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

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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.

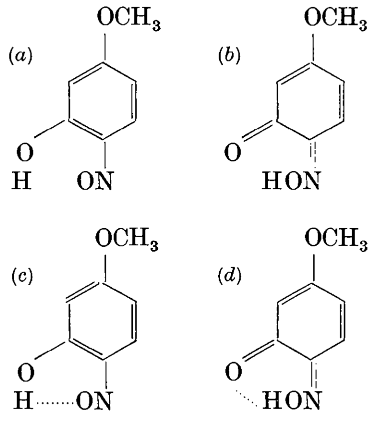

Fig. 1. (*a*) The 2-nitrosophenol tautomer. (*b*) The *o*-quinone monoxime tautomer. (*c*) The hydrogen bond in the 2-nitrosophenol tautomer. (*d*) The hydrogen bond in the *o*-quinone monoxime tautomer.

Table 1. *Table of observed* (F_o) *and calculated* (F_c) *structure factors for the* (010) *projection*

Origin on a 2_1-axis parallel to b

hkl	F_o	F_c
200	33	−32
400	43	−42
600	15	−12
800	31	−29
10,0,0	8	−10
12,0,0	12	11
14,0,0	4	0
16,0,0	5	−6
18,0,0	5	7
20,0,0	8	9
101	7	6
201	47	−45
301	40	−43
401	39	−36
501	26	27
601	17	−16
701	15	19
801	7	5
901	14	−13
10,0,1	19	19
11,0,1	8	9
12,0,1	8	−8
13,0,1	< 3	2
14,0,1	8	9
15,0,1	6	5
16,0,1	< 3	3
17,0,1	8	−10
18,0,1	4	4
19,0,1	< 2	−1
20,0,1	6	−8
21,0,1	< 2	2
002	< 3	−1
102	6	−6
202	13	17
302	22	32
402	17	−20
502	25	−30
602	7	−2
702	19	25
802	9	−11
902	< 3	2
10,0,2	8	12
11,0,2	5	−8
12,0,2	< 3	2
13,0,2	< 3	−4
14,0,2	< 3	−3
15,0,2	< 3	−3
16,0,2	< 3	0
17,0,2	< 3	2
18,0,2	5	−5
19,0,2	< 2	1
20,0,2	< 2	1
21,0,2	< 2	3
103	9	−7
203	6	6
303	5	−6
403	24	−29
503	12	11
603	6	−7
703	14	−15
803	< 3	0
903	5	5
10,0,3	8	5
11,0,3	6	4
12,0,3	12	12
13,0,3	5	4
14,0,3	< 3	−2
15,0,3	9	−9
16,0,3	< 3	−2
17,0,3	7	8
18,0,3	< 2	0
19,0,3	7	−6
20,0,3	< 2	−1
004	15	−18
104	< 2	4
204	3	−1
304	30	−37
404	14	−14
504	46	47
604	8	7
704	9	11
804	4	4
904	6	−7
10,0,4	19	22
11,0,4	8	6
12,0,4	4	4
13,0,4	18	−19
14,0,4	10	−11
15,0,4	10	−11
16,0,4	5	−2
17,0,4	8	9
18,0,4	< 2	0
19,0,4	< 2	3
20,0,4	< 2	0
105	3	3
205	13	−12
305	22	23
405	5	7
505	12	11
605	20	21
705	13	−14
805	10	−9
905	14	−18
10,0,5	< 3	−4
11,0,5	10	−12
12,0,5	14	14
13,0,5	5	−3
14,0,5	18	−19
15,0,5	19	15
16,0,5	< 2	3
17,0,5	< 2	2
18,0,5	< 2	3
19,0,5	< 2	0
006	20	21
106	< 3	−2
206	18	−20
306	16	−16
406	7	8
506	6	−8
606	< 3	−1
706	< 3	−1
806	11	9
906	8	−7
10,0,6	< 3	−1
11,0,6	8	11
12,0,6	6	−4
13,0,6	8	8
14,0,6	< 3	1
15,0,6	5	−5
16,0,6	< 2	−2
17,0,6	< 2	2
18,0,6	< 2	1
19,0,6	< 2	0
107	< 3	1
207	6	7
307	5	−7
407	< 3	1
507	< 3	2
607	4	5
707	8	11
807	6	−4
907	7	−7
10,0,7	< 3	1
11,0,7	< 3	−3
12,0,7	< 3	−2
13,0,7	< 3	0
14,0,7	< 2	1
15,0,7	< 2	1
16,0,7	< 2	−3
17,0,7	< 2	0
18,0,7	4	5
008	19	−19
108	11	−11
208	7	8
308	4	−4
408	< 3	−1
508	12	−15
608	< 3	−1
708	6	6
808	7	5
908	< 3	2
10,0,8	< 3	−2
11,0,8	< 3	1
12,0,8	< 3	−2
13,0,8	< 2	−1
14,0,8	< 2	1
15,0,8	< 2	3
16,0,8	< 2	2
17,0,8	4	6
109	19	−24
209	18	20
309	12	13
409	< 3	0
509	< 3	4
609	< 3	0
709	3	3
809	< 3	−1
909	8	9
10,0,9	4	−4
11,0,9	6	−6
12,0,9	< 2	1
13,0,9	< 2	1
14,0,9	< 2	1
15,0,9	< 2	−1
16,0,9	< 2	−1
0,0,10	5	−2
1,0,10	10	14
2,0,10	10	11
3,0,10	< 3	0
4,0,10	< 3	1
5,0,10	5	5
6,0,10	7	−8
7,0,10	4	3
8,0,10	< 2	−2
9,0,10	4	−3
10,0,10	< 2	2
11,0,10	< 2	−3
12,0,10	< 2	−1
13,0,10	< 2	−1
14,0,10	3	−3
1,0,11	3	−3
2,0,11	3	−2
3,0,11	3	5
4,0,11	< 2	1
5,0,11	< 2	−1
6,0,11	< 2	−1
7,0,11	< 2	−1
8,0,11	3	−3
9,0,11	< 2	1
10,0,11	< 2	−1
11,0,11	< 2	−1
12,0,11	4	6
0,0,12	< 2	1
1,0,12	< 2	−1
2,0,12	< 2	−1
3,0,12	< 2	1
4,0,12	4	4
5,0,12	3	1
6,0,12	5	−5
7,0,12	< 2	0
8,0,12	< 2	2
9,0,12	< 2	−2
1,0,13	< 2	2
2,0,13	< 2	4
3,0,13	< 2	0
4,0,13	< 2	−1
5,0,13	< 2	−3
6,0,13	5	−6

