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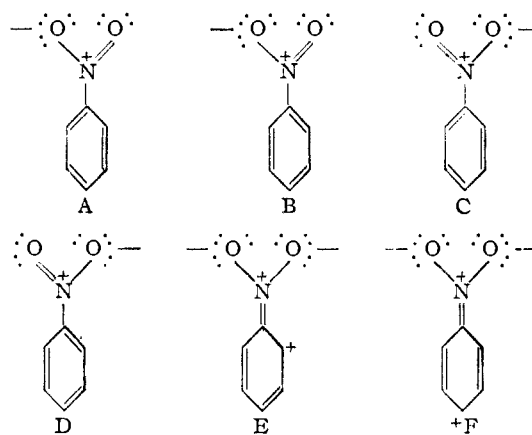
The Crystal Structure of m-Dinitrobenzene

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The diffraction of X-rays by crystalline m-dinitrobenzene has been investigated by several workers.[1,2,3] Hendricks pointed out that on the basis of X-ray data the space group is Pbnm if the crystal is holohedral and Pbn if hemihedral. Since the crystallographic investigation of Steinmetz[4] indicated holohedral symmetry, Pbnm was adopted as the space group. From this assignment and the low intensity of the (002) reflection, Hendricks concluded (a) that each molecule of m-dinitrobenzene lay on a mirror plane of the crystal which included the benzene ring, and (b) that one oxygen atom of each nitro group lay above the plane of the benzene ring and the other below. Since this publication evidence which favors hemihedral symmetry has accumulated. The observation of Hettick and Steinmetz[5] that m-dinitrobenzene is piezo-electric seems to demonstrate that the crystal is hemihedral. Indirect evidence is also afforded by the known van der Waals radius of oxygen.[6] The weight of evidence seems therefore to favor hemihedral symmetry and hence the space group Pbn.

If the suggestion of hemihedry is adopted it becomes possible to account for the weak (001) reflections even though all of the atoms in the molecule are in the same plane, since the plane of the molecule is no longer required to be on a symmetry plane of the crystal. This is fortunate since there is theoretical reason to believe that all the atoms in m-dinitrobenzene lie, at least approximately, in the same plane unless there are very strong interactions between adjacent molecules in the crystal.

The reasons for expecting a plane molecule can be most simply illustrated by considering nitrobenzene. In the ground state of nitrobenzene there is resonance between the following struc-

(1) E. Hertel, Z. physik. Chem., B7, 188 (1930).

(2) S. B. Hendricks, THIS JOURNAL, 53, 4280 (1931).

(3) Bauerjee and Ganguly, Indian J. Phys., 14, 231 (1940).

(4) Steinmetz, Z. Krist., 54, 467 (1915).

(5) Hettick and Steinmetz, Z. Physik, 76, 688 (1932).

(6) We are indebted to Anderson Pace, Jr., and P. M. Harris for a critical review of previous investigations of the crystal structure of m-dinitrobenzene and the suggestion that the crystal structure be re-examined since circumstances prevented their doing this. They pointed out that the only suggested structure consistent with X-ray diffraction data is that of Hendricks[2] and that it is inconsistent with the known dimensions of the nitro group[7] since the minimum value of c_0 compatible with this arrangement would then be 4.96 Å. (cf. 3.82 Å. observed). As a result, they measured the absolute values of F for certain pinacoid reflections (see Table I, column 3). These data indicated that Hendricks[2] visual estimates of intensities are substantially correct. They therefore concluded that the crystal of m-dinitrobenzene is not isomorphous with V_h^{16}(Pbnm) but with C_{2v}^9(Pbn)—i. e., that the crystal is not holohedral and therefore that the molecule does not lie in a mirror plane. Subsequently Professor Harris drew our attention to the work of Hettick and Steinmetz.[5]

tures.[7] Evidence that E and F contribute substantially to the ground state is afforded by the effect of a nitro group on orientation of entering substituents and also by the dipole moment of nitrobenzene as compared to the corresponding alkyl compound. The π bonds formed between nitrogen and carbon in structures E and F tend to keep the nitro group in the same plane as the benzene ring. This tendency is no doubt weak as in azo and other similar compounds[7] but in the absence of steric hindrance is expected to determine the configuration. In the case of m-dinitrobenzene the situation is more complex but similar.

