respectively are normal. These contacts are as follows:

$C(x, y, z)-C(\bar{x}, \bar{y}, z)$	4·02 Å
$C(x, y, z)-C(\bar{x}, 1-y, z)$	4·29
$C(x, y, z)-C(\bar{x}, y, z-\frac{1}{2})$	4·12
$C(x, y, z)-C(\bar{x}, y, z+\frac{1}{2})$	4·12

The structure analysis has been only recently completed, and it has therefore not yet been possible to compare quantitatively the observed and calculated intensities along the reciprocal lattice rods $(h+\omega, k, l)$. Such a comparison and a proper estimate of α will be published later.

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X-ray Diffraction Analysis of *o*-Nitrobenzaldehyde and Some Substituted *o*-Nitrobenzaldehydes

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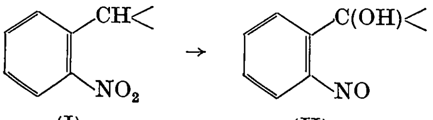
The structures of three halogen-derivatives of *o*-nitrobenzaldehyde have been partially determined in their short-axis projections while the structure of *o*-nitrobenzaldehyde itself has been analysed from partial three-dimensional data. Molecular distortions due to the proximity of the bulky *ortho* substituents are discussed and compared with the corresponding effects in *o*-chloro- and *o*-bromobenzoic acid.

The X-ray determination is to be supplemented by a neutron-diffraction analysis.

Introduction

The structure analyses of *o*-nitrobenzaldehydes reported in this paper form part of a research program on the chemistry of the solid state. One of us has pointed out elsewhere (Schmidt, 1957) that the aim of our combined X-ray and physico-chemical studies is the analysis of reaction mechanisms in terms of topochemical factors controlling solid-state reactions. The reaction type analysed here is the photochemical reaction of the system I → II such as *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid (Ciamician & Silber, 1901; Leighton & Lucy, 1934).



(I) (II)

To this end partial crystal-structure analyses of substituted *o*-nitrobenzaldehydes were undertaken in parallel with kinetic work (Cohen & Schmidt, unpublished). When this system was first being studied in 1951 we attempted to correlate reaction rates in the solid state with the distances between the reacting centres (CH and NO) in *o*-nitrobenzaldehyde, and its 4-iodo-, 5-bromo-, and 6-chloro derivatives. However, this approach had to be abandoned mainly because of the difficulty of establishing reproducible rates in the solid-state reaction. Parallel work on both the light-sensitive and the light-stable modifications of *p*-nitrophenol (Coppens & Schmidt, to be published) indicated that the geometry of the reacting centres rather than their distances was the controlling factor in the oxygen transfer reaction. Accordingly it became of interest to investigate the detailed structure of *o*-nitrobenzaldehydes; for the obvious reason the unsubstituted derivative was chosen for a three-dimensional X-ray analysis. One of us has followed up this work with a two-dimensional neutron-diffraction analysis (Coppens, 1964). No further X-ray work is contemplated on the three halogen derivatives.

Halogen derivatives

5-Bromo-2-nitrobenzaldehyde was prepared according to Einhorn & Gernsheim (1895). It crystallizes from aqueous ethanol in long colourless needles elongated along [010]. The crystallographic constants are listed in Table 1. The *h0l* intensities were estimated visually from Weissenberg photographs by means of the multiple-film technique. The Patterson projection

Table 1. *Crystallographic constants of o-nitrobenzaldehyde and halogen derivatives*

