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The Crystal and Molecular Structure of 4,4′-Dinitrodiphenyl*

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A more detailed account of the redetermination of the structure of 4,4′-dinitrodiphenyl, briefly reported earlier by van Niekerk & Boonstra (1961), is given. The structure was obtained by a combination of Patterson and intensity-distribution methods, and has now been refined by full-matrix least-squares analysis with individual isotropic temperature factors for non-hydrogen atoms. The residual R, based on 650 hkl reflexions (including 250 unobserved reflexions) has been reduced to 15%. The molecule is neither centrosymmetric nor planar as the approximately planar benzene rings are twisted about the central C–C bond through about 33°, relative to each other. The length of this bond is 1·499 Å, with an e.s.d. of $0{\cdot}01_6$ Å. The atomic coordinates (e.s.d. $\simeq 0{\cdot}02$ Å) are not known accurately enough to permit discussion of the variation of bond lengths. It is suggested that intermolecular bonding may be due to a weak type of C–H · · · O bond. The temperature motion is not discussed.

Introduction

The structure of 4,4′-dinitrodiphenyl, $C_{12}H_8(NO_2)_2$, was first determined by van Niekerk (1943). In order to facilitate computations, the molecules were assumed to be centrosymmetric, although packing considerations indicated a non-centrosymmetric space group Pc. Electron-density projections on the bc and ac planes supported but did not actually prove this assumption.

This structure received some attention as one of the few possible examples of the presence of centrosymmetric molecules in a non-centrosymmetric space group. Doubts about the space group assignment were removed by Herbstein & Schoening (1957), who confirmed the space group Pc. Thereafter Kitaigorodskii (1958) argued, on the basis of the theory of close packing, that the molecules should not be centrosymmetric when packed in a non-centrosymmetric space group. He has suggested that 'interactions between the hydrogen atoms in the *ortho* position prevent the molecule from being flat and hence centrosymmetric'.

In order to obtain further information on this apparent anomaly, it was decided to redetermine the structure of 4,4′-dinitrodiphenyl. The main results of the redetermination, *i.e.* that the molecules are not centrosymmetric, and that the benzene rings are twisted about the central C–C bond, have been reported by van Niekerk & Boonstra (1961). The present paper contains a description of the experimental procedure; how the new structure was determined; the initial and final refinement procedures, together with the more detailed results; and a discussion of the crystal and molecular structure.

* Part of the work described in this paper formed the basis of an M.Sc. thesis, submitted to the Department of Physics, University of Natal, Pietermaritzburg, South Africa in November 1961.

Experimental

4,4′-Dinitrodiphenyl was available from The British Drug Houses Ltd as a laboratory reagent in powder form. Well-faceted needle-like crystals were obtained by slow cooling and evaporation, in the dark, of a saturated solution of 4,4′-dinitrodiphenyl in a mixture of 70% ethyl acetate and 30% amyl acetate. The crystals showed oblique extinction and optical goniometer measurements agreed with earlier work.

Unit cell data

Preliminary oscillation and Weissenberg X-ray photographs showed that the needle-axis was the a axis, and that $\beta = 90{\cdot}0 \pm 0{\cdot}5°$. The symmetry relations $I(hkl) = I(h\bar{k}l)$, and the systematic absence $I(h0l) = 0$ for l odd, which were observed, are in accordance with the space group Pc. The density was measured as 1·46 g.cm^{-1} which, with the known cell dimensions, fixes the number of molecules in the unit cell at 2.

In order to minimize the uncertainty in bond lengths, the lattice constants were determined accurately by extrapolation techniques. A back-reflexion Weissenberg method was used to determine $d(010)$ and $d(001)$, while a special adaptor was used in the determination of a, the repeat distance along the needle-axis (Herbstein, 1963). The values, with e.s.d., found at 20 °C were:

$$\begin{aligned} a &= 3{\cdot}753 \pm 0{\cdot}003 \text{ Å} \\ d(010) = b &= 9{\cdot}5840 \pm 0{\cdot}0005 \text{ Å} \\ d(001) = c \sin\beta &= 15{\cdot}5080 \pm 0{\cdot}0005 \text{ Å} \end{aligned}$$

In the determination of a, Cu $K\alpha_1$ and α_2 radiation was used with wavelengths 1·54054 and 1·54436 Å respectively, while $d(010)$ and $d(001)$ were determined with Fe $K\alpha_1$ and α_2 radiation of wavelengths 1·93600 and 1·93994 Å rexpectively.

The value of β could not be measured readily, so that the uncertainties in the actual cell constants are somewhat greater than for the interplanar distances. The cell constants are

$$\beta = 90{\cdot}0 \pm 0{\cdot}5°,\ a = 3{\cdot}753 \pm 0{\cdot}003 \text{ Å},$$
$$b = 9{\cdot}5840 \pm 0{\cdot}0005 \text{ Å},\ c = 15{\cdot}5080 \pm 0{\cdot}0015 \text{ Å}.$$

Intensity data

Intensities were measured with Cu $K\alpha$ Ni-filtered radiation, a crystal of length 1·1 mm, width 0·6 mm and thickness 0·03 mm, mounted about the needle-axis being used. Under these conditions the absorption varied between 3 and 7%, and thus no correction was applied for absorption. With the use of the multiple-film technique, the intensities were recorded on zero, first and second-layer equi-inclination Weissenberg photographs. The intensities were measured by visual comparison with an exposure chart, and the data treated in the usual way with corrections for Lorentz-polarization, spot-shape and resolution factors, to give the experimental structure factors.

With this experimental arrangement 890 unique reflexions can theoretically be recorded with Cu $K\alpha$ radiation; of those which were experimentally recorded, 400 reflexions were intense enough to be measurable and a further 250 reflexions were weak and were given an intensity value corresponding to one quarter of the minimum measurable value. A few near-in reflexions were later recorded with Fe $K\alpha$ and Co $K\alpha$ radiation, but these were not determined with the same accuracy, and were therefore deleted in the final stages of the refinement. In the zero, first and second layers, reflexions up to $\sin^2\theta = 0{\cdot}85$ were recorded, *i.e.* $(\sin\theta/\lambda)^2_{\max} = 0{\cdot}36$. All the reflexions in the third and higher layer lines, which were not recorded, have $\sin^2\theta > 0{\cdot}35$.

Since $\beta = 90°$, the positive axial directions in this compound are not uniquely defined, and different observers may choose the positive axial directions differently. In order to obtain agreement between the present set of structure factors, and those of the original determination, it is in fact necessary to reverse the positive direction of the a axis in the earlier results, and to change the sign of the h index.

Determination of the structure

An attempt at least-squares refinement on a Stantec Zebra computer, using the program ZK 22 of Dr J. C. Schoone, showed that the atomic coordinates determined by van Niekerk (1943) were too inaccurate to be used as the initial values in such a process. At this stage there was some doubt about the structure as a whole, and hence a three-dimensional Patterson synthesis was computed on Zebra, using the program ZK 2 of Dr D. W. Smits. This could be interpreted on the basis of an approximately planar model of the molecule, and substantiated the main features of the molecular arrangement. In practice, this meant that the y and z atomic coordinates of the original structure were acceptable, but little information could be obtained about the x coordinates and the possible tilts about the long axis of the molecule.

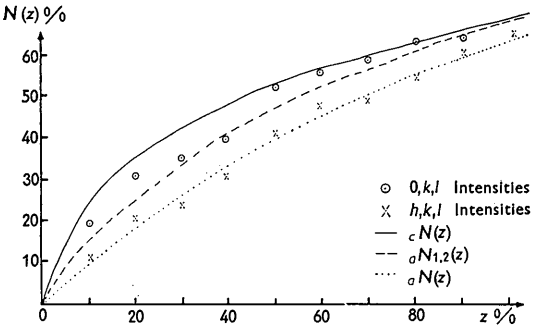

Fig. 1. Theoretical and experimental $N(z)$ curves.

