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A Three-Dimensional Analysis of the Crystal Structure of *m*-Dinitrobenzene

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Crystals of *m*-dinitrobenzene are orthorhombic with four molecules in a unit cell of dimensions

$$a = 13{\cdot}20,\ b = 13{\cdot}97,\ c = 3{\cdot}80\ \text{Å}\ ,$$

space group $Pbn2_1$. The x and y coordinates determined in a previous investigation have been refined by two-dimensional Fourier methods, the z-coordinates estimated by trial, and all the positional and temperature parameters then refined by three-dimensional least-squares methods. Details of the molecular geometry and dimensions, and of the intermolecular separations, have been obtained. The carbon and nitrogen atoms all lie on one plane but the nitro groups are twisted out of this plane about the C–N bonds by about 11°. The mean bond lengths are

$$\text{C–C} = 1{\cdot}38,\ \text{C–N} = 1{\cdot}47,\ \text{N–O} = 1{\cdot}20\ \text{Å}\ .$$

Introduction

The crystal structure of *m*-dinitrobenzene has been examined by several investigators. The most recent and most thorough analyses were reported by Archer (1946) and independently by Gregory & Lassettre (1947), and a resumé of all the earlier work has been given in these papers. In both these analyses x and y coordinates for all the carbon, nitrogen and oxygen atoms were determined reasonably accurately from the projection along the short crystal axis, but the z parameters were determined only rather roughly from the consideration of a few general reflexions.

Archer (1946) found the data to be consistent with a regular six-membered ring, with C–C distances 1·41 Å, the other bond lengths being C–N = 1·54 Å, N–O = 1·20 Å. The nitro groups were found to deviate from the plane of the benzene ring, but their size and shape were largely assumed from the results of other investigations. Gregory & Lassettre (1947) found C–C distances in the ring varying between 1·33 and 1·42 Å, C–N distances of 1·39 and 1·46 Å, and N–O distances of 1·10, 1·15, 1·18 and 1·22 Å.

The abstractor in *Structure Reports* (1947–48) comments that 'the considerable differences in the parameters obtained in these two investigations indicates that a redetermination of the structure will be necessary before any conclusions can be drawn regarding the precise values of the bond lengths'. The present paper describes such a redetermination; three-dimensional data have been used, and the final refinement has been made by least-squares methods.

Experimental

Crystals of *m*-dinitrobenzene, which were obtained by crystallization from aqueous ethanol, consist of yellow needles elongated along the c-axis. The density was determined by flotation in aqueous potassium-iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the c-axis, $hk0$ and $hk1$ Weissenberg films, and $0kl$ and $h0l$ precession films.

Crystal data

m-Dinitrobenzene, $C_6H_4N_2O_4$; $M = 168{\cdot}1$; m.pt. = 90 °C.

Orthorhombic,

$$a = 13{\cdot}20 \pm 0{\cdot}03,\ b = 13{\cdot}97 \pm 0{\cdot}03,\ c = 3{\cdot}80 \pm 0{\cdot}005\ \text{Å}\ .$$

Volume of the unit cell = 700·7 Å³.

Density, calculated (with $Z = 4$) = 1·583, measured = 1·570 g.cm.$^{-3}$.

Absorption coefficients for X-rays, $\lambda = 1{\cdot}542$ Å,

$\mu = 13{\cdot}5$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}65$ cm.$^{-1}$.

Total number of electrons per unit cell = $F(000)$ = 344.

Absent spectra: $h0l$ when $(h+l)$ is odd, $0kl$ when k is odd. Space group is $Pbn2_1$–C_{2v}^9 or $Pbnm$–D_{2h}^{16}. A positive piezoelectric test (cf. Archer, 1946) establishes the space group as $Pbn2_1$.

The intensities of the hkl reflexions were recorded on Weissenberg photographs for a crystal rotating about the c-axis, using Cu $K\alpha$ radiation, the multiple-film technique being used to correlate strong and weak reflexions. Layers with $l = 0, 1, 2, 3$ were recorded, the equi-inclination method being used for non-equatorial layers. $0kl$ and $h0l$ precession films (Mo $K\alpha$ radiation) were used for intensity correlation between the various layers. All the intensities were estimated visually, the range being about 20,000 to 1. The same crystal was used for all the photographs; the cross-section normal to the c-axis was $0{\cdot}30 \times 0{\cdot}30$ mm., and no absorption corrections were applied. 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 equi-inclination Weissenberg photographs (Tunell, 1939). The absolute scale was established later by correlation with the calculated structure factors.