We have examined the structure of m-dinitrobenzene by X-ray diffraction and have succeeded in determining the atomic positions. Our results support the suggestion of Harris and Pace concerning the hemihedry of m-dinitrobenzene and establish the geometrical arrangement of atoms in the molecule.

Experimental

The m-dinitrobenzene used in this work was obtained by recrystallizing a sample (Eastman Kodak Co.) from ethyl alcohol. Crystals for X-ray diffraction measurements were grown from a saturated solution in a 50% alcohol–benzene solvent. Crystallization was carried out in a dish fitted with a ground glass lid to reduce the rate of evaporation of the solvent. The crystals used were grown in a period of about two weeks and were well formed, the (100) and (010) planes being developed about equally with considerable elongation along the c axis. Several samples gave a constant melting point of 90.5°. These crystals were well adapted for oscillation or rotation photographs about the c axis.

The data used in this determination were obtained from oscillation photographs around the c axis at fifteen degree intervals. For low orders a crystal measuring slightly less than 0.1 millimeter in diameter was used, while for higher order reflections it was found necessary to use a crystal between 0.2 and 0.3 millimeter in diameter. A cylindrical camera was employed, the camera having a

(7) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

radius of 57.3 millimeters, with the multiple film technique (adapted from de Lange, Robertson and Woodward)[8] to facilitate intensity estimates of the observed reflections. The source of X-radiation was a General Electric Co. Model CA-6 X-ray tube with copper target, $\lambda = 1.539$ Å. This tube was operated at 34,000 volts with a filament current of 20 milliamperes. A nickel filter was used.

The exposure time for the smaller crystal under these conditions was one hour for the 15°-oscillation photographs, while thirty minutes were sufficient for the larger crystal. The crystals were mounted and lined up as well as possible using an optical telescope, the final adjustments being checked by taking complete rotation photographs. Agfa non-screen X-ray safety film was used for the measurements. All photographs were developed under identical timing and dark room conditions, the three films from each oscillation being developed simultaneously.

Reduction of Data

The reflections appearing on the oscillation photographs were assigned Miller indices by means of the graphical method of Bernal.[9] In this assignment the cell dimensions reported by Banerjee and Ganguly[3] were used. These are: $a_0 = 13.3$ Å., $b_0 = 14.2$ Å. and $c_0 = 3.82$ Å. The results lead to the extinction rules

(hkl)	appear in all orders
$(hk0)$	appear in all orders
$(h0l)$	appear when $(h + l)$ is even
$(0kl)$	appear when k is even.

These are in complete agreement with results reported by previous investigators.[1,2,3] As suggested by Harris and Pace, these extinctions lead to the hemihedral space group Pbn(C_{2v}^9).[10] There are four equivalent general positions whose coordinates are

$$(xyz); \quad (\bar{x}, \bar{y}, \tfrac{1}{2} + z); \quad (\tfrac{1}{2} + x, \tfrac{1}{2} - y; \tfrac{1}{2} + z); \quad (\tfrac{1}{2} - x, \tfrac{1}{2} + y, z)$$

The unit cell is reported to contain four molecules for which equivalent atoms occupy sets of the above points.

To obtain the value of the structure factor for each reflection, photographic intensity data were estimated. The triple film technique used by Robertson[8] was employed and was quite satisfactory. The intensities of the observed reflections were found to decrease by a factor of approximately two in going from one film to another, therefore the second and third films were used only in the case of very strong reflections.

A scale for the first relative intensity measurements was established by taking a series of timed exposures of the X-ray beam, reducing its intensity by a filter, so that a series of spots ranging from those only faintly visible to those of fair intensity were recorded. Each was assigned an arbitrary value proportional to its exposure time. By means of a visual comparison the relative intensities of reflections were obtained. Each estimated intensity was then multiplied by the reciprocal of the Lorentz polarization factor

(8) de Lange, Robertson and Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

(9) Bernal, *ibid.*, **113**, 117 (1926).

(10) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. I, Gebrüder Borntraeger, Berlin, 1935.

$$\frac{\sin 2\theta}{1 + \cos^2 2\theta} \quad (\theta \text{ is the glancing angle})$$

to convert it into a quantity which is proportional to the square of the structure factor.

$$I \alpha F^2 \left[\frac{1 + \cos^2 2\theta}{\sin 2\theta}\right]$$

To convert the square root of this quantity, F_{rel}, into the absolute structure factor, F_{abs}, the (020), (040), (060), and (080) relative values were compared with the spectrometer structure factors obtained by Pace.[6,16] This comparison is shown in Table I.