5-bromo-2-nitrobenzaldehyde
a = 13·16 Å
b = 3·95
c = 14·96
β = 94° 50′

$P2_1/c$
n = 4
D_x = 1·97 g.cm^{-3}

6-chloro-2-nitrobenzaldehyde
a = 14·61 Å
b = 13·81
c = 3·95
β = 93°20′

$P2_1/a$
n = 4
D_x = 1·55 g.cm^{-3}

4-iodo-2-nitrobenzaldehyde
d_{100} = 10·94 Å
b = 10·03
c = 7·81

$P2_1/a$
n = 4
D_x = 2·15 g.cm^{-3}

o-nitrobenzaldehyde
a = 11·37 Å
b = 3·960
c = 7·57
β = 90° 11′

$P2_1$
n = 2
D_x = 1·47 g.cm^{-3}

$P(x, z)$ located the bromine atom at (0, 0·125); a first electron-density projection based on the sign of the reflections $h0l$ ($l=4n$) derived from the bromine contribution gave a recognizable pattern containing, however, a spurious molecule due to a centre of symmetry at the bromine position. The signs of the structure factors $F(h0l)$ ($l=4n+2$) to which the bromine does not contribute, were calculated from the coordinates of the light atoms obtained from this first Fourier projection. The projection was refined by an isotropic least-squares procedure to an agreement factor $R=\Sigma|kF_o-|F_c||/\Sigma kF_o=0{\cdot}08$ (excluding $F_o=0$). The projections of the packing arrangement and the electron density down [010] are given in Fig. 1. Atomic parameters are listed in Table 2.

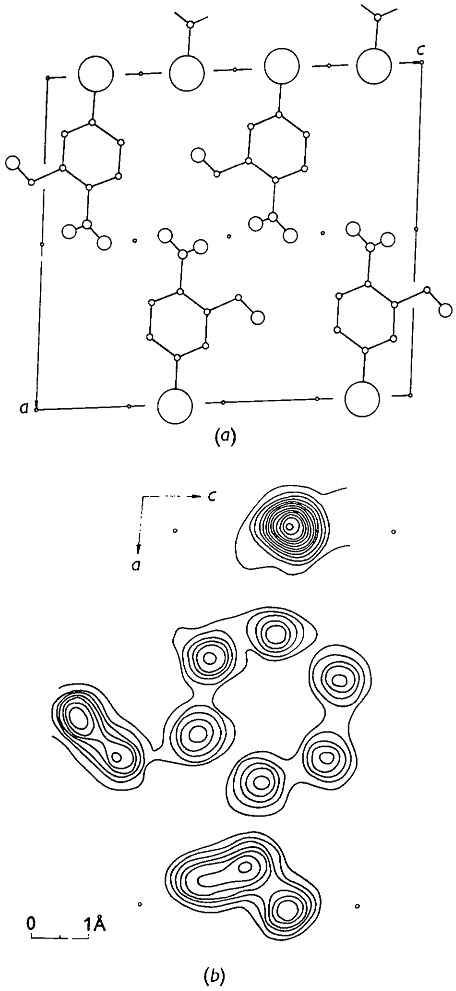


Fig. 1. Projection of 5-bromo-2-nitrobenzaldehyde along [010]. (*a*) Packing diagram. (*b*) Electron density. Contours at arbitrary intervals. Contours around Br at ¼ the regular interval.

6-*Chloro*-2-*nitrobenzaldehyde* (commercial material) crystallizes from aqueous ethanol or petroleum ether (60–80°) in colourless needles elongated along [001]. The crystallographic constants are given in Table 1. The Patterson projection $P(x, y)$ could not be interpreted; here, as in other chlorine-containing compounds, we have used a partially sharpened function

