*Crystal Structure of a Monoclinic Form of Naphthazarin**

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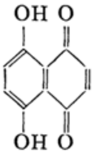
Introduction

There have been reported three monoclinic modifications of naphthazarin ($C_{10}H_4O_2(OH)_2$)[1-3]. We obtained one of these, a needle crystal with metallic lustre, from acetic acid solution colored red. To this crystal Palacios and Salvia[1] have given the space group of C_{2h}^5 with two molecules in the unit cell**. Thus the molecule should be situated on a center of symmetry in the crystal lattice, while the usual chemical formula, 5,8-dihydroxy-1,4-naphthoquinone (I), has no center of symmetry. Thus further investigations are required to deal with the molecular structure.


(I)

Naphthazarin is similar to quinhydrone, the molecular compound of quinone and hydroquinone, in color, lustre and shape of the crystal, and has the same functional groups and planar form. From the result of X-ray analysis of quinhydrone[4], it is shown that the crystal has a very interesting structure, in which there is an anomalously short distance of 3.16 Å between the planes of successively overlying planar molecules as compared with the graphite interplanar value of 3.4 Å, and in which quinones and hydroquinones are linked linearly one after the other through the intermolecular hydrogen-bridges, these two interactions causing a layered structure to be formed. Therefore it becomes interesting to discover whether or not such special interactions are operative in the crystal structure of naphthazarin.

In this paper is given some information about the form of the molecule and the intermolecular interactions from two-dimensional X-ray analysis.

Unit Cell and Space Group

Oscillation, Sauter and Weissenberg photographs were taken about the needle axis (a axis) and another axis (b axis), using Cu K_α radiation. The photographs have shown a monoclinic lattice. The dimensions of the unit cell, containing two molecules, were as follows;

$$a=3.74,\ b=7.63,\ c=14.53\ \text{Å}.\ \beta=97.1°.$$

From the Weissenberg photographs the intensities of reflexions were estimated visually, compared with a calibrated scale, multiple-film technique being used. Structure factors were deduced from these intensity data in the usual way.

At the first stage, the space group of $C_{2h}^5-P2_1/c$ was considered to be reasonable, since it appeared that no regular absences of reflexions were observed, except for $(0k0)$ when k is odd, and $(h0l)$ when l is odd. However, when the Weissenberg photograph of $(h0l)$ was examined carefully once more, some of the forbidden spectra were suspected to be appearing very faintly. On the long exposed oscillation photographs of the a axis, very weak but definite spectra of (101), (103), (103), (105) and (105) etc. were recognized. Therefore the symmetry element of glide plane is undoubtedly missing in the crystal.

In consequence, the space group is not $C_{2h}^5-P2_1/c$, but $C_2^2-P2_1$, although it may be said that the crystal has the symmetry of $C_{2h}^5-P2_1/c$ in a rough sense.

Application of Fourier-transform Method

It is reasonable to attempt the analysis of the structure of naphthazarin in assuming the space group of $C_{2h}^5-P2_1/c$, because the forbidden spectra are negligibly weak.

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* The major part of this paper was read at the 6th Annual Meeting of the Chemical Society of Japan, April, 1953.

1) J. Palacios and R. Salvia, *Anales Soc. espan. fis. quim.*, **32**, 49 (1934).

2) M. T. Rogers, *J. Am. Chem Soc*, **69**, 1506 (1947).

3) O. Borgen, *Acta Chem. Scand.*, **10**, 867 (1956)

** According to the reports 1-3), the other two modifications have the space groups of C_{2h}^5, their unit cells containing two and four molecules respectively, and the volumes occupied by one molecule are nearly equal in the three modifications.

4) I. Nitta, H. Matsuda and K. Osaki, 2nd Intern. Congr. Cryst. (1951).

When the space group is C_{2h}^{5} and the unit cell contains two planar molecules on its centres of symmetry, the best way of analysis is of application of the Fourier-transform method[5], and by this method the orientation of the reciprocal lattice to the molecule is found out easily.

