

## The Structure of *o*-Nitrobenzoic Acid\*

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*o*-Nitrobenzoic acid,  $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}$ , crystallized from aqueous alcohol mixture is triclinic, space group  $P\bar{1}$  with

$$\begin{aligned} a &= 7.55, b = 4.99, c = 12.50 \text{ \AA}; \\ \alpha &= 122.5^\circ, \beta = 95.3^\circ, \gamma = 108.9^\circ; \\ \rho_o(26^\circ\text{C}), & 1.567 \text{ g.cm}^{-3}; \rho_c \text{ for } Z=2, 1.568 \text{ g.cm}^{-3}; \\ \mu & \text{ for Cu } K\alpha, 13.5 \text{ cm}^{-1}. \end{aligned}$$

The structure has been refined with the help of three-dimensional data and the molecular dimensions are compared with those of similar compounds. The effect of intramolecular overcrowding is to cause the exocyclic carbon atom and the nitrogen atom to be displaced out of the aromatic plane in opposite directions by 0.209 and 0.160 Å respectively; the C–C and C–N bonds are displaced sideways as well. The *o*-nitrobenzoic acid dimers are held in a stable structure by normal van der Waals interactions.

### Introduction

The structure analysis of *o*-nitrobenzoic acid was undertaken as part of a programme to determine the structures of substituted benzenes in order to study the effects of the substituted groups on the molecular geometry. The structure of *p*-nitrobenzoic acid was recently determined (Sakore & Pant, 1965, 1966) and the analysis of *p*-nitrobenzaldehyde (Jose & Pant) is in progress.

### Experimental

The crystals, obtained from a water–alcohol mixture are triclinic, space group  $P\bar{1}$  with

$$\begin{aligned} a &= 7.55, b = 4.99, c = 12.50 \text{ \AA}; \\ \alpha &= 122.5^\circ, \beta = 95.3^\circ, \gamma = 108.9^\circ; \\ \rho_o(26^\circ\text{C}), & 1.567 \text{ g.cm}^{-3}; \rho_c \text{ for } Z=2, 1.568 \text{ g.cm}^{-3}; \\ \mu & \text{ for Cu } K\alpha, 13.5 \text{ cm}^{-1}. \end{aligned}$$

The axial lengths were obtained approximately from rotation photographs along the three axes, more accurate values being obtained from zero-layer Weissen-

berg photographs from which  $\alpha, \beta, \gamma$  were also determined. The data reported by Thaker *et al.* (1939) are:

$$\begin{aligned} a &= 7.58, b = 14.01, c = 5.05 \text{ \AA}; \\ \alpha &= 131^\circ 11', \beta = 109^\circ 37', \gamma = 61^\circ 54'; \rho_o, 1.559 \text{ g.cm}^{-3}. \end{aligned}$$

The *b* axis chosen by Thaker, Kapadia & Prasad (1939) corresponds to the [101] direction according to the cell chosen for the present analysis.

Reflexions of the type  $h0l$  and  $0kl$  to  $5kl$  were obtained from equi-inclination Weissenberg photographs, using copper radiation. The crystals used were platy with a maximum width of about 0.3 mm normal to the oscillation axes. Intensities of 694 reflexions out of nearly 1250 possible for these layers were estimated visually from extended spots in higher layer photographs; intensities were corrected for the Lorentz–polarization–Tunell factor as well as the effect of spot extension (*International Tables for X-ray Crystallography*, 1962); absorption was neglected.

