165. *The Crystal Structure of* p-*Dinitrobenzene.*

By F. J. Llewellyn.

The crystal structure of *p*-dinitrobenzene has been completely determined by utilising all the diffracted beams obtainable with Cu-$K\alpha$ X-radiation. The molecule is centrosymmetrical, and the carbon atoms of the benzene nucleus are located on a regular hexagon such that the C–C distance is $1{\cdot}38_5$ A. The nitro-group is planar, and coplanar with the rest of the molecule; its dimensions are C–N = 1·41, N–O = 1·23 A.

The crystal structure of *p*-dinitrobenzene has been previously investigated by Hertel (*Z. physikal. Chem.*, 1930, **7**, *B*, 188), Bannerjee (*Phil. Mag.*, 1934, **18**, 1004), and James, King, and Horrocks (*Proc. Roy. Soc.*, 1935, **153**, *A*, 225); in the last investigation Mo-$K\alpha$ radiation was used to determine the intensities of the diffracted beams from the $\{h0l\}$, $\{hk0\}$, and $\{0kl\}$ planes—about 200 in all—the atomic parameters being determined by means of Fourier projections on the (*a*), (*b*), and (*c*) faces. The main features of the results are as follows : (i) The molecule of *p*-dinitrobenzene is centrosymmetrical; the benzene ring is not, however, a regular hexagon, as has previously been reported in other solid benzenoid substances, *e.g.*, benzene (Cox, *Proc. Roy. Soc.*, 1932, **135**, *A*, 491), hexamethylbenzene (Lonsdale, *ibid.*, 1929, **123**, *A*, 494). (ii) The nitro-group and the carbon of the benzene ring to which it is bonded are not coplanar. (iii) The two oxygen atoms of the nitro-group are not equidistant from the nitrogen atom.

The irregularity of the benzene ring and the non-equivalence of the two oxygen atoms of the nitro-group are not compatible with the usual conceptions of the function of resonance which is to be expected in such a substance; various objections to, and criticisms of, these results have been made (see Pauling, "Nature of the Chemical Bond," p. 201). It seemed probable that, whilst the general arrangement of the molecules in the unit cell had been correctly determined, the detailed description of the molecule was inaccurate, mainly because the number of intensities used in computing the Fourier synthesis was insufficient, and also because of the considerable overlapping which occurs in projecting the structure on to both the *a*- and the *c*-planes.

It was decided, therefore, to repeat the structure determination, utilising all the $\{hkl\}$ intensities obtainable with Cu-$K\alpha$ X-radiation—about 450 in all—and to ascertain the atomic co-ordinates by means of three-dimensional Fourier lines and sections.

Preliminary Crystallographic Data.—Small, well-defined, single crystals of *p*-dinitrobenzene were readily obtained by slow evaporation of an acetone solution; they exhibited the forms $\{110\}$, $\{100\}$, $\{101\}$, $\{011\}$, $\{111\}$; the symmetry appeared to be monoclinic holohedral and the habit was variable. X-Ray rotation and oscillation photographs confirmed the monoclinic symmetry and the axial dimensions previously reported by James *et al.* (*loc. cit.*), *viz.*, $[a] =$ 11·05 A., $[b] =$ 5·42 A., $[c] =$ 5·65 A., $\beta = 92° 18'$; whence $a : b : c = 2{\cdot}039 : 1 : 0{\cdot}42$. Axial ratios quoted by Bodewig (*Ann. Physik*, 1876, **158**, 239) are $a : b : c = 2{\cdot}038 : 1 : 0{\cdot}43$, $\beta = 92° 18'$.

Various values for the density (g./c.c.) appear in the literature: 1·546 (Barker, *Z. Krist.*, 1908, **44**, 154), 1·625 (Lobry de Bruyn, *Rec. Trav. chim.*, 1894, **13**, 111), 1·623 (Brandl, quoted by Groth, "Chemische Kristallographie," **4**, 14), 1·64 (James *et al.*, *loc. cit.*); the density calculated from the X-ray data on the basis of two molecules in the unit cell is 1·64 (obs., by flotation, 1·63).

The only systematic halvings observed in the analysis of the X-ray oscillation photographs are $\{h0l\}$ absent when $h + l \neq 2n$, and $\{0k0\}$ absent when $k \neq 2n$. The space-group is therefore $P2_1/n(C_{2h}^5)$, which accommodates the four general positions $\pm (x, y, z)$ and $\pm (x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$ in each unit cell. Since there are only two molecules in the cell, it follows that these must be orientated about special two-fold positions, *i.e.*, each molecule is centrosymmetrical.