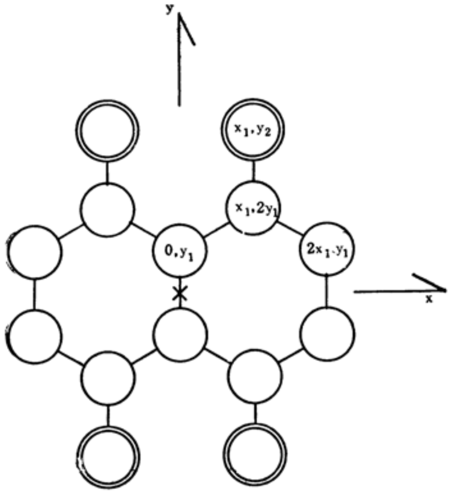

Fig. 1. Idealized molecular Model of naphthazarin for the Fourier transform. In this model $x_1=1.21$, $y_1=0.70$, $y_2=2.71$ Å, the atomic scattering factor of oxygen being assumed 3/2 of carbon. Single circles represent carbons and double circles oxygens.

An idealized molecular model was assumed as shown in Fig. 1. Then the Fourier transform of the molecule of naphthazarin was calculated, on the assumption of point-atoms, as follows (X, Y: the coordinates in reciprocal space):

$$\begin{aligned}T=&2\cos 2\pi y_1 Y\\&+2\cos 2\pi(2x_1X+y_1Y)+2\cos 2\pi(2x_1X-y_1Y)\\&+2\cos 2\pi(x_1X+2y_1Y)+2\cos 2\pi(x_1X-2y_1Y)\\&+3\cos 2\pi(x_1X+y_2Y)+3\cos 2\pi(x_1X-y_2Y).\end{aligned}$$

The transform map of Fig. 2 was obtained by the above calculations. From comparison between the observed structure factors and the transform map, the projection of the reciprocal lattice along the normal of the molecular plane could be determined without difficulty, as shown also in Fig. 2. The observed structure factors were fitted well with the values of the map in the following manner:***

Case (0*kl*);

$$T_{0kl(\text{crystal})}=T_{0kl(\text{molecule})}+\cos\pi(k+l)\times T_{0k\bar{l}(\text{molecule})}.$$

Case (*h*0*l*);

directly on the map****.

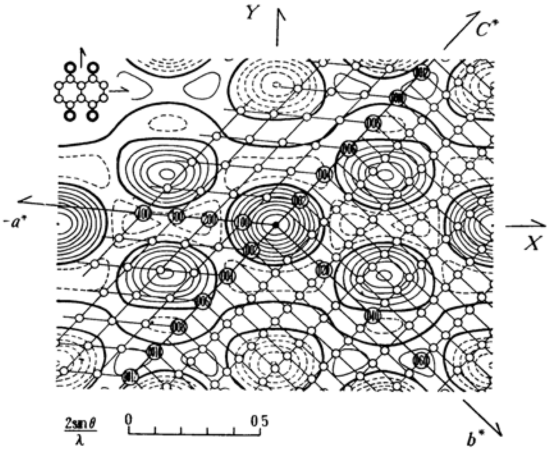

Fig. 2. The Fourier transform of naphthazarin showing the relation with the crystal reciprocal lattice. Solid, broad and broken contours are positive, zero and negative ones respectively, these intervals being of 2.

Thus the signs of the structure factors being given reliably, the Fourier summations of the electron-density projections along the *a* and *b* axes were then calculated, and by successive Fourier refinements the maps of Fig. 3 were derived after the signs of a few small structure factors had been changed. The atomic parameters obtained from the peaks of these maps are

(8.5/30, 9.8/60, 9.0/60),
(9.4/30, 16.2/60, 4.7/60),
(24.9/30, 29.1/60, 22.3/60),
(0.5/30, 26.3/60, 27.7/60) and
(4.3/30, 16.2/60, 29.2/60) for carbons,

and are

(25.3/30, 22.6/60. 18.3/60) and
(5.5/30, 9.5/60, 25.0/60) for oxygens.