### Determination and refinement of the structure

Possible trial structures in the (010) projection were postulated with the help of the Patterson map, assuming plane centrosymmetrical dimers and usual bond

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Table 1. *Final atomic and thermal parameters*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C(1)	$-0.2812 \pm 0.0009$	$-0.0628 \pm 0.0014$	$0.1928 \pm 0.0006$	$2.40 \text{ \AA}^2$
C(2)	$-0.2308 \pm 0.0009$	$-0.0972 \pm 0.0014$	$0.2931 \pm 0.0006$	2.20
C(3)	$-0.3639 \pm 0.0009$	$-0.1913 \pm 0.0014$	$0.3521 \pm 0.0006$	3.22
C(4)	$-0.5533 \pm 0.0009$	$-0.2327 \pm 0.0014$	$0.3130 \pm 0.0006$	3.53
C(5)	$-0.6118 \pm 0.0009$	$-0.1928 \pm 0.0014$	$0.2181 \pm 0.0006$	3.66
C(6)	$-0.4758 \pm 0.0009$	$-0.1073 \pm 0.0014$	$0.1568 \pm 0.0006$	3.05
C(7)	$-0.1553 \pm 0.0009$	$-0.0234 \pm 0.0014$	$0.1125 \pm 0.0006$	2.38
N	$-0.0243 \pm 0.0008$	$-0.0158 \pm 0.0012$	$0.3470 \pm 0.0005$	2.87
O(1)	$-0.0187 \pm 0.0007$	$-0.1066 \pm 0.0010$	$0.1047 \pm 0.0004$	3.27
O(2)	$-0.1984 \pm 0.0007$	$0.0952 \pm 0.0010$	$0.0486 \pm 0.0004$	3.69
O(3)	$0.1089 \pm 0.0007$	$0.2759 \pm 0.0010$	$0.3909 \pm 0.0004$	4.12
O(4)	$0.0045 \pm 0.0007$	$-0.2355 \pm 0.0010$	$0.3502 \pm 0.0004$	3.78



along with the angles between the different planes and the deviation of the atoms from them. The least-squares plane through the benzene ring was obtained by the method of Schomaker, Waser, Marsh & Bergman (1959).

The average C—C bond length in the benzene ring is 1.394 Å which is very close to the value found in crystalline benzene (1.393 Å; Cox, Cruickshank & Smith, 1958) and in *p*-nitrobenzoic acid (1.396 Å). However, the individual aromatic C—C bonds are of significantly different lengths in *o*-nitrobenzoic acid [Fig. 2(a)]; the bonds parallel to the exocyclic C—C bond are longest (1.406 and 1.427 Å) while those further away are the

shortest (1.362 and 1.377 Å); the remaining two bonds are nearly of normal length (1.389 and 1.403 Å). The general picture thus resembles the molecule of benzoic acid [Fig. 2(b)] where the corresponding bond lengths are 1.41 and 1.42 Å, 1.36 and 1.37 Å, 1.39 and 1.39 Å respectively. It thus appears that the substitution of the nitro group in the *ortho* position leaves the aromatic bonds of benzoic acid molecule almost undisturbed while its substitution in the *para* position has the effect of making the different aromatic bonds of nearly equal length.

It may be of interest to mention that the distribution of valency angles in the aromatic ring in *o*-nitrobenzoic

Table 3. *Intramolecular distances and angles*

Intramolecular distances		Bond angles	
C(1)—C(2)	1.389 ± 0.010 Å	O(1)—C(7)—O(2)	121.1 ± 0.6°
C(2)—C(3)	1.406 ± 0.010	C(1)—C(7)—O(2)	117.4 ± 0.6
C(3)—C(4)	1.377 ± 0.010	C(1)—C(7)—O(1)	121.4 ± 0.6
C(4)—C(5)	1.362 ± 0.010	C(7)—C(1)—C(2)	125.4 ± 0.6
C(5)—C(6)	1.427 ± 0.010	C(7)—C(1)—C(6)	118.4 ± 0.6
C(6)—C(1)	1.403 ± 0.010	C(6)—C(1)—C(2)	115.7 ± 0.6
C(1)—C(7)	1.489 ± 0.010	C(1)—C(2)—C(3)	124.3 ± 0.6
C(2)—N	1.466 ± 0.009	C(2)—C(3)—C(4)	117.6 ± 0.6
N—O(3)	1.234 ± 0.008	C(3)—C(4)—C(5)	121.3 ± 0.7
N—O(4)	1.204 ± 0.008	C(4)—C(5)—C(6)	120.0 ± 0.6
C(7)—O(1)	1.223 ± 0.009	C(1)—C(6)—C(5)	121.0 ± 0.6
C(7)—O(2)	1.295 ± 0.009	C(3)—C(2)—N	116.7 ± 0.6
C(1)—O(3)	2.931 ± 0.009	C(1)—C(2)—N	119.1 ± 0.6
O(1)—O(3)	2.864 ± 0.007	C(2)—N—O(3)	118.9 ± 0.6
C(7)—N	2.980 ± 0.009	C(2)—N—O(4)	117.5 ± 0.6
O(1)—N	2.817 ± 0.008	O(3)—N—O(4)	123.6 ± 0.6
O(1)—O(2)	2.645 ± 0.007		