Direct evidence on the molecular symmetry was obtained from a study of the intensity statistics using the ϱ and $N(z)$ tests. In Fig. 1, ${}_cN(z)$ is the theoretical curve for a centrosymmetric distribution of scattering material, and ${}_aN(z)$ is that for a non-centrosymmetric distribution. The curve ${}_aN_{1,2}(z)$ was derived by Herbstein & Schoening (1957) for an arrangement with a non-crystallographic molecular centre of symmetry, on the assumption that all positions are equally likely for the molecular centre. The experimental points for the $0kl$ intensities lie between the ${}_cN(z)$ and ${}_aN_{1,2}(z)$ curves, showing that the molecule possesses a centre or pseudocentre — at least in the bc projection. The points lie between these two possibilities since the molecular size and the space group symmetry prevent all positions for the molecular centre from being equally likely, and this is not taken into account in the derivation of the ${}_aN_{1,2}(z)$ curve. The results for the combined $1kl$ and $2kl$ intensities show that the molecule is non-centrosymmetric, although it seems centrosymmetric in the bc projection. The values obtained for ϱ are 0·715 and 0·775 for the $0kl$ and hkl intensities respectively. Comparison with the calculated values of 0·637 for a centric distribution and 0·785 for an acentric distribution shows that these results agree with the deductions made about the molecular symmetry.

The results from the first least-squares refinement suggested that the benzene rings differed in size as seen in the ac projection. This, together with the results of the statistical tests, was interpreted as indicating that the benzene rings and possibly the nitro-groups were twisted in opposite directions about the long axis of the molecule. Such an arrangement

would give a centrosymmetric *bc* projection, but this would not be readily detected in a Patterson synthesis. The least-squares program available at the time was not capable of refining temperature factors. The layer line intensities were therefore scaled by the Wilson-plot method, and then combined to give an overall isotropic temperature factor. The value deduced was $B=4{\cdot}0$ Å^2 and this was used in preliminary refinement of the new trial structure.

This three-dimensional trial structure was obtained in the following way. The zero-layer intensities were used to refine the y and z coordinates. From these the x coordinates were calculated by fixing the molecular 'centre' and assuming average bond lengths obtained from similar compounds. The directions of the bonds were chosen to comply with the proposed model of benzene rings tilted in opposite directions about the long axis of the molecule. By using all 400 measured structure factors, the structure was refined by the diagonal approximation least-squares method to a conventional R factor of 17%, the scale factors of the layer lines being included in the refinement. At this stage the preliminary account of the refinement by van Niekerk & Boonstra (1961) was written. Refinement was slow and an attempt was made to speed it up by computing a three-dimensional Fourier synthesis, for which all 650 reflexions, including the unobserved spots, were used. Before this one cycle of refinement by the Fourier method, the R factor was therefore at a higher value of 20%, but this process reduced it to 19%. In all the refinement procedures which have been described up to now, the effect of the hydrogen atoms had been neglected.

Refinement of the structure

The final refinement of the structure, after the trial structure had been found and shown to be correct by the Fourier synthesis, was done on an IBM 704 computer, using the least-squares refinement program ORXLS of Drs W. R. Busing & H. A. Levy (Oak Ridge National Laboratory, Report ORNL-54-4-37). With the 8K machine available, the maximum number of parameters which could be refined was 120. The molecule contains 26 atoms, and refinement with anisotropic individual temperature factors would therefore not have been possible even if the intensity data had been sufficiently accurate to warrant such treatment.

The original intensities of the individual layer lines 0*kl*, 1*kl* and 2*kl* were all on different arbitrary scales. Some consideration was given to the possibility of determining the absolute or relative intensities of these layers. It may be shown, however, that the requirements of experimentally determined relative scale factors and isotropic temperature factors obtained by refinement are not in general logically compatible. With the enforced assumption of isotropic temperature factors, it is therefore better to obtain the scale factors of the layer lines by refinement.

In the earlier refinement, no weighting scheme for the reflexion data could be introduced. Since experimental values for the estimated standard deviations (e.s.d.) of the intensity data were not available, an appropriate weighting scheme was used. (Relative weight proportional to the inverse square of the e.s.d.) The experimental structure factors F ranged in value from 0 to 40, and the relative weight w of a reflexion was defined as

$$w=F/F_o \text{ for } F \leq F_o$$
$$=F_o/F \text{ for } F \geq F_o ,$$

where F_o was taken to be 10.

The experimentally unobserved structure factors were treated in the following way. The relative exposure chart for measuring intensities ranged from 2 to 40 and values below 2 were labelled unobserved. Reflexions not observed on the innermost film were all given the same value for the uncorrected intensity equal to $\frac{1}{4}I_{\min}=\frac{1}{2}$. This is not strictly correct, since Hamilton (1955) has shown that for a non-centrosymmetric structure the average value of the unobserved intensities should be $\frac{1}{2}I_{\min}$ with absolute weight equal to $12/I^2_{\min}$. Since the weighting scheme adopted above does not give great weight to these terms, this minor error will not affect the refinement significantly, although it might increase the value of the R factor slightly.

Table 1. *Fractional atomic coordinates and temperature factors*

Glide planes at $y/b=\pm 0{\cdot}25$ and origin chosen to coincide with the molecular centroid in x/a and z/c directions

Atom	x/a	y/b	z/c	B (Å^2)
C(1)	0·056	0·068	0·024	2·9
C(2)	0·196	0·052	0·110	5·4
C(3)	0·288	0·178	0·155	3·9
C(4)	0·253	0·302	0·119	5·7
C(5)	0·120	0·324	0·035	4·1
C(6)	0·006	0·209	−0·013	4·6
C(1′)	−0·073	−0·057	−0·025	4·9
C(2′)	−0·028	−0·059	−0·114	3·4
C(3′)	−0·097	−0·177	−0·161	5·4
C(4′)	−0·220	−0·282	−0·116	4·5
C(5′)	−0·280	−0·293	−0·027	5·2
C(6′)	−0·196	−0·176	0·018	4·1
N(1)	0·341	0·438	0·165	5·4
N(1′)	−0·352	−0·415	−0·162	6·8
O(1)	0·510	0·406	0·231	7·6
O(2)	0·261	0·538	0·131	8·4
O(1′)	−0·305	−0·414	−0·242	7·1
O(2′)	−0·475	−0·513	−0·128	8·1
H(2)	0·224	−0·051	0·138	3·0
H(3)	0·394	0·167	0·218	3·0
H(5)	0·092	0·427	0·007	3·0
H(6)	−0·101	0·221	−0·076	3·0
H(2′)	0·072	0·033	−0·148	3·0
H(3′)	−0·059	−0·177	−0·230	3·0
H(5′)	−0·379	−0·385	0·007	3·0
H(6′)	−0·231	−0·176	0·087	3·0

Table 2. *Observed* (F_o) *and calculated* (F_c) *structure factors on absolute scale where* $F_c=(A_c^2+B_c^2)^{\frac{1}{2}}$

(– in F_o column for structure factors not measured, + for unobserved values, *i.e.* $F_o=\frac{1}{2}F_{\min}$ and × for observed reflexions which were given zero weight in refinement)