In the $hk0$, $hk1$, $hk2$ and $hk3$ zones, 75%, 93%, 80% and 90% respectively of the reflexions within the Cu $K\alpha$ sphere were observed. The $hk4$ reflexions have not been recorded, since they are outside the observable range for a crystal rotating about the c-axis in the conventional Weissenberg goniometer.

Structure analysis

[001] projection

A preliminary electron-density projection along the c-axis was computed with measured structure amplitudes and the signs of the calculated structure factors given by Archer (1946). On the resulting map (Fig. 1) all the carbon, nitrogen and oxygen atoms were well resolved. Centres were chosen and structure factors calculated for all the $hk0$ reflexions, using the scattering factors of Berghuis *et al.* (1955), corrected for thermal vibration, with $B=4{\cdot}8$ Å^2 for all the atoms. The R value was 23·5% over the observed reflexions.

Refinement proceeded by computing a difference synthesis and changing the positional and isotropic temperature parameters to minimize the slopes and difference densities at the atomic centres. Recalculation of structure factors indicated that R had dropped to 18·3%.

z-coordinates

By assuming that the molecule was completely planar, the z-coordinates of all the atoms were then deduced from a consideration of the bond lengths projected on (001). For the carbon atoms these trial z-coordinates were very similar to those given by Archer (1946), but for the nitrogen and oxygen atoms there were considerable differences, Archer having assumed a non-planar model for the molecule. The maximum difference was 0·79 Å for atom O_1. The coordinates were markedly different from those of Gregory & Lassettre (1947).

Taking the z-coordinate of the molecular centre as zero (it can of course be chosen arbitrarily) structure factors were calculated for the hkl reflexions; the discrepancy over the observed reflexions was 24·2%. This reasonable agreement indicated that further refinement could proceed by three-dimensional least-squares methods.

Three-dimensional least-squares refinement

The x- and y-coordinates and isotropic temperature parameters from the $hk0$ zone refinement, and the trial

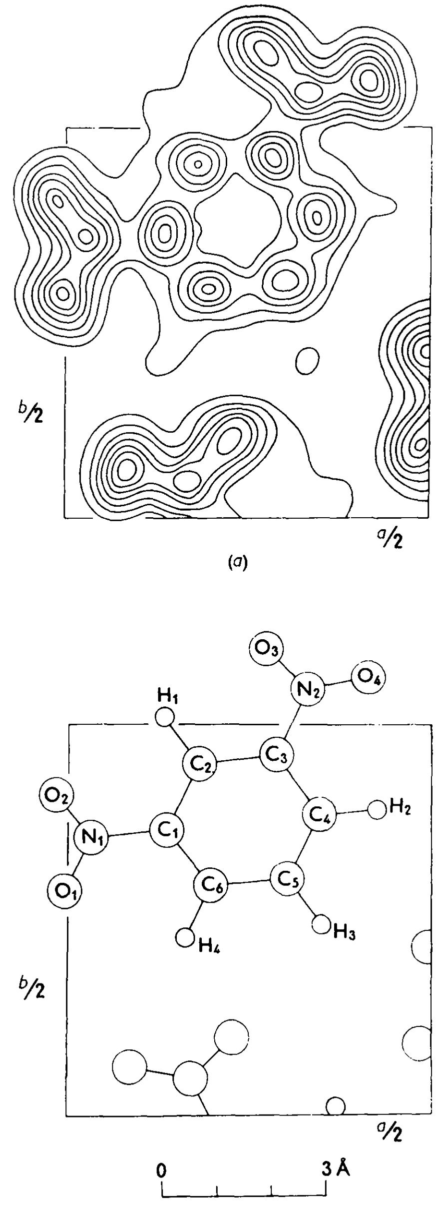

Fig. 1. (a) Preliminary electron-density projection along the c-axis. Contours at equal and arbitrary intervals (of about 1 e.Å^{-2}). (b) Projection of the structure onto (001).

z-coordinates were used as a starting point in the three-dimensional refinement. Hydrogen atoms were included, coordinates (Table 1) being obtained by assuming that they lay on the ring diagonals with

Table 1. *Assumed hydrogen fractional coordinates*

Atom	x	y	z
H_1	0·1321	0·5075	−0·2108
H_2	0·4254	0·3940	0
H_3	0·3479	0·2458	0·2108
H_4	0·1617	0·2309	0·2108

C–H = 1·08 Å and B being taken as 5·6 Å^2. Anisotropic temperature parameters for the carbon, nitrogen and oxygen atoms were introduced after the first cycle. The initial R value was 24·2% for all the observed hkl planes.