Measurement of Intensities.—In order to make the structure determination as accurate as possible, the intensities of the diffracted beams from all the $\{hkl\}$ planes with spacings greater than 0·77 A. were determined photographically. Since photographic density is proportional to X-ray intensity only over a limited range (from 0 to 1·2 approximately) it was necessary to take a number of oscillation photographs covering the same range of crystal orientation in order that all the diffracted beams which occur should be recorded as photographic spots whose density was within the proportionality limits. Two methods were adopted: (*a*) to vary the exposure, in which case the whole photograph was either more or less dense in proportion to this variation, or (*b*) to maintain the exposure constant but to screen (with aluminium sheets of known absorbing power) those parts of the photographic film on which the more intense diffracted beams fell such that their photographic impression lay within the proportionality limits.

The latter method was finally adopted, since it permitted an easy correlation between the strongest and weakest spots on a given photograph and considerably reduced the number of photographs necessary with (*a*) to achieve the same end. The actual measurement was carried out visually by matching each of the spots on the photographic film, in turn, with one of a series of spots of known density on a previously prepared comparator. The standard series of spots on the comparator was obtained as follows. A piece of X-ray film was exposed to a suitably collimated X-ray beam for a short measured time such that on development a photographic image was just discernible; a second piece of film was then exposed to the same X-ray beam for this time, then moved to a new position and exposed again for a longer time, this operation being repeated with successive increases in exposure until the necessary range of density was covered. The film was developed under conditions exactly similar to those obtaining in the photography of the crystal. In order to facilitate the matching of the spots, those on the comparator were made to approximate in both size and shape to those produced on the oscillation photographs.

A set of intensities on an arbitrary scale was thus produced, and these were converted to an absolute scale by direct photometric comparison of the intensities of the orders of (100) with the (400) reflection from the ground cleavage face of rock-salt. The experimental structure amplitudes ($F_{obs.}$) derived from the observed intensities Q by the relation

$$Q = \frac{N^2 e^4 \lambda^3}{2m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot F^2$$

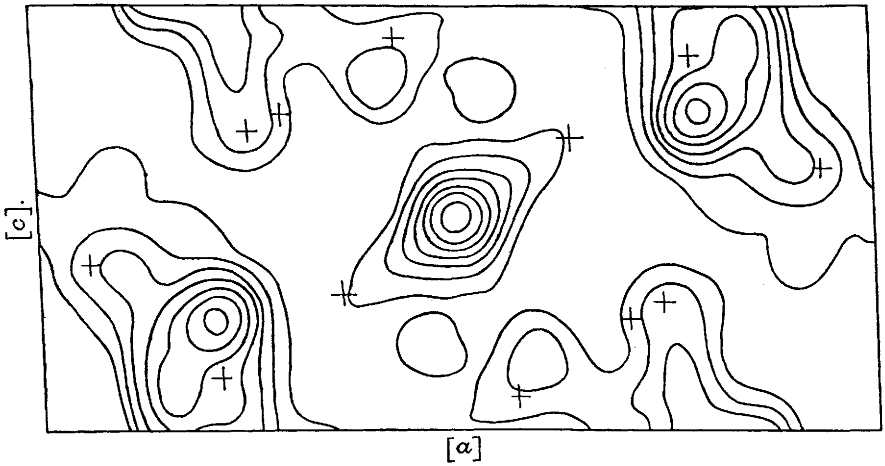
are listed in the table together with the calculated structure amplitudes ($F_{calc.}$) and the phase angles derived from the final atomic co-ordinates.

Determination of the Structure.—In order to define the structure it is necessary to determine the co-ordinates of six atoms, *viz.*, three carbons of the benzene ring, and one nitrogen and two oxygens of the nitro-group. The other half of the molecule is determinable by the operation of the centre of symmetry, and the second molecule by the operation of the glide plane. Since all the atoms in the structure are located in general positions, $\pm (x, y, z)$, $\pm (x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$, it is to be expected that a three-dimensional Harker–Patterson synthesis (*J. Chem. Physics*, 1936, **4**, 381) evaluated at $y = \frac{1}{2}$ would exhibit maxima in the Patterson function $P_{x\frac{1}{2}z}$, where

$$P_{x\frac{1}{2}z} = \overset{H}{\Sigma}\overset{L}{\Sigma} \cos 2\pi(hx + lz)(\overset{K}{\Sigma} F^2_{hkl} \cos 2\pi k/2)$$

at the points $\pm(\frac{1}{2} - 2x_r, \frac{1}{2} - 2z_r)$, (x_r, z_r) being the co-ordinates of an atom, and thus provide for the direct determination of the (xz) co-ordinates of all the atoms in the structure. Such a three-dimensional synthesis was evaluated, and the resulting contour map (Fig. 1) plotted over the whole unit cell; it is obvious that the maxima are too diffuse to be of any great service in determining accurate atomic co-ordinates.

