1,18 Å vom Schwerpunkt des Na^+-Ions entfernt. Zum Vergleich sind in der Tabelle 3 die Ionenradien nach Goldschmidt und Pauling angegeben.

Um den Einfluss der TDS-Korrektur auf die Elektronendichte zu bestimmen, wurde diese auch aus den nicht korrigierten Strukturfaktoren berechnet, wie sie mit der Spaltöffnung von 12×12 mm gemessen wurden. In Fig. 12 ist die Differenz zwischen der aus nicht korrigierten und korrigierten Intensitäten berechneten Elektronendichte gezeichnet. Man erkennt, dass sich die Korrektur nur bis zu einem Abstand von 0,5 Å von den Atomschwerpunkten auswirkt. Im gesamten Bereich zwischen den Ionen ist der Unterschied in den Elektronendichten kleiner als 0,1 e.$Å^{-3}$ und liegt im Bereich der Messgenauigkeit. Auf die Verteilung der Valenzelektronen und auf die Ionenradien hat die TDS-Korrektur keinen Einfluss.

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The Structure of 2,4,6-Trinitrophenetole

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The crystal structure of 2,4,6-trinitrophenetole has been determined and refined by three-dimensional least-squares methods. The crystals are orthorhombic, space group $Pca2_1$, with $a = 23\cdot7848$, $b = 7\cdot3577$, $c = 6\cdot2642$ Å and four molecules per unit cell. Intensity data were collected visually from Weissenberg photographs about two crystal axes. The final R index is $0\cdot059$; the average standard deviations are $0\cdot007$ Å for the atomic positions.

A particularly evident feature is the extensive rotation of the two nitro groups in *ortho* positions with respect to the ethoxyl group; the angles of these nitro groups with the phenyl plane are $31\cdot8°$ and $61\cdot3°$. The third nitro group is subject to a very slight rotation.

Small but significant displacements from the plane of the phenyl ring are observed, particularly in the case of the nitrogen atoms and of the oxygen atom directly joined to the ring.

Introduction

Since 2,4,6-trinitrophenetole, $C_2H_5OC_6H_2(NO_2)_3$, is the parent compound of two so-called 'Meisenheimer complexes' whose structures have been determined in this laboratory (Destro, Gramaccioli, Mugnoli & Simonetta, 1965; Casalone, Destro, Gramaccioli, Mariani, Mugnoli & Simonetta, 1966) in connexion with a recent surge of interest in the field of the mechanism of aromatic nucleophilic reactions (Bunnett, 1959; Carrà,

Raimondi & Simonetta, 1966; Simonetta & Carrà, 1964), we considered the determination of its structure particularly appropriate. A further interest in structures of aromatic derivatives of this kind derives from the recent attention given to the study of the conformations of overloaded molecules with spatial difficulties (Akopyan, Kitaigorodskii & Struchkov, 1965).

Experimental

Crystals of 2,4,6-trinitrophenetole were readily grown from solutions in ethanol. They are slightly yellow, elongated along **c**. A preliminary set of Weissenberg photographs indicated them to be orthorhombic, with space group either *Pcam* or *Pca2₁*, the latter group being confirmed by solution of the structure. (The systematic absences are: $0kl$ for l odd and $h0l$ for h odd). The unit-cell dimensions are: $a = 23·7848 \pm 0·0008$, $b = 7·3577 \pm 0·0007$, $c = 6·2642 \pm 0·0004$ Å. These results were obtained from a least-squares treatment of 48 measurements on zero-level Weissenberg photographs taken at 20°C about the crystallographic axes b and c, using Cu $K\alpha$ radiation (λ Cu $K\alpha_1 = 1·54051$ Å, λ Cu $K\alpha_2 = 1·54433$ Å); the film was held in the asymmetric position, essentially following the Straumanis technique. Eccentricity coefficients were included as parameters in the least-squares calculations and weights were assigned as inversely proportional to $\sin^2 2\theta$.