The weighting system in the least-squares program was such that

$$\sqrt{w} = |F_o|/|F^*| \quad \text{when} \quad |F_o| < |F^*|$$
$$\sqrt{w} = |F^*|/|F_o| \quad \text{when} \quad |F_o| \geq |F^*|$$

$|F^*|$ being taken as 12·0.

The refinement process is outlined in Table 2. After two cycles it became apparent that the shifts were too large, and coordinates for input to the third cycle were taken as the mean of the coordinates obtained by half-shifting in the first and second cycles. In the third cycle the shifts in the positional parameters were quite small (maximum 0·01 Å) and refinement was terminated at this point. The values of the measured structure amplitudes for the observed reflexions are listed in Table 5. The final calculated structure factors were not computed, but it is likely that the final R value is a little less than 14·6%. Throughout the refinement structure factors were calculated at each stage for all the unobserved reflexions, and no anomalies were found.

Table 2. *Refinement process*

Sources of coordinates	R (%)	$\Sigma w(\|F_o\| - \|F_c\|)^2$
1st $(F_o - F_c)$ synthesis $hk0$ + trial z-coordinates	24·2	298
1st LS cycle	18·5	191
Mean of $\frac{1}{2}$-shifts on 1st and 2nd LS cycles	14·6	134
3rd LS cycle	Not calculated	

Coordinates and molecular dimensions

The positional and temperature parameters of the carbon, nitrogen and oxygen atoms obtained from the third least-squares cycle are listed in Table 3, x, y and z being coordinates referred to the principal crystallographic axes, and expressed as fractions of the unit-cell edges, and b_{ij} the parameters in the expression

$$f = f_0 \times 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}lh + b_{12}hk)}$$

The equation of the mean molecular plane is

$$0·1055X - 0·4470Y - 0·8883Z + 2·0853 = 0\,,$$

where X, Y, Z are coordinates expressed in Å units. The deviations of the atoms from this plane are listed in the second column of Table 4. These deviations indicate that all the atoms in the molecule do not lie in one plane, and to obtain a better description of the deviations from coplanarity, the equation of the best plane through the carbon atoms only was calculated. It is

$$0·0871X - 0·4048Y - 0·9103Z + 1·8723 = 0\,.$$

The deviations of the atoms from this plane are listed in the final column of Table 4.

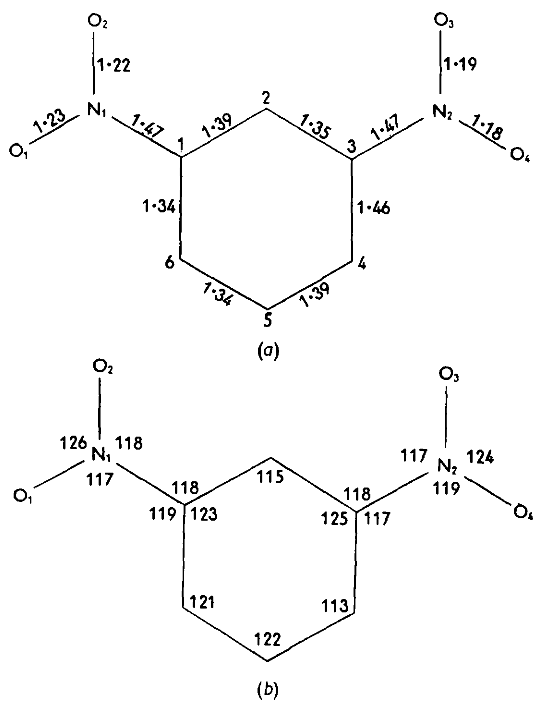

Fig. 2. (*a*) Bond lengths, and (*b*) valency angles in *m*-dinitrobenzene.