Fig. 1.



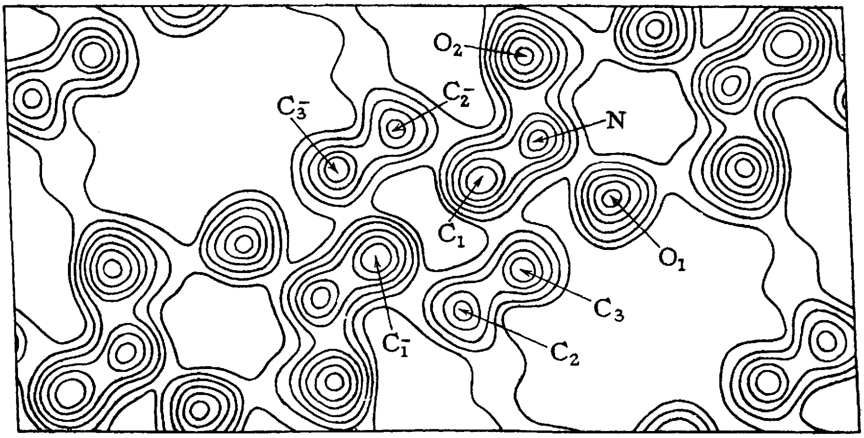
Patterson–Harker Section at y = ½.

This result is in sharp contrast with that obtained in the determination of the structure of pentaerythritol (Llewellyn, Cox, and Goodwin, *J.*, 1937, 883) in which a Patterson–Harker three-dimensional summation gave rise to sharp maxima in the function P_{xy0} and permitted the accurate determination of the (xy) co-ordinates of the pentaerythritol molecule. It is interesting to compare the positions of the maxima $P_{x\frac{1}{2}z}$ as represented by the peaks in Fig. 1 with the positions (represented by crosses) of the maxima calculated from the final atomic co-ordinates. Although it may be allowed that there is qualitative coincidence, yet the value of the Patterson synthesis in determining even approximate atomic co-ordinates is practically negligible. This question is further discussed by Booth and Llewellyn (this vol., p. 839).

It became necessary therefore to postulate a molecule and a molecular orientation and to refine the resulting atomic co-ordinates in three stages : (i) by trial-and-error methods using the $\{h0l\}$ structure amplitudes to determine the x and z co-ordinates; (ii) to refine these co-ordinates by two-dimensional Fourier syntheses; (iii) to obtain approximate y co-ordinates from a consideration of the x and z co-ordinates determined in (ii) and the bond lengths postulated in the molecule, and to refine these (xyz) co-ordinates by three-dimensional Fourier sections and lines.

The model used in the first stages consisted of a regular hexagon for the benzene ring with carbon–carbon separations of 1·39 A., a planar $R{\cdot}NO_2$ group which was coplanar with the benzene ring with carbon–nitrogen separation of 1·47 A., and a nitrogen–oxygen separation of 1·23 A. This model was placed in the unit cell with the centre of the benzene ring coincident with the centre of symmetry (origin) and orientated by trial-and-error methods until approximate agreement between the observed and calculated values of a few {*h*0*l*} structure amplitudes was obtained. The (*xz*) co-ordinates were then refined by means of a number of two-dimensional Fourier projections involving all the {*h*0*l*} amplitudes. The resulting contour map is shown in Fig. 2.