The density measured by flotation is 1·553 g.cm⁻³; that calculated on the basis of four molecules per unit cell is 1·557 g.cm⁻³.

For the determination of the structure, intensity data were collected from multiple-film equi-inclination Weissenberg photographs. The layers 0–2 around **c** were obtained from a needle-shaped crystal, almost square in section, whose diameter was about 0·12 mm. The layers 0–5 around **b** were obtained from an approximately square tabular crystal, whose diameter was about 0·20 mm. Copper $K\alpha$ radiation was used and the intensities were estimated visually and corrected for Lorentz and polarization factors. No corrections either for absorption or for extinction were made.

The processing of the observed data was first carried on within the single layers, using a method rather similar to the procedure mentioned by Rae (1965). The second stage, which involved the evaluation of relative scale factors for all the layers and subsequent averagings of the observed $|F|^2$, was performed according to the method proposed by Rollett & Sparks, modified to account for the dependence of weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964). The assignment of estimated standard deviations to the individual observations, which is the major difference between Rae's method and ours, will be described elsewhere (Gramaccioli & Mariani, 1967). Of 1372 reflexions within the effective sphere of copper radiation, 1164 were collected, of which 267 were too weak to be observed.

Determination and refinement of the structure

A sharpened three-dimensional Patterson synthesis gave an approximative indication about the possible orientation of the molecule with respect to the crystallographic axes. In order to determine the position of the molecule in the unit cell, a series of structure factor calculations, based on relatively low Bragg angle ($\sin^2\theta/\lambda^2 \leq 0·15$) reflexions, was carried out for the centrosymmetric (001) projection, each time assigning a different set of coordinates x and y to the centre of the phenyl ring and recording on a map the discrepancy with the observed structure factors. A program written for this purpose by Albano, Bellon, Pompa & Scatturin (1963) was employed, where the speed of calculation is substantially increased by the use of Fourier transforms. In this procedure, a planar model for the molecule was used, with the exception of the two carbon atoms of the OC_2H_5 group, which were assumed to be on a plane perpendicular to the phenyl ring.

These calculations ended in giving a few different possibilities, of which only one could very roughly explain the major features of the Patterson synthesis. Using this 'best' hypothesis, a calculation of the R index gave the values 0·44 for three-dimensional data and 0·55 for the $hk0$ structure factors. A refinement of this trial structure was attempted, using both normal and difference Fourier syntheses on the (001) and (010) projections, with no success. Refinement of the positions of the heavier atoms by least squares was then tried, minimizing the function $\sum w(|F|_{obs} - |F|_{cal})^2$ and including three-dimensional data. The first cycles were based on a relatively small number of reflexions (103), each of them characterized by a low Bragg angle ($\sin^2\theta/\lambda^2 \leq 0·08$) and by a rather large value of the structure factor ($|F| \geq 10$); later on, all the remaining reflexions were included by gradually extending these limits. Initially unit weights were assigned to all the included reflexions; later, weights of the form $w = 1/f^2$ were used, where f is the average scattering factor* for all the atoms at the calculated value of $\sin \theta/\lambda$. At the beginning isotropic temperature factors were held constant and equal to 5·4 Å², a value deduced by Wilson's statistical method. Later on, when there was a sufficient number of considered reflexions, temperature factors were included in the refinement for the first time.

After the first least-squares cycles a constant decrease of the R index was noticed; further confidence in the success of the procedure was given by the reasonable values of the interatomic distances and angles which resulted after each series of cycles. At the end of this stage of the refinement, the R index was 0·14 for all the observed three-dimensional data. At this point, a three-dimensional difference Fourier synthesis was calculated as a check of our results; this indicated

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* In this work, atomic scattering factors for hydrogen were taken from Forsyth & Wells (1959) and for the heavier atoms from Cromer & Waber (1965).

