oriented bundles of line scatterers is shown to be circularly symmetrical.

Equation (7) for the generalized model with a distribution of orientations cannot be integrated directly except when $g(\varphi)$ assumes certain favorable forms (such as $\sin\varphi$); neither does it generally lend itself to inversion by the Fourier–Bessel theorem. Therefore the present mathematical analysis does not lead to a definite conclusion concerning the validity of equation (1).

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The Direct Determination, by Optical-Transform Methods, of the Structure of the Red Form of 5-Methoxy-2-Nitrosophenol. I. Determination of the Trial Structure

BY M. M. CROWDER
Chemistry Department

AND K. A. MORLEY AND C. A. TAYLOR
Physics Department, College of Science and Technology, Manchester 1, *England*

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The direct determination of the crystal structure of a compound $C_7O_3NH_7$ has been carried out using optical-diffraction principles without recourse to knowledge of the chemical configuration. The $h0l$ weighted reciprocal-lattice section showed that the molecule probably contained a plane hexagonal ring of atoms and that it was elongated parallel to the c axis. With this assumption, the position of the ring was found by a molecular-location method, signs of the structure factors were deduced from optical transforms, and a Fourier synthesis was performed. Possible positions of the remaining atoms were selected from this and the most likely ones tested by optical-transform methods. This procedure led to a trial structure which, after re-application of the molecular-location method, was refined by normal Fourier methods.

1. Introduction

This investigation was deliberately conceived as an attempt to see whether optical methods could be used to determine a structure directly—in other words, to see whether a structure can be recognized from its X-ray diffraction pattern. The compound was chosen because preliminary work showed that there was some possibility of success, and it was felt to be better to attempt a problem of this sort rather than one of greater difficulty which might not provide as much experience. Two of the authors (K. A. M. & C. A. T.) were kept in ignorance of the probable chemical configuration, being given only the empirical formula, $C_7O_3NH_7$. An outline of the earlier stages of the work has already been published (Crowder, Morley & Taylor, 1957).

2. Preliminary crystallographic results

Oscillation and Weissenberg photographs showed that the space group is $P2_12_12_1$, the unit-cell dimensions being $a = 17{\cdot}11$, $b = 3{\cdot}80$, $c = 10{\cdot}67$ Å. The density, 1·46 g.cm.$^{-3}$, showed that there are four molecules of $C_7O_3NH_7$ in the unit cell.

The short b axis indicated that the (010) projection was likely to be the most informative, and thus a $h0l$ weighted reciprocal-lattice section was derived. The first photographs taken were rather underexposed and gave only about 70 measurable reflexions out of a possible total of 230; this number was however considered reasonable to start with. The intensities were estimated visually and the weighted reciprocal-lattice section using approximate unitary structure factors derived from them is shown in Fig. 1.

3. Preliminary deductions

From Fig. 1 it can be deduced that a prominent feature of the structure is a hexagonal arrangement of atoms, parallel to the plane of projection and roughly with the dimensions of a benzene ring (Hanson, Lipson & Taylor, 1953). If such a ring is assumed, it is then necessary to find the position within the unit cell, and it was decided to use the molecular-location method (Taylor, 1954) for this purpose; the method was originally intended to be used only when the complete molecule was known, but it was thought possible that it might give information about a single feature such as a hexagonal ring of atoms if reflexions associated particularly with such a ring were used.

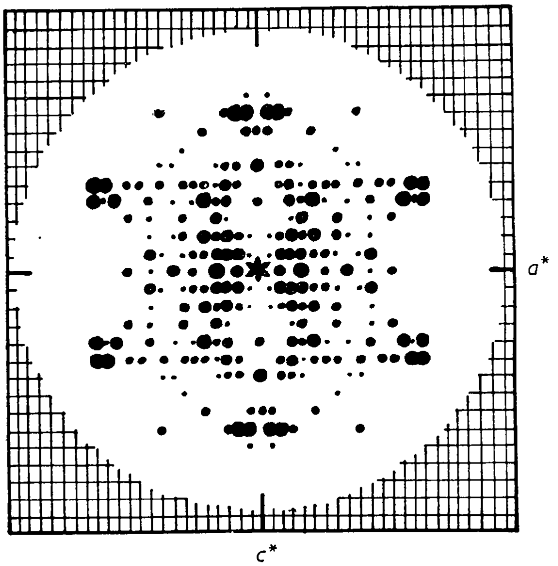

Fig. 1. *h0l* section of the weighted reciprocal lattice, based on the earlier limited data.

