continuous curve in Fig. 1, while the experimental data have been plotted as points. The crystal exhibits anomalous rotatory dispersion in the neighbourhood of the absorption band. However, except in the immediate vicinity of the band, the experimental points fall on the theoretical curve. The shaded portion in the graph represents the actual contribution of the absorption band to the rotatory power, and this is not large. We are, therefore, not unjustified in leaving it out in our formula. It is interesting to find that the same type of formula that holds good for quartz and cinnabar also represents the data for benzil fairly well.

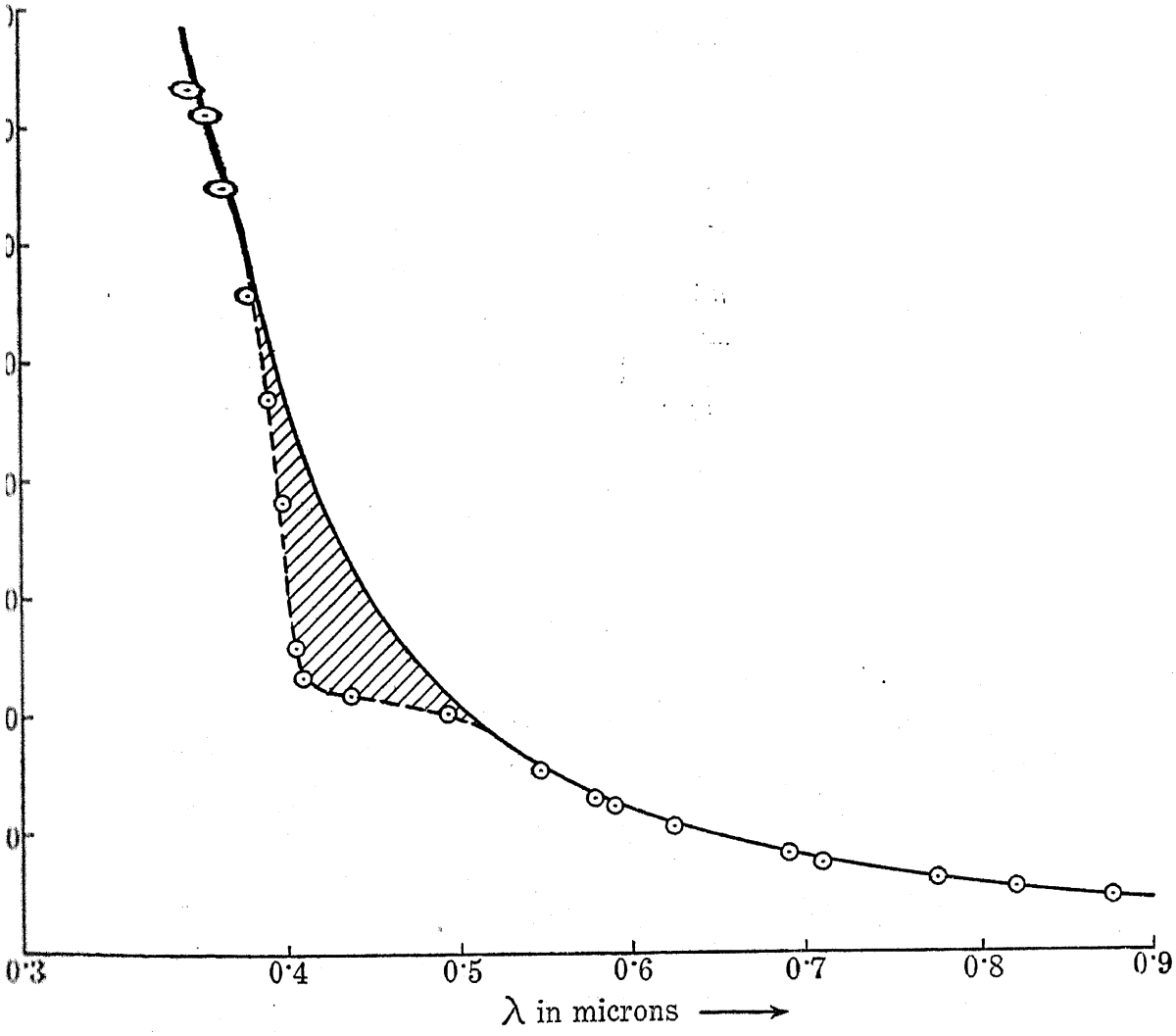


FIG. 1. The Rotatory Dispersion of Benzil.