l	F_o	F_c	A_c	B_c
00l				
0	–	252.0	252.0	0.0
2	–	18.1	17.5	4.7
4	13.2	14.5	-14.3	-2.1
6	28.6	29.1	27.7	8.6
8	40.0	39.5	39.1	5.9
10	8.2	7.6	-7.6	0.2
12	2.1+	2.8	-1.8	-2.1
14	9.1	8.2	-8.2	0.3
16	4.3	3.6	-3.6	0.0
18	2.1+	1.3	0.8	-1.0
01l				
0	–	3.9	3.9	0.0
1	–	3.9	1.8	3.4
2	44.5x	55.6	0.6	-55.6
3	39.8	43.5	-1.6	43.5
4	11.5	10.3	-3.0	9.8
5	3.9	3.0	-3.0	0.7
6	3.5	3.7	-0.1	3.7
7	4.7	3.5	3.5	0.3
8	9.5	8.3	3.1	-7.6
9	3.9	3.8	-2.6	2.8
10	7.0	6.4	1.4	-6.2
11	7.6	7.6	-0.9	7.5
12	2.1+	0.6	0.4	0.3
13	5.4	4.5	-1.1	-4.4
14	2.3+	2.3	-1.2	-2.0
15	2.3+	1.7	-1.2	-1.2
16	5.6	4.5	-0.1	4.5
17	2.3+	2.1	-1.0	-1.9
18	2.1+	1.5	-0.3	1.5
02l				
0	22.1	21.7	-21.7	0.0
1	20.6	20.3	-20.1	3.3
2	23.9	25.1	25.0	-1.7
3	22.5	22.4	22.1	3.7
4	20.0	18.2	18.0	3.1
5	23.5	21.6	-21.4	2.2
6	8.2	8.2	7.9	-2.2
7	4.9	4.7	-0.3	-4.7
8	8.5	7.1	-7.0	-1.3
9	5.6	5.1	-5.1	0.4
10	3.5	2.8	2.6	1.0
11	4.7	2.8	2.7	-0.8
12	2.1+	2.3	1.4	-1.7
13	5.4	3.2	-2.1	-2.4
14	2.1+	2.5	1.8	-1.7
15	2.3+	1.2	0.8	-0.9
16	2.3+	0.8	-0.6	-0.5
17	2.1+	1.2	-0.9	0.7
18	1.6+	0.7	0.2	-0.7
03l				
0	4.3	3.5	-3.5	0.0
1	4.3	3.0	1.3	2.7
2	11.1	11.8	1.4	11.7
3	22.5	21.1	2.1	-21.0
4	7.0	7.3	3.1	-6.6
5	10.7	7.1	1.8	6.8
6	16.3	15.0	-1.5	14.9
7	12.4	14.3	-5.3	13.2
8	5.4	5.0	-4.6	2.0
9	5.6	6.5	-0.2	-6.5
10	3.9	3.9	1.7	3.5
11	2.1+	2.1	0.4	2.1
12	4.3	3.0	-1.4	2.7
13	9.7	8.7	-3.0	8.2
14	7.4	6.5	-2.2	6.2
15	2.3+	2.7	-2.0	1.7
16	2.3+	1.9	-1.6	-1.1
17	2.1+	0.6	-0.2	-0.5
18	1.9+	1.3	-0.7	1.1
04l				
0	2.7	4.9	4.9	0.0
1	7.6	8.5	7.9	3.2
2	14.8	15.0	14.2	-4.7
3	40.0	41.3	-41.3	-1.0
4	19.2	18.7	-17.4	-7.0
5	14.4	12.8	-12.3	-3.3
6	3.3	4.0	2.6	-3.1
7	4.1	1.6	1.3	0.9
8	5.6	6.2	6.2	-0.4
9	10.7	11.0	-10.7	-2.4
10	7.6	8.0	5.6	-5.7
11	24.5	24.5	-23.9	-5.3
12	6.0	5.0	-4.0	-3.1
13	4.3	3.2	-2.5	-2.0
14	2.3+	0.7	-0.0	-0.7
15	2.3+	1.1	1.0	-0.4
16	2.1+	1.8	1.8	-0.3
17	3.9	3.4	-2.7	-2.1
05l				
0	3.5	4.1	4.1	0.0
1	7.0	6.6	-0.8	-6.5
2	2.9	6.3	-0.8	-6.3
3	6.4	6.3	-1.9	-6.0
4	6.2	6.3	-3.9	-4.9
5	16.3	15.2	0.7	15.2
6	8.5	5.7	-4.2	-3.9
7	3.9	3.0	2.8	-1.2
8	2.1+	3.0	2.8	1.0
9	6.4	5.0	1.0	-4.9
10	6.2	5.4	-1.3	-5.3
11	5.4	3.5	-2.2	2.8
12	6.4	7.5	-2.3	-7.2
13	9.1	8.8	-0.6	8.8
14	4.3	2.1	-0.6	-2.0
15	2.1+	0.6	-0.1	-0.6
16	2.1+	1.0	0.4	0.9
17	1.9+	0.4	0.2	0.3
06l				
0	4.7	5.7	5.7	0.0
1	5.4	6.2	5.1	-3.5
2	8.0	8.4	-8.0	-2.9
3	1.9+	3.8	1.0	-3.6
4	6.2	6.8	6.1	-3.1
5	3.9	2.9	-2.7	-1.2
6	6.2	5.8	-5.7	-1.0
7	6.2	4.4	-4.1	-1.6
8	2.1+	3.3	2.4	-2.2
9	2.1+	3.2	1.0	-3.0
10	2.1+	2.5	1.5	-2.0
11	2.3+	0.5	-0.5	-0.0
12	2.3+	1.4	1.0	-1.0
13	2.3+	0.9	-0.6	-0.7
14	2.1+	2.0	-1.9	-0.3
15	2.1+	0.3	-0.1	-0.3
16	1.9+	0.7	0.6	0.5
07l				
0	1.9+	2.2	2.2	0.0
1	2.1+	3.5	0.9	3.4
2	3.9	5.2	-1.4	5.0
3	7.6	8.3	0.7	8.3
4	2.1+	4.0	-3.8	1.0
5	4.1	3.7	-3.6	-0.3
6	2.1+	0.8	0.1	-0.8
7	2.1+	2.1	-1.2	1.7
8	2.3+	3.9	-1.2	3.7
9	2.3+	3.2	-1.3	2.9
10	2.3+	1.9	-1.7	-0.8
11	2.3+	0.8	-0.3	0.7
12	2.3+	1.1	-0.3	1.1
08l				
0	17.3	19.0	-19.0	0.0
1	10.1	11.5	-9.3	-6.7
2	7.4	7.1	-5.7	-4.2
3	4.3	4.3	-1.5	-4.0
4	2.1+	0.5	-0.4	-0.3
5	2.1+	4.4	3.1	-3.1
6	4.7	6.3	-6.3	-0.6
7	2.3+	4.5	3.6	-2.6
8	4.3	4.9	-3.5	-3.5
9	2.3+	2.9	-2.7	-1.0
10	2.3+	1.4	0.7	-1.2
11	2.1+	0.6	-0.3	-0.5
12	2.1+	0.5	0.3	-0.4
09l				
0	2.3+	0.9	0.9	0.0
1	5.6	6.9	-2.4	-6.5
2	7.4	6.1	1.2	6.0
10l				
0	–	11.7	11.6	-1.3
2	21.2	20.6	-18.8	-8.6
4	30.2	28.9	23.6	-16.7
6	–	26.7	25.4	8.3
8	10.0	10.5	-10.5	-0.1
10	1.8+	1.2	-1.1	0.4
12	4.0	4.4	-3.7	-2.5
14	5.4	5.3	-4.8	-2.1
16	2.2+	2.0	1.4	1.4
18	1.8+	0.2	-0.1	0.2
-2	86.1x	116.3	115.5	13.0
-4	41.2	41.9	5.1	-41.6
-6	6.8	6.5	-4.5	4.7
-8	15.8	16.0	14.2	-7.5
-10	16.4	16.0	15.8	-2.9
-12	6.6	4.5	-2.3	-3.9
11l				
0	–	62.4	9.3	-61.7
1	–	61.9	6.8	61.5
2	22.8	22.2	-14.6	-16.8
3	23.4	24.5	19.7	-14.6
4	10.0	10.2	-8.8	-5.3
5	9.2	9.6	-9.4	-2.1
6	7.8	7.8	-1.4	-7.7
7	11.4	10.9	1.3	10.9
8	13.8	12.3	6.1	-10.6
9	15.8	14.0	-1.6	13.9
10	1.8+	2.6	-2.1	1.6
11	6.6	5.6	2.9	-4.8
12	2.0+	1.8	1.5	-1.0
13	2.2+	1.8	-1.6	-0.9
14	5.4	5.7	-0.4	5.7
15	4.6	3.4	0.3	-3.4
16	3.2	3.3	-0.1	3.3
17	2.0+	1.2	-0.9	0.8
18	1.8+	1.0	0.5	0.8
-1	16.8	15.8	-5.0	15.0
-2	22.0	21.8	-20.7	-6.6
-3	17.4	18.5	-14.4	-11.6
-4	16.4	16.9	-14.6	8.4
-5	15.2	14.7	11.3	9.4
-6	15.4	15.4	-3.5	-15.0
-7	12.8	12.6	7.3	10.3
-8	7.8	7.7	-3.5	-6.9
-9	8.6	6.2	-6.2	0.7
-10	5.2	3.5	-1.2	3.3
-11	2.0+	2.1	-2.0	0.8
-12	2.0+	2.1	0.3	2.1
-13	2.2+	1.1	-0.1	-1.1
-14	2.2+	1.8	-0.5	1.8
12l				
0	24.0	23.1	19.2	-12.8
1	33.4	33.9	22.8	25.1
2	19.2	18.7	-2.3	-18.6
3	5.8	5.5	-1.9	-5.2
4	13.8	13.1	-8.8	9.7
5	3.8	1.1	-1.1	-0.2
6	5.4	4.0	3.3	2.3
7	1.4+	2.6	2.5	0.6
8	7.4	7.1	4.4	-5.6
9	7.4	5.8	5.1	2.9
10	4.6	5.3	-2.4	-4.7
11	2.0+	0.4	0.3	0.1
12	4.2	3.2	2.1	2.4
13	5.2	4.1	3.8	1.7
14	5.4	3.3	3.1	1.1
15	2.2+	0.9	0.5	0.8