(*x, y, z*) ( $\bar{x}, \bar{y}, \bar{z}$ )

Table 4.

Equations of planes	
(1) Benzene ring	$-0.1674x + 0.6816y + 0.7123z - 0.567 = 0$
(2) Nitro group	$-0.4019x - 0.1876y + 0.8965z - 3.817 = 0$
(3) Carboxylic group	$0.2159x + 0.5748y + 0.7895z - 0.062 = 0$
(4) Plane through O(1), O(2) & dimer centre	$0.2456x + 0.5989y + 0.7622z = 0$

Angles between different planes

	(2)	(3)	(4)
(1)	54.7°	23.4°	24.5°
(2)	—	59.1	—
(3)	—	—	2.6

Deviations of atoms from different planes

	Planes			
	(1)	(2)	(3)	(4)
C(1)	-0.013 Å		-0.034 Å	-0.133 Å
C(2)	0.020	0.065 Å		
C(3)	-0.012			
C(4)	-0.002			
C(5)	0.006			
C(6)	-0.001			
C(7)	-0.209			-0.029
N	0.160			
O(1)	-0.689			
O(2)	0.121			
O(3)	1.104			
O(4)	-0.635			
Dimer centre	-0.567	-3.187	-0.062	

acid is similar to that found in nitrobenzene (Trotter, 1959*a*) and nitrobenzene derivatives such as *o*-nitrobenzaldehyde (Coppens, 1964; Coppens & Schmidt, 1964),  $\beta$ -*p*-nitrophenol (Coppens & Schmidt, 1965), nitromesitylene (Trotter, 1959*b*) and *p*-nitrobenzoic acid (Sakore & Pant, 1966); in each case the angle at the carbon atom where the nitro group is attached is greater than  $120^\circ$ , the angles at the *ortho* positions are less than  $120^\circ$  and the other three angles are generally

close to  $120^\circ$ ; the effect is less marked in *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961). Trotter (1960) has attempted a correlation between the valency angles and the effective covalent radii in the aromatic ring on the postulate that changes in the hybridization of aromatic carbon atoms from those in benzene result in changes in the C-C bond lengths; he has given a graph of valency angle against covalent radius, which was obtained from the

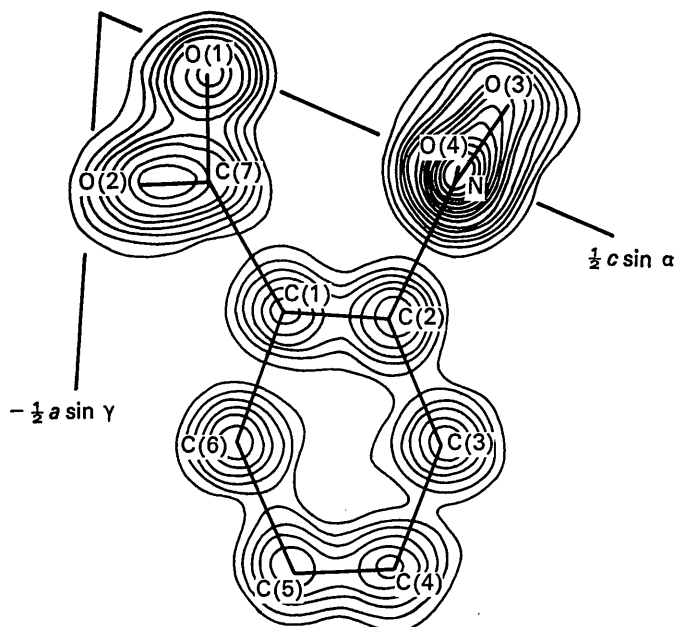


Fig. 1. Electron density projected onto (010). Contours are at intervals of  $1 \text{ e.}\text{\AA}^{-2}$ , starting from  $2 \text{ e.}\text{\AA}^{-2}$ .