An average conversion factor is seen to be 16. All of the relative structure factors were multiplied by this number to convert them to absolute values.

Determination of Atomic Positions

As a first step in the determination of atomic positions an approximate structure, of sufficient accuracy to determine the phases of the structure factors, is needed. Such an approximate structure was found by means of a trial and error procedure using the data for reflections of type $(h00)$ and $(0k0)$. In these calculations the positions of the atoms in one molecule were estimated, relative to axes fixed in the molecule, by making use of covalent radii[7] and the known dimensions of the benzene ring[7] and the nitro group.[11] All atoms in the molecule were assumed to be in the same plane. We were assisted in these calculations by the fact that with such a small value for c_0 the plane of the molecule could not be tipped appreciably with respect to the (001) plane. The reflections of type $(h00)$ and $(0k0)$ were relatively insensitive to this tip so it could be neglected in the preliminary calculations. The structure factors were calculated for various positions and orientations of the molecule until satisfactory agreement between calculated and observed F values was obtained. All $(hk0)$ structure factors were then calculated and since the agreement was fair the phases were assigned. In the case of $(hk0)$ structure factors the assignment of phase reduced to deciding whether the factor was positive or negative.

For the purpose of checking the structure and refining parameter values a Fourier projection on the (001) plane was computed from the formula

$$\rho_{xy} = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} F_{(hk0)} \cos 2\pi \left(\frac{hx}{a_0} + \frac{ky}{b_0}\right)$$

The experimental values of $|F_{hk0}|$ were used together with the phases obtained from the approximate structure. A projection was first calculated using only the data from the smaller crystal and the results confirmed the approximate structure in a qualitative way although many of the atoms were unresolved. Additional reflections were then obtained from the larger crystal and a

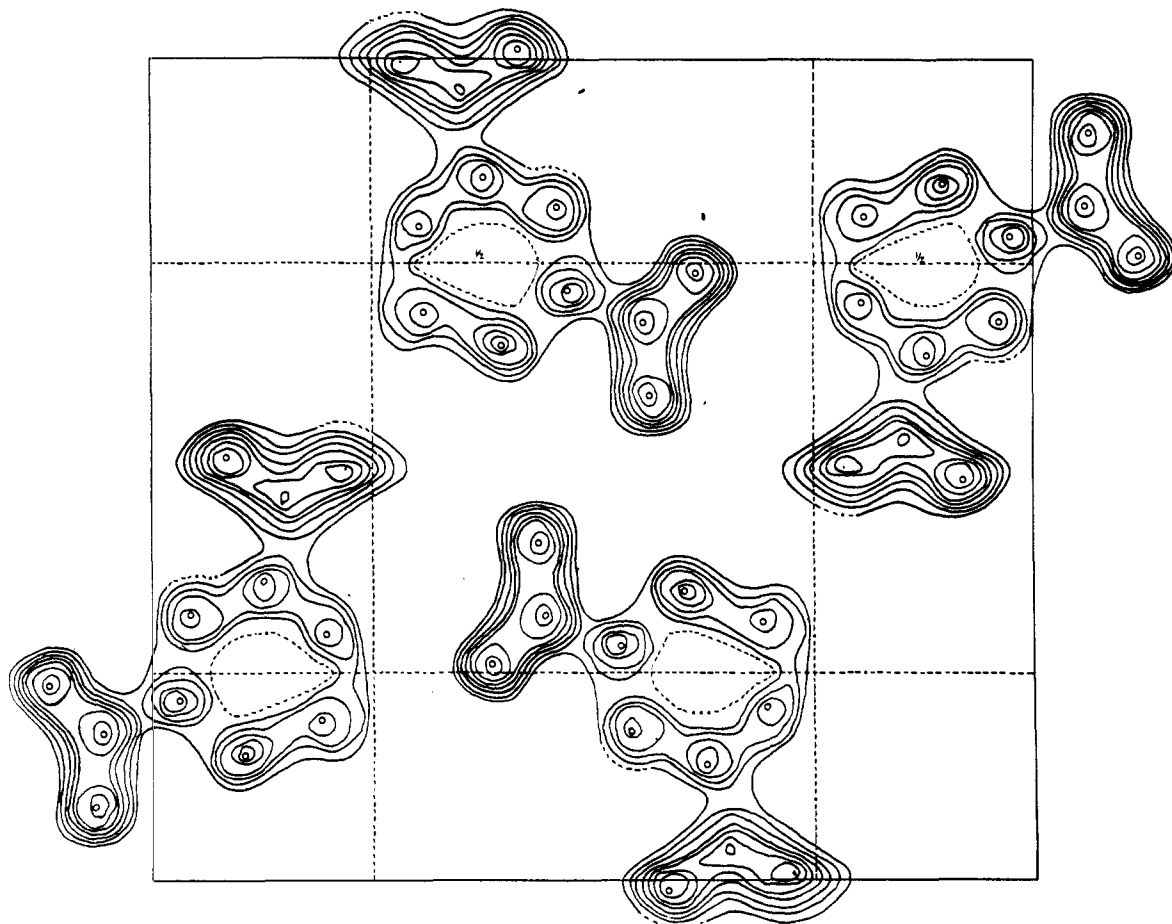(11) Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 (1935).