16	2.2+	2.1	1.7	-1.2
17	4.0	1.9	-1.9	0.1
18	1.8+	1.5	1.5	-0.2
-1	23.4	22.8	-20.1	-10.8
-2	14.0	14.4	-13.8	-3.9
-3	9.2	9.4	9.4	-0.3
-4	6.2	5.3	2.1	4.9
-5	4.6	6.0	-1.8	-5.7
-6	13.8	13.3	6.6	-11.6
-7	10.6	11.0	6.5	8.9
-8	1.8+	2.4	2.3	-0.6
-9	10.4	11.0	-2.2	-10.8
-10	5.2	4.5	-3.1	-3.2
-11	2.0+	1.9	1.9	-0.4
-12	4.2	2.4	2.3	0.7
-13	5.2	4.0	-1.8	-3.6
-14	2.2+	2.1	0.7	1.9
-15	2.2+	2.5	0.6	-2.5
-16	2.2+	1.6	0.1	1.5
-17	2.0+	1.0	-0.5	-0.9
-18	1.8+	0.4	-0.2	0.3
13l				
0	13.2	13.8	-12.5	5.9
1	13.8	13.3	3.1	-12.9
2	8.6	8.7	2.2	-8.5
3	17.2	16.3	5.5	15.3
4	26.6	24.9	-11.8	22.0
5	23.2	24.2	-1.5	24.2
6	3.8	2.2	1.9	-1.2
7	6.6	7.9	7.8	-1.1
8	4.2	4.2	-4.1	1.1
9	4.2	4.2	3.0	2.9
10	5.4	4.7	-2.2	4.2
11	13.4	13.5	-4.8	12.7
12	13.2	12.2	-5.8	10.7
13	7.8	6.5	-1.6	6.3
14	2.2+	1.2	0.6	-1.1
15	2.2+	1.4	1.4	0.2
16	2.0+	1.0	-0.6	0.8
-1	4.8	5.2	2.8	-4.4
-2	14.0	14.0	0.4	-13.9
-3	11.4	11.8	11.2	-3.7
-4	9.2	8.6	1.6	-8.4
-5	8.2	7.8	-1.2	-7.7
-6	3.2	2.5	2.2	1.3
-7	11.2	12.5	-12.3	-1.9
-8	8.6	7.8	-3.8	-6.8
-9	5.8	5.0	1.8	-4.7
-10	9.4	9.9	-2.7	-9.5
-11	7.2	7.7	3.0	-7.1
-12	6.0	5.1	4.2	-2.9
-13	2.2+	4.3	-4.0	1.6
-14	2.2+	1.3	0.0	-1.3
-15	4.2	2.7	-1.6	2.2
-16	4.0	2.9	-1.5	-2.4
14l				
0	3.4	5.6	2.3	5.1
1	24.0	24.1	-23.1	-7.2
2	9.4	10.9	-10.1	-4.0
3	14.4	14.2	-13.6	-4.1
4	4.2	4.8	4.0	-2.8
5	7.2	5.6	2.3	5.1
6	4.6	4.6	3.2	-3.3
7	7.2	9.2	-5.1	7.7
8	1.8+	2.2	2.1	-0.8
9	16.4	18.7	-16.5	-8.8
10	4.8	3.4	-3.2	-1.3
11	6.0	3.9	-2.8	-2.7
12	2.2+	0.8	-0.4	-0.7
13	3.2	4.1	2.2	3.5
14	2.2+	1.4	1.4	0.2
15	2.2+	1.4	-1.4	-0.1
16	2.0+	0.1	0.1	-0.0
-1	11.2	11.3	2.8	10.9
-2	9.2	10.0	2.4	-9.7
-3	6.8	5.8	-3.4	-4.7
-4	11.4	12.8	12.2	3.9
-5	22.2	22.7	21.6	6.8
-6	6.6	7.6	-7.2	2.3
-7	11.8	10.4	4.6	-9.3
-8	3.8	4.3	-0.5	4.3
-9	4.6	4.2	-1.4	-3.9
-10	5.4	4.8	4.5	-1.9
-11	9.8	9.9	9.4	-3.0
-12	6.0	5.4	4.2	3.4
-13	12.8	12.9	12.8	-1.5
-14	2.2+	1.7	-1.1	1.3
-15	5.2	4.5	0.0	-4.5
-16	2.0+	0.9	0.3	0.8
15l				
0	5.4	4.3	3.1	-3.0
1	9.2	9.8	9.7	-1.5
2	5.4	4.8	-4.2	-2.5
3	13.8	13.7	-1.2	13.6
4	10.8	8.9	-4.7	-7.6
5	4.8	4.3	3.2	2.9
6	6.6	6.0	-4.0	4.5
7	2.0+	4.4	1.9	4.0
8	2.0+	2.0	-1.9	-0.4
9	6.8	6.5	4.3	4.9
10	7.4	8.5	-1.6	-8.4
11	11.2	11.2	-2.4	11.0
12	6.2	4.7	-1.2	-4.5
13	2.2+	1.5	0.8	1.3
14	2.2+	2.9	-2.2	1.9
15	2.0+	1.8	0.9	1.6
16	1.8+	0.9	0.3	-0.9
-1	7.2	6.1	-5.0	3.5
-2	6.6	7.6	4.2	6.3
-3	11.8	10.6	-0.7	-10.6
-4	5.8	6.6	-1.9	6.4
-5	6.8	6.4	-0.3	-6.4
-6	1.8+	2.3	-2.2	0.4
-7	7.4	5.7	-3.0	4.9
-8	4.6	4.0	3.7	-1.4
-9	4.0	4.2	-3.3	-2.5
-10	6.8	6.0	4.8	3.6
-11	8.0	7.3	-2.1	-7.0
-12	5.4	4.3	-2.1	3.8
-13	2.2+	1.1	-0.9	0.6
-14	2.2+	2.1	-1.0	1.9
-15	2.0+	3.2	-1.3	2.9
-16	1.8+	1.4	1.4	-0.1
16l				
0	1.8+	5.3	-1.4	-5.1
1	1.8+	1.4	0.9	1.0
2	4.2	6.2	5.5	2.9
3	4.2	3.9	1.7	3.5
4	5.2	4.4	-3.9	-1.9
5	2.0+	1.9	-0.9	-1.6
6	3.8	3.3	-2.4	2.3
7	4.0	3.8	2.5	-2.9
8	4.2	3.4	3.0	1.6
9	2.2+	1.9	0.0	1.9
10	2.2+	1.4	1.4	0.1
11	3.2	2.0	1.2	1.5
12	5.4	4.5	-4.3	-1.3
13	2.2+	2.5	2.5	0.1
-1	1.8+	2.9	-0.6	-2.9
-2	9.4	10.4	6.9	7.7
-3	6.2	6.5	-3.4	-5.6
-4	5.2	5.0	-3.7	3.3
-5	2.0+	1.5	0.9	-1.2
-6	2.0+	2.7	1.3	2.4
-7	2.0+	0.4	0.1	-0.4
-8	4.2	4.0	2.0	-3.4
-9	2.2+	2.2	-0.2	-2.2
-10	6.6	7.2	4.5	5.7
-11	3.2	4.0	-1.3	-3.8
-12	2.2+	1.1	-0.0	1.1
-13	2.2+	1.4	0.0	-1.4
17l				
0	5.4	7.9	-3.5	7.0
1	11.4	13.7	-5.6	12.5
2	8.0	10.0	-4.7	8.8
3	2.0+	3.3	-1.6	2.9
4	2.0+	4.2	4.1	1.2
5	2.0+	2.3	-0.4	2.2
6	2.2+	5.4	-3.8	3.8
7	2.2+	2.1	-1.1	1.8
8	2.2+	2.7	-2.7	0.5
9	2.2+	3.6	-2.6	2.6
10	2.2+	2.2	-1.5	1.6
11	2.2+	1.1	1.1	-0.1
12	2.2+	1.8	-1.8	0.0
13	2.0+	1.0	1.0	-0.0
14	1.8+	1.5	-1.0	-1.1
15	2.0	2.2	0.9	-2.0
-1	2.0+	3.1	-2.2	2.2
-2	4.6	5.1	5.1	0.2
-3	4.0	4.0	-2.6	3.1
-4	4.0	4.5	4.5	0.1
-5	6.6	6.5	-1.2	6.4
-6	2.2+	4.5	-2.3	3.9
-7	2.2+	3.0	0.3	3.0
-8	2.2+	1.3	1.3	0.0
-9	2.2+	1.5	-1.4	0.6
18l				
0	7.4	8.1	-7.4	-3.4
1	2.2+	3.6	-3.2	-1.8
2	4.2	4.5	0.6	4.5
3	2.2+	3.5	2.2	-2.7
4	2.2+	3.3	-2.7	1.8
5	2.2+	2.3	2.3	0.0
6	4.6	4.7	-1.8	-4.4
7	2.2+	2.7	-2.6	-0.8
8	2.2+	0.7	-0.0	-0.7
9	2.2+	0.6	-0.5	-0.3
10	2.0+	0.3	-0.3	0.1
11	2.0+	0.3	-0.2	0.2
12	2.0+	2.0	1.9	0.5
13	1.8+	0.6	-0.0	0.6
14	3.2	2.4	2.3	0.5
-1	8.2	8.6	-6.9	-5.3
-2	11.2	12.8	-12.4	-3.3
-3	4.2	4.8	4.6	-1.3
-4	6.8	6.5	-0.7	6.5
-5	2.2+	4.3	-0.1	-4.3
-6	2.2+	3.2	-0.5	3.1
-7	2.2+	3.2	-2.9	-1.3
-8	4.6	5.9	-5.9	0.7
-9	2.2+	3.2	-2.5	-2.0
-10	2.0+	2.6	-2.1	1.5
19l				
0	6.2	6.9	0.7	6.9
1	2.2+	4.4	-4.3	-1.0
2	2.2+	1.3	1.3	0.2
3	2.2+	3.1	-2.1	2.3
4	2.2+	1.6	1.1	1.2
5	2.2+	1.2	-0.8	-1.0
-1	2.2+	4.9	-1.5	-4.6
-2	2.2+	3.7	3.4	1.4
-3	2.2+	1.3	-0.5	-1.2
-4	2.2+	2.4	1.9	-1.4
-5	2.2+	2.7	-1.9	2.0
20l				
0	–	8.1	-8.1	-0.0
2	19.5	19.3	9.4	-16.9
4	10.2	8.5	-1.6	8.3
6	11.4	9.5	-5.9	7.4
8	2.1+	3.5	0.8	-3.4
10	2.3+	3.4	-1.5	-3.0
12	4.6	5.7	-2.3	-5.3
14	2.3+	1.8	1.8	-0.1