Table 3. *Final positional and temperature parameters*

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
C_1	0·1402	0·3667	−0·0055	0·00610	0·00557	0·13088	−0·00211	0·00889	−0·00016
C_2	0·1800	0·4513	−0·1408	0·00525	0·00477	0·07293	−0·01347	−0·00510	−0·00060
C_3	0·2815	0·4589	−0·1177	0·00970	0·00437	0·06127	−0·00795	0·02280	0·00073
C_4	0·3490	0·3870	0·0330	0·00835	0·00776	0·08461	−0·02080	0·01488	0·00491
C_5	0·2994	0·3042	0·1366	0·01007	0·00569	0·09522	−0·00348	0·00553	0·00481
C_6	0·1982	0·2956	0·1223	0·00827	0·00605	0·05136	−0·00867	−0·00360	0·00168
N_1	0·0297	0·3538	−0·0213	0·00573	0·00800	0·15349	0·01216	−0·00247	−0·00066
N_2	0·3282	0·5486	−0·2419	0·00782	0·00930	0·11444	−0·01339	0·01917	−0·00775
O_1	−0·0059	0·2857	0·1440	0·01087	0·01315	0·17612	0·01260	0·01043	−0·00882
O_2	−0·0189	0·4109	−0·1945	0·00867	0·01113	0·16113	−0·00804	0·00037	−0·00088
O_3	0·2759	0·6021	−0·4028	0·01339	0·00904	0·18000	0·03895	−0·00148	−0·00100
O_4	0·4152	0·5603	−0·1934	0·01073	0·01292	0·28340	0·01269	0·01584	−0·00476

Table 4. *Deviations from the mean planes*

Atom	Deviation from molecular plane	Deviation from benzene ring plane
C_1	+0·01 Å	−0·02 Å
C_2	−0·01	+0·01
C_3	+0·01	+0·01
C_4	+0·04	−0·03
C_5	+0·14	+0·02
C_6	+0·10	+0·01
N_1	−0·01	−0·02
N_2	−0·07	−0·02
O_1	−0·19	−0·25
O_2	+0·15	+0·20
O_3	+0·07	+0·18
O_4	−0·18	−0·15

The equations of the planes of the nitro groups are

$$N_1O_1O_2: 0{\cdot}1031X - 0{\cdot}5827Y - 0{\cdot}8062Z + 2{\cdot}7745 = 0$$
$$N_2O_3O_4: 0{\cdot}2056X - 0{\cdot}4995Y - 0{\cdot}8415Z + 2{\cdot}1641 = 0\ .$$

The angle between the plane of the carbon atoms and the $N_1O_1O_2$ plane is 11·8°, and between the carbon atom plane and the $N_2O_3O_4$ plane 9·6°.

The bond lengths and valency angles in the molecule, calculated from the coordinates of Table 3, are shown in Fig. 2. No corrections for errors in atomic position due to rotational oscillation of the molecule have been applied. These corrections would increase all the bond lengths by small amounts, but leave the valency angles unaltered (Cruickshank, 1956).

Standard deviations

The standard deviations of the atomic positions were calculated from the least-squares formulae:

$$\sigma(x/a) = \Sigma w.(\Delta F)^2/(n-s).\Sigma w\left\{\frac{\partial \Delta F}{\partial (x/a)}\right\}^2,$$

where

n = number of reflexions = 706
s = number of parameters = 109 .

The r.m.s. values for all the atoms were

$$\sigma(x) = 0{\cdot}010,\quad \sigma(y) = 0{\cdot}010,\quad \sigma(z) = 0{\cdot}014\ \text{Å}\ .$$

(The values for C, N and O did not differ significantly.)

Discussion

The aromatic ring in the *m*-dinitrobenzene molecule is completely planar within the limits of experimental error, the maximum deviation of the carbon atoms from the mean plane being 0·03 Å and the root mean square deviation 0·02 Å. The nitrogen atoms also lie on this plane, but the oxygen atoms deviate significantly from the plane. In the nitro group $N_1O_1O_2$, O_1 lies below and O_2 above the plane of the ring at mean distances of 0·22 Å. This nitro group is thus rotated out of the plane of the aromatic ring about the C_1–N_1 bond, the angle of twisting being 11·8°. Similarly in the group $N_2O_3O_4$, O_3 lies above and O_4 below the aromatic plane at mean distances of 0·16 Å, so that this nitro group is rotated 9·6° out of the plane of the benzene ring about the C_3–N_2 bond. These departures from an ideal planar structure may be compared with the corresponding displacements in *p*-dinitrobenzene (Abrahams, 1950). This latter molecule is centrosymmetrical and both nitro groups make angles of 9·4° with the aromatic plane. Since it has been shown that the nitrobenzene molecule is completely planar (Trotter, 1959), the deviations from planarity in *m*-dinitrobenzene and *p*-dinitrobenzene are probably not due to intramolecular steric effects, but rather to intermolecular forces.