In this stage, the reliability factors ($R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$) are 0.19 and 0.22 for (0*kl*) and (*h*0*l*) respectively, using the value of $B=5.0$ Å^2 as the temperature factor. In these calculations unobserved reflexions are omitted. The observed values of T_{hkl}, which are the absolute values of the structure factors divided by the atomic scattering factor[6] of carbon and the temperature factor, are listed in Tables I and II for comparison in the same scale with the values of the transform map.

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5) G. Knott, *Proc. Phys. Soc.*, **52**, 229 (1940).

*** Because, in the present case, two molecules are in the unit cell and the space group is C_{2h}^5-$P2_1/c$.

**** $T_{h0l(\text{crystal})}=2T_{h0l(\text{molecule})}\times(\cos\pi l/2)^2$.

6) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

TABLE I

OBSERVED VALUES OF T_{0kl}

l \ k	0	1	2	3	4	5	6	7	8
0	—		− 5.8				+ 1.9		+ 4.0
1		+ 6.2	+ 1.4	+ 7.0	+ 8.5		− 3.5	− 7.6	− 4.0
2	+ 6.1	+ 2.4	− 5.0	+ 7.7	+ 9.4	− 1.9	− 8.2	+ 7.7	
3		− 5.7	− 5.7	+ 4.9	+ 8.8		+16.5	−14.7	− 7.5
4	− 4.6	+ 0.7	− 0.4	+ 4.6	+ 0.9	− 3.5	−17.0	+ 7.8	
5		+ 6.5	+ 4.2	−14.9			+13.3		− 8.3
6	+ 0.5	+ 7.6	+ 1.9	+10.1					
7		+ 5.0	+10.7	− 6.9	+ 1.8	+12.6	− 7.7		
8	− 3.4		+ 2.9	− 5.9	+15.9	+23.5			
9		− 1.2	− 1.4		+ 2.8	+ 3.7	+ 4.6		
10			− 4.9	− 3.5		+22.4			
11		− 9.8	+12.1						
12	+ 8.2	+12.0	−11.7						
13		−10.6							
14									
15									
16									