Table 1. *Observed and calculated structure factors (final)*

Items in order are $k,l,|F|$obs$,|F|$cal$,\alpha$. Reflexions marked with an asterisk were omitted from least squares. Negative values for $|F|$obs mean a 'less than' reflexion.

[Table 1 is a large multi-column numerical listing of observed and calculated structure factors, organized into blocks labelled H = 0 through H = 16. Each entry lists $k, l, |F|$obs$, |F|$cal$, \alpha$. The full numeric data are not reproduced here in digit-perfect form.]

Table 1 (cont.)

(Structure factor table — extensive numeric listing of reflexions arranged in columns by h index groups (H = 17, 18, 19, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, etc.), each entry giving k, l, Fo and Fc values.)

some shifts in the atomic coordinates, which brought the R index down to 0·12.

The final refinement was carried out by full-matrix least squares on an IBM 7040 computer, using the program OR-FLS written by Busing, Martin & Levy (1962). Anisotropic temperature factors were assigned to all the atoms in the structure except four hydrogen atoms, H(1) to (H4), which were considered as isotropic, with $B = 7·0$ Å^2, and included only in the structure factor calculations. For 21 of the strongest reflexions, which were suspected to suffer from extinction or from a particularly bad measurement, the weight was taken as zero; for the other reflexions weights were assigned according to Hughes's scheme. The reflexions too weak to be measured ('less than') were included in the least squares only when $|F|_{cal}$ exceeded the threshold value of $|F|_{obs}$. Since the assignment of such threshold values was less reliable for higher values of the Bragg angle, none of these reflexions was considered in the refinement when $\sin^2\theta/\lambda^2$ exceeded 0·27.

Convergence was first reached at a point corresponding to an R index of 0·063. A three-dimensional difference Fourier synthesis was then calculated in order to locate the remaining three hydrogen atoms H(5) to H(7). Whereas for H(5) and H(6) there were well-defined peaks at about the right distance from the carbon atom, for H(7) there was only an indistinct maximum, situated too far away (1·58 Å) to be significant. For this reason, coordinates were assigned to H(7) by assuming it to lie at the average of the positions that would be assumed by H(5) and H(6) if they

were both rotated by 120°, in the appropriate direction, around the adjacent C(7)–C(8) bond. As to the first four hydrogen atoms, the difference Fourier clearly indicated that their assigned temperature factors were too high, and also some shifts in their positions.

Starting with this more complete set of parameters, a new series of least squares brought the R index* to 0·059 in three cycles. Weights were still assigned according to Hughes's scheme and hydrogen atoms were included only in the structure factor calculations, just as in the previous cycles. The refinement was considered complete when no atom parameter was shifted by as much as one-half of its standard deviation. This occurred in practice only with the z coordinates of O(6) and O(7) and with the thermal parameter B_{33} of O(2), where the final shifts amounted to 0·3 to 0·5 times the corresponding σ's; for all the other parameters shifts were much smaller (0·1 times the standard deviation). The observed and calculated structure factors relative to the final model are listed in Table 1; the final parameters of the heavier atoms are given in Table 2 and of the hydrogen atoms in Table 3.

The difference between the initial model and the final structure is evident in Fig. 1. The average total atomic shift is 0·33 Å and the maximum shifts, which can be observed in O(6) and O(7), amount to 1·2 and 1·1 Å respectively.

* This R index – as the previous one of 0·063 – has been calculated omitting all the unobserved reflexions and the observed reflexions with zero weight (marked with an asterisk in Table 1).

Accuracy of the results

The standard deviations in the coordinates, derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties ranging from about 0·006 Å for the atoms of the phenyl ring to about 0·009 Å for the carbon atom C(8). The corresponding standard deviations in the bond distances are about 0·01 Å for the N(3)–O and O(1)–C(7) bonds, 0·012 Å for C(7)–C(8) and 0·008 Å for all the others. The standard deviations for the angles range from 0·5 to 0·7°. No discussion about the accuracy of the C–H bonds and angles is thought to be appropriate.