An ideal planar model for the *m*-dinitrobenzene molecule has symmetry *mm*2. The present results show that, in the crystalline state at least, all these symmetry elements are destroyed, although since the difference between the nitro-group twists (mean value 10·7°) is small and not definitely significant, the mirror plane perpendicular to the plane of the ring is possibly retained. It might be noted that the deviations from planarity are different from those deduced by Archer (1946). The C–N bonds lie in the aromatic plane, and only the oxygen atoms are displaced.

The dimensions of the two nitro groups are very similar, the mean dimensions being

$$\text{C–N} = 1{\cdot}47\ \text{Å},\quad \text{N–O} = 1{\cdot}20\ \text{Å},\quad \text{O–N–O} = 125°.$$

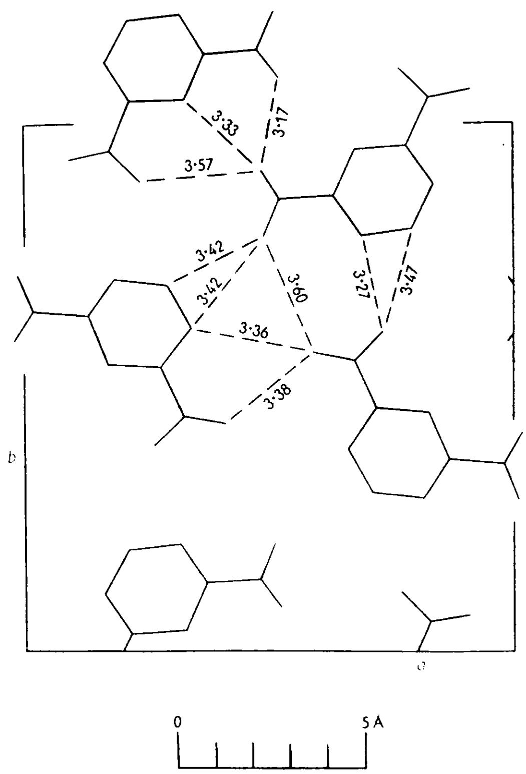

Fig. 3. Projection of the structure onto (001), showing the shorter intermolecular contacts.