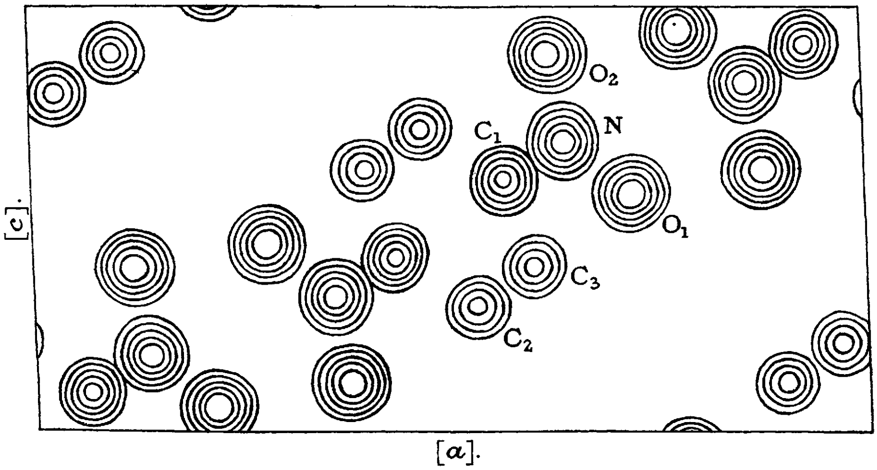
FIG. 2.



Fourier Projection on to 010.

These co-ordinates were then used in conjunction with the model to calculate approximate *y* co-ordinates. With these (*xyz*) co-ordinates the phase angles of all the {*hkl*} structure amplitudes were calculated, and then the co-ordinates refined by successive three-dimensional Fourier lines parallel to [010] at the *xy* co-ordinates of each atom in turn and by three-dimensional Fourier sections parallel to (010) at the *y* co-ordinates of each of the atoms. After two such complete cycles of operations the agreement between the calculated and the observed structure amplitudes became satisfactory; a third set of syntheses resulted in no alteration of the phase angles. The various Fourier sections are illustrated in a composite drawing in Fig. 3.

FIG. 3.



The final atomic co-ordinates are :

Atom.	*x*.	*y*.	*z*.	Atom.	*x*.	*y*.	*z*.
C_1	0·070	0·192	0·090	N	0·142	0·387	0·184
C_2	0·032	−0·117	−0·206	O_1	0·220	0·472	0·057
C_3	0·102	0·075	−0·115	O_2	0·124	0·460	0·385

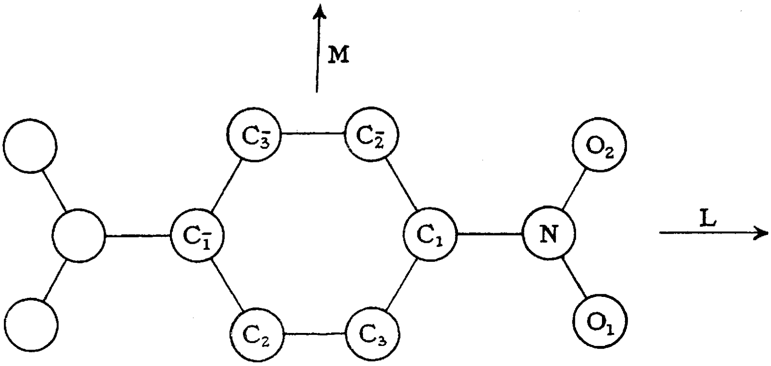
The average discrepancy between observed and calculated structure factors is 24%.