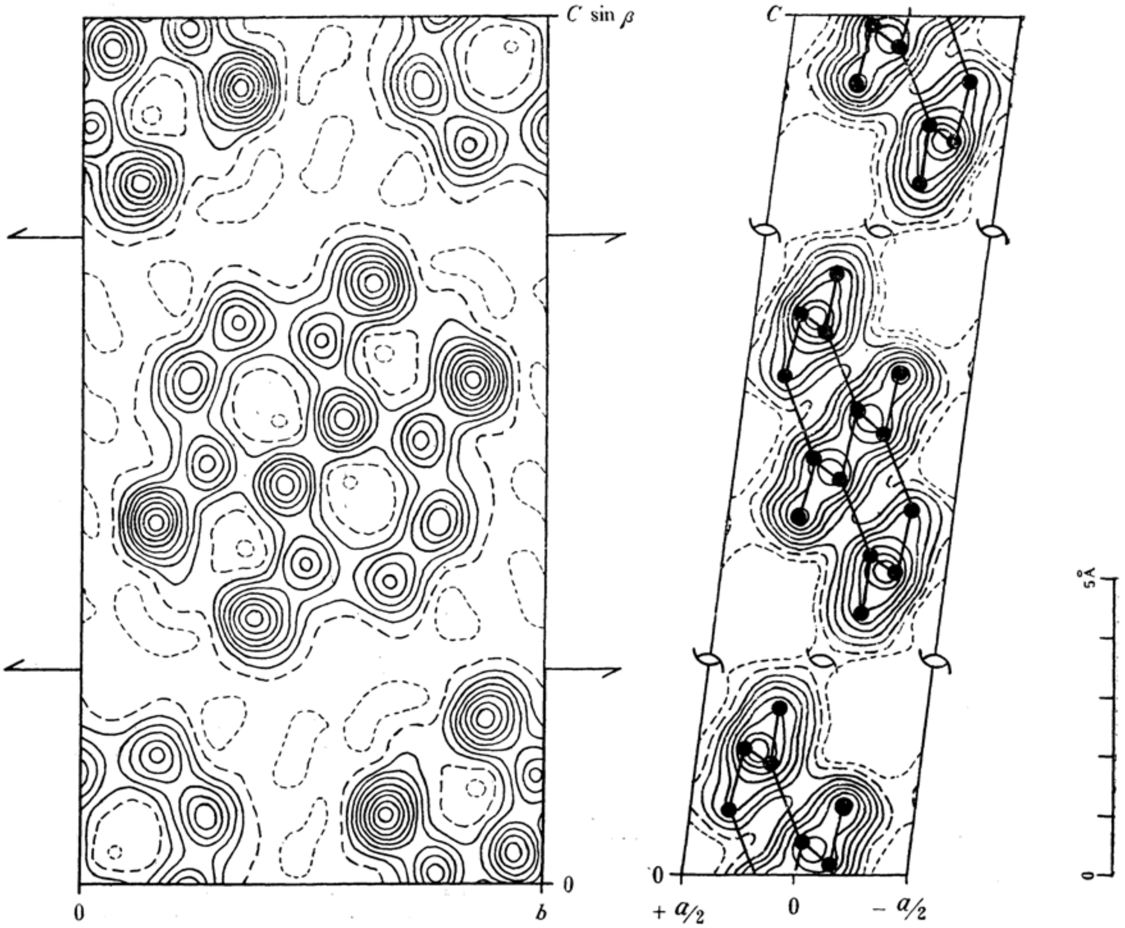

Fig 3. Electron-density projections along the *a* and *b* axes. Contours are drawn at equal intervals on an arbitrary scale for each map. Black circles in the *b* axis projection indicate the atomic positions.

TABLE II

OBSERVED VALUES OF $1/2\ T_{h0l}$

The odd cases of l are omitted, the intensities of these reflexions being too weak to be estimated

$l \backslash h$	4	3	2	1	0	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$
0	− 0.9	− 1.6	− 4.6	+ 5.4	—	+ 5.4	− 4.6	− 1.6	− 0.9
2		+ 0.9	+ 1.0	− 2.3	+ 3.2	+ 5.8	− 1.3	+ 1.1	+ 8.0
4			+10.9	+ 6.3	− 2.4	− 3.5	− 2.7	+ 0.6	+ 5.3
6			+ 1.3	+ 3.6	+ 0.3	+ 0.2			
8			+ 0.4	− 0.5	− 1.5	+ 0.7	+ 2.3	− 6.2	− 1.6
10		− 8.2	− 3.0		+ 0.8	+ 1.7		− 6.9	
12			− 1.9	− 1.3	+ 3.5	− 6.6	− 1.9	+ 1.5	
14					+ 1.2	− 6.9	−12.1	− 3.8	
16						+ 1.2			

Discussion

Although the electron-density projection maps, shown in Fig. 3, are not very accurate, the maps show the principal feature of the crystal structure, and the interatomic distances derived from these maps give some information, since it may be considered that the degree of approximation is fairly high. The atomic distances between the molecules are shown in Figs. 4 and 5. The crystal structure is of a type entirely different from that of quinhydrone.

In the projection along the a axis, all the atoms are completely separated because of the very short period of this axis, each molecule being surrounded by six molecules two-dimensionally (Fig. 4). The molecular plane is inclined at only about 28° to the (100) plane.

The projection along the b axis (Fig. 5) shows the feature of the planar molecules overlapping successively along the a axis (needle axis). The perpendicular distance between the planes of the molecules is found to be about 3.4 Å, the usual contact distance. There is no especially close approach as found in the structure of quinhydrone. This fact supports the discussion based on absorption spectra[7]; special interplanar interaction will not be operative in naphthazarine, since no such particular optical dichroism as shown by quinhydrone is detected.