Fig. 1.—Fourier projection of the structure on the (001) plane, showing positions of the atoms in the molecules assigned to the unit cell. Lines of constant electron density are in arbitrary units. The molecules marked with the number $^1/_2$ are those whose centers lie at z $^1/_2$, while the others lie in the (001) plane.

new projection calculated using the additional data. The contour lines of constant electron density (in arbitrary units) are shown in Fig. 1. It is evident that all of the atoms, except the hydrogens, are resolved. New x and y parameters were estimated from the positions of the maxima. These parameters are listed in the second and third columns of Table IV and the structure factors computed from them in Table II. The numbering of atoms in the molecule is indicated in Fig. 2.
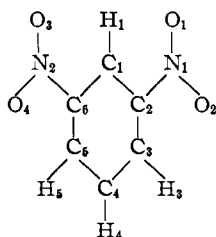

Fig. 2.—Diagram illustrating the numbering system used throughout this investigation to designate various atoms within the molecule.

TABLE I

CONVERSION OF $F_{relative}$ TO $F_{absolute}$

$(hk0)$	F_{rel}	F_{abs} (Pace)	Conversion factor	F_{abs} (Phot)
020	1.97	34.9	17.7	31.5
040	2.64	39.5	15.0	42.3
060	2.75	45.9	16.6	44.0
080	1.83	25.9	14.1	29.3

Av. 15.9

In order to determine the z parameters the reflections on the first layer line (which was the only layer line obtained) were indexed and intensities estimated in the same manner as before. To reduce the intensities to the same scale as that for the zero layer line each was divided by the factor[10]

$$D = \frac{\cos \theta}{\sqrt{\cos^2 \psi - \sin^2 \theta}}$$

where θ is the glancing angle and ψ the angle between the reflecting plane and the axis of rotation. Structure factors were then calculated as before. The results are shown in Table III.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR
(*hk*0) REFLECTIONS