Preliminary work

The material used in the investigations was supplied by Dr A. Burawoy and prepared by the method of Henrich & Eisenach (1904). Suitable crystals were grown by slow cooling of a solution of 5-methoxy-2-nitrosophenol in ethanol.

Oscillation and zero-layer-line Weissenberg photographs were taken with Cu $K\alpha$ radiation and showed that the unit cell is orthorhombic with dimensions

$$a = 17{\cdot}11,\quad b = 3{\cdot}80,\quad c = 10{\cdot}67\ \text{Å}\,.$$

The measured density was 1·46 g.cm.$^{-3}$ and the calculated density assuming four empirical-formula units in the unit cell is also 1·46 g.cm.$^{-3}$. The space group was found to be $P2_12_12_1$. Visually estimated intensities from Weissenberg photographs were used, the final refinement being made with 135 measured reflexions for the (010) zone and 60 for the (001) zone. Full details of the determination of the trial structure are given in Part I (Crowder, Morley & Taylor, 1959).

Results of the structure determination

(*a*) (010) *projection*

The trial structure was refined by repeated cycles of structure-factor calculation and Fourier synthesis. At a later stage new and more complete data were obtained and it became possible to include hydrogen atoms in the calculations. The residual for the final result (see Crowder, Morley & Taylor, 1959 for the precise method of calculating the residual) was 14·3 %. Table 1 gives the agreement between observed and calculated structure factors and shows that the main discrepancies are with the unusually large number of unobserved reflexions. The final Fourier synthesis is shown in Fig. 2. As can be seen it reveals a clear distinction between the oxygen, nitrogen and carbon peaks and indicates possible positions of the hydrogen atoms.

