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The Crystal Structure of Nitrobenzene at −30 °C

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Crystals of nitrobenzene at −30° C. are monoclinic, space group $P2_1/c$, with four molecules in the unit cell. The structure has been determined from the projection along the short *a*-axis, and refined by three-dimensional differential syntheses. The molecule is exactly planar, and values of the bond lengths, valency angles, and intermolecular distances are given.

Introduction

Detailed X-ray analyses of the crystal and molecular structures of 9-nitroanthracene, 9:10-dinitroanthracene (Trotter, 1958, 1959*a*, *b*) and nitromesitylene (Trotter, 1959*c*, *d*) have shown that the nitro groups are rotated out of the planes of the aromatic rings due to the steric effects of neighbouring carbon and hydrogen atoms, and examination of the characteristic nitro group vibration frequencies and the bond lengths in the molecules suggests resultant decreases in the resonance interaction between the nitro groups and the aromatic rings (Trotter, 1959*e*, *f*, *g*). It was noted during the course of the investigations that it would be useful to have for comparison with the molecular dimensions of these molecules an accurate measure of the molecular dimensions of a completely conjugated aromatic nitro compound, and since nitrobenzene is the simplest example, an analysis of its crystal structure at reduced temperatures has been undertaken.

Experimental

Low-temperature equipment similar to that described by Burbank & Bensey (1953) was used for growing suitable crystals in thin-walled glass capillaries, and maintaining them at −30 °C. during collection of the data. Provided the crystals were grown with care, the short *a*-axis (3·86 Å) of the monoclinic unit cell was invariably directed almost exactly along the length of the capillary, and most of the three-dimensional data could be readily recorded on a few Weissenberg films.

The cooling equipment, which was designed for the precession camera, could easily be fitted to a Weissenberg camera, but the conventional layer-line screen of our Weibenga integrating Weissenberg goniometer did not permit convenient viewing of the crystal or adjustment of the arc settings without disturbing the flow of cold air. The instrument was adapted for low-temperature work by fitting it with a screen from which a hemi-cylindrical section about 5 cm. long had been removed on the upper side. This arrangement had some useful advantages. With the screen in position, the alignments of the capillary, collimator, beam trap, and cold and warm air streams were in full view and could be inspected periodically; more efficient circulation of air helped to prevent ice formation; a telescope and polaroids could be inserted for viewing during crystal growth; the arc adjusting screws were easily accessible; and a thermocouple could readily be inserted for checking the temperature.

Once the apparatus was assembled any necessary adjustment of crystal setting or screen position could be made without discontinuing the cold air flow to the crystal. In order that the arrangement should not be disturbed during changing of films, a hemi-cylindrical film-holder was constructed, only the beams reflected through the slit on the lower side of the screen being recorded.

In assembling the equipment it was actually unnecessary to construct a new layer-line screen, since a double layer-line screen (Hanson, 1958) was available and could be adapted for the purpose. This screen was designed to record simultaneously, on the upper and lower halves of a Weissenberg film, two different levels of the reciprocal lattice, to facilitate correlation of scale factors. The upper slit of the screen is contained in a shell which slides within the outer cylinder, and this shell was completely removed, giving an arrangement similar to that described above.

The unit-cell dimensions were determined from rotation and oscillation photographs of a crystal rotating about the *a*-axis, and *h*0*l* and *hk*0 precession films; the space group was determined from these photographs and 0*kl* and 1*kl* Weissenberg films.

Crystal data (at −30 °C.)

Nitrobenzene, $C_6H_5NO_2$; $M = 123{\cdot}1$; m.pt. $= 5{\cdot}85$ °C.
Monoclinic, $a = 3{\cdot}86$, $b = 11{\cdot}65$, $c = 13{\cdot}24$ Å; $\beta = 95°\ 35'$.
Volume of the unit cell $= 592{\cdot}9$ Å^3.
D_m (measured density) $= 1{\cdot}344$ g.cm.$^{-3}$ at 0 °C.
$Z = 4$, D_x (calculated density) $= 1{\cdot}370$ g.cm.$^{-3}$ at −30 °C.
Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 10{\cdot}26$ cm.$^{-1}$.
Total number of electrons per unit cell $= F(000) = 256$.

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Absent spectra: $h0l$ when l is odd, $0k0$ when k is odd. Space group is $P2_1/c$–C_{2h}^5.

