Disordered Structure in Crystalline Cyclohexanoxime

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Since cyclohexanoxime $C_6H_{10}NOH$ is peculiar in that it dissolves readily not only in polar but also in non-polar solvents, and its molecular weight estimates in solution suggest that more than two molecules are associated, this substance in crystalline state was put under X-ray study. It was found that the crystal belongs to the hexagonal system with $a=12.18$, $c=8.10$ Å, and space group C_6^6-$P6_3$, the number of chemical units in the unit cell being six.

Projection of structure on (0001) was obtained as usual using Patterson Projection and trial-and error methods. It is evident from this projection that three molecules of cyclohexanoxime associate to form a trimeric molecule through three OH . . . N hydrogen bonds of the length about 2.75 Å around the threefold axis, and that such trimeric molecules arrange themselves in a hexagonal closepacked structure (Fig. 1). These results might well be compared with those of the structure of acetoxime as analysed by Bierlein and Lingafelter[1]. Anomalies in the molecular weight in solution will thus be accounted for by the existence of the trimeric form in solution.

It is quite remarkable that, while the $(hki0)$-reflexions are regular, the general $(hkil)$-reflexions with non-zero l show diffuse scattering which corresponds to non-integral h and k values, l being strictly limited to integral numbers. Such diffuse scattering is undoubtedly due to some disordering in the packing of molecules in the crystal. In order to explain such anomaly there are many possible ways, which it is difficult to deal with rigorously case by case. However, in view of chemical and structural considerations, the following explanation seems to be quite reasonable and probable.

On the assumption of the more stable chair-form configuration of the ring, the cyclohexanoxime molecules can be expected to exist in the enantiomorphic forms as shown in Fig. 2. They are equally stable and are supposed to be in solution in equal numbers. Let us call one "A" and the other "B". In forming the trimers, four types of combination are conceivable: AAA, BBB, ABA