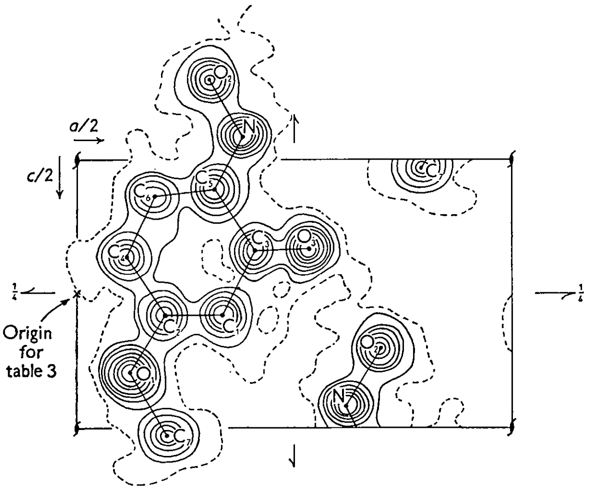

Fig. 2. The final Fourier synthesis for the (010) projection. Contours are drawn at intervals of approximately 1 electron per square Ångström unit. The 1 e.Å^2 contour is dotted. The origin is on the 2_1 axis parallel to *b*, as used in the computations of structure factors. The origin used for Table 3 is also marked.

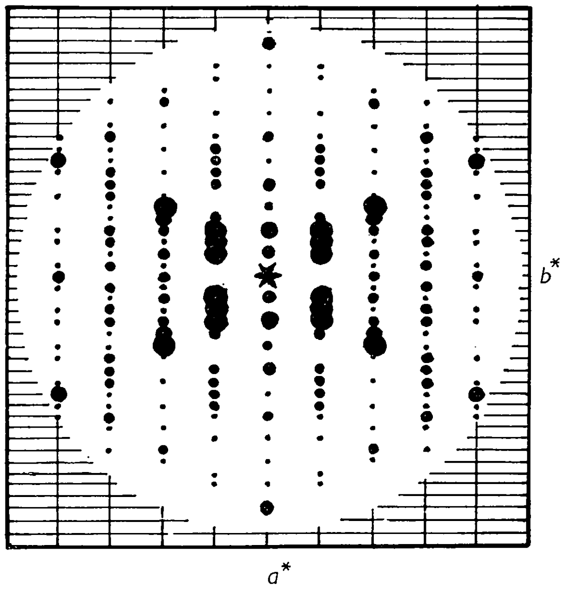

Fig. 3. *hk*0 section of the weighted reciprocal lattice derived from approximate unitary structure factors.

Table 2. *Table of observed* (F_o) *and calculated* (F_c) *structure factors for the* (001) *projection*

Origin on a 2_1-axis parallel to *c*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	33	35	11,1,0	15	6	10,2,0	< 3	−5	11,3,0	5	−5
400	43	−41	12,1,0	6	0	11,2,0	5	2	12,3,0	12	7
600	15	14	13,1,0	< 3	0	12,2,0	< 3	−3	13,3,0	5	−3
800	31	−26	14,1,0	7	−7	13,2,0	8	−4	14,3,0	< 2	1
10,0,0	8	10	15,1,0	< 3	3	14,2,0	< 3	4	15,3,0	4	4
12,0,0	12	11	16,1,0	< 3	2	15,2,0	11	−7	16,3,0	< 2	−1
14,0,0	4	0	17,1,0	6	−6	16,2,0	5	4			
16,0,0	5	−6	18,1,0	8	7	17,2,0	< 2	1	040	16	−18
18,0,0	5	−7	19,1,0	< 2	0	18,2,0	< 2	−5	140	6	−4
20,0,0	8	9	20,1,0	< 2	2	19,2,0	< 2	2	240	< 3	0
									340	6	−4
110	3	4	020	18	14	130	13	7	440	5	−4
210	70	−76	120	5	−7	230	8	7	540	< 2	1
310	80	−99	220	32	−28	330	17	−19	640	< 2	1
410	48	−52	320	9	2	430	17	16	740	6	−6
510	22	11	420	19	15	530	9	7	840	< 2	−2
610	< 3	0	520	28	20	630	5	3	940	8	−7
710	4	3	620	51	59	730	10	−5	10,4,0	10	9
810	13	14	720	8	8	830	18	−17	11,4,0	5	7
910	17	−15	820	< 3	2	930	14	−15	12,4,0	12	5
10,1,0	15	11	920	6	−3	10,3,0	5	−5			