We could not of course measure the density at −30 °C. The density of the crystals at 0 °C. is 1·344 g.cm.$^{-3}$ (see Heilbron & Bunbury, 1953).

Almost all of the crystals grown were twinned on (001); indeed only on one occasion was a single crystal obtained. However the cell dimensions are such that a regular and rather unusual array of points in reciprocal space is obtained (Fig. 1). On the $1kl$ and $2kl$ layers every third spot is apparently absent on the Weissenberg photographs, which can be very readily indexed and interpreted.

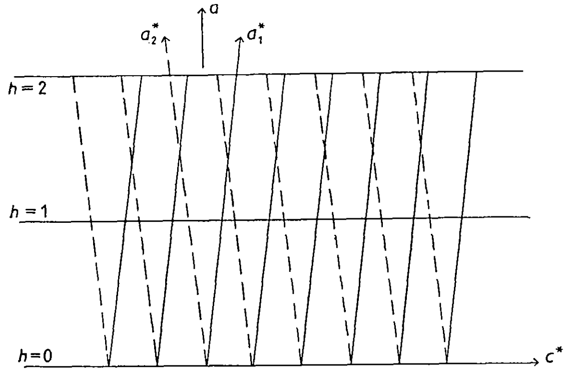

Fig. 1. Projection along b^* of the reciprocal lattice of a crystal twinned on (001).

The intensities of the hkl reflexions were recorded on Weissenberg photographs for a crystal rotating about the a-axis, using Cu $K\alpha$ radiation, the multiple film technique being used to correlate strong and weak reflexions. Layers with $h=0, 1, 2, 3$ were recorded, both normal-beam and equi-inclination methods being used for the non-equatorial layers. $h0l$ and $hk0$ precession films were used for intensity correlation between the various layers. All the intensities were estimated visually, the range being 14,000 to 1. The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal, Lorentz and polarization factors being applied together with the rotation factors appropriate to normal-beam and equi-inclination Weissenberg photographs (Cox & Shaw, 1930; Tunell, 1939). No absorption corrections were applied. The absolute scale was established later by correlation with the calculated structure factors.

In the $0kl$, $1kl$ and $2kl$ zones, 68%, 49% and 20% respectively of the reflexions within the Cu $K\alpha$ sphere were observed. No reflexions with $h=3$ or 4 were observed.

Structure analysis

[100] projection

In deriving an approximate trial structure it was assumed initially that the molecule was completely planar with C–C and C–N bond lengths 1·40 Å, N–O bond lengths 1·20 Å, and all valency angles 120°. The molecular orientation in the a-axis projection was determined from an examination of the $0kl$ weighted reciprocal lattice, and the position of the molecular centre then found by the usual methods (Taylor, 1954; Trotter, 1959*h*). Structure factors were calculated for the stronger reflexions and a Fourier series computed using measured structure amplitudes and calculated signs. On the resulting electron-density map all the carbon, nitrogen and oxygen atoms were well resolved; new atomic centres were chosen and structure factors calculated for all the $0kl$ reflexions, using McWeeny's scattering factors for carbon, nitrogen and oxygen, corrected for thermal vibration as usual, taking $B=5\cdot5$ Å^2 for all the atoms. The value of R, the usual discrepancy factor, was 34·3% over the observed reflexions.

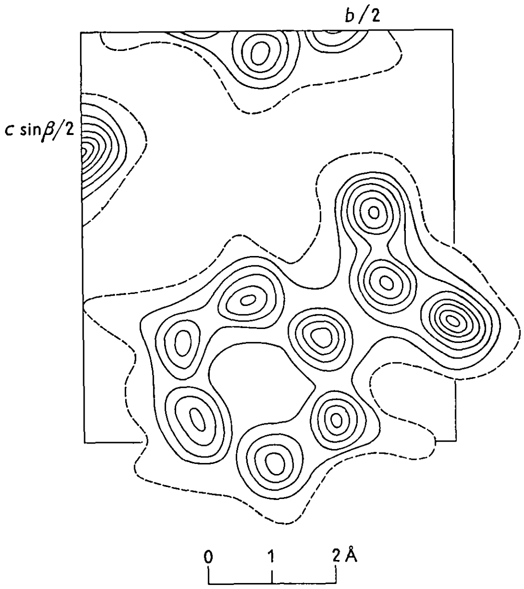

Fig. 2. Electron-density projection along the a-axis. Contours at intervals of 1 e.Å^{-2}, with the one-electron line broken