Discussion

The molecular structure

The molecule as viewed normal to the plane of the phenyl ring is shown in Figs.2 and 3. A most evident feature is the fact that the two nitro groups in *ortho*
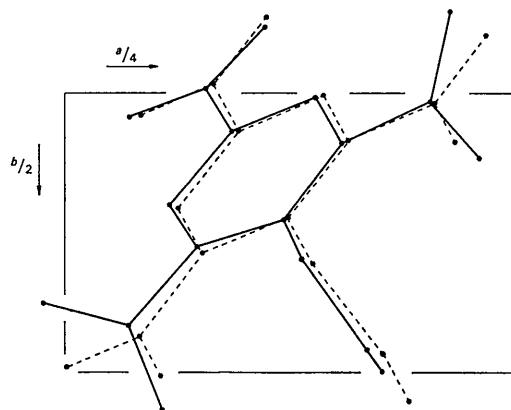
Fig. 1. Difference between the initial (dashed) and final models seen on the (001) projection.

Table 3. Parameters for the hydrogen atoms

	x	y	z	B
H(1)	0·1631	−0·0960	−0·3337	4·5
H(2)	0·0223	0·2330	−0·3793	5·0
H(3)	0·2080	0·4520	0·1367	4·5
H(4)	0·1510	0·5710	0·1407	4·5
H(5)	0·1940	0·3900	0·5127	4·5
H(6)	0·2050	0·6100	0·4907	4·5
H(7)	(0·1389)	(0·5302)	(0·5257)	6·0

positions with respect to the ethoxyl group are significantly rotated out of the plane of the phenyl ring, the dihedral angles between the corresponding planes being 31·8 and 61·3°. It is interesting to notice that, as an effect of these rotations, atoms O(2) and O(7) are situated on the same side of the plane of the phenyl ring, as the carbon atoms C(7) and C(8) of the ethoxyl group. The third nitro group (in the *para* position with respect to the ethoxyl group) is nearly coplanar with the phenyl ring (angle between the planes =3°).

The deviations of two carbon atoms C(1) and C(4) from the median plane of the ring, although small (up to 0·023 Å), definitely exceed the probable error and show that the molecule assumes a 'boat'-like shape. Considerably larger deviations from the phenyl plane are shown by the nitrogen atoms and especially by the oxygen belonging to the ethoxyl group [O(1)]; these correspond to an inclination of about 2 to 3° for the C–N bonds and of 5·5° for the C(1)–O(1) bond with respect to this plane. According to Akopyan, Kitaigorodskii & Struchkov (1965), these effects are not unusual in overloaded molecules; for instance, in the structure of 1,8-dinitronaphthalene the two nitro groups are rotated by 45·1 and 41·7° and the nitrogen atoms are displaced from the main molecular plane by 0·4 Å. In the structures of *o*-nitrobenzaldehyde (Coppens & Schmidt, 1964) and *o*-nitroperbenzoic acid (Sax, Beurskens & Chu, 1965) the nitro groups are rotated by 27 and 28°, respectively, and the nitrogen atoms

Table 2. The heavy-atom parameters and their standard deviations

All the values in this table have been multiplied by 10^4. The temperature factor is in the form