(*hk*0)	sin θ	|F|obs.	Fcalcd.
020	0.109	31.5	33.6
040	.217	42.3	−38.8
060	.325	44.0	−37.5
080	.433	29.3	−28.0
0100	.542	<5	4.1
0120	.656	24.5	−33.6
110	.079	17.5	−15.0
120	.123	35.9	−18.9
130	.173	64.6	48.7
140	.224	55.6	40.8
150	.277	19.9	−11.8
160	.330	26.3	−22.0
170	.384	11.0	− 2.0
180	.437	12.1	−10.3
190	.491	13.2	−19.9
1100	.545	20.0	−13.1
200	.116	22.0	−24.2
210	.128	38.9	28.1
220	.158	35.5	−28.4
230	.200	49.3	40.6
240	.246	16.6	2.0
250	.295	32.1	20.6
260	.345	<4	−18.3
270	.396	25.2	15.6
280	.449	12.3	− 8.3
290	.501	10.3	10.2
2100	.554	6.4	− 9.2
2110	.607	6.8	−16.2
2120	.661	15.8	31.9
310	.182	66.4	−64.8
320	.205	10.6	−12.7
330	.238	36.4	23.3
340	.278	20.0	21.1
350	.322	21.9	9.4
360	.368	67.6	59.2
370	.417	26.1	34.8
380	.467	<4	4.8
390	.518	4.3	− 2.5
3100	.569	9.3	−21.8
400	.231	53.6	54.9
410	.237	7.1	7.4
420	.255	36.0	−25.0
430	.283	20.2	− 8.5
440	.317	<4	1.5
450	.356	27.7	−16.0
460	.399	<5	0.0
470	.444	12.1	3.4
480	.491	10.2	4.2
490	.540	6.3	2.0
4100	.589	8.2	12.7
510	.294	27.7	−16.4
520	.309	47.7	34.9
530	.332	22.3	11.0
540	.361	18.3	20.3
550	.396	<5	− 3.6
560	.435	27.2	−25.2
570	.477	22.3	37.9
580	.521	23.8	−27.0
590	.567	<6	2.8
600	.347	69.0	48.2
610	.351	<4	1.1
620	.363	18.4	−16.5
630	.383	<5	6.6
640	.409	19.9	8.8
650	.440	<5	−12.7
660	.475	28.8	−10.3
670	.514	<6	0.2
680	.555	14.4	−16.2
690	.600	<6	3.1
6120	.737	4.3	− 4.6
710	.408	46.0	−41.5
720	.419	31.0	−36.5
730	.436	12.0	3.4
740	.459	12.5	17.5
750	.487	5.8	6.4
760	.519	4.3	2.1
770	.555	14.4	17.0
780	.593	<6	− 5.3
790	.634	<6	− 5.2
7120	.766	4.4	− 7.4
800	.463	12.6	7.6
810	.466	<5	− 5.4
820	.475	<5	−11.0
830	.490	13.1	−18.8
840	.511	19.1	−21.7
850	.536	<6	−11.7
860	.565	14.6	−22.7
870	.598	21.3	18.7
880	.634	22.0	34.3
890	.672	22.5	32.1
910	.523	<5	0.8
920	.532	<5	− 6.0
930	.545	<5	12.8
940	.564	<6	−13.0
950	.587	<6	− 3.5
960	.614	<6	5.5
970	.644	22.1	30.8
980	.677	10.1	− 6.9
990	.713	8.8	−10.2
1000	.578	20.8	26.8
1010	.581	<6	10.7
1020	.585	<6	− 2.4
1030	.600	21.4	−22.2
1040	.617	34.3	36.1
1050	.638	41.2	−44.0
1060	.663	5.0	− 7.2
1070	.691	16.0	−20.1
1080	.722	16.0(?)	−45.0
1150	.691	5.1	− 4.3
1160	.714	8.8	−14.4
1170	.740	7.1	4.9
1180	.770	7.0	−12.0
1230	.713	4.5	− 1.0

The *z* parameters were estimated by trial and error calculations assuming that all the atoms of the molecule are in the same plane and using the *x* and *y* parameters listed in Table IV. After a number of trials fair agreement was found when the molecule was rotated around its two-fold axis until the normal to the plane of the molecule

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (hkl) REFLECTIONS

(hkl)	Sin θ	|F|obs.	Fcalcd.
002	0.403	5.6	− 3.5
004	.806	<15	−12.6
021	.229	73.5	107.4
041	.296	29.1	22.8
061	.382	22.2	25.3
101	.210	81.4	121.5
111	.217	53.8	53.1
121	.236	53.0	40.9
131	.265	48.2	30.8
141	.301	35.4	19.3
151	.343	17.9	17.2
161	.387	17.4	22.2
211	.238	36.4	50.7
221	.256	32.4	24.7
231	.284	16.6	8.0
241	.318	18.7	10.0
251	.357	9.4	16.1
261	.397	29.1	37.8
301	.266	30.6	27.0
311	.271	39.0	20.1
321	.287	<8	10.8
331	.311	18.3	34.2
341	.343	25.5	19.7
411	.311	9.1	13.4
421	.325	21.0	10.6
431	.347	13.9	32.5
441	.371	26.2	19.0
501	.352	24.4	26.9
511	.356	20.9	38.4
521	.368	<9	9.0
531	.388	24.7	12.8
541	.413	18.4	7.3
621	.415	28.3	30.7
641	.456	16.4	13.6