$k =$	0.		1.		2.		3.		4.		5.	
hl.	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$F_{\text{calc.}}$
00	172·0	—	—	—	25·1	+27·2	—	—	4·1	−3·0	—	—
01	—	—	7·6	+8·2	8·5	+9·0	7·8	−6·0	9·6	+11·5	<1·2	0·5
02	2·5	+1·6	9·6	−10·6	3·9	+7·8	4·1	+3·0	7·7	+9·8	5·4	5·0
03	—	—	12·3	−10·1	7·2	7·4	4·9	−4·5	9·9	10·4	1·4	−1·7
04	14·0	−12·2	1·9	3·1	3·4	−4·5	5·6	6·6	<1·1	−2·0	<0·9	−2·7
05	—	—	4·1	−6·1	2·5	−3·1	<1·1	0·5	<1·0	0·3	—	—
06	2·8	−3·0	2·9	−4·6	<1·0	−1·5	—	—	—	—	—	—
10	—	—	1·9	−0·4	14·0	+12·5	15·6	−13·2	8·8	8·5	1·0	−0·5
11	1·7	0·8	23·8	−30·4	12·9	−13·6	12·4	−10·9	5·2	−4·5	1·5	0·8
12	—	—	7·2	6·8	4·5	−3·6	3·4	−0·5	7·6	6·8	1·7	−2·6
13	22·9	−22·0	1·7	2·8	4·9	−4·7	6·0	+6·4	2·6	1·0	1·4	−4·0
14	—	—	1·9	3·7	4·7	0	7·3	8·0	<1·2	+0·6	1·6	+2·7
15	<1·2	0·6	4·2	−1·0	2·8	0·9	1·6	−1·4	2·1	4·0	—	—
16	—	—	4·7	3·4	2·3	0·4	—	—	—	—	—	—
20	9·3	7·2	25·8	−28·6	17·8	−16·4	18·6	−16·1	7·7	−7·0	3·3	−5·2
21	—	—	38·3	52·0	16·3	−19·6	6·8	4·4	1·1	−1·5	2·9	−2·9
22	7·3	−4·4	6·2	−5·6	5·3	6·0	4·6	5·3	2·1	3·4	1·8	1·7
23	—	—	6·4	7·5	3·2	−1·9	12·4	13·2	2·9	2·7	1·1	2·0
24	1·6	−1·0	6·2	6·4	1·5	3·5	8·3	9·5	3·9	−2·0	3·1	4·7
25	—	—	3·3	−2·4	5·7	5·7	<1·1	−0·7	<1·0	1·4	—	—
26	4·3	−6·0	<1·1	0·5	1·1	−1·9	—	—	—	—	—	—
30	—	—	35·6	32·4	3·8	−2·4	<1·0	−0·5	1·4	0·9	1·5	−0·5
31	5·3	−2·4	9·6	−8·2	1·5	3·2	7·6	6·7	1·6	+0·2	4·5	5·4
32	—	—	10·9	−8·4	15·5	−13·6	1·8	2·7	<1·2	−0·1	2·9	−2·4
33	1·4	−3·0	3·8	3·0	4·8	4·4	5·2	5·8	1·6	−2·0	2·7	1·6
34	—	—	10·0	−9·9	9·3	6·6	<1·2	1·7	<1·1	−0·7	—	—
35	<1·2	1·9	1·8	0·9	2·6	2·9	<1·1	1·1	—	—	—	—
36	—	—	<1·0	−0·5	<0·9	−0·9	—	—	—	—	—	—
40	23·9	−18·0	1·7	−2·4	7·3	−5·9	8·3	7·1	2·5	2·4	<1·0	−0·1
41	—	—	18·0	−20·0	21·5	−25·4	8·0	−9·5	4·3	−5·3	4·7	−5·6
42	12·3	14·0	10·7	−9·2	11·8	13·0	9·8	−8·4	<1·2	0·3	2·3	−3·3
43	—	—	6·8	−7·5	<1·1	1·4	6·8	6·2	1·7	−1·7	<1·0	−0·8
44	5·2	9·4	2·5	1·7	8·3	11·0	<1·2	2·6	2·2	3·7	—	—
45	—	—	5·3	6·9	5·3	4·4	<1·2	−1·0	—	—	—	—
46	2·0	3·0	2·1	3·1	—	—	—	—	—	—	—	—
50	—	—	5·2	−4·4	7·0	−6·6	2·6	−2·4	2·9	1·3	2·3	−1·8
51	21·3	20·6	6·0	−5·7	15·9	13·2	4·0	−3·7	1·0	−1·5	2·2	−3·9
52	—	—	6·9	−3·2	2·7	−1·8	8·8	8·8	<1·2	1·8	<1·1	2·5
53	8·5	−5·4	2·7	−2·5	2·2	3·3	6·6	−6·5	<1·2	2·1	<1·0	−0·7
54	—	—	4·1	5·5	8·2	7·1	<1·2	0·8	<1·0	1·1	—	—
55	1·2	−3·0	2·1	5·0	1·6	−4·3	<1·0	1·9	—	—	—	—
56	—	—	2·0	2·2	—	—	—	—	—	—	—	—
60	10·5	−8·2	9·4	7·1	1·7	−1·2	11·7	10·9	3·4	−3·7	<1·0	−0·1
61	—	—	10·9	−7·2	5·7	3·7	3·7	4·0	3·8	4·4	1·1	2·8
62	24·0	−20·0	7·9	−6·8	8·9	−9·6	8·7	−9·0	2·1	−4·0	<1·0	0·3
63	—	—	<1·2	−0·4	<1·2	−0·4	1·2	2·3	<1·2	−0·4	—	—
64	6·8	−8·4	4·1	4·3	1·9	−3·5	1·2	−2·0	<1·0	0·3	—	—
65	—	—	5·3	6·6	1·1	−2·6	—	—	—	—	—	—
70	—	—	6·9	−5·0	4·2	4·8	7·4	5·9	1·0	0·1	1·1	1·2
71	6·2	−6·4	<1·2	−1·4	2·3	−3·1	2·4	−3·0	3·5	−5·0	<1·0	0·6
72	—	—	6·7	4·1	2·4	−2·8	3·7	3·1	5·0	−5·6	—	—
73	8·1	−5·6	2·8	2·4	<1·2	1·6	<1·1	−1·6	—	—	—	—
74	—	—	<1·2	0	1·7	−1·8	<1·1	1·4	—	—	—	—
75	7·5	8·0	2·7	3·4	<1·0	2·3	—	—	—	—	—	—
80	7·2	7·8	5·2	4·1	9·2	10·2	3·5	4·0	1·0	−0·3	—	—
81	—	—	3·6	4·0	10·1	8·1	<1·2	−0·5	<1·0	0·7	—	—
82	4·8	−1·6	4·2	3·0	<1·2	2·6	<1·2	2·0	1·9	5·5	—	—
83	—	—	7·8	−7·2	<1·2	−1·7	<1·0	−3·6	—	—	—	—
84	<1·0	0·2	2·4	3·0	1·9	−1·1	<1·0	0·7	—	—	—	—
85	—	—	1·3	−4·6	—	—	—	—	—	—	—	—
90	—	—	6·5	−4·7	10·5	11·1	<1·2	−2·4	1·7	2·1	—	—
91	1·8	−1·0	5·6	4·5	<1·2	1·1	<1·2	0·7	1·0	0·5	—	—
92	—	—	2·1	−4·0	<1·2	−0·9	3·4	−6·2	1·2	−0·5	—	
93	<1·0	1·3	1·4	1·3	<1·2	−0·5	<1·0	0	—	—	—	
94	—	—	2·5	−3·1	<1·0	1·7	—	—	—	—	—	—
10·0	1·7	−0·8	1·8	1·3	3·1	2·4	3·3	−4·5	—	—	—	—
10·1	—	—	8·5	8·0	2·7	1·8	<1·0	−0·3	—	—	—	—
10·2	7·7	7·0	3·9	1·6	<1·2	0·8	<1·0	0·2	—	—	—	—
10·3	—	—	1·8	0·2	<1·0	1·4	—	—	—	—	—	—
10·4	<1·0	2·0	—	—	—	—	—	—	—	—	—	—