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

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	1216 (2)	2267 (6)	0	14 (1)	166 (9)	222 (12)	−4 (2)	−1 (3)	0 (12)
C(2)	1536 (2)	883 (7)	−875 (13)	11(1)	181 (9)	233 (12)	5 (2)	6 (3)	20 (10)
C(3)	1393 (2)	73 (7)	−2803 (13)	14 (1)	161 (9)	235 (13)	6 (2)	11 (3)	12 (11)
C(4)	927 (2)	686 (7)	−3864 (13)	15 (1)	158 (8)	233 (13)	−2 (2)	4 (3)	27 (11)
C(5)	582 (2)	2005 (7)	−3013 (14)	14 (1)	192 (10)	258 (13)	4 (2)	0 (3)	−8 (12)
C(6)	735 (2)	2755 (7)	−1115 (12)	14 (1)	174 (9)	242 (14)	7 (2)	7 (3)	2 (11)
C(7)	1678 (3)	4581 (8)	2138 (18)	20 (1)	198 (11)	428 (23)	−17 (3)	1 (4)	− 32 (16)
C(8)	1762 (3)	4968 (10)	4432 (17)	31 (2)	242 (14)	412 (25)	−20 (4)	−45 (5)	−16 (17)
N(1)	2029 (2)	155 (7)	230 (13)	14 (1)	254 (11)	265 (13)	15 (2)	4 (3)	46 (11)
N(2)	783 (2)	−84 (7)	−5954 (13)	20 (1)	202 (9)	250 (13)	−12 (2)	0 (3)	−8 (10)
N(3)	360 (2)	4160 (8)	−211 (14)	21 (1)	253 (11)	303 (14)	30 (3)	−13 (3)	−87 (12)
O(1)	1314 (2)	2958 (5)	1994 (12)	18 (1)	207 (8)	217 (9)	−14 (2)	−3 (2)	−8 (8)
O(2)	2307 (2)	1149 (7)	1336 (14)	19 (1)	339 (13)	510 (22)	8 (2)	−41 (4)	−39 (14)
O(3)	2137 (2)	−1469 (7)	−42 (14)	22 (1)	278 (10)	417 (16)	28 (2)	3 (3)	48 (14)
O(4)	1105 (2)	−1198 (7)	−6726 (12)	30 (1)	283 (11)	306 (14)	9 (3)	15 (3)	−106 (11)
O(5)	354 (2)	442 (6)	−6812 (13)	20 (1)	345 (12)	298 (13)	−13 (3)	−18 (3)	−7 (11)
O(6)	−122 (2)	3760 (8)	96 (18)	20 (1)	418 (15)	720 (30)	30 (3)	32 (5)	−127 (21)
O(7)	543 (3)	5670 (7)	−15 (21)	31 (1)	276 (11)	929 (42)	24 (3)	−4 (7)	−211 (23)

are displaced from the phenyl plane by 0·065 and 0·154 Å. Concomitant with these effects, which are probably connected with spatial difficulties, a slight distortion of the aromatic ring is nearly always observed: in o-nitroperbenzoic acid the carbon atom directly joined to the nitro group is situated 0·025 Å from the plane and similar observations can be made for 1,8-dinitronaphthalene, where such deviations amount to 0·09 Å for one carbon atom.

In our compound, the rotation angle of 61·3° for a nitro group is very large; higher angles were found only for nitromesitylene (66·4°) (Trotter, 1959a), 9-nitroanthracene (85°) (Trotter, 1959b), 9,10-dinitro-anthracene (64°) (Trotter, 1959c) and 2,3,4,6-tetra-nitroaniline (64°) (Dickinson, Stewart & Holden, 1966). This extensive rotation is probably connected with the considerable difference in length (0·029 Å) between the two otherwise 'equivalent' bonds C(2)–C(3) and C(5)–C(6) in the phenyl ring. A further point of interest is given by the evident deviations from planarity (up to 0·033 Å) observable in this C–NO$_2$ group (see the third nitro group in Table 4), in contrast with the others, where no significant displacement from the median planes can be noticed.

Table 4. *Some planes of interest*

The coefficients q_i are the direction cosines relative to the crystallographic axes *a*, *b* and *c*. Atoms were omitted from the calculation of the least-squares plane where indicated with an asterisk; the remaining atoms were given equal weights.

