

## Short Communications

### A Preliminary X-Ray Investigation of Naphthazarin

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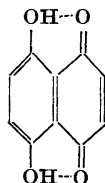
Naphthazarin has been isolated in three modifications at room temperature. Two of these have been reported previously by Palacios and Salvia<sup>1</sup> and Rogers<sup>2</sup>.

Our approximate X-ray data are as follows:

| Modification           | I                     | II       | III      |
|------------------------|-----------------------|----------|----------|
| <i>a</i> (Å)           | 3.81                  | 8.09     | 5.46     |
| <i>b</i> (Å)           | 7.63                  | 7.27     | 6.35     |
| <i>c</i> (Å)           | 14.52                 | 15.26    | 11.71    |
| $\beta$ (°)            | 97.2                  | 115      | 91.5     |
| Space group            | $P2_1/c$              | $P2_1/c$ | $P2_1/c$ |
| Molecules in unit cell | 2                     | 4        | 2        |
| Colour                 | green metallic lustre | red      | dark red |

The physical properties, especially the colours, of the various modifications are appreciably different. An investigation has therefore been commenced in order to study the influence of intermolecular forces and molecular orientation.

The structure of naphthazarin, based on chemical evidence, is given as 5,8-dihydroxy-1,4-naphthoquinone.



The space group of the modifications I and III is  $P2_1/c$ , and the unit cells contain 2 molecules. The molecules therefore have a centre of symmetry. This is incompatible with the above formula.

There exist a number of possible explanations, of which we may mention some.

- 1) The compound may be of the form 4,8-dihydroxy-1,5-naphthoquinone, in spite of certain chemical evidence.
- 2) The hydrogen bonds may be symmetrical, although such bonds are not known in any organic compound.
- 3) The protons of the hydrogen bonds may change positions between neighbouring oxygen atoms, giving a quasi-centrosymmetric structure.
- 4) The benzo- and keto-parts of the molecules may be statistically distributed in the lattice, giving a quasicentrosymmetric structure.

In the three later cases we would expect to find the four C—O distances equal.

The electron-density projection of naphthazarin I on (100) is shown in Fig. 1. The signs of the structure amplitudes have been determined from a model based on a Patterson projection.

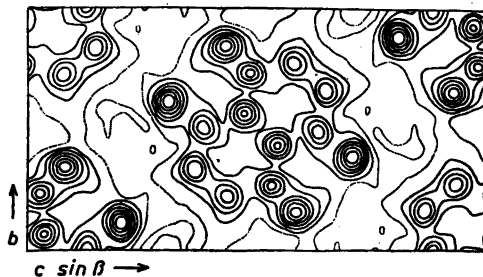


Fig. 1. Electron-density projection on (100) of naphthazarin I.

The molecules are oriented nearly parallel to the (100) plane, and a rough calculation of the atomic positions indicates short intramolecular O—H...O distances and rather close intermolecular approach. The length of the hydrogen bond is of great interest in connection with the recent studies of the infrared spectra of hydroxy-quinones<sup>3-5</sup>, but further discussion will have to await the final refinements of the calculations.

1. Palacios, J. and Salvia, R. *Anales soc. españ. fís. y quim.* **32** (1934) 49.
2. Rogers, M. T. *J. Am. Chem. Soc.* **69** (1947) 1506.
3. Josien, M.-L., Fuson, N., Lebas, J.-M. and Gregory, T. M. *J. Chem. Phys.* **21** (1953) 331.
4. Hadzi, D. and Sheppard, N. *Trans. Faraday Soc.* **50** (1954) 911.
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## X-Ray Crystallographic Data on Sodium and Potassium Thiosulphonates

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A study of unit cells and space groups of some alkali methane- and *p*-toluene-thiosulphonates has been made, with the following results. The axial lengths, from oscillation and Weissenberg photographs taken with copper radiation,  $\lambda(\text{CuK}\alpha) = 1.542 \text{ \AA}$ , are probably correct to within 0.5%. Densities were determined by a flotation method.