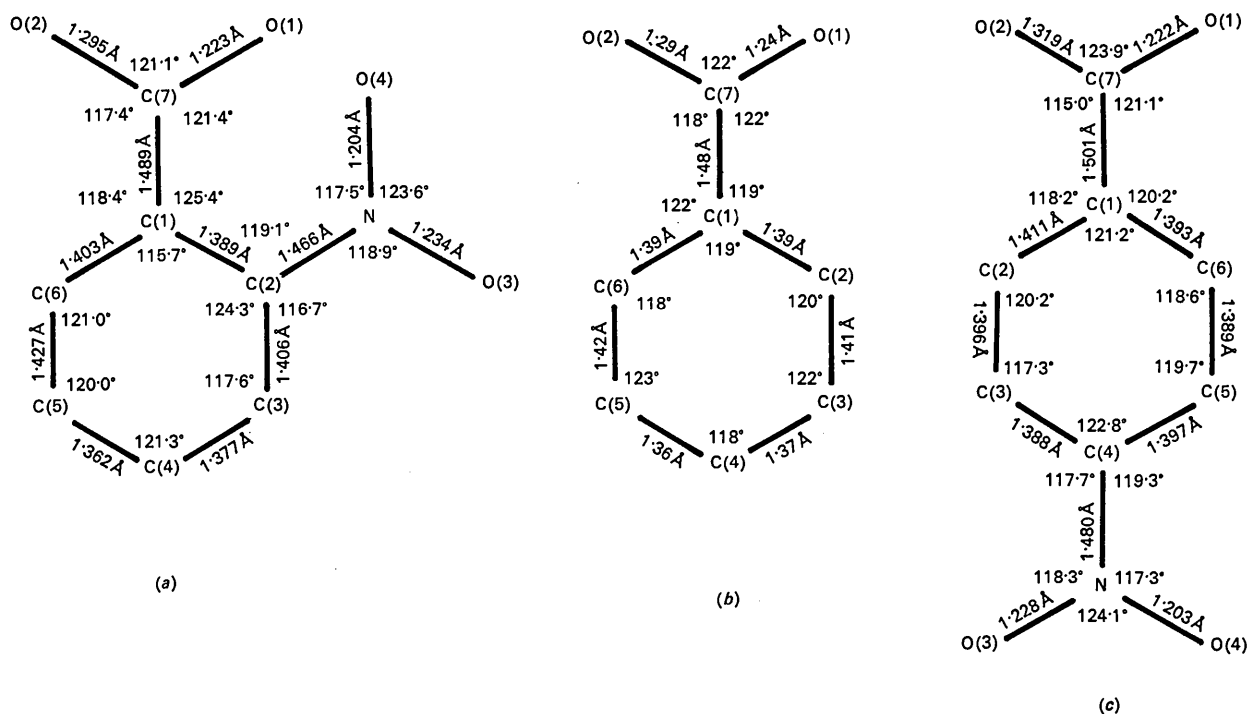


Fig. 2. Bond lengths and angles in (a) *o*-nitrobenzoic acid, (b) benzoic acid, and (c) *p*-nitrobenzoic acid.

nitrobenzene results. In some instances, the graph gives reasonable agreement with observed bond lengths; however, in the cases of benzoic acid and *o*-nitrobenzoic acid, there is no agreement between the observed values and those to be expected from the graph.

