The Crystal and Molecular Structure of *o*-Nitrobenzoic Acid

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It is of interest to elucidate the steric hindrance of two neighboring substituents –COOH and $-NO_2$ in an *o*-nitrobenzoic acid molecule, and it is also of significance to compare this compound with other *ortho*-substituted benzoic acids or with *p*-nitrobenzoic acid.[1]

The crystal of *o*-nitrobenzoic acid belongs to the triclinic system with the unit cell of the dimensions, $a=7.59$, $b=11.40$, $c=5.00$ Å, $\alpha=112°01'$, $\beta=109°22'$ and $\gamma=64°24'$.[2] The space group was found to be $P\bar{1}$ by the statistical test. The observed density was 1.55 g·cm^{-3} and there are two molecules in a unit cell, and the density is calculated to be 1.56 g·cm^{-3}.

The three-dimensional data such as *hk*0, *hk*1, *hk*2, *hk*3, 0*kl* and *h*0*l* were collected by the multiple-film equi-inclination Weissenberg photographs taken with Ni-filtered Cu$K\alpha$ radiation. The intensities of reflections were measured visually and corrected for the Lorentz-polarization factor and also for the spot extension.

Approximate *x*- and *y*-coordinates of atoms were obtained by Patterson projection along the *c*-axis, and the successive refinements of the Fourier projection and least-squares method were applied. *z*-Coordinates were obtained from 0*kl* and *h*0*l* reflections and refined by the least-squares method. The structure thus obtained was refined by the least-squares method with the three-dimensional data. A discrepancy index R is 0.18 at the present stage of refinement.

The crystal structure projected along the *c*-axis and the molecular configuration are shown in Figs. 1 and 2 respectively. Thus, the interesting features of the crystal and molecular structure were revealed, although the accuracy of the analysis is not sufficient to describe the details of the structures. As usually seen in benzoic acid and its derivatives, the hydrogen bonds of 2.65 Å between

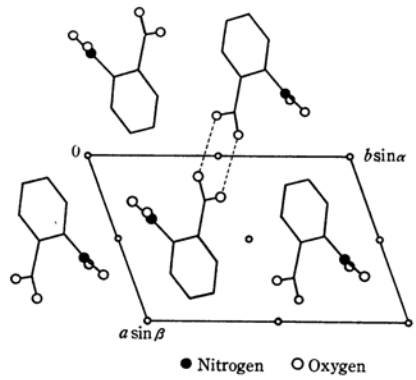

Fig. 1. The crystal structure projected along the *c*-axis.

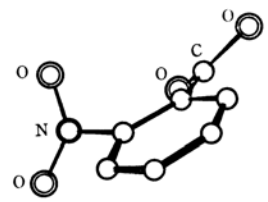

Fig. 2. The molecular configuration of *o*-nitrobenzoic acid.

two carboxyl groups are found around a center of symmetry with the formation of a dimer. The benzene ring is approximately planar within the deviation of 0.03 Å. But owing to the steric hindrance caused by the carboxyl and nitro groups in *ortho* positions, these substituted groups can no longer lie in the plane of the benzene ring. The carbon atom in the carboxyl group and the nitrogen atom in the nitro group is respectively about +0.25 Å and −0.12 Å away from the plane of the benzene ring. The plane of the carboxyl group and that of the nitro group make an angle of about 23° and 54° respectively with the plane of the benzene ring. The closest approach between an oxygen atom in the carboxyl group and that in the nitro group is 2.84 Å.

A full paper will be published soon.

1) T. D. Sakore and L. M. Pant, *Acta Cryst.*, **21**, 715 (1966).

2) The preliminary report of the crystal data of this compound was already done. (V. C. Thaker *et al.*, *J. Indian Chem. Soc.*, **17**, 555 (1940)).