TABLE IV

FINAL ATOMIC PARAMETERS

Atom	X parameter	Y parameter	Z parameter
C_1	0.317	0.042	0.000
C_2	.360	.123	.074
C_3	.298	.198	.074
C_4	.190	.192	.000
C_5	.152	.104	− .074
C_6	.217	.030	− .074
N_1	.465	.150	.149
N_2	.180	− .058	− .149
O_1	.512	.082	.144
O_2	.496	.217	.211
O_3	.238	− .117	− .144
O_4	.090	− .063	− .211
Center of molecule	.257	.114	.000

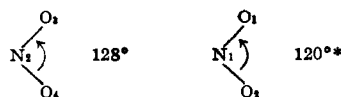These parameters are in units of the cell dimensions.

$$a_0 = 13.3 \text{ Å.} \quad b_0 = 14.2 \text{ Å.} \quad c_0 = 3.82 \text{ Å.}$$

makes an angle of 13.7° with the c axis. Further refinement seems to be impractical without

more data. We were unable to obtain crystals suitable for rotation around the a or b axes. The z parameters obtained are listed in the third column of Table IV and the calculated (hkl) structure factors are listed in Table III.

TABLE V

INTER-ATOMIC DISTANCES, Å.

C_1-C_2 = 1.33	C_2-N_1 = 1.46*	N_1-O_1 = 1.18*	N_2-O_3 1.15
C_2-C_3 = 1.33	C_5-N_2 = 1.39	N_1-O_2 = 1.10*	N_2-O_4 1.22
C_3-C_4 = 1.42			Mean 1.19
C_4-C_5 = 1.38		O_1-O_2 = 1.95*	O_3-O_4 2.13
C_5-C_6 = 1.37			
C_6-C_1 = 1.37			
Mean 1.37			

The agreement between the observed and calculated structure factors listed in Tables II and III is reasonably satisfactory with a few exceptions. The reflections (170), (240) and (260) are in poorest agreement. It has been found that proper adjustment of parameters within the limits of a reasonable error gives better agreement in these cases and it is likely that adjustment of all parameters by means of a least square method such as that of Hughes[12] will improve the agreement. We do not believe, however, that our data are sufficiently accurate to warrant such a treatment. It is also possible that some correction for extinction should be made in the case of the (021) and (101) reflections since these are so intense. We have not made such a correction, however.