The hexagon deduced from Fig. 1 has two opposite sides parallel to *a* and has mirror planes parallel to *a* and *c*; the four symmetry-related hexagons in the projection will thus appear identical. This fact leads to considerable simplification in the application of the molecular-location method, since all four hexagons are centrosymmetric and have the same transform. Thus, if G_o is the transform of the single hexagon with respect to its centre as origin, and G_{hl} is the transform of the four hexagons with the parameters X, Z defining their positions in the unit cell, then

$$\left.\begin{array}{l} G_{hl} = 4G_o \cos 2\pi hX \cos 2\pi lZ \\ \qquad \text{for points at which } h+l \text{ is even} \\ G_{hl} = 4G_o \sin 2\pi hX \sin 2\pi lZ \\ \qquad \text{for points at which } h+l \text{ is odd .} \end{array}\right\} \quad (1)$$

It is unnecessary to use the approximate equation involving the error due to a second pair of molecules as in the paper by Taylor (1954).

A few reflexions for which G_{hl} ($\simeq F_{\text{obs.}}$) was small but G_o was large were chosen, and a graphical solution of equation (1) was obtained. If G_{hl} is exactly zero then one of the separate terms in the appropriate equation (1) must be zero and the solutions are lines parallel to the axes of X and Z. Six reflexions were used and a solution found at $X = 0{\cdot}130$, $Z = 0{\cdot}225$.

This result had, of course, to be accepted with caution; it had been obtained with only 6 out of 11 atoms and since the form of Fig. 1 shows the hexagonal nature of the molecule so clearly it is probable that other atoms also lie upon the same hexagonal lattice of points. It is therefore quite possible that a pseudo-centre of an incomplete hexagon had been found, for example; contingencies of this sort must always be allowed for when using the molecular-location method.

An optical transform of the four hexagons in the relative positions corresponding to the X and Z values given above was prepared; the agreement with the weighted reciprocal lattice in the regions of the 'benzene' peaks was good and the signs of about half the reflexions—including most of the strong ones—were clearly indicated; they were determined optically (Pinnock & Taylor, 1955). The resulting Fourier synthesis (Fig. 2) showed the hexagons that had been used to derive it, together with some extra peaks.

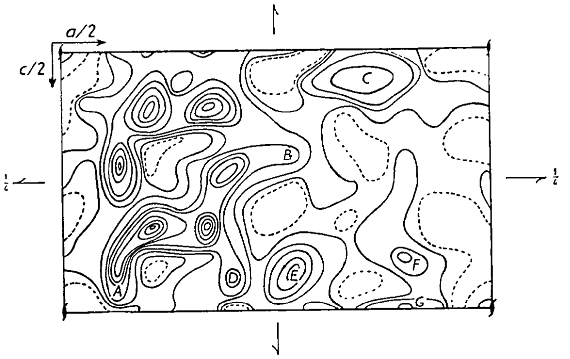

Fig. 2. First Fourier synthesis of the (010) projection based on signs derived from hexagons only. The peaks labelled *A*, *B* and *C* ultimately turned out to be significant and *D*, *E*, *F* and *G* to be spurious.