k =	0.		1.		2.		3.		4.		5.	
hl.	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$
11·0	—	—	6·1	7·5	1·9	3·0	0·7	3·9	—	—	—	—
11·1	3·1	1·9	6·2	5·4	1·1	−1·6	1·0	0·5	—	—	—	—
11·2	—	—	2·2	3·1	<1·0	0	—	—	—	—	—	—
11·3	1·5	−0·9	<1·0	−0·9	—	—	—	—	—	—	—	—
12·0	3·4	−5·8	3·6	4·3	2·6	−4·0	—	—	—	—	—	—
12·1	—	—	<1·0	3·1	—	—	—	—	—	—	—	—
12·2	7·2	8·1	—	—	—	—	—	—	—	—	—	—
$1\bar{1}$	32·7	−48·8	9·6	11·8	5·1	1·6	1·3	1·5	2·3	−2·4	3·8	−3·1
$1\bar{2}$	—	—	13·5	−10·6	0·7	−2·4	3·1	−1·0	1·3	−1·5	5·2	4·2
$1\bar{3}$	5·9	3·0	8·2	2·9	9·1	8·8	<1·1	−4·0	5·5	10·8	<1·0	−0·8
$1\bar{4}$	—	—	3·1	−0·4	2·9	2·4	2·9	−4·1	<1·0	−2·5	2·6	−2·8
$1\bar{5}$	3·6	5·0	1·4	+0·2	1·9	5·1	1·3	1·3	1·3	+2·0	—	—
$1\bar{6}$	—	—	2·7	−6·6	2·4	2·3	—	—	—	—	—	—
$2\bar{1}$	—	—	12·8	−9·0	6·0	5·2	1·1	−1·9	1·4	−2·6	7·8	6·9
$2\bar{2}$	21·0	−19·6	2·0	0·4	20·4	−20·0	4·1	−3·8	3·0	−2·8	5·1	−4·2
$2\bar{3}$	—	—	12·0	−11·1	3·8	−3·0	5·7	−5·1	<1·2	0·9	3·1	2·4
$2\bar{4}$	3·2	−4·0	5·4	5·4	4·4	−3·7	<1·2	0·9	<1·1	1·5	<1·0	1·4
$2\bar{5}$	—	—	4·0	2·8	9·5	11·4	<1·1	−1·6	1·8	4·1	—	—
$2\bar{6}$	2·5	6·0	3·8	2·0	3·2	7·2	—	—	—	—	—	—
$3\bar{1}$	5·2	4·4	7·2	−8·6	8·2	−5·0	1·6	1·1	<3·2	2·5	1·4	0·9
$3\bar{2}$	—	—	4·9	2·6	<1·0	−0·2	9·5	10·6	<3·2	−1·9	11·1	10·8
$3\bar{3}$	1·5	−0·8	3·1	1·4	10·1	−6·5	<1·2	−1·0	4·1	−3·0	1·1	−1·3
$3\bar{4}$	—	—	7·7	8·2	2·5	−1·3	3·2	−2·5	1·9	−1·6	—	—
$3\bar{5}$	1·7	−5·2	4·3	4·3	1·9	−3·9	<1·1	−0·3	—	—	—	—
$3\bar{6}$	—	—	2·4	−0·5	3·6	6·4	—	—	—	—	—	—
$4\bar{1}$	—	—	19·8	−17·9	7·9	8·9	9·6	−9·6	5·6	4·4	1·1	0
$4\bar{2}$	4·0	−3·6	6·4	−2·8	8·2	−6·0	5·9	6·8	2·0	3·7	5·9	8·3
$4\bar{3}$	—	—	5·4	2·9	<1·1	−0·8	2·9	3·1	2·1	1·4	4·9	5·7
$4\bar{4}$	13·8	15·6	6·5	6·4	1·5	1·2	1·2	5·3	3·1	−2·7	—	—
$4\bar{5}$	—	—	9·4	11·6	1·9	1·0	<1·1	1·8	—	—	—	—
$4\bar{6}$	2·5	−3·1	1·7	3·4	—	—	—	—	—	—	—	—
$5\bar{1}$	9·6	−8·8	6·2	−2·4	5·8	3·8	3·9	5·0	8·9	9·7	1·4	−2·6
