

2. Previous theories of the glass electrode are critically reviewed.
3. A differential thermodynamic equation for the glass electrode in terms of activities and transference numbers is given.
4. A new equation for the glass electrode is discovered and shown to agree with the data up to a  $P_H$  of 12. A similar equation may be theoretically derived for uniunivalent salts from the Henderson and Planck liquid junction equations if one allows the relative mobility of the positive ions to be a function of the hydrogen-ion activity.
5. The idea is expressed that the electric double layer at the glass aqueous solution interface determines the selective mobility of the ions across the boundary.

EVANSTON, ILLINOIS

---

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN DIVISION OF THE BUREAU OF CHEMISTRY AND SOILS]

**THE MOLECULAR ASSOCIATION, THE APPARENT SYMMETRY OF THE BENZENE RING, AND THE STRUCTURE OF THE NITRO GROUP IN CRYSTALLINE META-DINITROBENZENE. THE VALENCES OF NITROGEN IN SOME ORGANIC COMPOUNDS**

BY STERLING B. HENDRICKS AND GUIDO E. HILBERT

RECEIVED JULY 2, 1931

PUBLISHED DECEMBER 10, 1931

### Introduction

E. Hertel<sup>1</sup> has recently obtained x-ray diffraction data leading to space group determinations from crystals of ortho, meta and para dinitrobenzene. An unfortunate error in the analysis of the data from *m*-dinitrobenzene, however, resulted in an incorrect determination of the atomic positions relative to a plane of symmetry. The simple results obtained from a re-examination of this compound have far-reaching significance.

**The Structure of the Crystal and the Positions of the Hydrogen Atoms.**—*m*-Dinitrobenzene, in agreement with the analysis of Hertel, has an atomic arrangement derivable from space group  $Pbnm$  ( $V_h^{16}$ ). On the average the carbon and nitrogen atoms of a molecule must be in the same plane perpendicular to the  $c$  axis. The oxygen atoms are about 0.96 Å. from this plane as a plane of symmetry.

It is probable that the hydrogen atoms of *m*-dinitrobenzene occupy fixed positions coplanar with the nitrogen and carbon atoms. Earlier results of crystal structure analyses of some ammonium salts led to the belief that the hydrogen atoms in a crystal need not conform to the symmetry requirements of the crystal.<sup>2</sup> These results, and the apparently high symmetries

<sup>1</sup> E. Hertel, *Z. physik. Chem.*, **B7**, 188 (1930).

<sup>2</sup> R. W. G. Wyckoff, *Am. J. Sci.*, **5**, 209 (1923).

at room temperatures of the water molecule in certain hydrates and the ammonia molecule in some ammonium groups, can best be explained by molecular rotation in the solid state.<sup>3</sup> The analyses of the crystal structures of urea and hexamethylenetetramine, moreover, indicate that the hydrogen atoms occupy positions required by the crystal symmetries. The x-ray reflection data from *m*-dinitrobenzene clearly show that neither the rotation of the molecule nor of the nitro groups are excited at room temperatures.

**The Symmetry of the Benzene Ring and the Valence Directions of the Aromatic Carbon Atom.**—The crystal structure requirement that the carbon, nitrogen and hydrogen atoms of a *m*-dinitrobenzene molecule be coplanar supports the concept of a plane benzene ring. An *approximately* plane configuration is also indicated by the crystal structures of hexamethylbenzene<sup>4,5</sup> and naphthalene,<sup>6</sup> the only other aromatic compounds upon which trustworthy observations have been made.

The impossibility of predicting such a configuration from chemical evidence alone has resulted in the persistence of the concept of the tetrahedral carbon atom in aromatic compounds, a concept that has been signally unfruitful.<sup>7</sup> The oscillating "puckered" ring structures for benzene discussed at great length in the past and one more recently by Huggins<sup>8</sup> are in direct conflict with the results of crystal structure determinations.