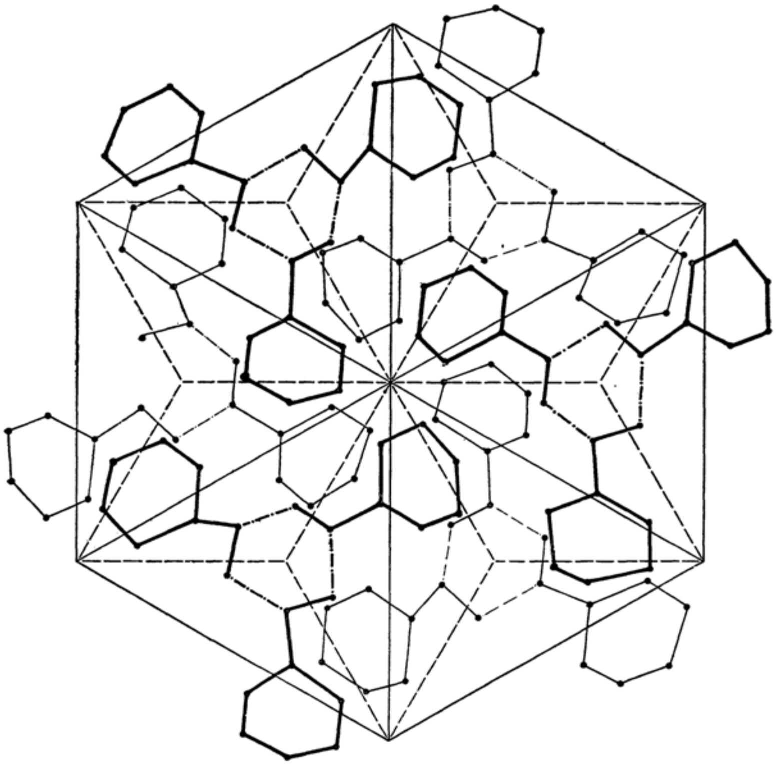

Fig. 1

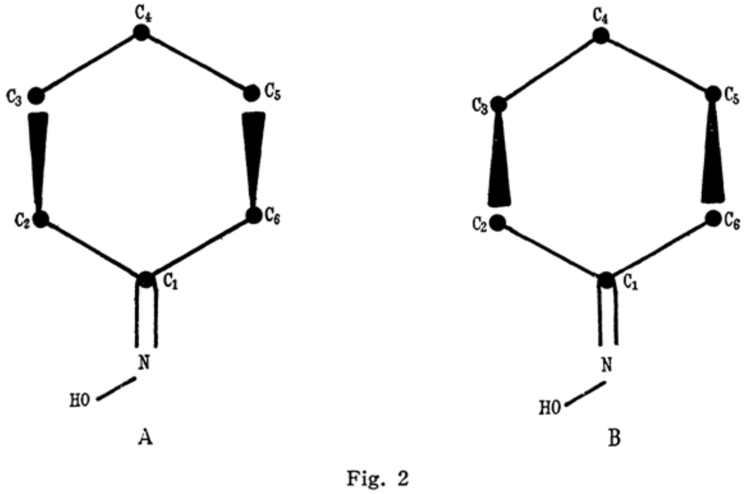

Fig. 2

and ABB. These four types can be arranged in the crystal with the same atomic x- and y- coordinates, but with partly different z-values, so that the $(hki\,0)$-reflexions are unaffected and regular, the projection of the structure on (0001) being the same. Further it seems to be required, from the consideration of the steric hindrance between adjacent cyclohexane rings, that each 6_3-axis should be always surrounded by the same kind of molecule, A or B. Such a condition can be fulfilled with the four types of trimers in many ways resulting in the two-dimensionally random distribution of the 6_3-(A) and 6_3-(B)-axes. One example of how such a structure can be reallized is illustrated by Fig. 3. Thus the situation very well explains the characteristics mentioned

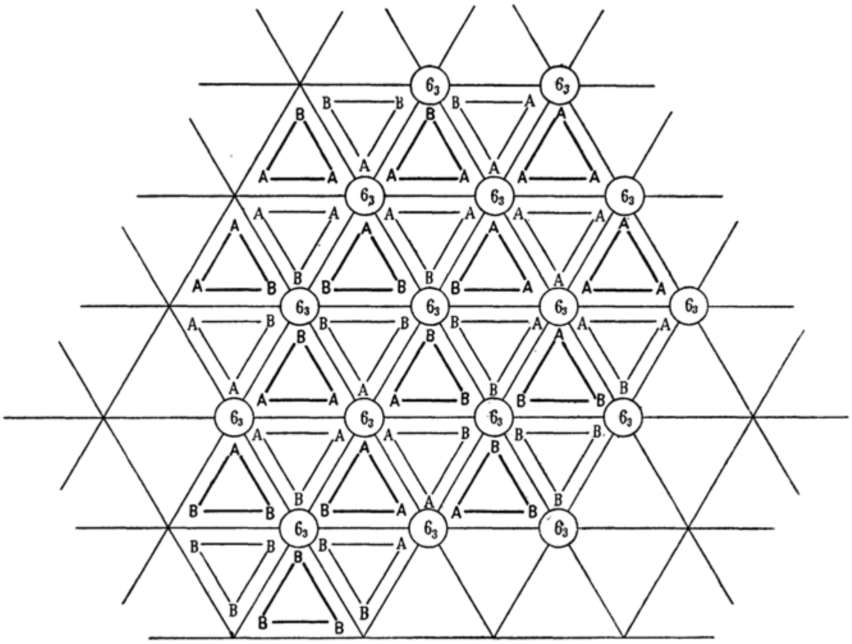

Fig. 3

before of the diffuse scattering observed in this crystal, because the crystal should have a quite constant repetition period in the z-direction, the only condition disturbing the periodicity being the random distribution of the two kinds of the 6_3-axes.

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1) T.K. Bierlein and E.C. Lingafelter, *Acta Cryst.*, 4, 450 (1951).