Phenyl ring		Atom	Deviation (Å)
q_1	= 0·5384	C(1)	0·019
q_2	= 0·6887	C(2)	−0·007
q_3	= −0·4856	C(3)	−0·014
D	= 2·688 Å	C(4)	0·023
		C(5)	−0·010
		C(6)	−0·011
		*N(1)	−0·081
		*N(2)	0·083
		*N(3)	−0·055
		*O(1)	−0·112

1st nitro group			
q_1	= −0·5705	C(2)	−0·000
q_2	= −0·2335	N(1)	0·001
q_3	= 0·7874	O(2)	−0·000
D	= −2·666 Å	O(3)	−0·000

Angle with the phenyl ring: 31·8°

2nd nitro group			
q_1	= 0·5098	C(4)	0·001
q_2	= 0·7345	N(2)	−0·004
q_3	= −0·4479	O(4)	0·001
D	= 2·578 Å	O(5)	0·001

Angle with the phenyl ring: 3·8°

3rd nitro group			
q_1	= 0·2627	C(6)	−0·009
q_2	= −0·2442	N(3)	0·033
q_3	= 0·9335	O(6)	−0·012
D	= −0·679 Å	O(7)	−0·012

Angle with the phenyl ring: 61·3°
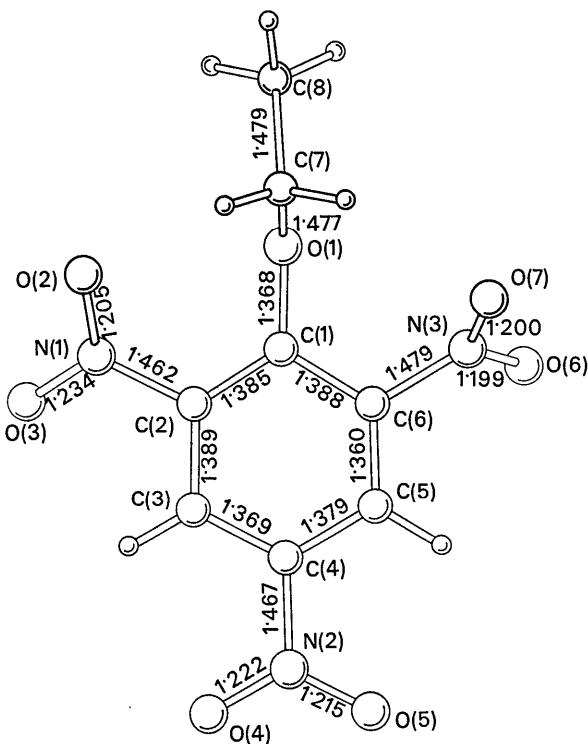
Fig. 2. Interatomic distances in the 2,4,6-trinitrophenetole molecule.
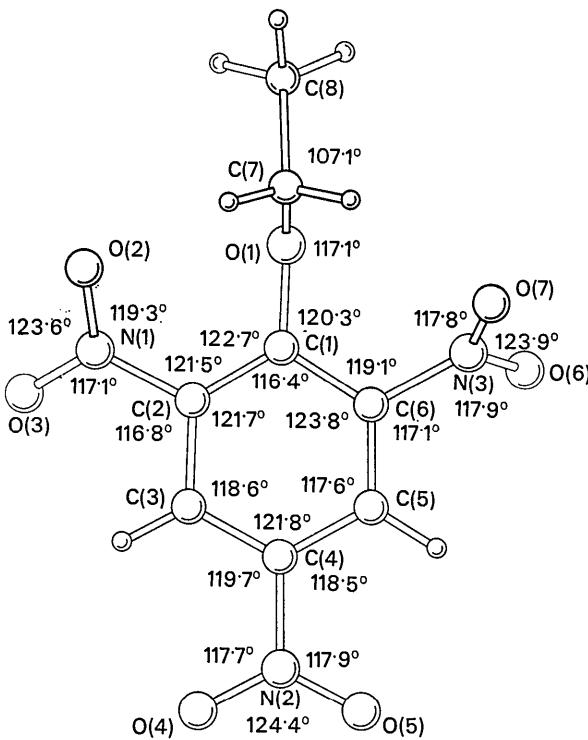
Fig. 3. Bond angles in the 2,4,6-trinitrophenetole molecule.