5. THE THERMAL VARIATION OF THE ROTATORY POWER

An attempt was then made to see if the rotatory power shows any marked anges when the temperature of the crystal is altered. A specimen about mm. thick was used for this experiment. The crystal was mounted inside solenoid suitably constructed for the purpose, so that it could be heated ectrically. The temperature of the crystal was measured by means of a pper-constantan thermocouple. The rotatory power was determined th at room temperature (28° C.) and at 68° C. The rotatory power is und to decrease slightly with rise of temperature. The values of the te of variation of the rotatory power with temperature, $d\rho/dt$, are given in able II for three wavelengths. High accuracy cannot however be claimed r these values as the changes in rotation are rather small.

TABLE II

λ	$d\rho/dt \times 10^4$ (28° to 68° C.)
·4916	2·5
·5461	2·0
·5780	1·5

In some earlier papers, the present author has shown that the thermal variation of the rotatory power of quartz and cinnabar can be satisfactorily explained by assuming that the characteristic frequencies shift with temperature. We shall not make a similar calculation in the case of benzil, as a detailed knowledge of the contribution of the negative term at 3900 Å is necessary before we can proceed to do so.

6. THE REFRACTIVE DISPERSION OF BENZIL

The following formulæ of the Sellmeier-Drude type have been found to fit the refractive dispersion of benzil over the whole range of available data:

$$\epsilon^2 - 1 = 1{\cdot}35 + \frac{0{\cdot}37\,\lambda^2}{\lambda^2 - (0{\cdot}24)^2} + \frac{0{\cdot}0138\,\lambda^2}{\lambda^2 - (0{\cdot}395)^2} \tag{3}$$

$$\omega^2 - 1 = 1{\cdot}08 + \frac{0{\cdot}535\,\lambda^2}{\lambda^2 - (0{\cdot}24)^2} + \frac{0{\cdot}015\,\lambda^2}{\lambda^2 - (0{\cdot}398)^2} \tag{4}$$

The characteristic absorption wavelength at 2400 Å which occurs in the rotatory dispersion formula (2) also appears in these formulæ. In addition, the extraordinary index has a characteristic dispersion wavelength at 3950 Å while the ordinary index has one at 3980 Å. This is based on the observations made earlier regarding the pleochroism of crystalline benzil in the region of 4000 Å. The contribution of the extreme ultraviolet term has been replaced by a constant in each formula. The calculated values are given in comparison with Bryant's experimental data in Table III.

The agreement between the experimental and the calculated values is quite good. The interesting way in which the birefringence of benzil varies as we proceed from one end of the visible spectrum to the other becomes immediately explicable in terms of these dispersion formulæ.

TABLE III

λ	ϵ (expt.)	ϵ (calc.)	ω (expt.)	ω (calc.)	$\epsilon - \omega$ (expt.)	$\epsilon - \omega$ (calc.)
·4205	1·737	1·737	1·737	1·737	0·000	0·000
·4358	1·720	1·720	1·716	1·714	0·004	0·006
·4380	1·718	1·718	1·712	1·712	0·006	0·006
·4620	1·705	1·705	1·694	1·694	0·011	0·011
·4860	1·695	1·697	1·682	1·683	0·013	0·014
·5461	1·684	1·684	1·667	1·666	0·017	0·018
·5780	1·680	1·680	1·660	1·660	0·020	0·020
·5893	1·679	1·679	1·658	1·658	0·021	0·021
·6560	1·672	1·673	1·648	1·648	0·024	0·023