Refinement proceeded by computing a difference synthesis and shifting the atoms to minimize the slopes at the atomic centres, no changes being made in the temperature parameters (although the map indicated that the B values of the atoms would have to be adjusted in later stages of the refinement). Recalculation of structure factors revealed that R had dropped to 21·5%, a significant improvement in agreement. An electron-density projection along the a-axis, computed using all the $0kl$ reflexions (measured amplitudes and calculated signs) is shown in Fig. 2.

x-Coordinates

The approximate orientation of the molecule in three-dimensions was then deduced from an examination of the three-dimensional weighted reciprocal lattice, and of the bond lengths in the a-axis projec-

Table 1. *Peak heights and curvatures in final cycle*

	ϱ (e.Å^{-3})		$\partial^2\varrho/\partial x^2$ (e.Å^{-5})		$\partial^2\varrho/\partial y^2$ (e.Å^{-5})		$\partial^2\varrho/\partial z^2$ (e.Å^{-5})	
Atom	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
C_1	5·58	5·49	−20·38	−20·21	−37·07	−34·56	−37·02	−36·60
C_2	4·97	5·09	−17·10	−16·95	−32·43	−34·06	−32·82	−34·18
C_3	4·62	4·57	−15·26	−14·95	−29·56	−28·87	−30·40	−28·57
C_4	4·46	4·61	−15·40	−15·60	−25·33	−26·71	−26·89	−28·80
C_5	4·52	4·57	−14·76	−14·55	−30·49	−30·36	−24·41	−27·03
C_6	5·07	5·01	−17·27	−17·63	−30·32	−30·08	−32·14	−31·94
N	5·93	6·30	−20·03	−21·58	−34·32	−34·87	−33·76	−32·96
O_1	5·70	5·91	−17·28	−18·99	−30·79	−31·12	−33·69	−32·18
O_2	5·80	5·77	−16·08	−17·09	−32·86	−29·94	−30·92	−30·33

tion. The x-coordinate of the molecular centre was obtained by computing the variation of the calculated structure factors of some of the low order $1kl$ reflexions, as the molecule was moved along the a-axis. The positional parameters giving best agreement between F_o and F_c for these reflexions were used in computing structure factors for all the $1kl$ reflexions; the discrepancy over the observed reflexions was 27·1%. Generalized projections were computed using the measured $1kl$ structure amplitudes and calculated signs, and new x-coordinates obtained from the relation

$$\tan 2\pi x_j = S_1(y_j, z_j)/C_1(y_j, z_j)$$

where $S_1(y, z)$, $C_1(y, z)$ are the sine and cosine generalized projections (shown in Fig. 3). Recalculation of the $1kl$ structure factors revealed that R had dropped to 22·0%.

Three-dimensional refinement

At this stage structure factors were calculated for the $2kl$ reflexions, and the R value was 26·3%. Refinement proceeded by computing a differential synthesis, using the measured structure amplitudes and calculated signs for all the observed hkl reflexions. New coordinates were obtained and structure factors calculated for all the observed reflexions; the R value was 19·2%.

Observed and calculated differential syntheses were then computed, and new positional parameters obtained from the corrections of the F_o synthesis (these were now quite small), combined with the back-shift (series-termination) corrections from the F_c synthesis. New temperature parameters were chosen to minimize the differences between the observed and calculated peak electron-densities and curvatures. These changes reduced R to 16·9%.

A second set of observed and calculated differential syntheses was computed, and some further small changes in the positional parameters were indicated. The values of the observed and calculated peak electron-densities and curvatures are listed in Table 1, and these indicate that some further small changes are required in the temperature parameters. The final B values adopted are included in Table 2.

Further refinement would require that allowance be made for the contribution of the hydrogen atoms, and for the anisotropic thermal vibrations of the carbon, nitrogen and oxygen atoms. It is doubtful