To decide which peaks were likely to be significant another indication from Fig. 1 was used; the central group of reflexions covers a region that is long in the *a** direction. We may thus expect the molecule to be long in the *c* direction and this criterion was used in selecting possible combinations of atoms that would improve the agreement between the transform and the weighted reciprocal lattice. There were several possibilities and these were tested by comparison of the optical transforms with the weighted reciprocal lattice. From the best a further sign determination was made and a second Fourier synthesis computed. It showed the expected molecule fairly clearly, and by the use of the variable structure-factor graph (Morley & Taylor, 1957) some improvement of the agreement

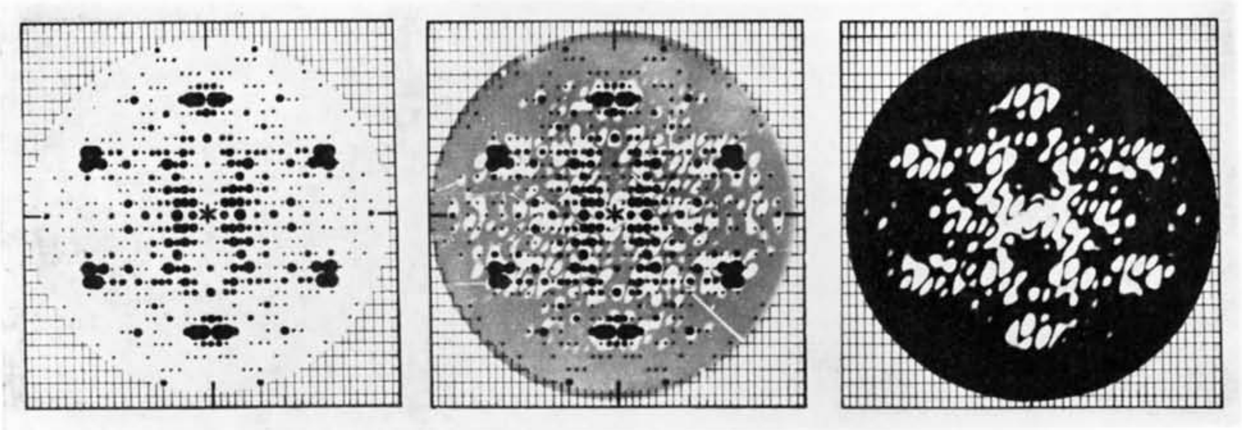

Fig. 3. The final optical agreement. On the left is the $h0l$ section of the weighted reciprocal lattice with approximate unitary structure factors and the complete data; on the right is the optical transform of one unit cell; in the centre the two are superimposed.

between calculated and observed intensities was obtained. But the residual remained high (about 0·50) and the Fourier synthesis contained some spurious detail. The residual did not decrease greatly when the larger peaks—including one in the ring—were assumed to be oxygen and nitrogen, and it was therefore considered worth while to re-determine the position of the molecule assuming that the atoms were in the correct relative positions. It is well known that correct molecular orientation can produce fair agreement (Pinnock, Taylor & Lipson, 1956) even if the position of the molecule is wrong.

4. Re-determination of molecular location

Equations (1) cannot be used, since the molecule is not now symmetrical. On the other hand, because of the predominance of the diffraction by the hexagon, it is difficult to find reflexions satisfying the conditions laid down by Taylor (1954). A new and more general procedure was therefore worked out and is described in a separate paper (Taylor & Morley, 1959). In this paper the results of the application of the new method to the present problem are described; they indicate that the centre of the hexagon has co-ordinates (0·133, 0·175), a movement of about 0·5 Å (parallel to c) from the previous position. The agreement residual dropped to 0·30, but could not be further reduced; a Fourier synthesis showed no clear distinction between carbon, oxygen and nitrogen and there was some spurious detail including, for example, a small peak at the centre of the hexagon. Since the methods now seemed certain of success, it was decided to obtain more extensive data and new photographs were taken with reflexions out to the limit obtainable with Cu $K\alpha$ radiation.

5. Refinement of the (010) projection

There were still many unobserved $h0l$ reflexions; out of a possible 230 only 135 were observed, presumably because the projection is pseudo-hypercentric (Lipson & Woolfson, 1952). Nevertheless, comparison of the new observed structure factors with those calculated for the last structure described in section 4 gave a residual of 0·19 and the Fourier synthesis, using the same signs as before but with the new observed structure factors, showed clearly the oxygen, nitrogen and most of the hydrogen atoms.