Table 2. *Atomic parameters of substituted nitrobenzaldehydes**

x, y and z in fractions of the unit cell edges

	5-bromo-2-nitrobenzaldehyde			6-chloro-2-nitrobenzaldehyde			4-iodo-2-nitrobenzaldehyde		
	x	z	$B/4$	x	y	$B/4$	x	y	$B/4$
O(1)	0·4669	0·0668	1·62 Å^2	0·1088	0·4484	1·87 Å^2	0·464	0·010	2·0 Å^2
O(2)	0·5055	0·1723	1·30	0·2366	0·4457	1·01	0·517	0·818	1·9
O(3)	0·2477	−0·0899	1·18	−0·0675	0·3085	1·88	0·149	0·154	1·3
N	0·4486	0·1197	1·09	0·1727	0·4162	1·68	0·442	0·894	1·1
C(1)	0·3373	0·1222	0·98	0·1513	0·3080	0·98	0·326	0·845	0·9
C(2)	0·2699	0·0464	0·95	0·0686	0·2714	0·88	0·230	0·934	0·8
C(3)	0·1688	0·0559	0·81	0·0547	0·1770	1·11	0·133	0·876	0·6
C(4)	0·1357	0·1304	0·94	0·1311	0·1169	1·33	0·106	0·732	1·2
C(5)	0·1991	0·2063	0·91	0·2132	0·1603	0·93	0·210	0·659	1·6
C(6)	0·3064	0·1983	1·02	0·2310	0·2570	1·14	0·318	0·710	0·5
C(7)	0·3026	−0·0397	0·95	−0·0168	0·3370	1·70	0·256	0·099	1·2
Hal	−0·0485	0·1331	1·12	−0·0508	0·1175	1·23	0·1851	0·4465	0·99

* For numbering of the atoms see Fig. 4.

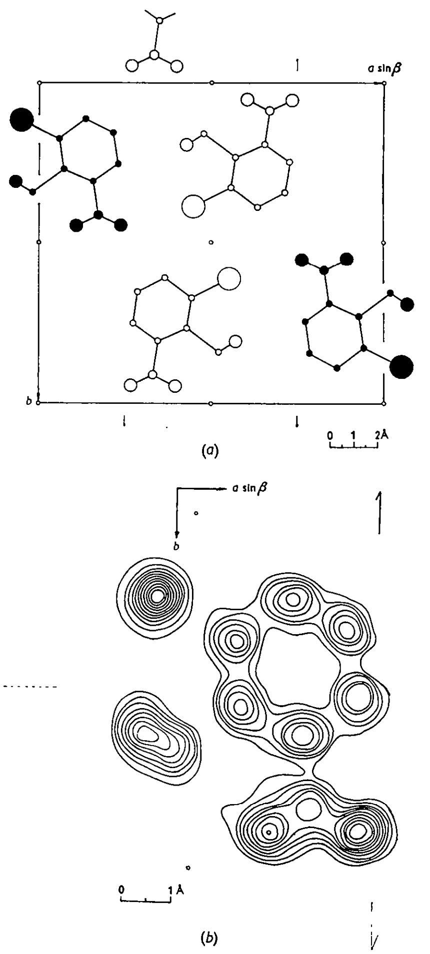


Fig. 2. Projection of 6-chloro-2-nitrobenzaldehyde along [001]. (a) Packing diagram. (b) Electron density. Contours each 1 e.Å^{-2}, around Cl each 2 e.Å^{-2}. Lowest contour 2 e.Å^{-2}.

$P_s(x, y) = \Sigma\Sigma(F^2/f_{\mathrm{Cl}}) \cos 2\pi hx . \cos 2\pi ky$ as a helpful substitute for the conventionally sharpened series involving $F^2/\langle f^2 \rangle$ requiring a special smoothing function. The positions of the chlorine and the light atoms could be derived from this projection; the structure was refined by an isotropic least-squares program to $R = 0{\cdot}15$ (excluding $F_o = 0$). The projections of the packing arrangement and the electron density down [001] are given in Fig. 2. Final parameters are listed in Table 2.

4-*Iodo-2-nitrobenzaldehyde* was prepared according to Sachs & Kantorowicz (1906). It crystallizes from aqueous ethanol in light-yellow prisms elongated along [001]. It is by far the most light-sensitive of the four nitrobenzaldehydes described here and must be completely shielded from light. The crystallographic constants are recorded in Table 1. The (x, y) parameters of the iodine atom were immediately obvious from the distribution of the $(hk0)$ intensities; a first electron density projection based on the iodine contributions showed the general arrangement of the light atoms. The structure was refined by an isotropic least-squares program to $R = 0{\cdot}14$. The projections of the packing arrangement and the electron density along [001] are given in Fig. 3. Atomic parameters are listed in Table 2.