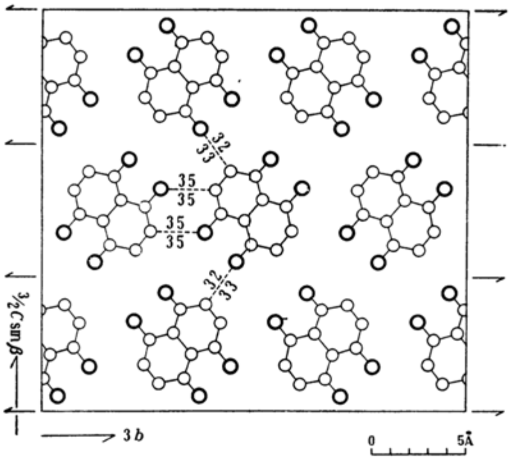

Fig. 4. Grouping of the molecules in the crystal, viewed along the a axis. The intermolecular distances are shown in Å. Single circles represent carbons and double circles oxygens.

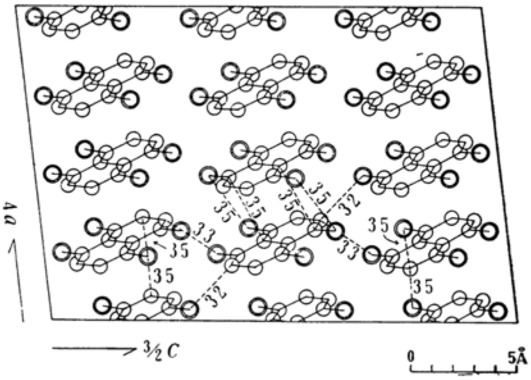

Fig. 5. Grouping of the molecules in the crystal, viewed along the b axis. The intermolecular distances are shown in Å. Single circles represent carbons and double circles oxygens.

As a whole, the crystal structure resembles that of typical aromatic compounds. In an approximation, only suitable van der Waals attractive forces may be said to operate between the molecules so as to form the observed crystal structure, and each molecule is surrounded by fourteen neighbours in a manner of closest packing.

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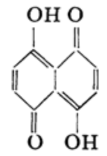
[7] K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952); This Bulletin, **26**, 172 (1953).

That there is no intermolecular hydrogen bond, is also a point which differs from the case of quinhydrone. The intramolecular O—O distance is roughly 2.5 Å and six-membered hydrogen-bonded ring is considered to be formed here. The latter point is also revealed from the missing of the free O—H stretching vibration in the infrared spectra[8].

Quite recently, Borgen[3] has analysed the crystal structure of this modification to be of the space group of $C_{2h}^5-P2_1/c$, deriving the *a* axis electron-density projection by the use of the Patterson function, and has discussed some possible molecular models of centro-symmetry and molecular arrangements from this space group, since the usual chemical formula (I) is by itself incompatible with the space group. However, as we have pointed out above that the crystal has this symmetry only in a sense of approximation, it appears likely that those models and arrangements should be modified from this point of view, the formula (I) being not incompatible with the real crystal symmetry of $C_2^2-P2_1$.

In the classical sense the usual formula (I) and the centro-symmetric one (II) are to be considered as possible from the electron-density projection maps based upon $C_{2h}^5-P2_1/c$.



(II)

However it seems that the formula (II) is hardly suitable, since in such a manner of molecular grouping as shown by Figs. 4 and 5, it will be natural to suggest the crystal symmetry of $C_{2h}^5-P2_1/c$, if the molecule be of this formula. On the other side, from the stand point of the resonance stabilization, it may be said that the structure (II) is less stable than the formula (I).

Further, regarding the molecular structure, the spectra forbidden to the space group of $C_{2h}^5-P2_1/c$ are generally so weak that it may be supposed, as a probable explanation, that the molecule will have the structure considerably deviating from that corresponding in the classical sense to the formula (I) so as to approach the centro-symmetric form (II) to some extent. We can not of course conclude further what the real molecular structure is without more accurate determination of the atomic parameters. However, no further analysis is being attempted at present.

Finally, it is of interest to remark again that naphthazarin has at least three modifications in the region of ordinary temperatures.

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[8] H. Brockmann and B. Franck, *Naturwiss.*, **42**, 45 (1955).