7. DISCUSSION

The structure of the benzil molecule is not definitely known. Caldwell and Le Fevre (1939), from a measurement of the dipole moment of benzil dissolved in various organic solvents, suggest that the molecule has a skew configuration in which the two $C_6H_5-\overset{|}{C}-O$ groups lie in planes which are nearly mutually perpendicular. In such a case, the molecule can obviously exist in either a right-handed or a left-handed form. The optical activity of benzil should consequently be of molecular origin, as is the case, for instance, with the sugars, the tartrates, etc. But remarkably enough, the rotatory power of this substance exists only in the crystalline state. The reason for this perhaps lies in the fact that in the state of solution, an interchange or equilibrium between the *d* and the *l*-forms of the molecule exists—a possibility which cannot be precluded if the potential barrier between these two enantiomorphous forms is not large. Or it may be that there is a free rotation of the two halves of the molecule about the central C—C bond. In fact, the measured value of the dipole moment of benzil in solution agrees closely with the value computed assuming a free rotation. But Caldwell and Le Fevre are inclined to dismiss such a possibility. In the crystal, on the other hand, the molecule would assume a relatively fixed configura-

tion, as is evident from the fact that the rotatory power does not exhibit any catastrophic change when the crystal is heated.

A large amount of experimental data concerning various properties of crystalline benzil is available. However, these data still await interpretation on account of the fact that the structure of the crystal is not known. For instance, the magnetic anisotropy of benzil is quite large and comparable in magnitude with that of naphthalene, biphenyl, etc. (Krishnan, Guha and Banerjee, 1933). The optical anisotropy, on the contrary, is quite feeble. In fact, the crystal is optically isotropic in the violet region of the spectrum. An explanation for this in terms of the crystal structure and the anisotropies of the individual molecules would be of the highest interest. But, only a preliminary analysis of the crystal structure has been made so far and that is by Knaggs and Lonsdale (1939), who have come to the conclusion that the molecule must be of a skew type. Mann and Thompson (1951) have examined the polarisation of the infra-red absorption of benzil with a view to get some information about the structure, but have not arrived at anything significant from their observations. A detailed investigation of the Raman effect in crystalline benzil does not appear to have been made. The dynamic X-ray reflections of benzil have been studied thorow by Mrs. Lonsdale (1942) and also by R. V. Subrahmanian (1942). A careful inspection of these photographs will, no doubt, throw considerable light on the orientations of the benzene rings in the crystal.

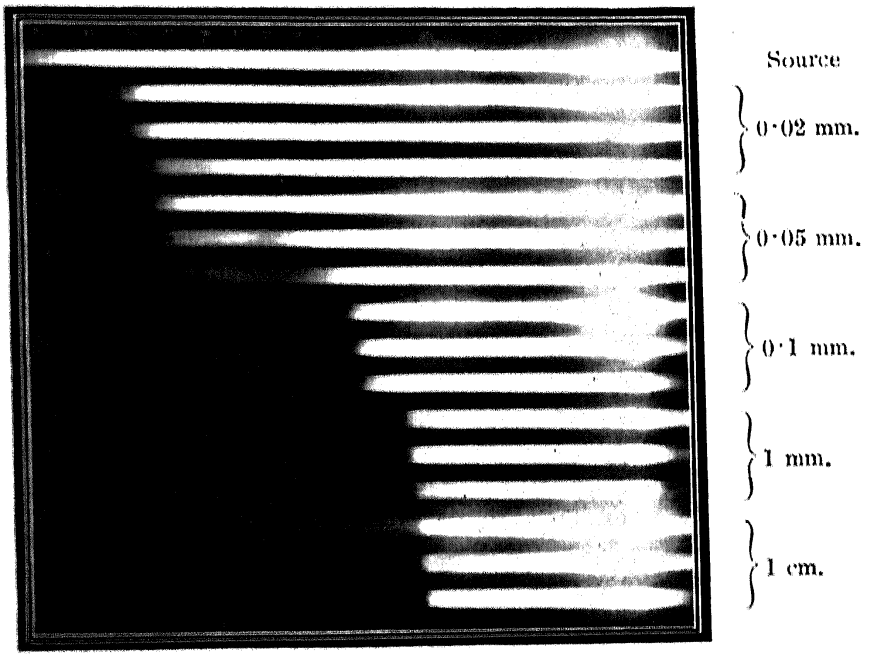
But this still leaves the question about the origin of the optical rotatory power of benzil unanswered. A more detailed knowledge of the structure of the benzil molecule and crystal is certainly necessary before we can proceed to a deeper analysis of this aspect of the problem.