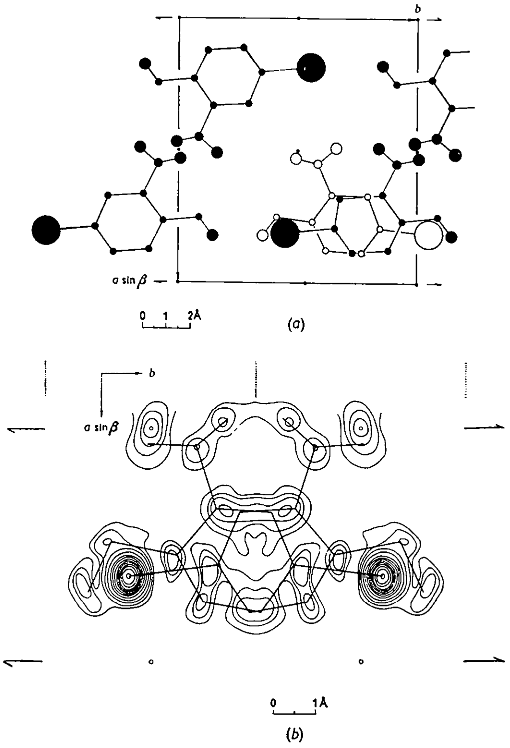


Fig. 3. Projection of 4-iodo-2-nitrobenzaldehyde along [001]. (a) Packing diagram. (b) Electron density. Contours each 2 e.Å^{-2}, lowest contour at 4 e.Å^{-2}. Around I contours at 4, 6, 12, 20, 28 *etc.* e.Å^{-2}. The indicated outline of the molecule is based on the least-squares parameters.

o-Nitrobenzaldehyde

Experimental

o-Nitrobenzaldehyde is dimorphic (Groth, 1917; Kofler & Kofler, 1954). The stable modification crystallizes from benzene in light-yellow needles elongated along [010]; its cell dimensions were measured on $h0l$ and hkh Weissenberg films calibrated by superposition of aluminum powder lines on the single-crystal diffraction pattern. The cell dimensions are listed in Table 1; their estimated standard deviations are 0·2%. Calculated density for $n = 2$: 1·47 g.cm^{-3}. Systematic absences: $0k0$ absent for k odd. Space group: $P2_1$ or $P2_1/m$, corresponding to molecular symmetry 1 or m. The higher symmetry space group is ruled out by the results of this structure analysis.

Intensity measurements were taken on a needle with average cross section $0{\cdot}5 \times 0{\cdot}5$ mm; to prevent loss of material by sublimation the crystal was covered with a very thin film of glue. Intensity photographs of the *h0l*, *h1l*, *h2l*, and *h3l* levels were taken with a Nonius integrating Weissenberg camera by means of the multiple-film multiple-exposures technique. Intensities estimated visually ranged over 8000–1, 2100–1, 2000–1, and 210–1 respectively in the four levels. No attempt was made to measure the few and very weak *h4l* reflections. The number of reflections in each level is given in Table 3.

Table 3. *Refinement of levels*

Level	r	$\Sigma w\Delta^2/(n-s)$	w_0	Number of reflections Obs.	Unobs.
h0l	0·059	3·09	1·0	189	34
h1l	0·076	4·10	0·8	204	13
h2l	0·057	3·31	1·0	182	8
h3l	0·047	7·83	0·4	132	12

Method of analysis

Comparison of the cell dimensions of *o*-nitrobenzaldehyde with those of the 5-bromo derivative indicates resemblance between the unit cells of the two compounds (see Table 1). The glide plane of the latter compound is apparently replaced in the former by a translation accounting for the halving of the *c* axis; on the other hand, the smaller size of the molecule accounts for the shortening of the *a* axis.