Failure in realizing that only the minimum molecular symmetry is fixed by the crystal symmetry has resulted in many probably incorrect deductions from crystal structure determinations.<sup>9</sup> The explanation proposed by Bergmann and Mark<sup>10</sup> for the possible isomerism<sup>11</sup> of some derivatives of fluorene prepared by W. Schlenk and E. Bergmann<sup>12</sup> is based upon an assumed "gewellte" benzene ring that incorrectly was said to be required by molecular symmetries of compounds such as hexamethylbenzene. The possible existence of geometrical isomers of fluorene and of optical isomers

<sup>3</sup> L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

<sup>4</sup> K. Lonsdale, *Proc. Roy. Soc. (London)*, **A123**, 494 (1929).

<sup>5</sup> The gradual transition of hexamethylbenzene at about 151°K. [H. M. Huffman, G. S. Parks, and A. C. Daniels, *THIS JOURNAL*, **52**, 154 (1930)] is best to be explained by rotation of the methyl groups, the hydrogen atoms not occupying fixed positions.

<sup>6</sup> K. Banerjee, *Nature*, **125**, 456 (1930); *Indian J. Phys.*, **4**, 557 (1930).

<sup>7</sup> Note for instance, A. W. Stewart, "Stereochemistry," London, 1907, pp. 502 *et seq.*

<sup>8</sup> M. L. Huggins, *THIS JOURNAL*, **53**, 1182 (1931).

<sup>9</sup> Note for instance G. L. Clark and L. W. Pickett, *ibid.*, **53**, 175 (1931).

<sup>10</sup> E. Bergmann and H. Mark, *Ber.*, **62**, 750 (1929).

<sup>11</sup> The isomerism of fluorene derivatives has not yet been accurately proven. Neither the structures of these products were determined, nor was evidence given excluding polymorphism. It has recently been shown that many of the "isomers" are structurally different compounds; see Kliegl and co-workers, *Ber.*, **62**, 1327 (1929); **63**, 1262, 1631 (1930); and Pfeiffer and Lübke, *ibid.*, **63**, 762 (1930).

<sup>12</sup> W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

of diphenyl derivatives is not incompatible with the presence of plane benzene rings. It is not necessary for two or more benzene rings of a molecule to be coplanar.

In *m*-dinitrobenzene, hexamethylbenzene and naphthalene, the centers of the atoms adjacent to the benzene ring are coplanar with it. The failure of all attempts to form meta or para rings of benzene compounds<sup>13</sup> indicates that these valences are not easily deformed in direction and that the benzene ring is very rigid.

**The Atomic Arrangement and Molecular Association of Crystalline *m*-Dinitrobenzene.**—The arrangement along the *c* axis of the nitro groups of several molecules of *m*-dinitrobenzene is shown in Fig. 1.

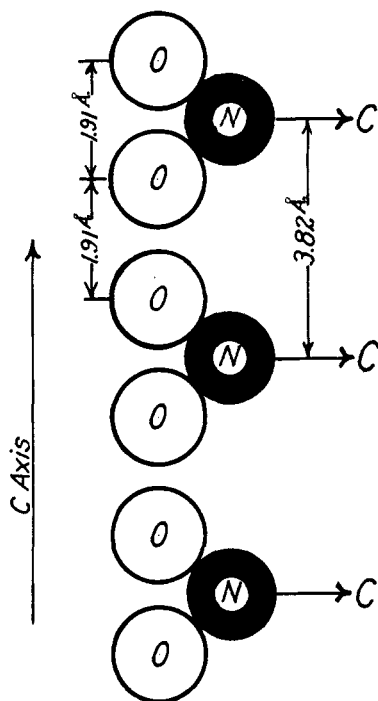


Fig. 1.—Arrangement of the nitro groups of *m*-dinitrobenzene along the *c* axis.

