ON THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: IV. BENZIL

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1. Introduction

Early in the history of the study of X-ray diffraction in crystals following Laue’s discovery of 1912, it was realised that the disturbing effect of the thermal agitation on the X-ray phenomena was a matter of considerable importance. About the same time, the theory of the specific heat of solids due to Debye in which the thermal energy of crystalline solids was identified with that of the elastic vibrations in them was coming into general favour. It was therefore natural that the considerations of the temperature effect in X-ray diffraction should be based on the same hypothesis. In fact, the first attempt in this direction was made by Debye himself, and the further improvements of the theory both by Debye and by later workers in the field rested on his basic concepts. Even in the specific heat theory of that time, however, it was recognised that the thermal energy of crystals which were not of the simplest chemical composition included what were called “Einstein” terms arising from modes of molecular vibration with specific frequencies. That these vibrations had any part to play in the X-ray phenomena does not however, appear to have been realised either by the experimenters or by the theorists. The great importance of the Einstein vibrations in X-ray physics, and the striking and distinctive phenomena to which they give rise, were first pointed out by Sir C. V. Raman and Dr. P. Nilakantan in their article in Current Science for April 1940. The study of these phenomena, in fact, has opened up a new approach to the problems of the solid state. The importance of the Einstein or characteristic frequencies of the crystal lattice is particularly evident in considering the X-ray behaviour of organic crystals. Taking for instance the case of benzil, it is known (Allen, 1927 and Banerjee and Sinha, 1937), that the hexagonal lattice of this crystal contains 3 molecules per unit cell. Even ignoring the numerous possible “internal” modes of their vibration, we have still to consider no fewer than 18 degrees of freedom of molecular movement, of which no less than 15 are necessarily represented by specific frequencies of vibration; the remaining three degrees of freedom alone of translatory movements of the lattice cell are the maximum number which can possibly be assigned to “elastic
vibrations" of the Debye type. It is thus evident that, in organic crystals, the Einstein vibrations of the lattice involving hindered rotations or translations of the molecules are of far greater importance than any possible vibrations of the elastic solid type.

In the three preceding papers of this series, Dr. C. S. Venkateswaran has considered respectively the cases of naphthalene, benzophenone and hexamethylene-tetramine. His work has proved conclusively that the situation is as described in the preceding paragraph. In the two crystals of the aromatic class dealt with by him, the very striking result emerged that the lattice planes which are parallel or nearly parallel to the planes of the aromatic rings give Raman reflections of marked intensity, while those perpendicular or nearly perpendicular to them are, by comparison, practically inactive in this respect. In fact, a striking disproportion was evident in the relative intensities of the classical and quantum reflections by the crystal planes differently situated with respect to the planes of the aromatic rings. Dr. Venkateswaran has remarked that these results find a simple explanation in the nature of the molecular oscillations which vary the structure amplitudes of the crystal planes. The hindered rotations and translations of the molecules as well as the deformational oscillations of low frequency would almost exclusively vary the structure amplitudes of the planes parallel to the aromatic rings, leaving unaffected those nearly perpendicular to them.

The fact that benzil is very similar in chemical composition to benzophenone, the former being diphenyldiketone and the latter diphenylketone, made it desirable to include this substance in the present series of investigations. It may be mentioned in this connection that a few photographs obtained with benzil were reproduced with a note in Nature (1940) published by four workers of the Royal Institution in London.

2. Crystal Structure of Benzil

Benzil belongs to the same crystal type as α-quartz, and has, in fact, an optical rotatory power stronger than that of quartz along the hexagonal axis. As already mentioned, the unit cell contains three molecules. The dimensions of the cell are \( a_0 = 8.15 \text{ A.U.} \) and \( c_0 = 13.46 \text{ A.U.} \) and the X-ray evidence indicates that the three molecules are arranged in equivalent positions within the cell about the threefold screw axis. Krishnan, Guha and Banerjee have studied the diamagnetic behaviour of the crystal and found that the gram-molecular susceptibility along the trigonal axis is \( \chi_t = -80.0 \times 10^6 \) e.m. units and that perpendicular to the trigonal axis is \( \chi_l = -125.6 \times 10^6 \) e.m. units. The crystal shows a noticeable birefringence, \( \omega = 1.6588 \), and \( \epsilon = 1.6783 \) (Groth, Chemische Krystallographie) for the sodium line. Suggestions regarding the molecular structure and the molecular
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orientation in benzil were made by Banerjee and Sinha (loc. cit.), but these conclusions have been disputed by Lonsdale and Knaggs (1939) in a brief note. No definite conclusions regarding the structure of benzil appear, however, to have been published by these latter authors.

3. Experimental Arrangements

Benzil is usually crystallised from ether. Due to the rapid evaporation of ether, most of the crystals are often found to be of disproportionate growth, forming a cluster. In the present work, the crystals were grown out of a solution of the substance in alcohol diluted with an equal volume of water. The smaller solubility of the substance in alcohol, assisted by the slow evaporation of the liquid facilitates a good growth of crystals suitable for X-ray work. The crystals were yellow hexagonal prismatic needles, approximately \( \frac{1}{2} \) mm. in diameter. The source of X-rays was a Siebert ‘Spektro-Analyt’ tube of the non-demountable type, with a copper anticathode, run at 41000 volts, and 10 m.a. A fine beam of X-rays collimated by means of a lead slit 1 mm. in diameter and 9 cm. deep was incident on the crystal which was mounted on a goniometer with its trigonal axis nearly vertical. Initially one of the external prism planes of the crystal was normal to the X-ray beam, this having been judged by the optical reflection from that face. The crystal was turned through an angle of about 20° from this position about the vertical axis of the goniometer, which was adjusted to coincide with the triad axis of the crystal. The plane giving an intense Raman reflection along the horizontal was found to be the 2\( \bar{2} \)00 plane, and a series of pictures was then taken up to a limit of about 4° on either side of this setting. In these extreme positions, exposures varying from about 2 to 2\( \frac{1}{2} \) hours were required.