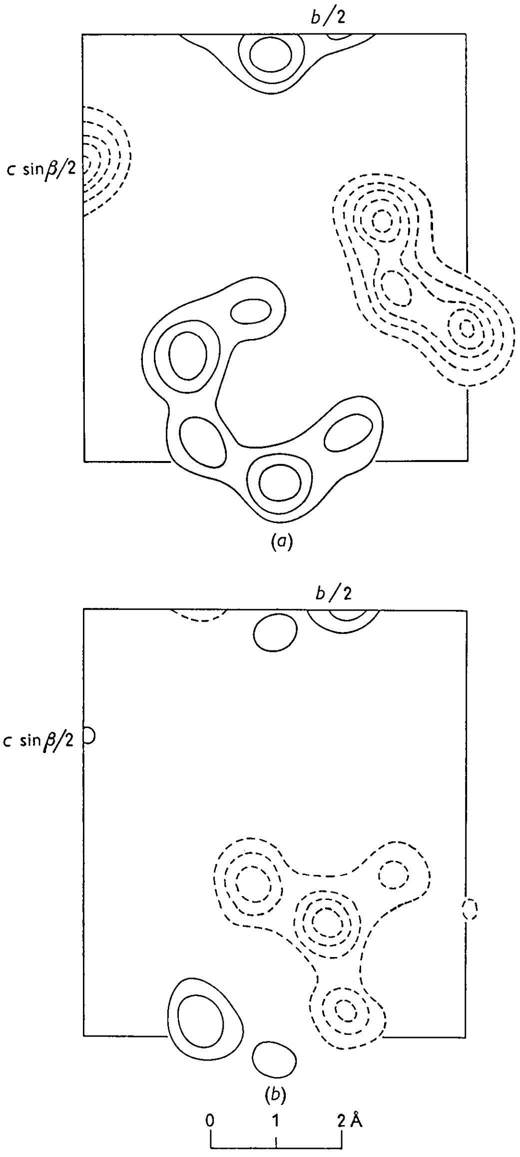

Fig. 3. (*a*) Cosine, and (*b*) −sine generalized projections along the a-axis, using the $1kl$ data. Contours at intervals of 1 e.Å^{-2}, negative contours broken, zero contour omitted.

Table 2. *Final positional and temperature parameters* (and deviations, Δ, from the mean plane)

Atom	x	y	z	B (Å^2)	Δ (Å)
C_1	0·2267	0·3183	0·1300	4·9	−0·005
C_2	0·1338	0·3415	0·0291	4·9	+0·033
C_3	−0·0569	0·2553	−0·0258	5·7	−0·015
C_4	−0·1231	0·1516	0·0178	5·7	−0·006
C_5	−0·0156	0·1299	0·1161	5·7	+0·011
C_6	0·1653	0·2181	0·1775	4·9	−0·012
N	0·4216	0·4102	0·1890	5·3	+0·014
O_1	0·5099	0·3900	0·2779	7·5	+0·002
O_2	0·4673	0·5002	0·1484	7·5	−0·021

whether such further refinement would be of much value, since the coordinates of the heavier atoms would probably not be changed significantly, and so refinement was terminated at this point. We did not trouble to compute the final values of the structure factors, but the calculated values at the penultimate stage for all the observed reflexions ($R=16\cdot9\%$) are listed, together with the measured structure amplitudes in Table 3. Throughout the refinement structure factors were calculated at each stage for many of the unobserved reflexions, and no anomalies were found.

Coordinates and molecular dimensions

The positional and temperature parameters of the atoms obtained from the final observed and calculated differential syntheses are listed in Table 2, x, y, and z being coordinates referred to the principal crystallographic axes, and expressed as fractions of the unit-cell edges.

The equation of the mean molecular plane, obtained by the least-squares method, is

$$0\cdot8674X'-0\cdot3610Y-0\cdot3426Z'+1\cdot1382=0\,,$$

where X', Y, Z' are coordinates expressed in Å units and referred to orthogonal axes a', b, c, where a' is perpendicular to b and c. The deviations of the atoms from this plane are listed in the final column of Table 2.

The bond lengths and valency angles in the molecule were calculated from the coordinates of Table 2. The symmetry of the molecule does not differ significantly from $mm2$, and the mean values of the bond lengths and valency angles are shown in Fig. 4.