16	2.3+	0.6	0.6	-0.2
-2	21.1	21.7	-0.9	21.7
-4	25.5	23.5	20.9	10.9
-6	20.6	21.3	4.6	-20.8
-8	7.9	6.5	-3.0	5.7
-10	9.0	7.5	7.3	1.6
-12	2.3+	3.2	3.2	-0.4
21l				
0	12.1	12.6	-9.3	-8.5
1	13.7	12.3	12.0	-2.7
2	8.6	9.4	-8.9	-3.0
3	1.4+	6.1	-5.5	-2.6
4	6.0	9.1	-7.9	-4.4
5	10.2	13.1	9.5	9.0
6	7.2	8.9	7.7	-4.3
7	4.6	3.5	-2.9	1.9
8	3.9	3.4	-3.1	-1.3
9	4.4	3.2	1.5	-2.9
10	2.3+	1.6	1.6	0.5
11	2.3+	1.2	-1.1	-0.3
12	4.6	3.6	1.0	3.4
13	7.0	5.4	4.2	-3.3
14	2.3+	1.5	0.3	1.4
-1	20.6	21.9	-6.3	21.0
-2	17.8	18.1	-1.1	-18.1
-3	8.3	8.6	5.9	6.3
-4	22.5	21.5	-20.7	-5.8
-5	5.6-	6.7	-5.4	-3.9
-6	8.3	8.0	-7.5	2.8
-7	8.6	7.3	3.8	6.2
-8	7.0	6.8	-5.6	-4.0
-9	4.9	4.1	-1.4	3.8
-10	7.6	6.2	-5.5	-3.0
-11	2.3+	2.2	-2.2	0.1
-12	2.3+	2.6	-2.0	1.6
-13	2.3+	2.0	-1.8	0.7
22l				
0	13.9	12.3	-10.2	-6.9
1	11.4	11.3	11.3	-0.8
2	15.5	17.8	-13.3	11.8
3	8.3	9.6	3.9	-8.8
4	10.9	11.1	7.2	8.4
5	7.0	7.8	7.5	-2.3
6	8.3	8.8	4.6	-7.5
7	7.2	6.7	6.7	-0.7
8	6.3	7.3	-3.4	-6.5
9	2.3+	3.4	3.4	-0.3
10	2.3+	3.5	1.7	3.1
11	5.6	5.8	5.6	1.5
12	7.2	6.4	5.8	2.7
13	4.9	3.5	3.1	1.5
14	4.6	4.7	4.0	-2.5
15	4.4	2.3	-1.4	-1.8
16	2.1+	2.7	2.6	-0.9
17	1.6+	2.0	0.0	2.0
-1	12.3	12.3	3.5	11.8
-2	5.6	6.7	-0.2	-6.7
-3	16.0	15.9	-6.7	-14.4
-4	4.9	3.4	-3.4	0.2
-5	5.3	3.6	2.7	-2.4
-6	8.6	9.9	-3.8	9.2
-7	5.3	2.9	2.6	1.2
-8	3.9	3.5	-3.4	-0.7
-9	6.7	5.7	-4.2	3.9
-10	7.0	5.1	-4.1	-2.9
-11	7.2	5.7	-1.9	-5.4
-12	4.6	2.7	1.0	-2.5
-13	2.3+	1.5	-1.5	0.1
-14	2.3+	3.0	1.3	2.7
23l				
0	2.3	2.8	2.2	-1.8
1	16.2	16.6	14.1	8.8
2	19.0	21.4	-17.0	13.0
3	6.3	6.2	1.3	6.0
4	9.5	9.2	3.8	8.4
5	3.7	3.1	3.0	-0.6
6	2.1+	1.9	-1.1	-1.6
7	8.3	8.4	7.1	4.5
8	4.4	4.0	-0.1	3.9
9	7.9	7.4	0.4	7.4
10	11.6	11.6	-8.6	7.9
11	4.6	3.6	-1.7	3.2
12	2.3+	1.7	1.3	1.1
-1	3.9	2.0	0.4	-2.0
-2	10.7	9.4	-9.4	-0.2
-3	10.0	6.6	-2.3	-6.2
-4	4.9	3.9	3.4	-1.9
-5	9.3	9.0	7.5	-5.0
-6	7.2	5.0	-4.1	-2.9
-7	2.1+	2.9	-1.8	-2.3
-8	2.3+	1.5	-1.5	0.3
-9	8.6	9.0	-8.9	-1.7
-10	7.6	6.1	-3.6	-5.0
-11	4.6	3.2	-0.4	-3.2
-12	7.2	6.2	1.0	-6.2
-13	2.5+	3.1	-1.0	-3.0
-14	2.3+	2.0	1.8	-1.0
-15	4.4	4.6	-4.6	0.5
24l				
0	1.6+	2.2	-0.4	-2.1
1	12.3	11.2	-6.4	-9.1
2	2.1+	2.6	0.9	-2.4
3	6.0	4.4	4.1	-1.5
4	2.1+	2.1	2.0	0.7
5	6.3	5.9	-2.9	5.1
6	2.1+	3.5	2.2	2.7
7	7.9	8.2	-4.0	-7.2
8	2.3+	1.0	0.2	1.0
9	9.0	8.8	2.3	-8.5
10	2.3+	1.3	0.4	-1.2
11	2.3+	2.8	2.1	1.9
12	2.3+	1.6	0.9	1.3
-1	9.0	8.8	-7.1	-5.3
-2	4.4	5.2	0.7	5.2
-3	5.3	3.9	-0.6	3.8
-4	3.9	2.5	0.6	-2.4
-5	2.1+	1.2	-0.7	0.9
-6	2.1+	1.2	1.2	-0.1
-7	7.1	5.2	1.9	4.9
-8	2.3+	1.5	-0.7	-1.3
-9	8.6	7.0	2.8	-6.4
-10	2.3+	2.5	-0.9	2.4
-11	2.5+	0.9	-0.5	-0.7
-12	2.5+	1.5	1.4	-0.5
-13	4.9	4.0	3.3	2.3
-14	2.3+	1.1	0.9	0.6
-15	3.9	3.5	3.5	-0.3
25l				
0	3.9	2.8	-2.8	-0.1
1	7.2	5.1	-0.9	5.1
2	6.3	4.5	2.8	-3.6
3	6.3	6.6	5.3	3.9
4	2.1+	2.3	-2.2	-0.4
5	2.3+	3.2	2.6	1.9
6	4.4	4.3	-4.0	1.4
7	8.6	9.4	8.3	4.3
8	2.3+	4.1	-0.4	-4.1
9	6.3	5.7	-1.9	5.4
10	5.3	4.0	2.6	-3.0
11	2.3+	1.5	0.8	1.2
-1	8.3	8.1	8.1	-0.3
-2	3.9	2.9	2.5	-1.6
-3	2.1+	1.4	-1.4	0.6
-4	2.1+	2.2	1.3	1.8
-5	2.3+	2.8	2.1	-1.8
-6	2.3+	2.2	-0.2	2.2
-7	7.0	5.9	-4.8	-3.4
-8	2.3+	1.6	0.6	-1.5
-9	4.6	3.3	-3.3	0.1
-10	4.6	3.6	3.5	-0.6
-11	2.3+	2.2	-2.0	-1.0
-12	2.3+	2.0	0.5	1.9
-13	4.4	3.5	-2.5	-2.5
-14	2.1+	1.5	-1.5	0.3
-15	2.3	3.1	-3.1	0.1
26l				
0	5.3	4.6	2.8	3.7
1	7.2	7.4	5.3	5.1
2	5.3	4.9	4.1	2.6
3	6.0	5.5	4.6	-3.0
4	2.3+	1.0	-0.1	-1.0
5	4.6	6.6	4.2	-5.0
6	2.3+	3.6	1.6	3.2
7	2.3+	1.0	1.0	0.1
8	2.3+	4.1	1.2	3.9
9	2.3+	2.4	2.2	1.0
10	2.3+	2.4	-2.3	0.6
11	2.3+	3.8	3.8	0.3
12	2.3+	2.4	-2.4	0.6
13	2.1+	1.7	1.1	-1.2
14	1.6+	2.4	-1.2	2.1
-1	2.3+	2.1	0.3	2.0
-2	5.3	6.4	3.3	-5.4
-3	4.4	4.5	-1.5	-4.2
-4	7.0	6.0	5.2	2.9
-5	2.3+	3.6	1.2	-3.4
-6	2.3+	1.7	1.4	1.0
-7	4.6	2.9	1.6	2.4
-8	2.3+	1.3	0.3	-1.2
-9	4.6	2.3	-1.7	1.5
-10	4.6	4.0	3.2	-2.3
-11	2.3+	2.6	-2.3	-1.2
-12	2.3+	2.7	1.1	2.4
-13	2.1+	2.3	-1.0	-2.1
-14	1.6+	1.1	-0.1	-1.1
27l				
0	6.3	6.0	-4.2	4.4
1	6.3	5.6	1.0	5.5
2	4.6	5.6	4.7	3.1
3	2.3+	2.1	2.0	0.6
4	2.3+	3.0	-1.6	2.5
5	2.3+	0.6	0.6	0.1
6	2.3+	2.0	-1.0	1.6
7	2.3+	3.7	-3.6	0.4
8	2.5+	1.4	-0.6	1.3
9	2.3+	1.3	1.0	1.0
10	2.3+	1.3	-1.3	0.3
11	2.3+	1.7	1.7	-0.4
12	2.1+	1.8	-1.8	-0.1
13	2.3	3.3	1.8	-2.8
-1	10.7	11.7	-6.6	9.7
-2	2.3+	3.8	1.3	3.6
-3	2.3+	2.6	-1.6	2.1
-4	5.6	6.5	6.4	1.0
-5	2.3+	1.5	-0.6	1.3
-6	2.3+	3.1	3.0	0.6
-7	7.2	6.4	1.0	6.3
-8	2.3+	1.1	-1.0	0.5
-9	4.6	4.8	-1.7	4.4
-10	2.3+	2.9	2.8	-0.8
-11	2.3+	2.0	-2.0	0.5
28l				
1	2.3+	2.3	2.2	-0.8
12	1.6+	2.4	1.2	2.1
-2	4.9	5.9	-1.7	-5.6
-4	6.0	4.6	-4.1	-2.0
-6	4.9	4.1	-1.0	4.0
-8	2.3+	0.5	-0.5	-0.0
-10	2.1+	3.0	-2.9	-0.9
-12	1.6+	1.0	-0.7	0.7
29l				
4	2.3+	3.2	2.2	2.3
-2	4.9	3.2	1.0	3.0
-4	5.6	4.8	4.5	1.4
-5	2.3+	2.3	-1.9	1.1
-6	2.3+	1.8	1.7	-0.3
-7	2.3+	1.8	-1.5	0.8