Assuming that intermolecular contacts between the oxygens of the nitro-groups, and the angle between the C(4) · · · C(1)–N axis of the molecule and the *a* axis should be similar in the two structures we derived a model of the nitrobenzaldehyde structure, which failed to converge however. The maxima and minima of a few high-order *h0l* reflections were plotted, and the structure-factor graph thus obtained showed that in the *b*-axis projection the angle between C(4) · · · C(1)–N and the *a* axis had to be increased from 2° to about 12°. This corrected model could be refined by the least-squares program.

Next, the *y* coordinates were derived from the projected shape of the molecule. (The origin can be chosen anywhere on the polar *b* axis.)

Refinement

Both two- and three-dimensional refinements were carried out with a least-squares program on WEIZAC (the electronic computer of the Weizmann Institute), written by Dr F. L. Hirshfeld of this Department. This program, which uses the diagonal-matrix approximation, seeks to minimize the function:

$$r = \Sigma w(k^2F_o^2 - F_c^2)^2/\Sigma wk^4F_o^4$$

with respect to the scale factors k and the positional and thermal parameters of each atom in the asymmetric unit.

Unobserved reflections are included in the refinement only when their calculated value is larger than an estimated threshold value F_t.

In the present analysis all atoms except hydrogen were treated anisotropically. The four levels were first refined separately; when these refinements had been completed the residuals were used to estimate the relative accuracies of the levels, as described below.

The weights w were assumed to be equal to w_0/F_o^3. Here w_0 is a constant which varies from level to level owing to different experimental conditions such as exposure time and spot shape. The value of w_0 for the various levels was estimated from the weighted sum of the residuals $\Sigma w\Delta^2$ (where $\Delta = k^2F_o^2 - F_c^2$) in each level as obtained after completion of its refinement. If s parameters have been refined to minimize r for a set of n reflections, then approximately:

$$\Sigma w\Delta^2 = (n-s)\Sigma w\sigma^2(k^2F_o^2)/n$$

on the assumption that errors in the measured values of F_o are the only source of discrepancy between kF_o and F_c. After calculation of the averages of $w\sigma^2(k^2F_o^2)$ in the four levels the weights were scaled in order to make these averages equal in all four levels. Numerical details are given in Table 3.

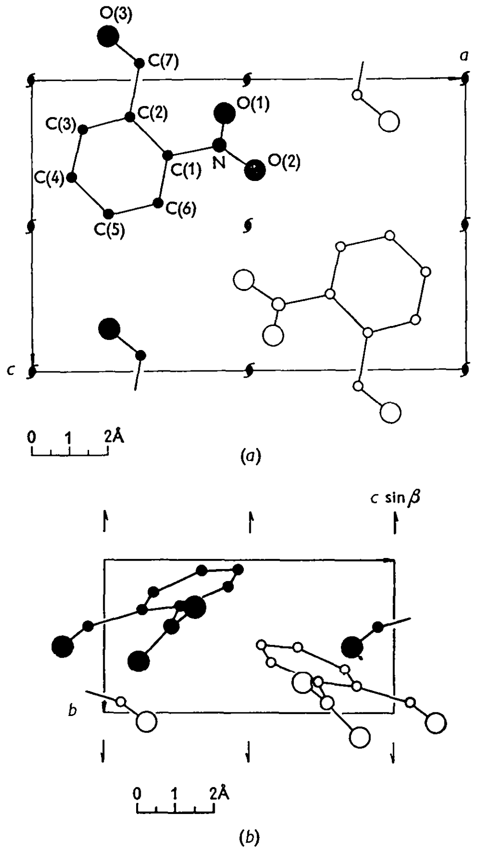


Fig. 4. Packing diagrams of nitrobenzaldehyde. (*a*) Seen along [010]. (*b*) Seen along [100].