The distance between the oxygen atoms of a nitro group is about 1.91 Å., which is somewhat smaller than the corresponding value 2.20 Å. for the oxygen atoms of a nitrate ion in sodium nitrate. The distance of closest approach between oxygen atoms of separate molecules also is about 1.91 Å. This value is markedly smaller than the comparable distance in some other molecular compounds such as urea (N—O, 3.15 Å.), hexamethylenetetramine (N—C, 3.72 Å.) and carbon dioxide (O—O, 3.23 Å.).

*m*-Dinitrobenzene is associated in its benzene solutions from which crystals were obtained. The close distance of approach between groups of separate molecules is probably indicative of association in the solid, the associated groups being limited only by the boundaries of the perfect crystals. This concept is supported by the lack of cleavage parallel to (001), *i. e.*, parallel to the plane of the benzene rings (compare hexamethylbenzene).

The crystals show characteristic elongation normal to (001).

In crystalline *m*-dinitrobenzene the two oxygen atoms of a nitro group are crystallographically equivalent. This requires them to be equidistant from the nitrogen atoms and to occupy geometrically equivalent positions relative to the molecule as a whole. This indicates similarity in the type of binding between the oxygen and nitrogen atoms of a nitro group.

<sup>13</sup> Titley, *J. Chem. Soc.*, 2571 (1930).

**The Valences of Nitrogen. Ammonium and Inner Ammonium Compounds.**—Heitler's and London's<sup>14</sup> extension and more quantitative formulation of the Lewis valence theory supports the concept of a maximum valence of three for a *free nitrogen atom*. Since the valence shell of nitrogen is an L shell it is impossible for more than three electrons to have unpaired spins. This is in agreement with the term multiplicity of the nitrogen arc spectra and a valence of one or three for the atom. It does not, however, prevent the five valence electrons of a nitrogen atom from having parallel spins, *in a compound of nitrogen*.<sup>15</sup>

Both Lewis and Langmuir and later London in agreement adduced evidence against the quinquevalence of nitrogen in ammonium compounds in the solid state and in solution. The formation of an ammonium ion, which results in the loss of an electron by the nitrogen atom of the group, might be expected on account of the high electron affinity of acid radicals. It also seems to occur in a number of compounds such as  $(C_6H_5)_3C(N(CH_3)_4)$  and  $C_6H_5CH_2(N(CH_3)_4)$  prepared by Schlenk and Holtz.<sup>16</sup> These compounds form conducting solutions in pyridine and in general have salt-like characteristics. The difficulty of obtaining molecular  $NH_4Cl$  is indicated by the great dissociation of gaseous  $NH_4Cl$  into  $HCl$  and  $NH_3$ .<sup>17</sup> This is also true for hypothetical  $NCl_5$  which is dissociated into  $NCl_3$  and  $Cl_2$ . In most, if not all, such cases the nitrogen atom instead of sharing five homopolar bonds, loses one electron, which results in a configuration similar to that of an excited carbon atom,  $2s\ 2p^3\ ^5S$ , and shares four homopolar bonds with other groups.

Lewis believed that the properties of the amine oxides justified the formula,  $R_3N^+ - O^-$ , corresponding to an inner ammonium salt, the nitrogen having a valence of four. The ready formation of addition compounds such as  $(CH_3)_3NO \cdot C_6H_5NH_2$ ,  $(CH_3)_3NO \cdot 2C_6H_5OH$ , and  $(CH_3)_3NO \cdot C_6H_5OH \cdot C_6H_5NH_2$  clearly indicates that there is a large separation of charge in the amine oxide molecule. Two other striking properties of trimethylamine oxide are that it melts with decomposition above  $200^\circ$  and is insoluble in non-polar solvents. These properties, together with its easy conversion into a true ammonium compound both with methyl iodide and water, characterize this type of binding.

**The Existence of Some Aldehydes, Ketones and Nitrogen Compounds as Free Radicals.**—It is known that nitrosobenzene exists in the solid state as a colorless polymer, probably a dimer, of  $C_6H_5NO$  and in solution and in the melt as a green monomer. It has been suggested, on a chemical

<sup>14</sup> Heitler and London, *Z. physik*, **44**, 455 (1927); London, *ibid.*, **46**, 455 (1928); **50**, 24 (1928).