Standard deviations

The standard deviations of the atomic positions were calculated from Cruickshank's (1949) formulae. The r.m.s. values for all the atoms were $\sigma(x)=\sigma(y)=\sigma(z)=0\cdot014$ Å. The corresponding standard deviations

Table 3. *Measured and calculated structure factors*

hkℓ	F_o	F_c	hkℓ	F_o	F_c	hkℓ	F_o	F_c	hkℓ	F_o	F_c	hkℓ	F_o	F_c	hkℓ	F_o	F_c
002	3.0	-5.5	057	7.4	-7.7	0,12,2	3.1	+2.7	130	5.8	+3.5	161	3.7	+5.6	20$\bar{8}$	4.7	+6.3
004	5.2	+2.4	058	10.3	+10.2	0,12,4	1.4	+2.0	132	12.6	-7.1	162	6.8	-6.8	20$\bar{4}$	8.9	-13.2
006	43.8	+38.7	059	8.0	-8.1	0,12,6	3.4	+2.5	133	26.7	-23.4	164	5.2	+5.1	20$\bar{2}$	11.0	-11.5
008	9.6	+8.6	0,5,10	14.0	+12.0	0,13,3	1.4	+0.1	134	17.0	-20.1	165	4.7	-5.4	202	6.8	-6.7
0,0,10	1.4	+1.5	0,5,11	12.5	+9.4	0,14,1	1.3	+0.9	136	3.4	-1.6	166	4.9	+4.6	21$\bar{5}$	12.6	-12.9
0,0,12	5.8	-5.1	0,5,12	3.5	+3.8				138	3.7	+2.5	167	4.4	-4.6	21$\bar{4}$	8.9	+8.6
0,0,14	2.6	-3.4	0,5,13	2.3	-1.8	1,0,$\overline{14}$	3.3	-5.2	139	7.8	-9.8	168	3.1	-2.9	21$\bar{3}$	4.5	-0.1
011	13.7	-15.4	0,5,14	1.8	+1.3	1,0,$\overline{10}$	2.5	+2.9	1,3,10	12.7	-10.5	169	2.7	+2.5	21$\bar{1}$	5.9	+7.4
012	57.0	-55.9	060	6.7	+7.7	10$\bar{8}$	12.3	+17.8	1,3,11	10.0	-8.9	1,7,$\overline{13}$	2.4	-1.0	211	5.3	-7.9
013	25.0	+27.4	061	11.9	-11.0	10$\bar{6}$	9.3	+6.3	1,3,12	2.1	+1.9	1,7,$\overline{12}$	3.6	+4.9	212	12.6	+12.2
014	13.7	+10.4	062	12.9	+17.4	10$\bar{4}$	9.8	-9.4	1,4,$\overline{11}$	6.0	+6.2	1,7,$\overline{11}$	2.5	-3.0	213	8.9	+9.6
015	1.0	-2.1	063	15.2	+16.5	10$\bar{2}$	109.4	+114.9	14$\bar{9}$	4.8	-6.4	1,7,$\overline{10}$	3.0	+1.9	215	5.1	+4.9
016	10.6	+10.0	064	14.5	-12.8	102	27.4	+30.6	14$\bar{8}$	5.0	-6.4	17$\bar{6}$	5.3	+4.0	219	11.1	+9.8
017	12.7	-13.9	065	5.2	-5.0	104	21.3	+23.3	14$\bar{7}$	6.0	-5.6	17$\bar{5}$	6.8	-7.0	2,1,10	5.4	+4.3
018	10.7	-10.8	066	5.5	+3.8	106	4.3	+0.5	14$\bar{6}$	4.3	-4.6	17$\bar{4}$	6.3	+6.1	22$\bar{9}$	7.7	+9.1
019	12.2	+11.6	067	8.0	-8.3	1,0,10	2.1	+0.8	14$\bar{5}$	8.8	+8.6	17$\bar{3}$	2.5	-2.9	22$\bar{8}$	3.8	-5.6
0,1,10	1.4	+0.2	068	10.0	+11.2	1,0,14	2.6	-2.0	14$\bar{4}$	23.8	+23.3	17$\bar{2}$	2.3	-2.7	22$\bar{6}$	2.5	+1.7
0,1,12	5.2	-6.1	069	4.4	+4.1	1,1,$\overline{10}$	5.1	+6.5	14$\bar{3}$	16.1	-17.7	17$\bar{1}$	2.0	+1.9	22$\bar{5}$	7.0	-9.5
0,1,13	1.8	+1.3	0,6,10	5.2	-4.6	11$\bar{9}$	7.4	-9.5	14$\bar{2}$	13.4	-13.2	170	5.1	-6.2	22$\bar{4}$	6.8	-6.0