Initial values for the coordinates of the atoms (excluding hydrogen) were obtained from the Fourier synthesis. The positions of the hydrogen atoms were calculated from the carbon positions, assuming that the benzene rings were planar and regular with C–C distances of 1·40 Å, and a C–H distance of 1·08 Å. The individual isotropic temperature factor for each atom was set at 4·0. The atomic scattering factors which were used were those determined by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) without any corrections.

The space group Pc is polar or non-centrosymmetric, and the origin coordinates are not fixed in the x and z directions. In the table of final atomic coordinates (see Table 1) the values of the x and z coordinates have been adjusted so that the centroid of the molecule is at zero in x and z. In least-squares analysis, such indeterminacy is permissible when the diagonal approximation is used, but this is not so for the full-matrix treatment used here (Templeton, 1960). Consequently the origin had to be fixed in these two directions by not refining the x and z coordinates of the atom C(1) — this choice being arbitrary. The effect which this has on the accuracy of the bond lengths is discussed in the next section.

Throughout, the hydrogen atoms were excluded from the refinement process. In the first cycle of refinement, the scale factors alone were adjusted, yielding the value of 19% for the unweighted R factor as expected, a weighted R' factor of 13·9% and an error of fit E of 46·7%. The various functions used in the refinement are defined as follows:

s = scale factor
w = relative weight of a reflexion
F_o = observed structure factor (relative scale)
F_c = calculated structure factor (absolute scale)
$\Delta = F_o - sF_c$
Unweighted $R = \Sigma|\Delta|/\Sigma F_o$
Weighted $R' = (\Sigma w|\Delta|^2/\Sigma wF_o^2)^{\frac{1}{2}}$
Error of fit $E = (\Sigma w|\Delta|^2/(m-n))^{\frac{1}{2}}$

where m = number of reflexions with non-zero weight, n = number of parameters adjusted in least-squares cycle and summations are taken over all the reflexions. The observed and calculated structure factor values are regarded as real positive numbers, and the minimization of the weighted R' value serves as the criterion of the refinement process.

After five cycles of refinement with the scale factors, coordinates and temperature factor of all atoms (excluding hydrogen) as adjusted parameters, successive changes in the parameters were less than 10% of the e.s.d.; the values for R, R' and E were 15·6, 10·7 and 38·2% respectively. Comparison with the initial values showed that many parameters had changed by amounts greater than three times the e.s.d. of the parameters. This was particularly true of the parameters associated with the nitro-groups. The temperature factors had mostly increased.