The carbon atom C(1) and the centre of the dimer are not exactly in the plane of the carboxylic group; these are on the same side of the plane and respectively 0.034 and 0.062 Å away from it. This suggests that, as in the case of *p*-nitrobenzoic acid, the oxygen atoms O(1) and O(2) of the carboxyl group are drawn towards

the centre of the dimer, presumably because of the force exerted by the hydrogen bonds. The angle between the plane of the carboxyl group and the one passing through O(1), O(2) and the dimer centre is 2.6° (2.4° in the case of *p*-nitrobenzoic acid).

The intramolecular overcrowding between the nitro group and the carboxyl group is relieved partly by the rotation of the substituted groups away from the aromatic plane and partly by the displacement of the nitrogen atom and the exocyclic carbon atom C(7) away from each other. The nitro group is rotated 54.7°

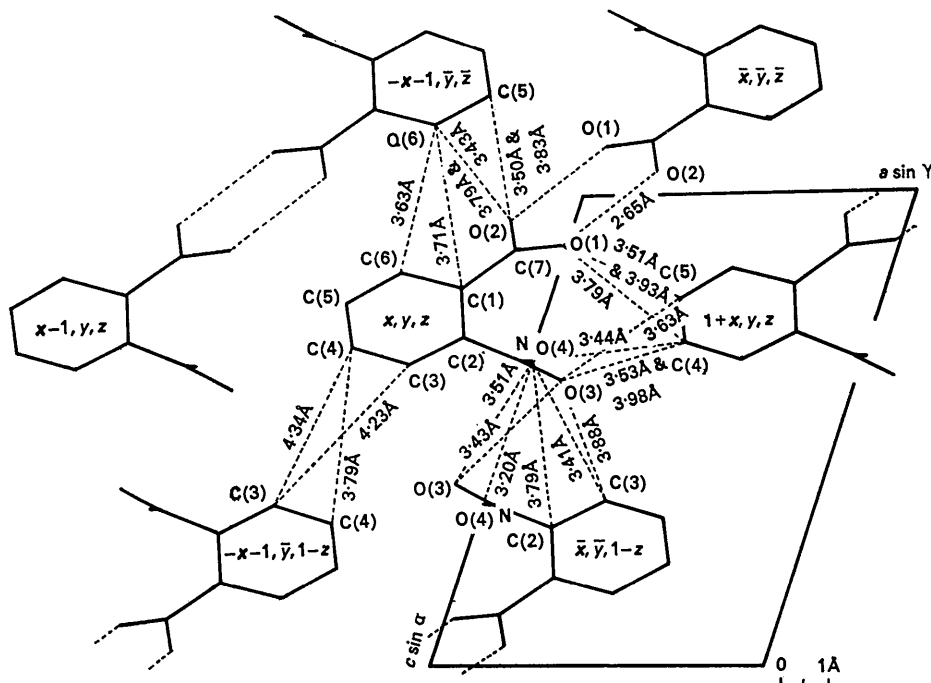


Fig. 3. Structure of *o*-nitrobenzoic acid projected onto (010).