$5\bar{2}$	—	—	15·4	14·8	1·2	1·2	8·8	−10·5	4·8	3·5	<1·0	−1·8
$5\bar{3}$	12·5	10·6	9·8	−5·9	<1·1	−1·0	1·2	−0·9	<1·2	−1·9	<1·0	4·6
$5\bar{4}$	—	—	1·2	−3·5	<1·2	−0·4	<1·2	−2·2	<1·1	−0·3	—	—
$5\bar{5}$	7·3	7·0	5·1	6·0	<1·8	0·1	<1·1	1·8	—	—	—	—
$5\bar{6}$	—	—	1·0	2·6	—	—	—	—	—	—	—	—
$6\bar{1}$	—	—	3·2	5·0	2·3	4·8	3·6	5·8	7·7	9·7	<1·1	−1·5
$6\bar{2}$	3·1	1·8	7·8	−7·0	8·5	7·2	<1·2	0·4	7·6	7·1	1·8	1·4
$6\bar{3}$	—	—	8·6	8·2	<1·2	−0·2	<1·2	−1·8	<1·2	3·5	—	—
$6\bar{4}$	18·3	18·7	5·4	−4·3	2·7	3·1	1·2	− 5·0	<1·0	−2·1	—	—
$6\bar{5}$	—	—	2·1	−4·0	<1·1	−4·1	—	—	—	—	—	—
$7\bar{1}$	21·5	−19·2	4·6	5·2	6·9	−7·0	7·6	8·9	1·8	−3·7	1·0	2·5
$7\bar{2}$	—	—	5·2	5·2	8·2	−4·5	2·0	2·4	2·4	5·0	1·1	−1·3
$7\bar{3}$	<1·2	−1·6	7·1	−7·2	1·2	−3·0	<1·2	−1·6	<1·1	0·7	—	—
$7\bar{4}$	—	—	7·9	7·1	1·2	3·0	<1·1	−0·4	—	—	—	—
$7\bar{5}$	4·4	7·8	<1·2	−1·4	1·0	1·5	—	—	—	—	—	—
$8\bar{1}$	—	—	1·0	1·5	2·7	−3·0	8·4	10·0	1·2	−2·2	—	—
$8\bar{2}$	1·9	−2·2	2·4	−2·7	2·3	2·0	<1·2	0·4	<1·2	−0·5	—	—
$8\bar{3}$	—	—	6·8	6·1	10·3	−9·0	<1·2	−1·2	<1·1	−3·1	—	—
$8\bar{4}$	3·7	−5·7	4·0	−3·5	4·9	−6·7	<1·1	−1·6	—	—	—	—
$8\bar{5}$	—	—	<1·0	−0·9	—	—	—	—	—	—	—	—
$9\bar{1}$	3·1	4·0	<1·2	0·6	7·0	10·0	1·1	1·8	<1·1	1·4	—	—
$9\bar{2}$	—	—	2·3	−2·8	6·3	−6·1	4·4	4·1	<1·0	−0·7	—	—
$9\bar{3}$	3·9	5·1	4·4	−1·7	3·7	5·4	1·1	1·4	—	—	—	—
$9\bar{4}$	—	—	1·8	4·9	2·3	−3·3	—	—	—	—	—	—
$10\bar{1}$	—	—	5·1	−5·9	1·8	2·2	1·4	0·9	—	—	—	—
$10\bar{2}$	<1·1	−0·3	4·4	−2·9	1·9	1·9	5·6	−4·8	—	—	—	—
$10\bar{3}$	—	—	1·7	−6·6	3·1	−4·1	1·0	−2·5	—	—	—	—
$10\bar{4}$	1·9	−0·2	—	—	—	—	—	—	—	—	—	—
$11\bar{1}$	5·2	−3·6	1·2	−1·6	1·2	1·8	3·7	−5·4	—	—	—	—
$11\bar{2}$	—	—	2·0	1·1	<1·2	0·8	—	—	—	—	—	—
$11\bar{3}$	1·0	1·3	1·0	−2·8	—	—	—	—	—	—	—	—
$12\bar{1}$	—	—	1·3	−0·1	1·2	1·1	—	—	—	—	—	—
$12\bar{2}$	4·9	−6·4	<1·0	1·1	—	—	—	—	—	—	—	—