For another series of pictures, the crystal was mounted in such a way that the X-ray beam passed along the trigonal axis. By suitable manipulation of the crystal this way or that about the goniometer axis, and aided by a number of trial pictures, the exact direction of the beam along the trigonal axis was secured. In this position, exposures varying from 2 to 3 hours were found necessary to secure a well-exposed pattern.

4. Description of the Experimental Results

Only two of the typical photographs obtained have been reproduced, although a number of others in different settings of the crystal have been taken. Fig. 1a in Plate XXXI represents a symmetric Laue photograph with the X-rays passing along the trigonal axis of the crystal, while Fig. 1b represents one with the X-rays perpendicular to the trigonal axis. Both photographs reveal some very interesting features. It will be observed from Fig. 1a, that the Laue pattern exhibits hexagonal symmetry with respect to the positions of the spots. The intensities, however, exhibit only a trigonal
symmetry, alternate sectors showing noticeable differences in the intensity of the spots. This feature is particularly striking in the Raman pattern of six spots at the corners of a regular hexagon; the alternate spots are of the same intensity, but differ greatly from the intervening ones in this respect. Though no quantitative measurements of intensity have been made, it is fairly clear that these differences are much greater than those of the corresponding Laue spots forming a hexagonal pattern. It is also noticed that streamers emerge from the primary Raman spot, proceeding approximately parallel to the adjacent sides of the hexagon, a noteworthy feature being that these alternately point in opposite directions. The three pairs of spots showing the intense Raman reflections have been identified as belonging to the form (2201). Lying on the same radial lines as these and forming an outer hexagon are the spots of the form (3302) which have however much less intensity. In two of them the Raman Ki spots are just visible beyond the Laue position, two of the other spots of this group coinciding with the Bragg reflection. Here again in the neighbouring Raman spots, the intensities appear to differ.

Equally remarkable are the features seen in Fig. 1 b, obtained as has already been mentioned with the direction of the X-ray beam normal to the trigonal axis of the crystal. There are two groups of Laue spots lying along two ellipses. These are accompanied by two groups of Raman spots lying on vertical lines in the photograph. The group to the left of the picture is much more intense than the group to the right, while in each group, the spots differ notably in intensity among themselves; the order of relative intensities is exactly reversed on the two sides of the picture. The zone to which the more intense Raman spots belong has been identified to be the (110) zone, while the other is the (1T0) zone. On the left, the central Raman spot lying along the horizontal has the index 2200, the one immediately above and below belong to the 2201 planes, and the one further up that of the 2202 plane. On the other zone the corresponding spots which appear belong respectively to the 2110, −2111 and −2112 planes. Of all the Raman spots seen, by far the most intense is that given by the 2201 plane. It is thus exactly the same set of planes which give the intense reflections seen in Fig. 1 a.

5. Discussion of the Results

Bearing in mind what has been said already in the introduction, it is clear that the only possible explanation for the results indicated is that the plane of the aromatic rings in the benzil crystal lie in or very close to the alternate planes of the form (2201). It is readily seen that this explains every one of the features indicated above. The angle between the triad axis of the crystal and the (2201) plane is by calculation 14° 6'. It is thus evident that the plane of the aromatic rings in the crystal are inclined to the triad axis at an
FIG. 1

Raman X-ray Reflections in Benzil
angle about the same as that stated above. The inclination of the plane of the aromatic rings thus directly inferred from the X-ray photographs, agrees closely with the angle 13° calculated by Banerjee and Sinha from the magnetic measurements of Krishnan, Guha and Banerjee. It should be remembered that the X-ray method is definitely superior to the magnetic method as it indicates both the azimuth and the orientation of the planes and not merely the latter.

The explanation of the configuration of the streamers accompanying the Raman reflections is fairly simple. By symmetry, the phase waves of the lattice must be along the three planes inclined at 120° to each other and passing through the triad axis of the crystal, these planes being perpendicular to the longer axis of the benzil molecules. The directions of the streamers as observed conform to this situation.

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6. Summary

In a series of well-exposed Laue diagrams of benzil taken with a pencil of Cu X-radiation along the trigonal axis, three alternate planes of the form (2201) are found to give intense Raman reflections, the alternate planes of the same form being much less active in this respect. A similar feature is also observed in photographs taken with the beam transverse to the trigonal axis. The facts find a very simple explanation when it is assumed that the three molecules of benzil in the unit cell lying in equivalent positions along the threefold screw axis, have the planes of their aromatic rings practically coinciding with the planes mentioned. The inclination of 14° of the aromatic planes thus inferred from the X-ray results is in close agreement with the angle of 13° deduced from the diamagnetic susceptibilities of the crystal. The X-ray method is however obviously superior as it gives both the azimuth and orientation of the aromatic rings.

REFERENCES

5. ——— and Lonsdale, K. Ibid., 1939, 143, 1023.