The bond C(1)–O(1) is surprisingly short (1·368 Å) and its length is comparable to the values observed for the corresponding C–O distances in other aromatic alkoxy-compounds, such as, for instance, 1,4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950), β-5-n-propoxy-o-quinone-2-oxime (Romers, 1964) and α-5-(2′-chloroethoxy)-o-quinone-2-oxime (van Oijen & Romers, 1966), where a considerable amount of double-bond character is evident. In our case, however, the plane determined by the three heavier atoms of the OC$_2$H$_5$ group is nearly perpendicular to the phenyl ring, the angle between the two planes being 88°. This geometry precludes the possibility of a strong π-interaction, and the cause of this shortening must therefore be connected with some other reason.

Considering the angles in the phenyl ring, it can be observed that they are alternately larger and smaller than 120°, the larger values being relative to the carbon atoms immediately adjacent to a nitro group. A similar situation is found in other 'symmetric' aromatic trinitroderivatives, such as 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965) and the 1:1 complexes of s-trinitrobenzene with anthracene (Brown, Wallwork & Wilson, 1964), skatole (Hanson, 1964) and azulene (Hanson, 1965).

Molecular packing

Assuming as van der Waals radii for carbon, nitrogen and oxygen respectively the values 1·6, 1·5 and 1·4 Å and 2·0 Å for the methylene and the methyl groups, in agreement with Pauling (1960), we see that in a very few cases two atoms belonging to different molecules are situated at a smaller distance than the sum of the corresponding van der Waals radii; a summary of these distances is given in Table 5. However, none of them is particularly short.

Table 5. *Intermolecular contact distances*

C(5)–O(5′)	$-x, -y, \frac{1}{2}+z$	2·961 Å
C(7)–O(3′)	$x, 1+y, z$	3·392
C(8)–O(4′)	$x, 1+y, 1+z$	3·305
N(2)–O(1′)	$x, y, z-1$	2·874

Considering the nitro group in position 6, which is subjected to the most extensive rotation, we have made a calculation of intermolecular distances, assuming it to be affected by the same rotation angle (31·8°) with respect to the phenyl ring as the nitro group in position 2. In this case the distance from O(6) to O(7) of another molecule at $x, 1+y, z-\frac{1}{2}$ [and the equivalent distance O(7)–O(6)] becomes too short (2·50 against 3·24 Å in the structure as found). If both the nitro groups lay in the plane of the phenyl ring, intermolecular distances would obviously become even more critical. Furthermore, in this case we cannot neglect a considerable intramolecular strain: in the same molecule, the distances O(1)–O(2) and O(1)–O(7) would fall from 2·74 and 2·99 Å to 2·57 and 2·42 Å.

Table 6. *Magnitudes and direction cosines, relative to the crystallographic axes, of the principal axes of the thermal ellipsoids*