Description of the Structure.—A diagrammatic representation of the *p*-dinitrobenzene molecule is shown in Fig. 4. The atoms $C_{\bar{1}}$, $C_{\bar{2}}$, etc., are obtained by inversion of the atoms C_1, C_2, etc., across the centre of symmetry coincident with the centre of the molecule. Within the limits of experimental error all the atoms lie in a plane which is so orientated within the unit cell that the molecular axes, *L* and *M*, make angles of 48° 42′ and 5° 42′ respectively with the plane 010. Bond angles and bond lengths calculated from the measured atomic co-ordinates and cell dimensions are as follows :

FIG. 4.

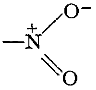


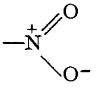
$C_1–C_{\bar{2}} = 1{\cdot}38_5$ A. $C_1–N = 1{\cdot}41$ A. $<O_1–N–O_2 = 124°$
$C_2–C_3 = 1{\cdot}38_5$ A. $N–O_1 = 1{\cdot}23$ A. $<O_1–N–C_1 = 117\frac{1}{2}°$
$C_3–C_1 = 1{\cdot}38_5$ A. $N–O_2 = 1{\cdot}23$ A. $<O_2–N–C_1 = 118\frac{1}{2}°$

Other distances within the molecule are : $O_1–O_2 = 2{\cdot}17$; $C_1–O_1 = 2{\cdot}25$; $C_1–O_2 = 2{\cdot}25$ A. The error in the bond lengths is probably not more than ± 0·02 A., and the angles are probably accurate to within ± 2°.

The anomalies in the bond lengths and bond angles reported by James (*loc. cit.*) are not substantiated by the present investigation. The benzene ring is a regular hexagon, and in this respect falls into line with the results of earlier structural work on benzenoid substances.

The two oxygen atoms of the nitro-group are equidistant at 1·23 A. from the nitrogen atom. This result is in agreement with the resonance mechanism suggested by Pauling in which the two principal forms are :





The observed distance, 1·23 A., is greater than the calculated value of 1·19 A. and agrees more nearly with the value of 1·21 ± 0·02 found in nitromethane. The ONO bond angle is 124° as compared with 127° found in nitromethane and the theoretical value of 125° 16′.

This work forms part of a programme of fundamental research sponsored by the Ministry of Supply at the University of Birmingham; approval for publication has been granted by the Director General of Scientific Research and Development, Ministry of Supply.

THE UNIVERSITY, BIRMINGHAM 15. [*Received, September 9th*, 1946.]