Table 5. *Measured structure amplitudes*

h	*k*	*l*	F_o	*h*	*k*	*l*	F_o	*h*	*k*	*l*	F_o	*h*	*k*	*l*	F_o	*h*	*k*	*l*	F_o	*h*	*k*	*l*	F_o
2	0	0	28·8	11	4	0	4·8	2	9	0	12·3	4	14	0	· –	9	2	1	18·4	14	6	1	
4			36·6	12			– –	3			6·0	5			3·3	10			6·7	15			2·0
6			56·8	13			2·4	4			7·8	6			· ·	11			5·1	1	7	1	5·3
8			6·2	14			· –	5			1·8	7			3·3	12			4·5	2			16·6
10			13·0	15			– ·	6			2·1	8			1·5	13			1·7	3			16·3
12			4·5	16			4·4	7			1·9	9			1·1	14			1·6	4			17·5
14			2·8	1	5	0	10·9	8			17·9	10			2·6	15			2·0	5			4·3
16			3·9	2			25·0	9			4·8	11			–	16			3·1	6			3·2
1	1	0	11·3	3			15·0	10			5·0	1	15	0	3·6	1	3	1	52·5	7			
2			30·3	4			16·1	11			2·4	2			– ·	2			18·2	8			7·0
3			57·4	5			2·7	12			2·8	3			7·0	3			12·1	9			14·7
4			5·4	6			2·4	13			· –	4			—	4			8·9	10			10·0
5			18·2	7			3·8	14			· · ·	5			2·7	5			26·2	11			7·2
6			–	8			1·7	0	10	0	1·4	6			1·2	6			9·5	12			2·4
7			35·6	9			2·4	1			12·1	7			2·3	7			10·5	13			1·9
8			3·3	10			24·5	2			4·8	8			1·3	8			—	14			2·6
9			– ·	11			3·9	3			4·4	9			–	9			7·8	15			2·2
10			3·3	12			4·6	4			11·4	10			·	10			10·6	0	8	1	15·4
11			–	13			3·4	5			2·2	0	16	0	1·9	11			11·8	1			9·6
12			· ·	14			· –	6			2·7	1			3·7	12			3·9	2			16·5
13			8·7	15			–	7			– ·	2			·	13			4·6	3			16·6
14			3·3	16			4·0	8			4·8	3			–	14			2·2	4			11·5
15			–	0	6	0	39·7	9			2·5	4			5·6	15			1·7	5			9·5
16			· ·	1			17·5	10			4·0	5			–	16			2·5	6			4·8
17			–	2			2·7	11			3·4	6			1·3	0	4	1	27·0	7			5·0
0	2	0	34·6	3			57·9	12			2·4	7			·	1			6·4	8			–
1			33·8	4			7·9	13			– ·	8			· –	2			24·0	9			16·1
2			26·1	5			17·7	14			1·9	1	17	0	2·4	3			35·2	10			7·2
3			1·5	6			1·3	1	11	0	4·3	2			·	4			34·9	11			3·0
4			22·8	7			2·6	2			8·1	3				5			18·3	12			3·9
5			38·3	8			2·3	3			5·1	4			3·2	6			21·3	13			4·0
6			14·2	9			18·0	4			3·8	5				7			9·4	14			2·6
7			17·2	10			5·5	5			3·9	6			· ·	8			3·6	1	9	1	8·2
8			10·9	11			11·1	6			1·6	0	18	0	·	9			15·6	2			3·9
9			4·2	12			6·3	7			4·8	1			·	10			9·5	3			5·6
10			5·6	13			3·8	8			4·2	2			–	11			4·5	4			3·7
11			3·5	14			· ·	9			1·5	3				12			4·4	5			2·7
12			5·3	15			4·4	10			–					13			2·4	6			5·3
13			7·7	16			· ·	11				1	0	1	84·2	14			1·6	7			6·2
14			– –	1	7	0	6·7	12			–	3			17·2	15			3·2	8			10·6
15			– ·	2			16·3	13			2·0	5			24·0	16			1·7	9			6·0
16			1·9	3			17·9	0	12	0	23·2	7			19·3	1	5	1	16·6	10			2·1
17			– –	4			4·8	1			3·5	9			8·6	2			10·6	11			3·7
1	3	0	51·6	5			17·8	2			15·5	11			8·5	3			14·1	12			3·8
2			41·3	6			5·6	3			–	13			4·3	4			8·9	13			
3			29·8	7			8·6	4			·	15			2·5	5			2·5	14			2·2
4			12·1	8			18·5	5			4·1	1	1	1	33·5	6			19·1	0	10	1	14·9
5			14·0	9			· ·	6			8·1	2			23·7	7			– –	1			19·3
6			3·5	10			12·4	7			2·2	3			30·7	8			5·5	2			2·9
7			8·7	11			7·5	8			4·4	4			11·1	9			13·5	3			3·8
8			10·2	12			2·4	9			7·6	5			10·9	10			10·5	4			5·0
9			5·5	13			–	10			2·1	6			14·9	11			15·5	5			9·1
10			11·1	14			3·0	11			2·3	7			17·5	12			5·1	6			5·7
11			4·4	15			·	12			·	8			7·9	13			2·0	7			11·3
12				0	8	0	19·2	13			– ·	9			3·6	14			2·6	8			4·8
13			·	1			11·5	1	13	0	6·8	10			4·2	15			1·2	9			9·7
14			– –	2			11·7	2			11·8	11			·	16			—	10			2·1
15			·	3			2·2	3			2·3	12			3·2	0	6	1	23·1	11			2·5
16			1·0	4			6·5	4			3·0	13			2·8	1			16·0	12			1·7
17			–	5			18·1	5			7·4	14			6·4	2			22·1	13			2·2
0	4	0	34·1	6			·	6			–	15			1·4	3			12·2	1	11	1	6·6
1			49·1	7			2·4	7				16			2·0	4			18·2	2			7·5
2			12·9	8			15·3	8			6·2	0	2	1	83·8	5			11·1	3			2·9
3			13·4	9			9·8	9			– –	1			51·5	6			10·6	4			3·1
4			2·9	10			13·6	10			3·0	2			28·6	7			8·6	5			2·6
5			14·6	11			8·3	11			2·7	3			15·0	8			10·8	6			3·4
6			2·3	12			· –	12			· –	4			19·3	9			14·5	7			·
7			9·6	13			3·0	0	14	0	· –	5			12·8	10			18·2	8			10·0
8			14·1	14			2·8	1			13·1	6			27·8	11			6·0	9			2·1
9			5·8	15			2·0	2			8·2	7			10·8	12			3·0	10			1·9
10			12·5	1	9	0	11·1	3			6·5	8			9·4	13			1·6	11			4·4