At this stage the positions of the hydrogen atoms were recalculated on the same basis as before, and isotropic temperature factors of 3·0 assigned to them. The two strongest reflexions ($10\bar{2}$, 012) were given zero weight because they appeared to suffer from extinction. With these changes the values of R, R' and E reduced to 15·3, 8·7 and 29·8% respectively and again the changes in the parameters in the last cycle were smaller than 10% of the e.s.d. of the parameters. The values of the scale factors as applied to the calculated structure factors of the $0kl$, $1kl$ and $2kl$ layers, were 0·49, 0·51 and 0·43 respectively. The final fractional atomic coordinates and temperature factors are given in Table 1. For the non-hydrogen atoms, the averaged e.s.d.'s of the atomic coordinates are 0·023, 0·016 and 0·019 Å in the x, y and z directions, and the averaged e.s.d. of the temperature factors is 0·4 Å^2. For the hydrogen atoms no e.s.d.'s are given since the atomic coordinates were calculated from the carbon coordinates, and the temperature factors were set equal to 3·0 Å^2. The origin chosen is not the standard one since the glide planes are placed at $y = \pm\frac{1}{4}$ and not at 0, $\frac{1}{2}$ (*International Tables for X-ray Crystallography*, 1952). The observed and final calculated structure factors (all on absolute scale) are given in Table 2, where F_o is the observed value, and $F_c = (A_c^2 + B_c^2)^{\frac{1}{2}}$ is the calculated value.

Discussion of the structure

The geometrical details of the structure were calculated by using the IBM 704 program ORXFE of Drs Busing & Levy (Oak Ridge National Laboratory, Report 59-12-3), and use was made of the data as produced on magnetic tape by the related least-squares refinement program ORXLS. In the calculation of the e.s.d. of bond lengths, it is often assumed that the coordinate errors are uncorrelated. This being so, the e.s.d. of a bond length is often 1·4 times the average e.s.d. of the individual atom coordinates. In the present work the x and z coordinates of any one atom, C(1), have to be kept fixed, and there exists a correlation between coordinate errors which cannot be neglected. The program ORXFE allows for this effect by taking into account the covariant terms of the inverse least-squares matrix. Consequently the e.s.d.'s of bond lengths are not simply related to the e.s.d.'s of atom coordinates, and the bonds involving the atom C(1) are not necessarily known any more accurately than other bonds.

The nomenclature used is indicated in Fig. 2(*a*). The bond lengths with the e.s.d. in brackets are given in Fig. 2(*b*), whilst the values of the bond angles and their e.s.d.'s are given in Fig. 2(*c*). Although the hydrogen atoms were included, but not refined in the least-squares analysis, they are not included in these diagrams. The average e.s.d. for bond lengths is about 0·02 Å, and for the bond angles about 1·6°, but the results indicate variation between chemically identical

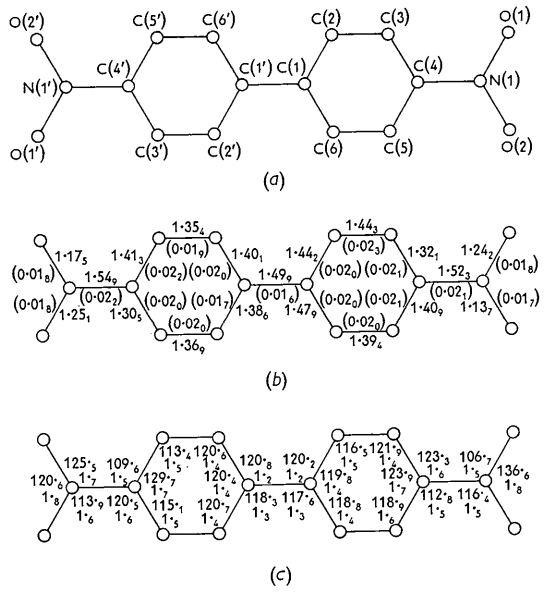

Fig. 2. Diagrammatic representation of molecule of 4,4′-dinitrodiphenyl showing

(*a*) nomenclature used,
(*b*) bond lengths with e.s.d. (in brackets) in Å,
(*c*) bond angles (upper values) with e.s.d. (lower values) in degrees.

bonds and angles, in excess of what would be expected from the e.s.d.'s. Although some of this variation may be due to real differences resulting from the effect of the non-centrosymmetric packing forces, the overall impression is that the e.s.d.'s are not physically meaningful since there exists the possibility of various systematic errors such as the absence of absolute layer line scaling, or those made in measuring the high-angle intensities, particularly with the double-coated film used.* The isotropic temperature factors for the nitro-group atoms are unusually high; this may indicate some measure of disorder, or may be due to the vibrations executed by the molecule. These possible vibrations were not analysed at all, and no corrections for this motion have been applied to the bond lengths.

In view of the lack of high accuracy in the results, a detailed analysis of the bond lengths would not be warranted. The value of 1·50 Å (e.s.d. 0·01$_6$ Å) for the central C–C bond is in good agreement with the values found by Robertson (1961*a*, *b*) and Hargreaves & Hasan Rizvi (1962) for diphenyl. The variation of bond lengths in the benzene rings (from 1·30 to 1·48 Å) is only slightly greater than that found by Trotter (1961) for *m*-dinitrobenzene. The difference in the two sets of nitrogen–oxygen distances (1·25 and 1·16 Å) in the nitro-groups seems to be significant. The carbon–nitrogen distance (average value 1·53 Å) found for this compound is much larger than the values found for *p*-dinitrobenzene (1·48 Å, Abrahams, 1950), nitrobenzene (1·49 Å, Trotter, 1959) and *m*-dinitrobenzene (1·47 Å, Trotter, 1961). The e.s.d. for all the values is about 0·02 Å, and the difference appears to be significant.

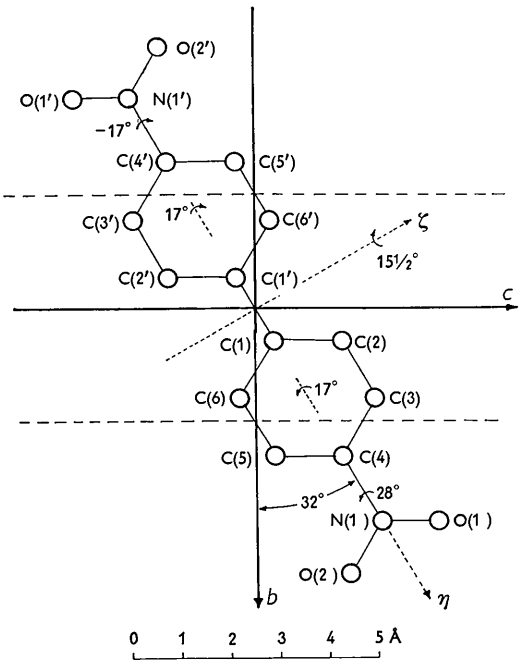

Fig. 3. The molecular orientation and configuration of 4,4′-dinitrodiphenyl.

The description of the molecular configuration in terms of a regular model is no longer as exact as when provisionally described by van Niekerk & Boonstra (1961). The angle between the long axis η of the molecule and the *b* axis in the *bc* projection is $32 \pm \frac{1}{4}°$, and it is tilted out of this plane by about $15\frac{1}{2} \pm \frac{1}{2}°$ about ζ. The mean plane of the molecule is not tilted about this long axis, but the benzene rings are twisted relative to one another about the central C–C bond by about 33°. These angles are shown in Fig. 3, and the axes used are also indicated. The molecular shape as given by the final atomic coordinates is somewhat irregular — in particular the atoms which define the long axis are not exactly collinear. Some of the departures of the atomic positions from the best least-squares fit for this axis may have some physical meaning, but these departures are ignored in view of the remarks made about the validity of the e.s.d.'s. The first nitro-group is inclined to the first benzene ring by about 11° about the long axis, this twist being in the same direction as that of the benzene ring. The second nitro-group is not significantly inclined to the second benzene ring, so that the approximate molecular symmetry 222 has disappeared. The conformation of the molecule is

* I am indebted to Prof. K. Lonsdale for stressing the importance of these effects.

unusual in that the benzene rings are twisted relative to one another. Such an effect was found for diphenyl in the vapour phase (Bastiansen, 1950), but in the solid the benzene rings are coplanar (Robertson, 1961*a*, *b*). In the structure determination of the molecular complex of 4,4′-dinitrodiphenyl with 4-hydroxydiphenyl (Saunder, 1946), symmetry considerations demand that the benzene rings in the different diphenyl groups are coplanar. The benzene rings in 4,4′-dihydroxydiphenyl are also coplanar (Farag & Kader, 1960). The relation of the benzene rings observed for this compound is therefore surprising. This cannot be due solely to the overcrowding effect of the hydrogen atoms in the *ortho* position, but no further explanation is offered. The observation that the first nitro-group is twisted out of the plane of the corresponding benzene ring agrees with the C–N bond twists found in *p*-dinitrobenzene (Abrahams, 1950) and *m*-dinitrobenzene (Trotter, 1961), whereas the apparent coplanarity of the second nitro-group is as found for nitrobenzene (Trotter, 1959).