<sup>15</sup> Compare L. Pauling, *Proc. Nat. Acad. Sci.*, **14**, 361 (1928).

<sup>16</sup> Schlenk and Holtz, *Ber.*, **49**, 603 (1916).

<sup>17</sup> Rodebush and Michalek, *Proc. Nat. Acad. Sci.*, **14**, 131 (1928).

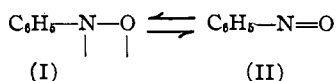
basis only,<sup>18</sup> that this behavior and many of the chemical properties of the monomer are similar to those of a free radical.

Pascal<sup>19</sup> from measurements of diamagnetic susceptibilities of some compounds having nitroso, keto or aldehydo groups calculated that the oxygen atoms of these groups were paramagnetic, with a susceptibility of  $1.8 \times 10^{-6}$ . Molecular oxygen, a free radical as shown by the term multiplicity of its electronic levels, is known to be paramagnetic, with a susceptibility of *ca.*  $2 \times 10^{-3}$ . An appreciable magnetic moment in a system is, at the present time, supposed to arise from unpaired electronic spins.

If it is true that some nitroso, keto and aldehydo groups are in part paramagnetic, as indicated by Pascal's measurements, then they must have formulas of the types

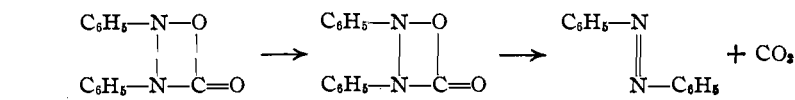


Such molecular species, however, should probably be decidedly paramagnetic rather than diamagnetic with slightly paramagnetic parts. Taylor's measurements of the molal magnetic susceptibility of  $\alpha$ -naphthylidiphenylmethyl<sup>20</sup> in 7% benzene solution, in which it is about one-third dissociated into the free radical, gave a value  $-50 \times 10^{-6}$ . He calculated that the paramagnetic correction for a mole of the free radical would be about  $570 \times 10^{-6}$ . It is thus probable that Pascal's measurements were made upon systems such as



in which the concentration of (I) was of the order of 1% or less.

The similarities in the structures of nitroso compounds and ketones is illustrated by their strikingly analogous chemical behaviors. We wish to emphasize only their reactions with phenyl isocyanate, with which they add to form ring compounds that usually, being unstable under the conditions of the experiment, break down forming acyclic products. This is exemplified by the following reaction between nitrosobenzene and phenyl isocyanate, and *p*-dimethylaminobenzaldehyde and phenyl isocyanate.<sup>21</sup>

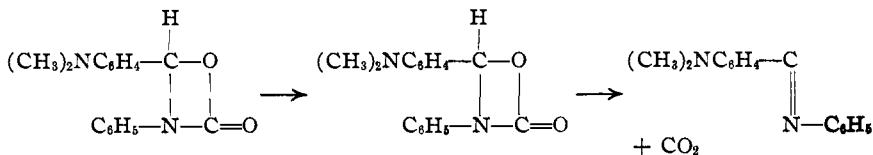


<sup>18</sup> Walden, "Chemie der Freien Radikale," Leipzig, 1924, p. 235; Goldschmidt and Christman, *Ann.*, **442**, 248 (1925); Gattermann-Wieland, "Die Praxis des organischen Chemikers," 1927, p. 161.

<sup>19</sup> Pascal, *Bull. soc. chim.*, [4] **9**, 6, 79, 134, 177, 336 (1911).

<sup>20</sup> Taylor, *THIS JOURNAL*, **48**, 854 (1926).