In conclusion, I express my sincere thanks to Prof. Sir C. V. Raman for the valuable suggestions he gave me during the course of this work.

8. SUMMARY

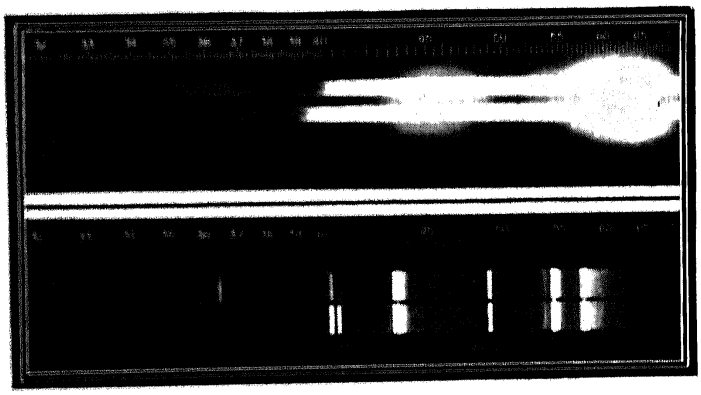
The paper reports a study of the rotatory dispersion and the ultraviolet absorption spectrum of crystalline benzil. Transmission spectra have been photographed with varying thicknesses of the crystal. Even with the thinnest specimens (0·02 mm.) there is an almost complete cut off in the transmitted intensity beyond 3400 Å marking the presence of an intense absorption band farther out in the ultraviolet. There is another comparatively feeble absorption which extends from 4500 Å onwards into the shorter wavelength region of the spectrum with a maximum at 3900 Å. This band is markedly pleochroic. The rotatory dispersion has been measured from 9000 Å in the

FIG. 1



Transmission by various thicknesses of crystalline benzil

FIG. 2



Photographs showing pleochroism in benzil. Thickness of crystal about 0·05 mm.

infrared upto 3600 Å in the ultraviolet right through the absorption band. A specimen of 0·03 mm. thick had to be used in order to penetrate the band. The crystal exhibits anomalous rotatory dispersion in the region of absorption. The one-term rotatory dispersion formula

$$\rho^2 = 6{\cdot}27\,\lambda^2/[\lambda^2 - (0{\cdot}24)^2]^2$$

fits the data quite well except in the immediate vicinity of the absorption band. The temperature variation of the rotatory power has been measured for three wavelengths in the visible. The rotatory power decreases slightly when the crystal is heated. Dispersion formulæ have been proposed in terms of observed absorption frequencies which give a satisfactory explanation for the interesting fact that the crystal, which is uniaxial and positive for λ 5893 A, becomes optically isotropic at λ 4205 Å.

References

1. Bryant, W. M. D. .. *J. Amer. Chem. Soc.*, 1943, **65**, 96.
2. Caldwell and Le Fevre .. *J. Chem. Soc.*, 1939, 1614–22.
3. Chandrasekhar, S. .. *Proc. Ind. Acad. Sci.*, 1952, **35A**, 103; 1952, **36A**, 118; 1953, **37A**, 458; 1953, **37A**, 468; 1953, **37A**, 697.
4. Des Cloizeaux .. *Comp. Rend.*, 1869, **68**, 308; 1870, **70**, 1209.
5. Ganguly and Choudhury .. *J. Chem. Phys.*, 1953, **21**, 554.
6. *International Critical Tables*, 1930.
7. Jelley, E. E. .. *Ind. Eng. Chem. Anals. Ed.*, 1941, **13**, 196.
8. Knaggs and Lonsdale .. *Nature*, 1939, **143**, 1023.
9. Krishnan, Guha and Banerjee .. *Phil. Trans.*, 1933, **231A**, 247.
10. Lonsdale and Smith .. *Proc. Roy. Soc.*, 1942, **179A**, 8.
11. Mann and Thompson .. *Ibid.*, 1951, **211A**, 168.
12. Subrahmanian, R. V. .. 1942, **14A**, 445.