0,1,14	2.6	+2.0	0,6,11	1.4	+2.1	11$\bar{7}$	7.6	+10.2	14$\bar{1}$	1.7	-0.8	171	9.6	+9.7	22$\bar{3}$	38.2	+37.0
020	21.7	-25.2	0,6,14	2.2	+1.3	11$\bar{6}$	11.1	-9.3	140	2.3	-0.8	172	6.3	-5.3	22$\bar{2}$	28.6	-27.9
021	33.7	+39.0	072	5.7	-4.7	11$\bar{4}$	10.3	+13.8	141	25.3	-23.3	175	4.5	-6.0	22$\bar{1}$	9.8	+4.1
022	31.5	-39.1	073	6.8	+5.9	11$\bar{3}$	35.0	-38.4	142	25.9	-22.3	176	2.6	-3.6	220	15.1	+16.9
023	29.0	-29.3	074	5.4	-6.0	11$\bar{2}$	33.7	+35.3	144	30.2	+23.5	177	11.9	+9.8	221	19.8	+18.0
024	17.4	-19.4	076	5.1	-4.9	11$\bar{1}$	6.8	+9.7	145	4.3	+3.6	178	12.0	-9.8	224	17.5	-16.3
025	10.2	+9.2	077	3.0	-2.7	110	27.1	-27.4	146	3.3	-3.3	179	3.1	+4.5	225	6.1	+4.9
026	1.6	-5.3	078	3.8	-3.6	111	46.6	+39.9	147	9.5	-8.7	18$\bar{9}$	2.2	+1.4	226	4.5	+8.1
027	5.7	+6.0	079	7.0	+5.8	112	0.9	-2.0	148	9.4	-11.3	18$\bar{3}$	6.1	+7.1	227	10.1	+10.7
028	2.3	-2.2	0,7,10	9.9	-8.1	113	22.5	-17.9	149	2.3	-2.7	18$\bar{2}$	2.8	+4.0	228	5.3	+4.6
029	1.7	-1.6	0,7,13	1.6	-1.2	114	23.3	+17.6	1,4,10	5.8	+3.2	180	2.8	-0.6	2,3,$\overline{11}$	5.4	+8.5
0,2,10	1.8	-2.0	0,7,14	2.5	-1.4	115	7.4	-5.6	1,4,11	3.1	+3.0	181	14.3	+16.6	23$\bar{6}$	3.8	+3.3
0,2,11	3.1	+1.3	080	14.5	+13.0	116	7.0	-5.5	1,4,12	2.9	-0.2	182	11.7	+10.6	23$\bar{5}$	12.3	+9.5
0,2,12	1.4	+1.2	081	3.1	-4.5	117	19.7	+17.2	1,5,$\overline{13}$	5.6	+5.7	183	2.5	-1.7	23$\bar{4}$	5.6	-4.5
0,2,13	4.0	-2.6	083	5.5	+5.6	118	5.3	+5.3	1,5,$\overline{12}$	5.6	-6.6	184	2.6	+0.4	23$\bar{3}$	22.0	+22.4
0,2,14	3.8	+2.9	087	2.9	+2.2	119	2.8	-0.3	1,5,$\overline{11}$	2.7	-4.1	185	4.3	+3.2	23$\bar{1}$	10.0	-9.2
031	15.0	-16.4	089	2.0	+2.5	1,1,10	2.1	-3.5	1,5,$\overline{10}$	8.2	-10.3	186	5.3	-2.5	230	7.7	+8.7
032	8.4	-8.5	0,8,12	1.6	+0.1	1,1,11	8.2	+5.7	15$\bar{9}$	6.7	-7.0	187	6.9	+7.5	231	16.4	-16.8
033	24.4	+26.3	0,8,13	1.4	+0.8	1,1,12	2.7	+1.1	15$\bar{7}$	9.8	+6.5	19$\bar{7}$	3.4	+5.6	232	22.4	-18.3
034	17.5	-15.5	0,8,14	0.8	-0.4	12$\bar{8}$	5.6	-5.5	15$\bar{6}$	9.8	-9.4	19$\bar{6}$	2.2	+2.2	233	5.3	+3.8
035	9.2	-7.4	091	2.7	+2.5	12$\bar{7}$	5.7	+5.1	15$\bar{5}$	4.2	+3.2	19$\bar{4}$	2.8	-3.5	234	6.3	-4.5
036	1.4	-3.0	092	3.4	+3.3	12$\bar{6}$	20.6	-20.6	15$\bar{4}$	10.4	-8.0	19$\bar{3}$	3.0	-2.9	238	11.2	-7.9
037	2.8	-3.6	094	6.0	-5.3	12$\bar{5}$	5.1	+6.8	15$\bar{3}$	19.9	-17.0	19$\bar{2}$	2.8	+3.8	239	11.2	-9.6
038	7.9	-8.0	096	1.4	+2.0	12$\bar{4}$	1.3	+2.3	15$\bar{2}$	8.9	-7.6	19$\bar{1}$	5.8	+7.3	24$\bar{9}$	4.7	-4.0