Discussion

The accuracy of the parameters in Table IV is estimated as ±0.03 Å. in all cases except N_1 and O_2. In these two cases the error is estimated to be ±0.05. These estimates of error are based partly on the calculation of another Fourier projection on the (001) plane. Five of the small (hk0) structure factors listed in Table II were found to have different signs from those assigned on the basis of the approximate structure. New calculations indicated only slight shifts in the parameters of atoms other than N_1 and O_2. These two atoms, however, were unresolved, which indicated that the limit of refinement by the Fourier method had been reached and showed that the positions of N_1 and O_2 were sensitive to small errors. The positions of the atoms in the other nitro group were but little affected and hence we believe that the dimensions calculated from these parameters are more reliable. In order to test this hypothesis we assumed that the two nitro groups were identical (which seems very probable) and calculated the positions for N_1 and O_2 on this basis (no change in the position of O_1 was required). Using these parameters all (hk0) structure factors were recalculated and were in as
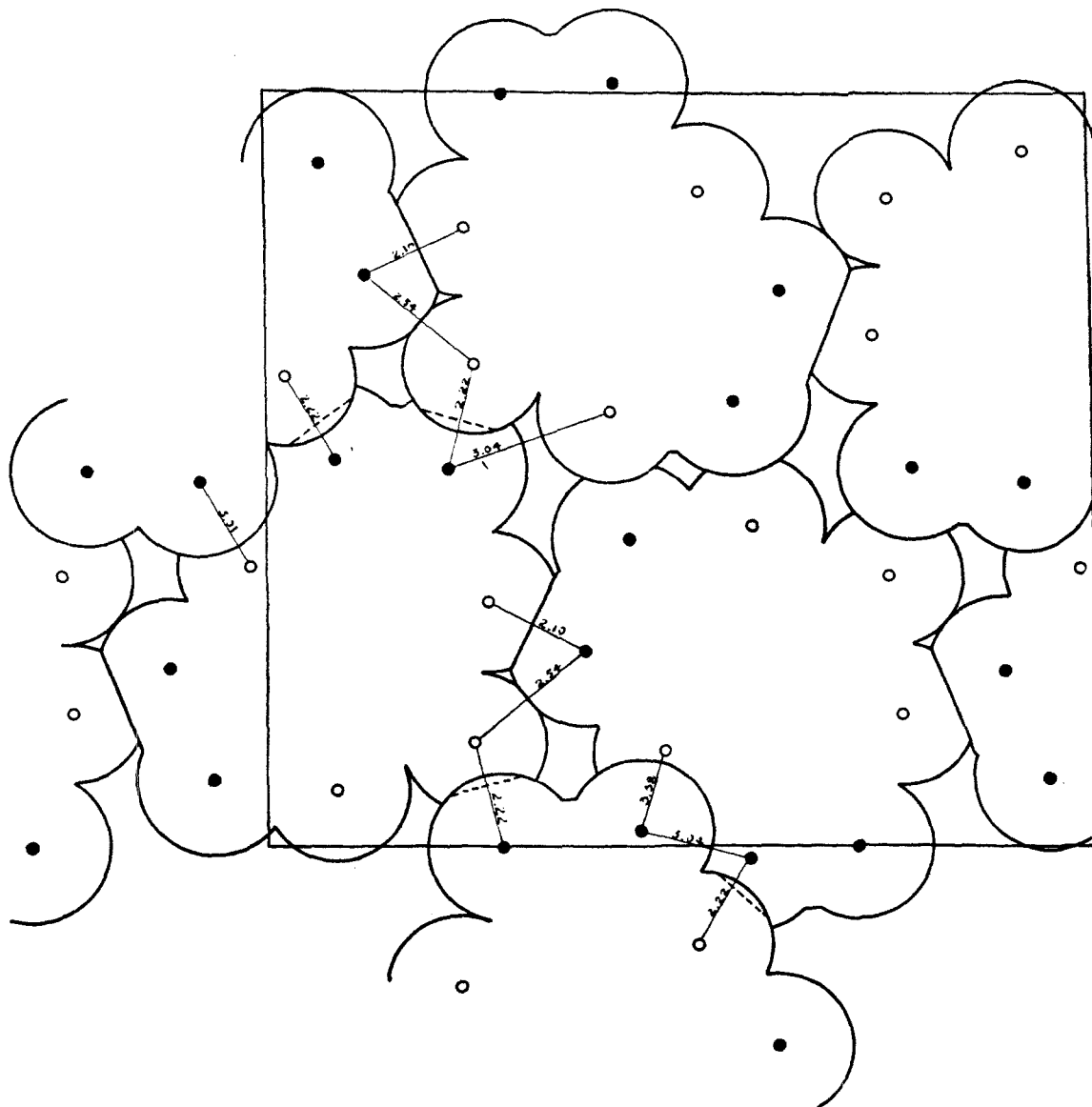
(12) Hughes, THIS JOURNAL, **63**, 1737 (1941).

Fig. 3.—Packing model of the molecules lying in and surrounding the unit cell. Only the oxygen atoms (black circles) and the hydrogen atoms (open circles) in the molecules are shown. Model is projected on the (001) plane and is constructed on the basis of the non-bonded van der Waals radii of the hydrogen and oxygen atoms.

good or slightly better agreement with observation than are those in Table II. Better resolution can be obtained only if higher order reflections are found.

The assigned errors seem, therefore, to be justified. There are in addition errors which arise due to inaccuracy in the intensity data.

From the atomic parameters tabulated in Table IV the interatomic distances within the molecule may be computed. Allowing for the uncertainty in locating the positions of the atoms, the accuracy of the interatomic distances is estimated to be ±0.04 Å. with the exception of those involving N_1 and O_2, whose positions were not determined as accurately. The calculated interatomic dis-

tances are given in Table V. An asterisk indicates less reliable distances involving the coördinates of N_1 or O_2. The average carbon–carbon distance agrees within experimental error with the accepted value of the carbon–carbon distance in the benzene ring. The carbon–nitrogen distance in *m*-dinitrobenzene is 1.39 ± 0.04 Å. units. This interatomic distance corresponds to 18% double bond character for the carbon–nitrogen bond. While it is odd that one nitro group is well resolved and the other is not, the results from the former are sufficient to fix the internal dimensions, as it is extremely unlikely that any difference exists between the two groups. On this basis, the nitrogen–oxygen distances appear to be equal

within experimental error, having an average value of 1.19 ± 0.04 Å., while the oxygen–oxygen distance is 2.13 ± 0.04 Å. This fixes the angle between the two bonds as 128°. It is interesting to compare these dimensions with those reported[11] for nitromethane. The nitrogen–oxygen distance is 1.21 ± 0.02Å., the oxygen–oxygen distance 2.16 ± 0.02Å., and the angle between the bonds 127 ± 3°. From these results it appears that the nitro group in m-dinitrobenzene is very similar to that of nitromethane.