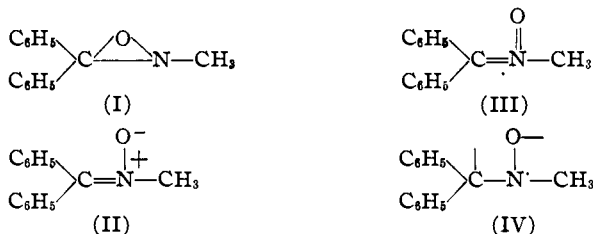
<sup>21</sup> Staudinger and Endle, *Ber.*, **50**, 1042 (1917).



It is not surprising that free radicals of this type are more inert chemically than triphenylmethyl, since they are probably analogous in their chemical behavior to normal oxygen, which is the free radical  $\begin{array}{c} \text{O} \\ | \\ \text{O} \end{array}$ .

It is possible that the existence of such free radicals is to be explained as arising from the geometrical constraints afforded by the fixed valence directions of nitrogen, oxygen and carbon, and the requirement of a certain distance of approach between such atoms sharing two or more homopolar bonds.

**The Valence of Nitrogen in Some Nitrones, Nitrenes, Azoxy and Nitro Compounds.**—There are four possible formulas for nitrones



The work of Semper and Lichtenstadt<sup>22</sup> eliminated the possibility (I) of a ringed structure. (II) is not compatible with the properties of a nitron. Methyl diphenyl methylene nitron has a low melting point for a molecule of its complexity, melting at 103° without decomposition. It is also quite soluble in such a non-polar solvent as ligroin. Moreover, on treatment with methyl iodide it does not react in a manner similar to trimethylamine oxide.

The nitrones readily combine with phenyl isocyanate and ketenes<sup>23</sup> forming cyclic compounds. Thus structure (IV) in which nitrogen is trivalent explains best the properties of the nitrones. However, the determinations of the magnetic susceptibility of the grouping in question is required to fix this more definitely. This discussion applies equally well to the nitrenes and azoxy compounds<sup>24</sup> which are closely analogous to the nitrones.

<sup>22</sup> Semper and Lichtenstadt, *Ber.*, **51**, 928 (1918).

<sup>23</sup> Staudinger and Miescher, *Helv. Chim. Acta*, **2**, 554 (1919).

<sup>24</sup> The recent work of Bachmann [THIS JOURNAL, **53**, 1524 (1931)] on the reduction of azobenzene, azoxybenzene and nitrosobenzene by the system magnesium and magnesium iodide in which the active reducing agent is magnesium subiodide, an inorganic free radical, would seem to be evidence for the above structures postulated for azoxybenzene and nitrosobenzene. It also seems possible that azo and diazo compounds, isocyanates, ketenes, azides and unsaturated systems such as the fulvenes and certain compounds containing coordinated double bonds have electrons with unpaired spins.

An inner ammonium salt structure for nitro compounds has been suggested by Sidgwick.<sup>25</sup> He supported his point of view by considerations of the "parachor" values of Sugden for various compounds of nitrogen.<sup>26</sup> These arguments are now known to be insufficient, since similar results were obtained for some compounds of quinquevalent phosphorus. Phosphorus, unlike nitrogen, since the valence shell is an *M* shell, in one state shows six-fold multiplicity of its term values. It can thus have a valence of five, which is supported by the observed low or zero dipole moment of  $\text{PCl}_5$ .<sup>27</sup>

The properties of nitro compounds are not similar to those of the amine oxides. They have low melting points, high solubility in non-polar solvents, and are inert toward methyl iodide. The observed equivalence of the oxygen atoms of a nitro group in *m*-dinitrobenzene could not readily be explained if the compound is an inner ammonium one. With the exception of their behavior toward reducing agents, nitro groups are relatively inert. They do not react, as one might expect on the basis of a formula similar to (IV), with phenyl isocyanates or ketenes. The nitro group is known to be diamagnetic. The structure of *m*-dinitrobenzene does not

permit of ring formulas. A formula for the nitro group such as  $-\text{R}-\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$  has usually been considered impossible on account of the "strain in the three-membered ring." This concept has been given a secure footing by the recent studies of directed valence.<sup>28</sup>