0,3,11	2.3	-2.2	097	2.9	-1.8	12$\bar{3}$	2.6	-9.4	15$\bar{1}$	2.7	+2.9	190	6.7	+6.6	24$\bar{6}$	7.9	+11.2
0,3,12	8.2	-6.2	098	1.4	+1.0	12$\bar{2}$	14.1	-14.9	150	5.9	+1.7	192	3.8	-4.3	24$\bar{4}$	2.9	-6.2
0,3,13	4.1	-2.3	099	2.0	+1.1	12$\bar{1}$	68.6	+75.6	151	2.9	-1.3	193	6.8	-6.5	24$\bar{3}$	9.4	-5.2
0,3,16	1.1	-1.0	0,9,10	1.8	-1.6	120	68.4	-64.8	152	22.6	+19.7	196	2.2	+2.4	24$\bar{2}$	17.5	+15.4
040	20.0	-22.2	0,9,13	1.4	-1.0	121	16.9	-15.9	154	3.3	+5.7	199	2.6	-3.6	24$\bar{1}$	17.3	-17.9
041	18.2	+19.6	0,10,0	3.3	+1.6	122	15.5	+12.4	155	2.8	+3.2	1,9,10	3.4	+0.5	240	3.2	-5.1
042	2.3	+6.0	0,10,1	6.7	-6.9	123	14.8	+16.2	156	7.7	+4.9	1,10,$\bar{7}$	2.6	-2.5	242	6.5	+6.0
043	21.0	-19.2	0,10,2	15.4	-17.3	124	2.6	+0.3	157	4.4	-4.6	1,10,$\bar{6}$	2.6	-4.1	243	2.9	-2.4
044	20.6	-17.7	0,10,3	6.0	-4.3	125	9.4	+6.3	158	7.3	+7.0	1,10,$\bar{4}$	4.9	-5.9	244	3.2	+1.3
045	2.5	+0.8	0,10,4	6.3	-6.0	126	13.5	-16.5	159	5.9	+5.5	1,10,$\bar{3}$	6.3	+5.0	245	8.9	-5.4
046	11.7	+11.9	0,10,5	3.6	+4.2	127	6.8	+6.6	1,5,10	3.5	+5.1	1,10,$\bar{2}$	2.7	+1.1	25$\bar{5}$	3.2	-5.0
047	7.4	+9.5	0,10,6	1.4	-0.2	128	2.7	+3.1	1,6,$\overline{11}$	4.6	-5.0	1,10,0	10.5	-11.5	251	3.2	-4.2
048	3.3	-3.9	0,10,7	1.5	-2.2	129	8.4	+7.0	1,6,$\overline{10}$	6.6	+7.6	1,10,1	7.1	-6.8	252	3.4	+4.2
049	8.5	-9.0	0,10,8	2.0	-2.7	1,2,10	2.2	+2.7	16$\bar{9}$	2.4	+0.9	1,10,2	3.8	-3.9	254	6.9	+5.2
0,4,10	8.4	-7.0	0,10,9	1.9	-0.9	1,2,11	4.9	-5.6	16$\bar{8}$	3.0	-1.1	1,11,$\bar{5}$	5.8	+5.0	26$\bar{4}$	3.8	-7.1
0,4,11	1.4	-0.2	0,10,11	1.5	-1.7	1,3,$\overline{10}$	10.7	+10.5	16$\bar{7}$	7.9	+6.0	1,11,$\bar{1}$	3.1	-4.1	260	3.6	-6.0
0,4,12	5.7	+3.7	0,11,1	8.2	-6.0	13$\bar{9}$	4.9	+6.0	16$\bar{6}$	9.5	-8.5	1,11,1	2.8	+3.5	270	8.3	-6.1
0,4,13	4.0	+2.9	0,11,3	9.8	+7.4	13$\bar{6}$	3.2	+4.2	16$\bar{5}$	9.1	-8.7	1,12,$\bar{5}$	3.3	+0.2	271	7.0	+7.0
051	19.9	-17.1	0,11,6	1.5	+2.2	13$\bar{5}$	9.4	+11.0	16$\bar{4}$	13.4	+13.1	1,12,$\bar{4}$	5.4	+4.5	276	8.1	-6.8
052	13.0	+13.7	0,11,7	4.0	-2.4	13$\bar{4}$	10.5	+8.6	16$\bar{3}$	2.3	+1.8	1,12,$\bar{3}$	5.2	-4.8	28$\bar{1}$	11.9	+14.6
053	5.8	+6.6	0,11,10	1.5	+1.6	13$\bar{3}$	6.7	+3.7	16$\bar{2}$	2.3	-1.3	1,12,$\bar{2}$	5.1	+4.5	280	9.7	+10.8
054	26.4	+23.8	0,12,0	5.4	+4.2	13$\bar{2}$	1.5	-1.4	16$\bar{1}$	18.2	-16.3	1,12,0	2.5	-1.1	284	3.8	-3.8
055	11.0	+11.0	0,12,1	5.9	+4.5	13$\bar{1}$	11.0	+8.8	160	7.4	+7.3				285	7.9	+7.6