Table 5 (*cont.*)

h	k	l	F_o
12	11	1	5·0
13			—
0	12	1	4·1
1			17·8
2			10·0
3			6·3
4			1·8
5			3·8
6			5·6
7			6·0
8			3·1
9			3·5
10			—
11			2·3
12			1·3
1	13	1	8·1
2			4·4
3			8·1
4			3·1
5			4·6
6			3·8
7			3·4
8			2·8
9			4·4
10			2·7
11			1·7
0	14	1	8·6
1			8·6
2			6·9
3			5·9
4			3·3
5			2·3
6			4·6
7			2·0
8			2·3
9			1·8
10			—
1	15	1	4·6
2			4·5
3			6·6
4			2·4
5			4·7
6			3·9
7			—
8			2·9
9			—
0	16	1	3·1
1			3·3
2			4·3
3			1·3
4			1·2
5			2·2
6			—
7			—
1	17	1	—
2			2·8
3			2·4
4			2·5
0	0	2	7·9
2			15·0
4			12·7
6			3·6
8			6·3
10			11·7
12			6·0
14			2·3
1	1	2	8·4
2			4·7
3			9·3
4			10·0
5	1	2	13·0
6			5·8
7			6·6
8			6·6
9			5·7
10			9·2
11			3·6
12			—
13			5·5
14			—
15			—
0	2	2	54·8
1			22·4
2			11·4
3			23·6
4			12·9
5			10·2
6			14·7
7			14·5
8			7·2
9			12·7
10			9·2
11			—
12			2·8
13			—
14			2·2
15			4·2
1	3	2	6·9
2			11·7
3			8·2
4			12·1
5			—
6			10·8
7			6·6
8			5·1
9			4·5
10			17·6
11			9·2
12			—
13			3·1
14			—
15			2·0
0	4	2	34·5
1			35·2
2			21·4
3			29·5
4			12·2
5			8·7
6			12·0
7			6·3
8			2·8
9			14·8
10			10·1
11			4·5
12			—
13			3·4
14			—
15			3·2
1	5	2	17·4
2			19·8
3			3·8
4			2·3
5			16·7
6			6·4
7			2·7
8			7·8
9			4·1
10			10·9
11			—
12			—
13	5	2	2·3
14			—
0	6	2	9·8
1			5·8
2			12·4
3			7·8
4			3·5
5			3·7
6			4·3
7			2·8
8			2·9
9			11·3
10			—
11			—
12			—
13			2·7
14			2·4
1	7	2	13·2
2			7·8
3			7·0
4			4·1
5			4·3
6			5·3
7			5·0
8			5·1
9			3·6
10			2·8
11			4·9
12			4·7
13			2·0
14			—
0	8	2	18·7
1			12·2
2			2·6
3			4·3
4			4·4
5			3·5
6			8·7
7			5·5
8			2·9
9			4·9
10			3·3
11			5·6
12			4·4
13			—
1	9	2	6·8
2			4·0
3			4·0
4			4·1
5			5·4
6			4·6
7			4·6
8			5·7
9			5·1
10			3·6
11			6·9
12			—
13			1·6
0	10	2	25·7
1			7·9
2			18·3
3			—
4			8·0
5			7·2
6			3·6
7			—
8			6·8
9			3·6
10			5·3
11			2·0
12	10	2	3·9
1	11	2	8·8
2			4·1
3			3·6
4			2·9
5			5·0
6			—
7			6·6
8			5·1
9			4·4
10			—
11			2·7
12			—
0	12	2	—
1			4·1
2			3·5
3			—
4			3·4
5			3·4
6			—
7			4·4
8			2·8
9			—
10			2·1
11			—
1	13	2	—
2			4·3
3			2·7
4			—
5			—
6			3·8
7			—
8			2·4
9			—
10			—
0	14	2	4·4
1			4·0
2			3·0
3			—
4			2·3
5			2·7
6			2·0
7			—
8			—
1	15	2	2·2
2			5·6
3			—
4			4·7
5			1·7
6			1·8
0	16	2	—
1			7·8
2			—
3			5·0
1	0	3	7·5
3			18·0
5			11·4
7			3·0
9			18·0
11			3·2
13			—
1	1	3	2·4
2			7·9
3			2·3
4			10·4
5			3·8
6			4·0
7			2·1
8	1	3	11·0
9			3·3
10			10·6
11			4·5
12			4·0
13			—
0	2	3	3·6
1			10·7
2			8·4
3			11·0
4			14·1
5			3·1
6			3·1
7			2·1
8			7·2
9			6·1
10			8·2
11			3·5
12			—
13			2·6
1	3	3	4·1
2			7·0
3			4·4
4			6·0
5			2·3
6			2·4
7			2·2
8			6·5
9			5·7
10			5·3
11			2·7
12			2·8
13			—
0	4	3	18·0
1			20·0
2			13·6
3			3·0
4			2·2
5			5·3
6			7·4
7			7·4
8			7·8
9			6·3
10			4·4
11			—
12			—
13			—
1	5	3	14·4
2			2·2
3			5·3
4			4·7
5			7·3
6			2·2
7			6·7
8			2·2
9			3·8
10			—
11			1·4
12			1·1
0	6	3	26·0
1			5·1
2			10·4
3			4·1
4			1·7
5			—
6			11·1
7			2·2
8			2·7
9			2·0
10			2·1
11	6	3	—
12			2·5
1	7	3	2·4
2			6·7
3			6·6
4			3·8
5			3·3
6			2·2
7			3·3
8			4·5
9			2·2
10			2·2
11			3·3
12			—
0	8	3	17·9
1			15·1
2			9·8
3			2·2
4			6·1
5			5·6
6			4·7
7			3·4
8			2·8
9			—
10			2·8
11			1·3
1	9	3	7·4
2			3·1
3			3·3
4			5·0
5			2·1
6			2·0
7			3·9
8			—
9			2·4
10			3·2
0	10	3	3·3
1			5·0
2			1·7
3			2·1
4			5·1
5			2·0
6			3·8
7			2·5
8			1·8
9			2·6
1	11	3	2·4
2			3·5
3			—
4			2·5
5			1·9
6			3·1
7			2·5
8			2·8
0	12	3	6·5
1			3·4
2			3·2
3			4·2
4			1·7
5			2·6
6			1·4
7			2·7
1	13	3	—
2			2·7
3			2·3
4			1·8
5			3·1
0	14	3	4·2
1			2·8
2			3·0