It is thus probable that nitrogen is quinquevalent in organic nitro compounds. The high dielectric constant of nitro compounds and their ready formation of addition compounds is indicative of some separation of charge in the nitro group. With one possible exception the nitrogen atoms in all compounds of quinquevalent nitrogen are joined to at least two oxygen atoms. Exemplars of these various types of compounds are  $\text{CH}_3\text{NO}_2$ ,  $\text{C}_6\text{H}_5\text{NO}_2$ ,  $\text{C}_6\text{H}_5\text{NHNO}_2$ ,  $\text{CH}_3\text{ONO}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$  and the free radical  $-\text{NO}_2$ . The free radical  $-\text{NOCl}_2$  is the exception mentioned. It is possible, however, that this is a compound of trivalent nitrogen.

### Experimental

**X-Ray Data. Crystallographic Description.**<sup>29</sup>—Rhombic bipyramidal

$$a:b:c = 0.9435:1:0.5434 \text{ (from many different forms)}$$

<sup>25</sup> Sidgwick, "The Electronic Theory of Valence," London, 1928.

<sup>26</sup> We are deeply indebted to Professor Sidgwick for a discussion concerning this portion of our paper. He suggested that the observed equivalence of the oxygen atoms of a nitro group in *m*-dinitrobenzene might be explained by oscillation of the two types of binding from one to the other oxygen atom.

<sup>27</sup> J. H. Simons and G. Jessop, *THIS JOURNAL*, **53**, 1263 (1931).

<sup>28</sup> J. C. Slater, *Phys. Rev.*, **37**, 481 (1931); L. Pauling, *THIS JOURNAL*, **53**, 1367 (1931).


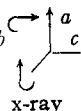
<sup>29</sup> Steinmetz, *Z. Krist.*, **54**, 467 (1915).





TABLE III

ESTIMATED INTENSITIES OF REFLECTIONS FOR SOME PLANES OF *m*-DINITROBENZENE.  
30° OSCILLATION FROM INDICATED POSITIONS

(1)		MoK radiation, x-ray beam normal to photographic plate. (0 <i>kl</i> ) with <i>k</i> odd required to be absent					
	I	II	III	IV	V	VI	VII
	(001)a.	(011)a.	(021)v.s.	(031)a.	(041)m.	(051)a.	(061)m.
	(101)s.	(111)m.	(121)s.	(131)s.	(141)a.	(151)w.	(161)m.w.
	(002)v.w.	(010)a.	(022)s.	(032)a.	(042)m.s.	(052)a.	(062)v.w.
		(112)v.w.		(132)v.w.		(152)m.w.	
	(202)v.w.	(212)v.w.	(222)v.w.	(232)v.w.			
(2)		CuK radiation, x-ray beam normal to photographic plate (0 <i>kl</i> ) with ( <i>k</i> ) odd } required to be absent ( <i>h</i> 0 <i>l</i> ) with ( <i>h</i> + <i>l</i> ) odd }					
	(001)a.	(101)v.s.	(201)a.	(301)m.			
	(011)a.	(111)m.s.	(211)m.s.	(311)s.			
	(021)v.s.	(121)v.s.	(221)s.	(321)m.	(421)m.s.	(521)w.	
	(031)a.	(131)v.s.	(231)m.	(331)m.w.	(431)w.	(531)m.	
	(002)a.	(102)a.					
	(012)a.	(112)v.w.					
	(022)m.s.	(122)m.	(222)w.	(322)m.			
	(032)a.	(132)a.	(232)w.				
	(042)m.w.	(142)m.	(242)v.w.	(342)m.			

of the type (0*kl*) with *k* odd and (*h*0*l*) with (*h*+*l*) odd were observed to be absent in odd orders. The rhombic holohedral space groups *Pmmm*, *Pmma*, *Pmnm* and *Pbnm* could possibly account for the above absences of reflections. These reflections are systematically required to be absent only by space group *Pbnm*.