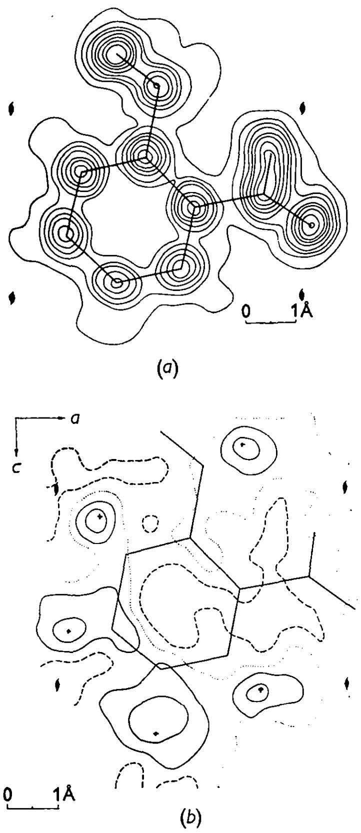


Fig. 5. (*a*) Electron-density projection of nitrobenzaldehyde along [010]. Contour interval 1 e.Å^{-2}; lowest contour 1 e.Å^{-2}. (*b*) (F_o-F_c) syntheses showing hydrogen atoms. Contours each 0·2 e.Å^{-2}. Zero contour dotted, negative contours broken. Crosses indicate least-squares hydrogen positions.

Subsequently all the data were refined together. The scale factors of the higher levels interact with the β_{22} temperature factors since an increase $\Delta\beta_{22}$ in all the β_{22}'s changes the scale factor of level *hnl* by a factor $\exp(-\Delta\beta_{22}n)$. Exposure times, upper level correction factors and the zero level scale factor were used to calculate initial values of the higher level scale factors, which were then refined together with the other parameters.

Final overall agreement factors are $r=0{\cdot}057$ and $R=0{\cdot}096$. For 23 out of 67 unobserved reflections $|F_c|$ was bigger than F_t, while for 5 of the 774 reflections $|2F_c|<kF_o$. The values of the observed and calculated structure factors are listed in Table 4.* Views of the packing arrangements down [010] and [100] are given in Fig. 4, while the electron-density projection $\varrho(x,z)$ and the corresponding difference map showing the hydrogen atoms, are reproduced in Fig. 5. Final positional and temperature parameters can be found in Tables 5 and 6.

Discussion

Molecular structure

Bond lengths and angles and their standard deviations are listed in Table 7. The bond lengths in the benzene ring are equal within the experimental error, and do not differ significantly from the standard value; the $>C=O$ length of the aldehyde group (1·200 Å) compares well with the bond lengths in acetaldehyde, 1·22 Å (Stevenson, LuValle & Schomaker, 1939) and glyoxal, 1·20 Å (LuValle & Schomaker, 1939). Information on the planes through the benzene ring, the nitro group, and C(2), C(7), and O(3) is given in Tables 8 and 9.

Rotation of the two substituent groups out of the

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* Table 4 has been deposited as Document No. 7588 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document No. and remitting $2·50 for photoprints or $1·75 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 5. *Positional parameters and their standard deviations* as fractions of the unit cell edges*

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
O(1)	0·4452	0·659	0·1179	0·0005	0·002	0·0008
O(2)	0·5147	0·303	0·3119	0·0004	0·003	0·0007
O(3)	0·1793	0·565	−0·1466	0·0004	0·002	0·0006
N	0·4336	0·433	0·2274	0·0005	0·002	0·0007
C(1)	0·3150	0·301	0·2594	0·0005	0·002	0·0008
C(2)	0·2304	0·326	0·1285	0·0004	0·002	0·0006
C(3)	0·1190	0·213	0·1681	0·0004	0·002	0·0006
C(4)	0·0931	0·081	0·3336	0·0005	0·002	0·0010
C(5)	0·1788	0·0600†	0·4605	0·0006	—†	0·0010
C(6)	0·2918	0·174	0·4254	0·0005	0·003	0·0009
C(7)	0·2533	0·433	−0·0569	0·0006	0·003	0·0009
H(3)	0·075	0·20	0·071			
H(4)	0·019	−0·05	0·362			
H(5)	0·170	−0·07	0·627			
H(6)	0·368	0·20	0·514			
H(7)	0·321	0·27	−0·111			