	B_i	$q_i{}^a$	$q_i{}^b$	$q_i{}^c$
C(1)	3·73	0·453	−0·886	−0·095
	3·49	0·047	0·130	−0·990
	3·03	0·890	0·444	0·101
C(2)	4·33	0·262	0·775	0·576
	3·39	0·055	−0·607	0·793
	2·25	0·964	−0·176	−0·201
C(3)	4·37	0·565	0·452	0·690
	3·57	0·001	−0·837	0·547
	2·72	0·825	−0·309	−0·473
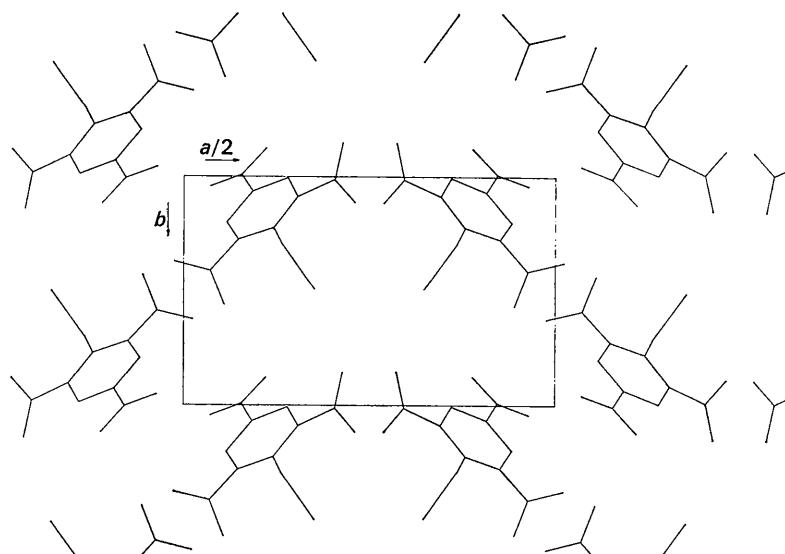
Fig. 4. Molecular packing seen along c.

Table 6 (cont.)

	B_i	q_i^a	q_i^b	q_i^c
C(4)	4·06	0·124	0·591	0·797
	3·42	0·846	−0·483	0·226
	2·88	0·519	0·646	−0·560
C(5)	4·29	0·191	0·853	−0·486
	3·97	0·169	0·459	0·872
	3·03	0·967	−0·249	−0·056
C(6)	4·22	0·514	0·607	0·606
	3·74	0·029	0·694	−0·719
	2·73	0·857	−0·387	−0·339
C(7)	6·91	0·152	−0·279	0·948
	5·40	0·737	−0·607	−0·297
	3·16	0·659	0·744	0·113
C(8)	9·54	0·750	−0·202	−0·630
	5·81	0·221	−0·821	0·527
	3·28	0·624	0·534	0·571
N(1)	6·26	0·313	0·866	0·389
	3·79	0·188	0·345	−0·919
	2·69	0·931	−0·361	0·054
N(2)	5·30	0·728	−0·682	0·070
	3·96	0·260	0·179	−0·949
	3·57	0·634	0·709	0·308
N(3)	8·13	0·537	0·707	−0·460
	3·99	0·536	0·135	0·833
	2·78	0·651	−0·694	−0·306
O(1)	5·28	0·638	−0·770	−0·006
	3·61	0·493	0·414	−0·765
	3·10	0·592	0·485	0·644
O(2)	9·62	0·429	0·369	−0·825
	6·99	0·125	−0·928	−0·351
	3·12	0·895	−0·048	0·444
O(3)	7·96	0·487	0·712	0·506
	6·14	0·414	0·322	−0·852
	3·43	0·769	−0·624	0·138
O(4)	7·53	0·003	0·814	−0·581
	7·10	0·958	0·163	0·234
	3·07	0·286	−0·557	−0·780
O(5)	7·75	0·301	−0·951	−0·064
	5·59	0·605	0·243	−0·758
	3·39	0·737	0·190	0·649
O(6)	12·81	0·068	−0·499	0·864
	9·22	0·503	0·765	0·403
	2·79	0·862	−0·407	−0·303
O(7)	16·15	0·095	0·369	−0·925
	7·64	0·901	0·363	0·237
	3·79	0·423	−0·856	−0·298

Thermal vibrations

The lengths and direction cosines of the principal axes of thermal vibration are given in Table 6. The thermal motions are relatively large, especially for the more external atoms of the molecule, some of which show a particularly marked anisotropy: see, for instance, the oxygen atoms in the third nitro group. For these two atoms, the directions of maximum motion form angles of 18 and 22° with the normal to the plane of the group; in the other nitro groups, a similar angle (11°) is found relative to O(2). This situation can prob-

ably account for some differences observed in the N–O distances, which are given uncorrected for thermal libration. For the other atoms, including C(7) and C(8), the situation appears to be more difficult to interpret.

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