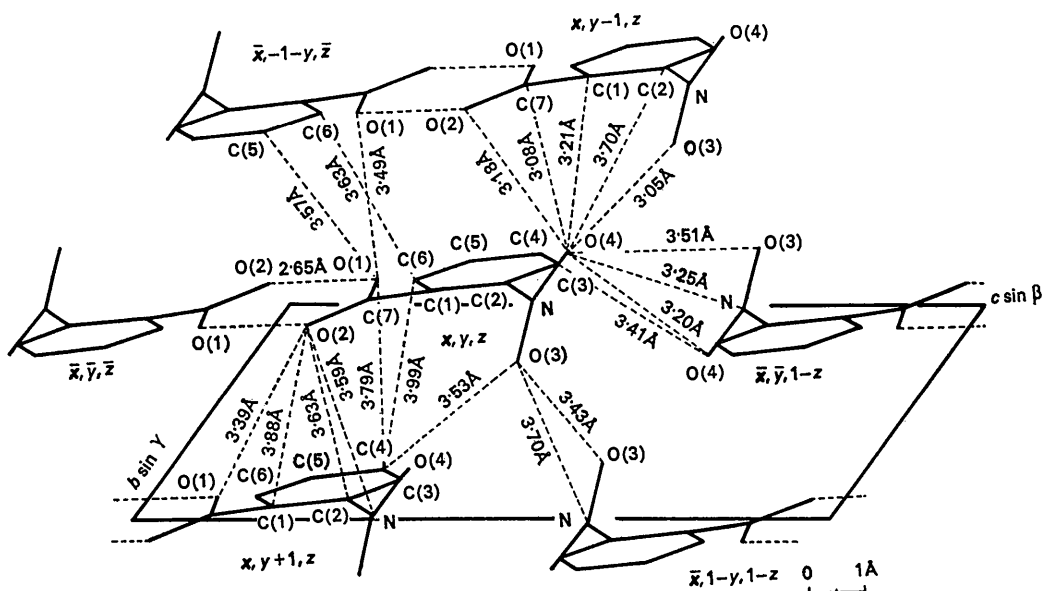


Fig. 4. Structure of *o*-nitrobenzoic acid projected onto (100).

and the carboxyl group  $23.4^\circ$  from the aromatic plane. The exocyclic carbon atom and the nitrogen atom are displaced 0.209 and 0.160 Å respectively from the aromatic plane in opposite directions. The carbon atoms C(1) and C(2) are displaced respectively 0.013 and 0.020 Å from the least-squares plane; the displacements of these atoms are, as expected, small and in the same directions as the atoms C(7) and N respectively (Table 4). The C(1)–C(7) and C(2)–N bonds are displaced sideways as well (Fig. 2).

The dimensions of the carboxyl group and the nitro group in *o*-nitrobenzoic acid show only minor differences from those in *p*-nitrobenzoic acid (Fig. 2).

The projections of the structure along the *b* and *a* axes are shown in Figs. 3 and 4 respectively, in which the principal intermolecular distances are also shown. The *o*-nitrobenzoic acid dimers are held in a stable structure by normal van der Waals interactions. The hydrogen bonds forming dimers are 2.645 Å in length (2.653 Å in *p*-nitrobenzoic acid).

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## The Crystal Structure of D-Galactono- $\gamma$ -lactone

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The crystal structure of D-galactono- $\gamma$ -lactone,  $C_6H_{10}O_6$ , has four molecules in a cell,  $a=6.746$ ,  $b=10.67$ ,  $c=10.98$  Å, with space group  $P2_12_12_1$ . The structure was determined from three-dimensional photographic data by means of a resolved centrosymmetric projection and the Harker sections of the Patterson synthesis. The molecule consists of a 1,4 lactone ring to which is attached a  $CHOH.CH_2OH$



chain. While the lactone group, C–C–O–C, is planar, the fifth atom of the lactone ring is 0.64 Å out of this plane, forming the puckered furan-type configuration very similar to that found in furanose sugars. The C–O bond adjacent to the carbonyl is 0.10 Å shorter than the other C–O bonds, which do not differ significantly from a mean of 1.421 Å. The intermolecular hydrogen bonding forms a three-dimensional network which includes all the hydroxyl groups as donors and acceptors, but excludes the two oxygen atoms of the lactone group.

### Introduction

This crystal structure determination of D-galactono- $\gamma$ -lactone forms part of a program aimed at providing data pertaining to the effects of intermolecular and intramolecular environments on the stereochemistry of groups of atoms commonly found in the carbohydrates and their derivatives. In this structure (I), and that of D-glucurono- $\gamma$ -lactone (II) described in the following paper (Kim, Jeffrey, Rosenstein & Corfield, 1967), the

lactone group C–C–O–C is observed in a 1,4 lactone



ring, which in the former is attached to a chain and in the latter is fused to a furanose ring. Therefore, we postulate that this group is generally planar, by reason

of the valence-bond resonance form  $C-C=O^+-C$  (cf.  $O^-$ )