* Standard deviations of hydrogen atom parameters are not sufficiently reliable to justify publication. More accurate information on the hydrogen atoms will be given in the description of the neutron-diffraction analysis (Coppens, 1964).

† The *y* parameter of C(5) is kept constant at this arbitrary value.

Table 6. *Temperature factors**

	β_{11}	β_{22}†	β_{33}	β_{12}	β_{23}	β_{13}
O(1)	0·0097	0·075	0·0411	−0·009	−0·015	0·012
O(2)	0·0078	0·200	0·0304	0·010	−0·043	−0·010
O(3)	0·0122	0·161	0·0179	0·008	0·040	−0·003
N	0·0059	0·082	0·0240	0·003	−0·032	−0·001
C(1)	0·0066	0·056	0·0155	0·003	−0·013	0·001
C(2)	0·0057	0·059	0·0142	0·002	−0·006	0·001
C(3)	0·0063	0·063	0·0162	0·002	0·006	0·001
C(4)	0·0072	0·074	0·0209	0·001	0·015	0·005
C(5)	0·0127	0·083	0·0173	0·005	0·008	0·008
C(6)	0·0105	0·074	0·0149	0·011	0·004	−0·003
C(7)	0·0081	0·107	0·0150	0·009	0·006	0·001

* The temperature factors are the coefficients in the expression

$$\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{13}hl)]$$

† The absolute scale of the β_{22}'s is unknown since no *experimental* information on the correlation between the *hnl* levels is available.

Table 7. *Bond lengths and angles*

	Length observed	Standard deviation
N–O(1)	1·226 Å	0·010 Å
N–O(2)	1·234	0·006
C(1)–N	1·468	0·008
C(2)–C(7)	1·490	0·009
C(7)–O(3)	1·200	0·009
C(1)–C(2)	1·382	0·006
C(2)–C(3)	1·377	0·006
C(3)–C(4)	1·390	0·009
C(4)–C(5)	1·367	0·009
C(5)–C(6)	1·388	0·009
C(6)–C(1)	1·380	0·009

Angle*		Angle*	
O(2)–N–O(1)	125·0°	C(6)–C(1)–C(2)	123·0°
O(2)–N–C(1)	116·8	C(1)–C(2)–C(3)	117·3
O(1)–N–C(1)	118·2	C(2)–C(3)–C(4)	121·1
N–C(1)–C(6)	117·3	C(3)–C(4)–C(5)	120·2
N–C(1)–C(2)	119·5	C(4)–C(5)–C(6)	120·2
C(3)–C(7)–C(2)	122·2	C(5)–C(6)–C(1)	118·2
C(7)–C(2)–C(1)	125·0		
C(7)–C(2)–C(3)	117·5		

* Average standard deviation in the angles 0·6°.

Table 9. *Deviations from the planes through the benzene ring and the nitro group atoms*

Atom	From benzene ring	From NO_2
C(1)	−0·006 Å	−0·030 Å
C(2)	0·002	—
C(3)	0·001	—
C(4)	0·000	—
C(5)	−0·004	—
C(6)	0·007	—
N	0·065	0
O(1)	0·580	0
O(2)	−0·426	0
C(7)	−0·128	−1·312
O(3)	0·335	−1·345

plane of the benzene ring may be ascribed to intramolecular overcrowding of the two *ortho* substituents. The resulting strain is also manifested in the bending of the exocyclic C(2)–C(7) (4·9°) and C(1)–N (2·5°) bonds in opposite directions out of the plane of the benzene ring, and in the in-plane bending of the two bonds resulting in a C(1)C(2)C(7) angle of 125·0° and a C(2)C(1)N angle of 119·5°; the latter two values are to be compared with their adjacent exocyclic bond angles of 117·5° and 117·3°.

