Chemistry

1958

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structural formula I

Figure 1: structural formula I

Abstract

Full Text

Chemistry

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X-ray Structural Study of Naphthazarin

(Presented by Academician N. V. Belov, 20 XI 1957)

Among the oxyketone dyes derived from naphthoquinone, naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) is widespread. Naphthazarin was first investigated radiographically by Palacios and Salvia (^1), who established a monoclinic cell with dimensions: $a = 3.85$, $b = 8.02$, $c = 14.5$ Å, with angle $\beta = 97°6'$; $Z = 2$ and space group $C_{2h}^5 = P2_1/n$. In order to reconcile the presence of a center of symmetry in the molecule, following from the X-ray data obtained, with the structure associated with formula I given, Palacios and Salvia suggested that the hydrogen atom oscillates between neighboring oxygen atoms of both rings.

Benerji (^2), studying the magnetic anisotropy of naphthazarin crystals, considered that the susceptibility values observed by him could not be reconciled with the presence of two molecules in the unit cell, and proposed that the cell contains four non-centrosymmetric molecules. He found for the magnetic susceptibility $K_1 = K_2 = -60.7 \cdot 10^{-6}$ and $K_3 = -132.8 \cdot 10^{-6}$. Billi (^3) investigated the structure of naphthazarin in another modification (2), the unit-cell dimensions of which differ from those given earlier (^1) for modification 1: $a = 5.40$, $b = 6.40$, $c = 11.86$ Å, $\beta = 91°23'$, $Z = 2$; space group $C_{2h}^5 = P2_1/c$. The position of the molecule in the crystal and the atomic coordinates were determined mainly from Patterson projections along three crystallographic directions, since the author did not succeed in obtaining a satisfactory resolution of atoms from electron-density projections. The author interprets his results on the basis of an assumption of a statistical distribution of non-centrosymmetric molecules or the presence of pseudosymmetry associated with a very small number of observed reflections.

Table 1

Results of X-ray measurements of three modifications of naphthazarin crystals

Fig. 1. Projection of the electron density onto the yz plane

Figure 2: Fig. 1. Projection of the electron density onto the yz plane

Modification	Color and form of crystals	a	b	c	β	Z	Space group
1	Dark-green needles	3.76	7.72	15.2	109°36′	2	$C_{2h}^5 = P2_1/c$
2	Dark-red prisms	5.41	6.40	12.86	92°24′	2	$C_{2h}^5 = P2_1/c$
3	Light-red plates	7.92	7.26	13.8	96°	4	$C_{2h}^5 = P2_1/n$

In crystallizing naphthazarin from a solution in benzene, in addition to the two modifications already known and listed above, we obtained a third modification (3), whose crystals are elongated prismatic plates colored light red.

Table 1 gives the X-ray diffraction data we obtained for all three modifications of naphthazarin.

It should be noted that in those cases where all three modifications crystallized from solution, well-faceted crystals of modification 3 were encountered most often. When naphthazarin crystals were obtained by sublimation, modifications 1 and 2 were formed.

The assignment of crystals of modification 1 to the space group $C_{2h}^5 = P2_1/c$ and the presence of two molecules in the unit cell confirm the previously stated suggestion of the authors cited above ([1]) that a center of symmetry is present in the molecule of the naphthazarin crystal in modification 1.

Fig. 1. Projection of the electron density onto the yz plane

The inclusion of the intramolecular bond O ... H—O in the conjugated system of bonds should cause a substantial change in the π-electron interaction throughout the molecule, which, in turn, should lead to a redistribution of the electron density in the molecule. In this connection, it was of interest to carry out a complete X-ray structural analysis of crystals of this modification.

The synthesis and crystallization of naphthazarin were carried out by Z. P. Glushkova.

In the Patterson projection $P(0yz)$ that was constructed, the maxima could not be explained by definite interatomic distances in the molecule; however, their arrangement on parallel lines forming an angle of $\sim 55^\circ$ with the c axis could be interpreted as the direction characterized by the largest number of atoms, i.e., the direction coinciding with the C–C and C–O distances in the molecule. On the basis of this assumption, the signs of the structure amplitudes $F(0kl)$ were calculated for a planar model of the molecule; for the bond lengths, distances were adopted in accordance with structural formula 1.

After construction of the fifth approximation of the electron-density projection $\rho(0yz)$ (Fig. 1), recalculation of the structure amplitudes from the atomic coordinates obtained from the projection did not lead to a change in signs or to an improvement of the value

$$R = \Sigma\left(|F_{\text{obs}}| - |F_{\text{calc}}|\right)/\Sigma|F_{\text{obs}}|,$$

which at this stage was 0.18. The yz coordinates of the atoms relative to the origin, located at the center of symmetry of the cell, are given in Table 2. The period of the unit cell along the a axis (3.760 Å) in the crystal, which is approximately equal to the thickness of the molecule, does not permit a large deviation of the molecule from the (100) plane of the crystal.

On the basis of the atomic coordinates obtained from the projections of the electron density $\rho(0kl)$ (Table 2), the bond lengths between atoms in molecule (II) were calculated.

The calculations of interatomic distances were carried out under the assumption that the molecule is situated parallel to the yz plane. The angle formed by the line of the C_9—C_{10} bond in the molecule and the y axis of the cell is 50°. The shortest distance between carbon and oxygen atoms in different molecules is 3.10 Å.

Table 2

Coordinates (yz) of atoms, calculated from the projection of the electron density $\rho(0yz)$

Atom	y/b	z/c	Atom	y/b	z/c
C(1)	0.0194	0.132	C(10)	0.062	0.040
C(2)	0.835	0.144	O(1)	0.130	0.198
C(3)	0.713	0.072	O(2)	0.341	0.087
C(4)	0.245	0.029			

II

Figure 3: II

III

Figure 4: III

As is evident from the data of the X-ray structural analysis presented, the presence of a center of symmetry in the molecule of modification 1 of naphthazarin is confirmed. The structure of the naphthalene nucleus is determined in this case by the character of the bonds between carbon and oxygen atoms, of which one is a double bond (1.1817 Å), and the second a single (1.35 Å) bond.

As was mentioned above, during crystallization from solution all three modifications precipitate simultaneously: two centrosymmetric (A) and one non-centrosymmetric (B). Recrystallization of any of these modifications again leads to the formation of the indicated three modifications (though often with a considerable predominance of one of these types). Therefore it may be assumed that there is a transition of an isomer with structure A into an isomer with structure B (and conversely), which can be represented as follows (III), as was proposed in their work by D. N. Shigorin and N. S. Dokunikhin ([4]). These authors, studying the vapor spectra of naphthazarin, found the presence of two bands corresponding to the valence vibrations of the OH group, which confirms the existence of an equilibrium between the indicated isomers.

It should be noted that the orientation of the molecule in the yz plane obtained by us is very similar to the orientation of the molecule given in the work of Bily ([3]) for crystals of the centrosymmetric modification 2.

To determine the third coordinate x and to refine the results obtained, it is necessary to carry out a three-dimensional synthesis.

We consider it a pleasant duty to express our gratitude to N. S. Dokunikhin and D. N. Shigorin for a number of valuable suggestions during the work and for discussion of the results.

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Received
16 VIII 1957

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Note: Figure translations are in progress. See original paper for figures.