As with many other nitro compounds and other types of derivative (Trotter, 1960), these dimensions indicate that there is no 'resonance' involving excited structures.

The bond distances and angles in the six-membered ring vary widely and haphazardly, many of the variations being too large to be real. It is considered that part at least of this variation is the result of errors in positional parameters due to the inadequacy of the block diagonal least-squares approximation, or perhaps of the weighting system, used in the present refinement. It would have been very useful to repeat the refinement using either full-matrix least-squares or differential syntheses for comparison of the results, but we did not have computational facilities for carrying out these refinements. It is considered that the finer details of the bond-length variations in the benzene ring are still obscure. The mean C–C distance is 1·38 Å.

Intermolecular dimensions

All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between the aromatic planes of molecules related by translation *c* is 3·46 Å. The shorter lateral contacts are illustrated in Fig. 3.

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The Molecular and Crystal Structure of $(PCF_3)_5$

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Visual estimates of 2078 reflections obtained from a single crystal at −100 °C. indicated four molecules of $(PCF_3)_5$ in a unit cell of symmetry $P2_1/n$ and having parameters

$$a = 9{\cdot}87,\ b = 9{\cdot}78,\ c = 16{\cdot}67\ \text{Å};\ \beta = 103°\ 0'.$$

The sterically distorted P_5 ring shows also one short P · · · F interaction of 3·04 Å.

Average distances are P–P = 2·223 ± 0·007, P–C = 1·91 ± 0·02 and C–F = 1·35 ± 0·03 Å. The P–P–P angles vary from 94·6 to 107·5 ± 0·4°. Values of

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}18 \quad \text{and} \quad r = \Sigma w||F_o|^2 - |F_c|^2|^2/\Sigma w F_o^4 = 0{\cdot}14$$

do not include the anisotropic thermal motions of the P_5 ring along x and the torsional oscillations of CF_3 and the P–C bonds.

Introduction

Recognition of the ability of the CF_3 group to stabilize unusual molecular and valence structures had led to the recent preparation of many new compounds in recent years. Among these are some new fluorocarbon–phosphorus compounds, and especially the two new ring compounds $(PCF_3)_4$ and $(PCF_3)_5$ (Mahler & Burg, 1958). The nature of the P–P bond in small rings, the role of the unshared pairs on P in the valence structures, and especially the not-directly bonded P · · · P interactions were of interest. In particular, the unshared pair might play a role in stabilizing the ring structure in several possible ways. Also, a comparison of the structures of $(PCF_3)_5$ and $(AsCH_3)_5$ (Burns & Waser, 1957) is of interest because CF_3 is larger than CH_3 and P is smaller than As, thus increasing the steric effects greatly.