These combined distortions have increased the C(7) · · · N distance to 2·97 Å, essentially equal to the corresponding value of 2·99 Å in 1,5-dinitronaphthalene (Trotter, 1960) where the nitro groups are twisted by 49° in order to clear the '*ortho*' carbons held rigidly in the planar aromatic ring. The effect of these distortions on the C–N bond length is insignificant: our value of 1·468 Å is identical with the C–N length both in planar nitropyridine *N*-oxide, 1·472 Å (Eichhorn, 1956) and nitrobenzene, 1·48 Å (Trotter, 1959*a*), and in nitromesitylene, 1·476 Å (Trotter, 1959*b*) whose angle of twist is 66·4 Å. This constancy of the C–N bond lengths is all the more striking when one considers the good correlation

Table 8. *Equations of planes and interplanar angles*

	m_1	m_2	m_3	d	Angle with best plane through benzene ring
Benzene ring	−2·7915	3·6191	2·4509	0·8502	
Nitro group	−1·3147	2·7134	5·4457	1·8437	27° 29′
Atoms C(2), C(7) and O(3)	3·3393	3·5564	2·4706	2·2466	31° 17′

m_1, m_2, m_3 and d are the coefficients in the equation $m_1x+m_2y+m_3z-d=0$ in which x, y, and z are fractional coordinates. The benzene ring plane is the best plane through the six ring-carbons derived according to Schomaker, Waser, Marsh & Bergman (1959).

of the intensity of the 2500 Å absorption band of nitro compounds in iso-octane solution with the angle of twist (Wepster, 1958); lowered conjugation between the nitro group and the ring is responsible for the decrease in intensity of this band with increasing size of the *o*-substituent, but appears not to influence the C–N bond length.

A second line of comparison can be attempted with *o*-chloro- and *o*-bromobenzoic acids recently analysed by Ferguson & Sim (1961, 1962). However, these two structures are not entirely consistent for, while the angle of twist of the carboxyl group to the benzene ring increases from 13·7° to 18·3° with increasing size of the *ortho* substituent, the exocyclic C–C bond decreases from 1·521 to 1·487 Å. The variations reported by Ferguson & Sim in the bond lengths of the benzene ring of the *o*-chloro-acid only, are not observed in *o*-nitrobenzaldehyde. The large discrepancy between the angles of twist in the NO_2 and COOH groups may be due to the difference in size of the *ortho* substituents, and perhaps also to contact requirements: while carboxylic groups are, as a rule, paired through hydrogen bonds across a centre of symmetry no such constant contact type is evident in the nitro compounds analysed so far. We note in this connection that *o*-nitrobenzaldehyde shows short $O \cdots O$ contacts across the screw axes at $x=\frac{1}{2}$, $z=0$ (2·95 Å) and between adjacent molecules in the stacks parallel to [010] (3·05 Å); in other nitro compounds, such as 9,10-dinitroanthracene (3·06 Å) (Trotter, 1959*c*) and 1,4-dinitrobenzene (3·24 Å) (Abrahams, 1950), short centric or screw-axis related $O \cdots O$ contacts have been observed though these are usually longer than the shortest distances reported in the present structure.

Thermal motion

Exceptionally large motion of the substituents in overcrowded molecules has been predicted as a result of the expected flatness of the curve describing total potential energy *versus* angle of twist (Wepster, 1958). In the *crystal* of *o*-nitrobenzaldehyde no abnormally large motion takes place: the observed amplitudes are similar to those in *para*-substituted nitro compounds such as *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961) and (α- and β-) *p*-nitrophenol (Coppens & Schmidt, to be published).

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