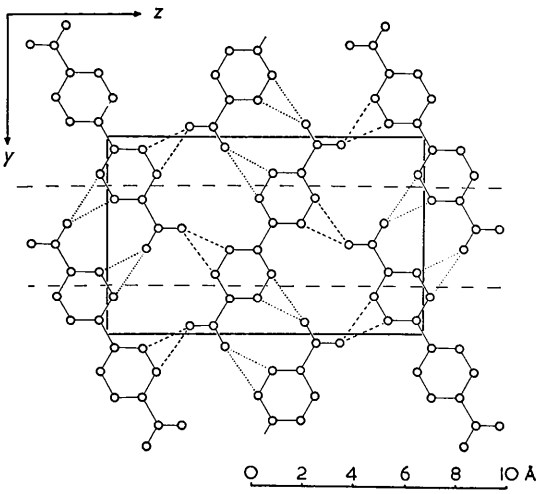

Fig. 4. The molecular arrangement of 4,4′-dinitrodiphenyl as seen in the *bc* projection indicating the possible weak hydrogen bonds. Dotted lines indicate the *p*-type bond between parallel molecules and dashed lines indicate the *q*-type bond between molecules inclined to each other.

Although the *bc* projection of the structure as determined does not differ much from that found in the original determination, the introduction of the different twists on the various parts of the molecule has greatly altered the *x* coordinates. The packing and bonding of the molecules must therefore be reconsidered. There exist the normal type of van der Waals approaches, but the only intermolecular distances which merit attention are those which were designated *p*- and *q*-type C–H · · · O linkages by van Niekerk (1943). They are indicated in Fig. 4, as seen in the *bc* projection, and the revised values of the distances are given in Table 3. The e.s.d.'s for the C · · · O distances are about 0·025 Å, while the values of the H · · · O distances are very uncertain, since they are based on calculated hydrogen positions obtained with the aid of simplifying assumptions.

Table 3. *Approach distances of possible weak* C–H · · · O *bonds*

(Tabulated for the molecule at the origin with *p*-type bonds from carbon atoms, and *q*-type bonds from oxygen atoms)

Type	Separation of molecular centres	Numbering of atom pairs		Approach distances	
		x	*y*	C(*x*) · · · O(*y*)	H(*x*) · · · O(*y*)
p	$+b$	5	2′	3·72 Å	3·04 Å
p	$+b$	6	2′	3·68	3·02
p	$-b$	5′	2	3·57	3·17
p	$-b$	6′	2	3·68	3·37
p	$+a+b$	5	2′	3·34	2·71
p	$+a+b$	6	2′	3·75	3·51
p	$-a-b$	5′	2	3·40	2·47
p	$-a-b$	6′	2	3·84	3·40
q	$+(b+c)/2$	2′	1	3·46 Å	2·57 Å
q	$+(b+c)/2$	3′	1	3·84	3·41
q	$-(b+c)/2$	2	1′	3·24	2·74
q	$-(b+c)/2$	3	1′	3·72	3·62
q	$+a+(b+c)/2$	2′	1	3·30	2·88
q	$+a+(b+c)/2$	3′	1	3·42	3·11
q	$-a-(b+c)/2$	2	1′	3·25	2·59
q	$-a-(b+c)/2$	3	1′	3·36	2·75

Any discussion of the significance of these C–H · · · O distances is hampered by the uncertainty in the hydrogen positions. It is clear however, that the distances cannot be associated with normal hydrogen bonding, since this is not found between carbon and oxygen atoms (Robertson, 1953). A weaker type of C–H · · · O bond may well exist, as shown by the recent survey of Sutor (1962). On comparing the tabulated values of the C · · · O and H · · · O distances with the effective van der Waals radii given by Nyburg (1961) *i.e.* C = 1·7, O = 1·4 and H = 1·0–1·4 Å, it appears that such bonds may be present, particularly since they need not be linear. The shorter of the distances found are in agreement with the longest of the results quoted in the survey, so that there is some evidence for suggesting that weak type C–H · · · O bonds are present in this compound.

The author wishes to acknowledge the help and interest received from Dr J. N. van Niekerk, who introduced him to the subject, and with whom he collaborated closely in the earlier stages of the work.

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The Crystal Structure of Ammonium Nickel Sulphate Hexahydrate $(NH_4)_2Ni(SO_4)_2 . 6H_2O$

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Crystals of ammonium nickel sulphate hexahydrate are monoclinic with space group $P2_1/a$. The unit cell of dimensions $a = 9{\cdot}181$, $b = 12{\cdot}459$, $c = 6{\cdot}239$ Å, $\beta = 106° 57'$ contains two formula units.

Projections of the structure on three crystallographic planes are given. The sulphate group and nickel–water complex have bond lengths and orientations somewhat different from those published for the isomorphous salt $(NH_4)_2Mg(SO_4)_2 . 6H_2O$.

A system of hydrogen bonding is suggested for the water molecules and the ammonium group. The former is in good agreement with recent proton resonance data and the latter has been used to explain the cleavage parallel to (010).

Introduction

During the past few years the technique of paramagnetic resonance has been extensively applied to investigate the lower energy levels of paramagnetic ions subjected to a crystal field such as occurs in hydrated salts. The interpretation of the resonance spectra depends upon a knowledge of the spatial structure of the magnetic ion complex and can be tested quantitatively only if this structure is known with precision. We were also interested in investigating probable hydrogen bonding in the structure.

The Tutton salts, of which isomorphous series ammonium nickel sulphate is a member, have been much investigated by the resonance technique, but the only published crystal structure is that of $(NH_4)_2Mg(SO_4)_2 . 6H_2O$ (Hofmann, 1931). The structures of the other members of the series have been assumed to be similar.

Crystal data

Crystals of ammonium nickel sulphate are monoclinic and bluish green in colour. The unit-cell dimensions from oscillation photographs taken of carefully oriented and machine-turned cylindrical crystals are

$$a = 9{\cdot}181 \pm 0{\cdot}001,\ b = 12{\cdot}459 \pm 0{\cdot}001,$$
$$c = 6{\cdot}239 \pm 0{\cdot}001 \text{ Å},\ \beta = 106° 57' \pm 2'.$$

These figures differ from those published by Mukherjee (1935) who gave

$$a = 8{\cdot}98,\ b = 12{\cdot}22,\ c = 6{\cdot}10 \text{ Å},\ \beta = 107° 4'.$$

However, our calculated density is $1{\cdot}922 \pm 0{\cdot}003$ g.cm^{-3} in excellent agreement with Tutton's (1916) measured value of 1·923 g.cm^{-3} whereas Mukherjee's dimensions give a calculated density of 2·04 g.cm^{-3}.

Systematic absences occur for $h0l$ with h odd and for $0k0$ with k odd. The space group is therefore $P2_1/a$. The number of formula units in the unit cell is two.

Determination of the structure

For evaluating the (100), (010) and (001) projections, the relevant intensities were recorded on zero-layer integrating-Weissenberg photographs by the multiple-film technique. Filtered Mo $K\alpha$ radiation was used. Roughly two-thirds of the intensities were measured photometrically with reference to a calibrated grey wedge. The very faint reflexions were estimated visually. The corrections for the Lorentz and polariza-