

correct. It must be emphasized, however, that this finding does not imply that Anderson's equations are erroneous. The present author has in any case been unable to detect mistakes in Anderson's deductions. The result suggests on the other hand either

(1) a shortcoming of Anderson's comparatively simple model, or

(2) an alternative interpretation of Biltz and Juza's<sup>7</sup> pressure-composition diagram, *e.g.* that the shape of the isotherms reflects non-equilibrium conditions of their experiments.

Anderson's statistical thermodynamic treatment of the PtS phase is referred to in review articles (*cf.* Prener<sup>10</sup>) and books (*cf.* Rees<sup>6</sup>). It is the hope of the present author that this contribution will prevent further utilization of this particular example in the literature, especially, that it may be avoided in textbooks of inorganic or physical chemistry. The present results also demand some caution in the interpretation of vapour pressure data of similar systems in terms of the same theory.

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Received December 21, 1965.

## Crystal Structure of Cyclohexane-1,4-dioxime

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The crystal structure of cyclohexane-1,4-dione has been determined with considerable care both at room temperature<sup>1</sup> and at low temperature<sup>2</sup> using three-dimensional X-ray methods. The results of the two investigations are, within the probable limits of error, identical, and they show that the molecular conformation may be described in terms of a "twisted boat" form with an angle between the two C—O bonds of 154°, an angle which is in good agreement with that to be expected from the dipole moment found in solution.

This "movable" form of the ring has been observed also in two addition compounds of the dione. In the (1:1) addition compound formed with diiodo-acetylene,<sup>3</sup> which has a statistically disordered crystal structure, the charge transfer bond is relatively weak with an I—O distance of 2.95 Å, and the angle between the two C—O directions, (155.6°), is practically the same as that of the dione itself. In the corresponding (1:1) compound formed with HgCl<sub>2</sub>,<sup>4</sup> however, the bonds between oxygen and mercury are apparently much stronger, and here the angle between the two C—O bonds is found equal to 176°.

An X-ray crystallographic investigation of cyclohexane-1,4-dioxime has now been undertaken with the chief aim of determining the hydrogen bonding system, and

to establish the configuration of the six-membered ring in this compound.

The dioxime crystals belong to the orthorhombic system and the space group is *Pbca*. The unit cell containing 8 molecules has the following parameters:

$$a = 7.14_1 \text{ \AA}, b = 13.25_1 \text{ \AA}, c = 14.72_4 \text{ \AA}$$

Of the 87 observed *Ok*l-reflections, signs were determined for 67 using a computer procedure based on the Cochran-Douglas method<sup>5</sup> (programmed in FORTAN IV for UNIVAC 1107 by the author). Since 65 of these signs turned out to be correct, the corresponding Fourier map is practically identical with the final one, which

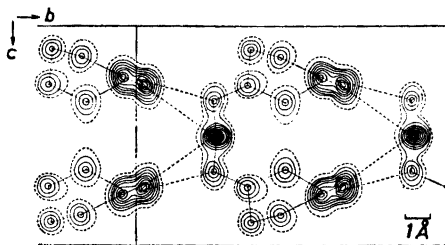


Fig. 1. Fourier projection along *a*-axis.

is shown in Fig. 1. The *R*-value thus arrived at for this projection is  $R_{0kl} = 7.4\%$ .

Using the known *z*-parameters, approximate values for the *x*-coordinates were found by allowing the *h0l*-projection of the molecule (determined from a model) to move in small steps parallel to the *x*-axis. The *R*-factors were calculated for each step, and the parameters corresponding to the minimum *R*-value were chosen as starting coordinates in a three-dimensional full matrix least squares refinement based on about 1300 reflections of which 990 are observed. The final *R*-value including all the observed reflections is  $R = 5.6\%$ . At the present stage the following results may be stated with confidence:

The carbon skeleton of the molecule corresponds to that of a "twisted boat" form, with interatomic distances and angles not very far from those found for the dione itself. The angle between the two C—N bonds is, however, about 26° smaller than the corresponding angle between the C—O bonds of the dione.

The two independent C—N bonds are, respectively, 1.27<sub>4</sub> Å and 1.27<sub>4</sub> Å, while

the two N—O bonds are 1.41<sub>1</sub> Å and 1.41<sub>2</sub> Å.

The hydrogen bonds link each dioxime molecule to four others, the two independent bonds having the lengths 2.77<sub>1</sub> Å and 2.83<sub>0</sub> Å. The hydrogen atoms in these bonds have been localized from a three-dimensional difference synthesis and found to be situated at normal distances from the oxygen atoms, and approximately on the straight line joining O and N.

Further details of the structure will be given later.

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Received December 22, 1965.

## A New Compound in the System $\text{Sb}_2\text{O}_3\text{-Nb}_2\text{O}_5$

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Hitherto the only known compound in the system  $\text{Sb}_2\text{O}_3\text{-Nb}_2\text{O}_5$  has been  $\text{SbNbO}_4$ ,<sup>1</sup> which is orthorhombic,  $a = 5.561$ ,  $b = 4.939$ ,  $c = 11.810$  Å, and is isostructural with the mineral stibio-tantalite. The crystal structure of  $\text{SbNbO}_4$  has recently been revised.<sup>2,3</sup>

During attempts to prepare single crystals of pure  $\text{SbNbO}_4$ , equimolar mixtures of antimony trioxide and niobium pentoxide were heated for 24 h in sealed platinum capsules. At 1000°C,  $\text{SbNbO}_4$  was formed, whereas at 1200°C the specimen melted and was lost from the platinum tube; both these observations are in agree-

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