These results may also be compared with those of de Lange, Robertson and Woodward[8] who report the carbon–nitrogen distance in $trans$-azobenzene to be 1.41 ± 0.03Å. and those of Van Niekerk[13] who gives the following values for 4,4'-dinitrodiphenyl (ångströms): C–C = 1.41; C–N = 1.56; N–O = 1.21, N–O = 1.14; O–O = 2.00.

James, King and Horrocks[14] arrive at the following distances in p-dinitrobenzene (ångströms): C–C = 1.39, C–C = 1.41, C–C = 1.32; C–N = 1.53; N–O = 1.25, N–O = 1.10; O–O = 2.14.

Some of these values compare favorably with the results obtained in this determination, while others are not in such good agreement. James, King and Horrocks state that one of the nitrogen–oxygen bonds is longer than the other. Within the limits of experimental error, we find no evidence of such a distortion in m-dinitrobenzene.

The contacts between atoms in different molecules appear to be of two types, first, those between oxygen and hydrogen atoms and, second, those between the benzene nuclei. The oxygen hydrogen distances are shown in Fig. 3. In placing the hydrogen atoms it was assumed that the carbon–hydrogen bond distance is 1.07Å. and the hydrogen lies on the extension of a line connecting opposite carbon atoms. The oxygen and hydrogen atoms have been given their van der Waals radii. No other atoms are shown. The sum of the oxygen and hydrogen van der Waals radii is 2.60Å. It appears that several of these distances have been shortened by as much as 0.5Å. This suggests that hydrogen bonds are formed in these cases and the association of m-dinitrobenzene in benzene solution[2] is to be attributed in part to this fact. The distance along the normal from one benzene ring to another is

found to be 3.70Å. The half thickness of the benzene ring according to Mack[15] is 1.85Å. and twice this value gives 3.70Å. which suggests that the benzene nuclei are in contact in m-dinitrobenzene.

The principal magnetic susceptibilities of m-dinitrobenzene have been determined by Pace,[16] the susceptibilities being $\chi_a = -38.2 \times 10^{-6}$, $\chi_b = -50.1 \times 10^{-6}$, $\chi_c = -99.8 \times 10^{-6}$. Using these and the theory of Lonsdale and Krishnan[17] the molecular susceptibilities are found to be

$$K_1 = -72.0 \times 10^{-6}$$
$$K_2 = -8.8 \times 10^{-6}$$
$$K_3 = -105.2 \times 10^{-6}$$

Here K_3 refers to the direction perpendicular to the plane of the molecule, K_1 along the two-fold axis and K_2 perpendicular to the two-fold axis and in the plane of the molecule. It is interesting that $|K_2|$ is smaller than that for benzene, $i.e.$, 32×10^{-6}.

We have found no additional evidence for the hemihedry of m-dinitrobenzene other than that afforded by the agreement between the intensities calculated from the proposed structure and those observed experimentally. The space group Pbnm can be obtained as a special case of Pbn by properly adjusting the parameters. Such special parameter values did not lead to agreement with experiment and hence are excluded.

Summary

1. The positions of the atoms in m-dinitrobenzene have been determined, the x and y coordinates from an electron density projection and the z coördinates by a trial and error procedure.

2. The atoms in one nitro group were well resolved and the dimensions of the group were found to be very similar to those for the nitro group in nitromethane as reported by Brockway, Beach and Pauling.[11]

3. The crystal structure determination supports the suggestion, by Harris and Pace, that the crystal is hemihedral.

(13) Van Niekerk, $Proc. Roy. Soc.$ (London), **181**, 314 (1943).

(14) James, King and Horrocks, $ibid.$, **153A**, 225 (1936).

(15) Mack, $J. Phys. Chem.$, **41**, 221 (1937).

(16) Pace, Thesis, The Ohio State University, 1943. We are indebted to the author for permission to use these values in advance of publication.

(17) Lonsdale and Krishnan, $Proc. Roy. Soc.$ (London), **A156**, 597 (1936).