(*b*) (001) *projection*

The determination of the trial structure for the (001) projection proceeded quite normally. The weighted reciprocal-lattice section, shown in Fig. 3, shows rows of strong peaks inclined at about 30° to the b^*-axis indicating a molecule which appears almost linear and inclined at 30° to the a-axis in the projection. Using this fact and the x co-ordinates from the first projection a trial molecule was obtained which gave quite reasonable optical agreement. The modified molecular-location method (Taylor & Morley, 1959) was then used to determine the Y co-ordinate of the molecule, signs were determined optically and a Fourier synthesis prepared. It was clear that considerable overlapping of atoms within the molecule occurred and that refinement would not produce a clearly resolved projection. The refinement, by successive Fourier syntheses and structure-factor calculations, was carried out in two stages. First, the molecule was considered to be completely planar and in the second stage atoms were located at points of maximum electron density consistent with the x co-ordinates from the first projection without regard for the assumed planarity of the molecule. Table 2 shows the agreement between observed and calculated structure factors; the final residual for this projection was 20%.

The atomic co-ordinates

Table 3 shows the final co-ordinates obtained. The standard deviation in atomic co-ordinates for the (010) projection was determined by Booth's method (1947) and found to be 0·016 Å for carbon, 0·014 Å for nitrogen and 0·012 Å for oxygen. The y co-ordinates could not be assessed in the same manner.

A second method of assessing the probable error in co-ordinates was suggested by Dr M. M. Woolfson. All the values of $|F_o-F_c|$ were collected into groups limited by $\sin\theta$ values. Within each group the values of (F_o-F_c) were redistributed at random between the various structure factors and a new hypothetical value of F_o obtained. In this way a set of 'F_o's' with the same *residual* as that used in the structure determination but with a different error distribution was obtained. A Fourier synthesis calculated from the new hypothetical F_o's would then give some indication of the error to be expected if the errors in the original determination were *all* due to errors in observation. Changes in co-ordinates were of the order of 0·015 Å, which agrees very well with the result found by Booth's method.

Table 3. *Atomic co-ordinates*

(Hydrogen atoms were not included in the calculations for the 001 zone). Origin half-way between three non-intersecting pairs of screw axes parallel to *a*, *b* and *c*.

Atom	x/a	y/b	z/c
C_1	0·1667	−0·253	0·0400
C_2	0·1033	−0·451	0·0417
C_3	0·2050	−0·167	−0·0783
C_4	0·0567	−0·520	−0·0700
C_5	0·1583	−0·260	−0·1933
C_6	0·0900	−0·460	−0·1833
C_7	0·1017	−0·455	0·2633
N	0·1900	−0·193	−0·2933
O_1	0·0600	−0·500	0·1450
O_2	0·1500	−0·273	−0·4000
O_3	0·2667	0·000	−0·0833
H_1	−0·008	—	−0·058
H_2	0·072	—	−0·297
H_3	0·200	—	0·125
H_4	0·325	—	−0·008
H_5	0·053	—	0·320
H_6	0·107	—	0·327
H_7	0·167	—	0·263

Discussion

In the final Fourier projection on the (010) plane the atoms are completely resolved and the carbon, nitrogen and oxygen peaks are clearly distinguishable. The Fourier projection on the (001) plane does not show the atomic positions clearly owing to considerable overlapping; nevertheless a certain amount of useful information could be derived. The molecule is practically planar and tilted at an angle of 30° to the (010) plane. The molecules are arranged in layers and adjacent molecules joined by hydrogen bonds in a manner analogous to the arrangement in boric acid, for example (Zachariasen, 1934).