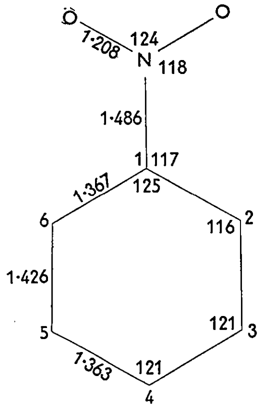

Fig. 4. Bond lengths and valency angles.

of the mean bond lengths are 0·014 Å (0·020 Å for the C–N bond).

Discussion

The molecule is completely planar within the limits of experimental error, the maximum deviation from the mean plane being 0·033 Å and the root mean square deviation 0·016 Å. This completely planar arrangement may be compared with the configurations of 9:10-dinitroanthracene (Trotter, 1959*b*) and nitromesitylene (Trotter, 1959*d*) where the nitro groups are rotated about the C–N bonds 64° and 66° respectively out of the aromatic planes, due to the steric effects of neighbouring carbon and hydrogen atoms. An X-ray investigation of the structure of *p*-dinitrobenzene has shown that the nitro groups are twisted 9° 25′ out of the plane of the benzene ring (Abrahams, 1950); the results of the present investigation of the nitrobenzene structure suggest that the most stable configuration of an isolated molecule of *p*-dinitrobenzene is completely planar, but that in the solid state, crystal forces cause a small deviation from planarity. This is similar to the situation in 9-nitroanthracene, where crystal forces increase the angle between the planes of the nitro group and the aromatic rings from 64° (the value in the corresponding dinitro derivative) to 85°.

The bonds C_2–C_3 and C_5–C_6 are significantly longer than the other aromatic bonds; the mean C–C length is 1·385 Å. The C–N bond length (1·486 Å) is longer than might have been expected, considering the single bond distance is usually quoted as 1·475 Å, but it agrees well with the length in *p*-dinitrobenzene (1·48 Å). The N–O bond distances are normal for nitro compounds. These bond length variations, and their relation to the corresponding distances in other nitro compounds, will be discussed in greater detail elsewhere.

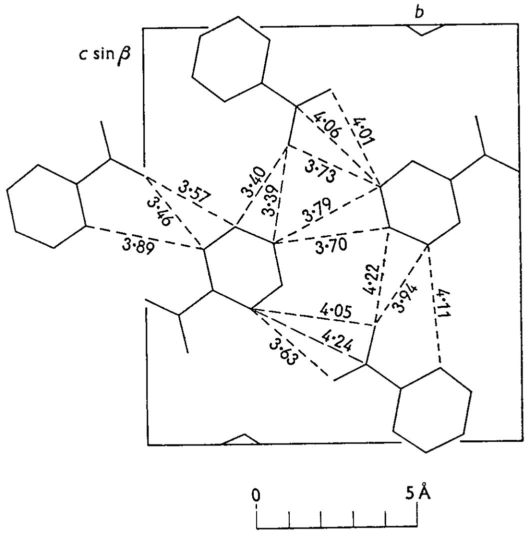

Fig. 5. Projection of the structure along [100], showing the shorter intermolecular contacts.

Intermolecular distances

All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between the planes of molecules related by translation *a* is 3·36 Å. The shorter lateral contacts are illustrated in Fig. 5.

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