Inclusion of hydrogen atoms and normal methods of refinement reduced the residual to 0·143. (In calculating the residual, unobserved reflexions were assessed at half the minimum observable value in calculating $\Sigma|F|_o$, and were omitted in calculating $\Sigma\{|F|_o-|F|_c\}$ if F_c was less than F_o).

The final optical agreement is shown in Fig. 3; the final Fourier synthesis, determination of the 001 projection, and tables of observed and calculated F's are given in part II of this paper (Bartindale, Crowder & Morley, 1959).

6. Discussion

This work shows that, in a favourable case, it is possible to deduce a structure from its diffraction pattern by the aid of optical principles. The methods described are not as direct or as objective as those described by Cochran & Douglas (1954), Woolfson (1957) and others, but the physical principles are probably more easily grasped by the generality of research workers. It is hoped to apply the methods to more complicated structures in the near future.

The work also demonstrates the importance of accurate data. The policy of testing the methods on data inadequate in extent and accuracy was not justified by the course of the work, which would almost certainly have proceeded more quickly and smoothly if the final data had been available at the beginning.

We wish to record our indebtedness to Prof. H. Lipson for his advice and help in the preparation of this paper.

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The Direct Determination, by Optical Transform Methods, of the Structure of the Red Form of 5-Methoxy-2-Nitrosophenol. II. Results and Chemical Discussion

By G. W. R. Bartindale, M. M. Crowder and K. A. Morley
College of Science and Technology, Manchester, England

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Details of the crystal structure of the red form of 5-methoxy-2-nitrosophenol are given; the determination is based on the preliminary work described in the preceding paper (Crowder, Morley & Taylor, 1959). Interatomic distances have been determined with a standard deviation of about 0·015 Å.

The compound is shown to be the *o*-quinone monoxime tautomer with molecules linked by hydrogen bonds.

Introduction

Henrich & Eisenach (1904) have shown that 5-methoxy-2-nitrosophenol crystallises in green rectangular plates from benzene and in red needles from ethanol. At a temperature of 128–130 °C., the green modification changes to the red form, subsequently melting at 154 °C. They suggested that the green material is the 2-nitrosophenol tautomer (Fig. 1(*a*)) and the red form the *o*-quinone monoxime tautomer (Fig. 1(*b*)).

Burawoy *et al.* (1955) confirmed the observations of Henrich & Eisenach (1904) and also found that in solution both forms possess identical electronic spectra. They also obtained conclusive evidence that in solutions 5-methoxy-2-nitrosophenol exhibits solvent-dependent tautomeric equilibria and that an intramolecular hydrogen bond exists in molecules of both tautomers (Fig. 1(*c*) and (*d*)).

X-ray powder photographs showed that the crystal structures of the two solid forms are completely different. It was, therefore, thought that the X-ray analysis of the two crystalline forms of 5-methoxy-2-nitrosophenol would provide valuable information. The crystal structure of the red form has now been determined and the analysis shows that it corresponds to the *o*-quinone monoxime tautomer, and that, in contrast to its solutions, it forms intermolecular hydrogen bonds.

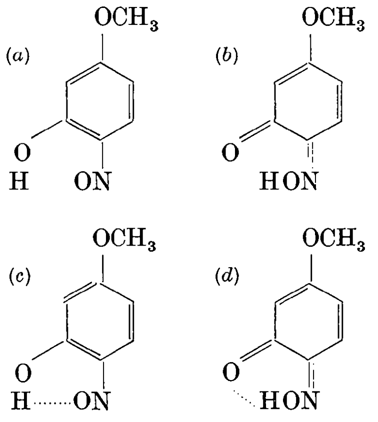

Fig. 1. (*a*) The 2-nitrosophenol tautomer. (*b*) The *o*-quinone monoxime tautomer. (*c*) The hydrogen bond in the 2-nitrosophenol tautomer. (*d*) The hydrogen bond in the *o*-quinone monoxime tautomer.