Bond lengths, interbond angles and intermolecular distances have been calculated and are shown in Figs. 4 and 5. The molecule clearly possesses the

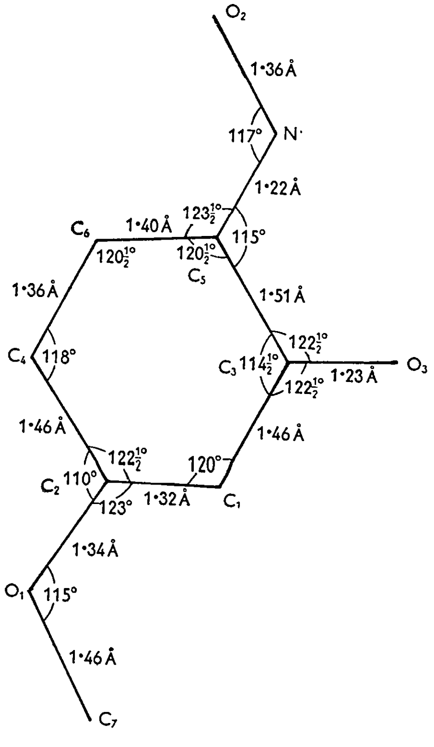

Fig. 4. Bond lengths and interbond angles.

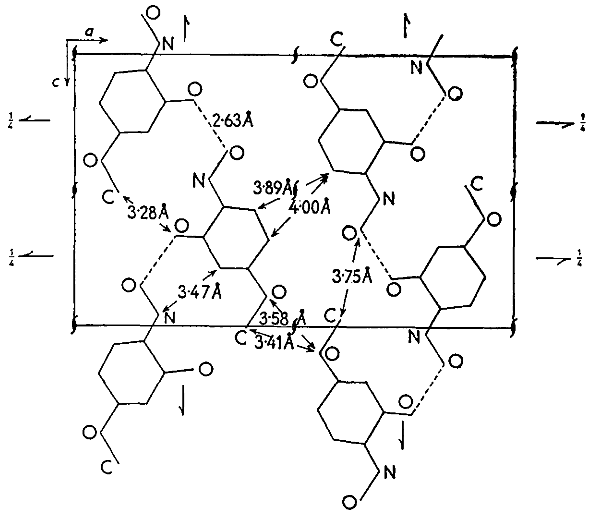

Fig. 5. Intermolecular distances in the structure.

o-quinone monoxime structure; this is borne out in several ways. The ring system is alicyclic with two double bonds (1·32 and 1·36 Å) in positions consistent with this structure. The lengths of the double bonds are similar to those found in, for example, *p*-benzoquinone (1·32 Å) (Robertson, 1935).

The four other bonds in the ring are single bonds, although one of these (1·40 Å) is shorter than might have been anticipated. The length (1·23 Å) of the carbon–oxygen bond (oxygen numbered 3) is that of a double bond rather than that of a phenolic hydroxyl group, as, for example, 1·36 Å in resorcinol (Robertson, 1936).

The lengths of the bonds in the side chain $>C=N-O-$ are consistent with values obtained for other compounds containing this oxime grouping, for example, dimethylglyoxime, $>C=N-$, 1·27 Å; $=N-O-$, 1·38 Å and interbond angle C–N–O, 114° (Merritt & Lanterman, 1952). Finally, bond lengths and interbond angle for the methoxy group do not show any significant deviation from the expected values.

Hydrogen bonding

There is evidence that each molecule in the crystal is joined by two external hydrogen bonds to two adjacent molecules. The O–O distances indicated in Fig. 5 are 2·63 Å; this, although short, is of the usual order of distance between two oxygen atoms linked by a hydrogen atom. Similar short hydrogen bonds occur in a number of other substances (Donohue, 1952).

All other intermolecular distances are in excess of those of closest approach between non-bonded atoms.

This investigation leaves no doubt that the red form of 5-methoxy-2-nitrosophenol has the *o*-benzoquinone monoxime structure. The observation that in the crystalline state it forms intermolecular hydrogen bonds between adjacent molecules, as distinct from intramolecular hydrogen bonds observed in solutions (Burawoy *et al.*, 1955), is also a most significant result of this investigation.

The authors wish to record their appreciation of the constant encouragement and helpful advice so generously given by Prof. H. Lipson and Dr A. Burawoy in this work. Thanks are also due to Mr F. A. Underwood for assistance with computations.

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