*Sodium methanethiosulphonate monohydrate*,  $\text{CH}_3\text{SO}_2\text{SNa} \cdot \text{H}_2\text{O}$ . Orthorhombic,  $a = 6.49 \text{ \AA}$ ,  $b = 5.55 \text{ \AA}$ ,  $c = 16.23 \text{ \AA}$ . Four formula units per unit cell; density, calc. 1.73, found 1.72 g/cm<sup>3</sup>. Systematic absences,  $0kl$  when  $k + l$  is odd,  $h k 0$  when  $h$  is odd. These absences are characteristic of the space groups,  $D_{2h}^{16} - Pnma$  and  $C_{2h}^2 - Pn2_1a$ . If the former is the correct one, the carbon and both sulphur atoms of the methanethiosulphonate ion lie in a crystallographic mirror plane of symmetry.

From water, the salt crystallized as plates {001} with plate edges parallel to the  $a$  and  $b$  axes. There is perfect cleavage along the plate face, and also a pronounced tendency of cleavage along another, not identified plane parallel to the  $a$  axis.

*Potassium methanethiosulphonate*,  $\text{CH}_3\text{SO}_2\text{SK}$ . Monoclinic prismatic,  $a = 8.76 \text{ \AA}$ ,  $b = 8.12 \text{ \AA}$ ,  $c = 7.42 \text{ \AA}$ ,  $\beta = 92^\circ$ . Four formula units per unit cell; density, calc. 1.89, found 1.88 g/cm<sup>3</sup>. Systematic absences,  $h0l$  when  $l$  is odd,  $0k0$  when  $k$  is odd. The space group is thus  $C_{2h}^2 - P2_1/c$ .

The salt crystallized from water or methanol as thick plates {100} bounded by {011}, {010} and occasionally {111}. There is perfect cleavage along the plate face.

*Potassium p-toluenethiosulphonate monohydrate*,  $\text{C}_7\text{H}_7\text{SO}_2\text{SK} \cdot \text{H}_2\text{O}$ . Monoclinic,  $a = 8.56 \text{ \AA}$ ,  $b = 9.67 \text{ \AA}$ ,  $c = 13.01 \text{ \AA}$ ,  $\beta = 95^\circ$ . Four formula units per unit cell; density, calc. 1.51, found 1.49 g/cm<sup>3</sup>. Systematic absences,  $hkl$  when  $h + k$  is odd. The monoclinic prismatic morphology<sup>1,2</sup> of the crystals points to the centrosymmetric space group,  $C_{2h}^2 - C2/m$ , the correctness of which would imply that the *p*-toluenethiosulphonate ion possesses mirror plane symmetry in the crystals.

The salt was first prepared by Blomstrand<sup>3</sup> and Wahlstedt<sup>4</sup>, and by these authors noted to crystallize particularly well. Brugnatelli<sup>1,2</sup> described the crystals as monoclinic prismatic, with  $a : b : c = 0.8854 : 1 : 1.5436$  and  $\beta = 119^\circ 52'$ . Transforming according to the matrix,  $100/010/101$ , these data become  $a : b : c = 0.8854 : 1 : 1.344$ ;  $\beta = 94.9^\circ$ , as compared with  $a : b : c = 0.8853 : 1 : 1.345$ ;  $\beta = 95^\circ$  from the X-ray data.

There is perfect cleavage along the  $c$  plane.

*Sodium p-toluenethiosulphonate*,  $\text{C}_7\text{H}_7\text{SO}_2\text{SNa}$ . Monoclinic,  $a = 7.36 \text{ \AA}$ ,  $b = 9.72 \text{ \AA}$ ,  $c = 12.96 \text{ \AA}$ ,  $\beta = 93^\circ$ . Four formula units per unit cell; density, calc. 1.51, found 1.51 g/cm<sup>3</sup>. Systematic absences,  $hkl$  when  $h + k$  is odd.

Except for the length of the  $a$  axis, the cell dimensions are close to those found for potassium *p*-toluenethiosulphonate monohydrate. The systematic absences are the same, and the intensity distribution of the  $0kl$  reflections of the two salts are very similar. It appears likely that the space group of the sodium salt is that of the potassium salt, and thus probably  $C_{2h}^2 - C2/m$ .

Crystallized from 96% ethanol above room temperature, the salt occurred as