The hemihedral sub-group *Pna* requires the above classes of planes to be absent. The extensive crystallographic measurements, however, give no indication of a possible hemihedral character. Lath-shaped crystals elongated parallel to *c* gave no evident separation of charge upon cooling in liquid air. It would seem to be very improbable that the crystals are isomorphous with a point group of lower than holohedral symmetry.

**Molecular Symmetry.**—If the space group is *Pbnm* ( $V_h^{16}$ ) then each molecule is required to have at least a center of symmetry or a plane of symmetry. The former is precluded by the formula of *m*-dinitrobenzene. The required plane of symmetry of the molecule must be perpendicular to the *c* axis. There are two possible positions for this plane compatible with the formula of the compound (considered as 2,6-dinitrobenzene). The carbon atoms 1 and 4 can be in the plane of symmetry with 2 and 6, and 3 and 5 spaced equally on each side of it. The value of  $d_{(001)}$ , however, is but 3.82 Å., a distance far too small to permit of any such arrangement.

In the alternative case the carbon, nitrogen and hydrogen atoms are required to be in the plane of symmetry. The oxygen atoms of a molecule might either be in the same plane as the other atoms or equally spaced on each side of it. The former arrangement would require all of the atoms in the crystal to scatter in phase for the second order reflection from (001), which would make this reflection a very intense one. Experimentally, it is observed to be absent or present with a very low intensity. The low intensity of (002) can, however, be explained by the second of the above arrangements. If the oxygen atoms are  $1/4 c_0$  from the plane of the benzene ring, then the intensity of (002) would be proportional to  $(2F_O - F_N - 3F_C)^2$  where  $F_O$ ,  $F_N$  and  $F_C$  are the  $F$  values for oxygen, nitrogen and carbon, respectively, for a value of  $\sin \theta/\lambda$ , equal to 0.262. A low value for this factor is in accord with the very approximately known  $F$  values for atoms of low atomic number. If the oxygen atoms should be appreciably less than a distance  $1/4 C_0$  from the plane of the benzene ring, the calculated intensity of (002) would be greater than the observed.

The atomic positions are

$$\begin{array}{l} \text{Oxygen at } xyz; \bar{x}, \bar{y}, z + \frac{1}{2}; \bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}; x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} \\ \bar{x}\bar{y}\bar{z}; x, y, \bar{z} + \frac{1}{2}; x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}; \bar{x} + \frac{1}{2}, y + \frac{1}{2}, z \end{array}$$

with  $z$  approximately equal to 0 or  $1/2$ . Carbon, nitrogen and hydrogen at

$$uw\frac{1}{2}; \bar{u}\bar{v}\frac{3}{2}; \bar{u} + \frac{1}{2}, v + \frac{1}{2}, \frac{1}{2}; u + \frac{1}{2}, \bar{v} + \frac{1}{2}, \frac{3}{2}$$

There are 20 parameters defining the arrangement of the carbon, nitrogen and oxygen atoms in the  $a$  and  $b$  directions. It is not necessary that the positions of the molecules should have any simple relationships to these directions.

It is very probable that absolute intensity measurements would permit a complete structure determination. By assuming a structure of the *m*-dinitrobenzene molecule only three parameters, defining the positions of the molecules in the unit of structure, remain to be determined.

**Chemical Experiments.**—The inner ammonium salt structure of trimethylamine oxide indicates a separation of charge in the system and suggests that it should readily form addition compounds with many organic substances. Trimethylamine oxide is soluble in benzene, about one gram in 500 cc. at  $78^\circ$ , from which it separates with benzene of crystallization (m. p.  $70^\circ$ ). It forms addition compounds with both the weakly acidic substance phenol and the mildly basic substance aniline.

**The Addition Compound  $(\text{CH}_3)_3\text{NO} \cdot 2\text{C}_6\text{H}_5\text{OH}$ .**—One mole of anhydrous trimethylamine oxide was heated with two moles of phenol until there was complete solution. On cooling it solidified to a mass of long thin colorless plates melting at  $105.4^\circ$ . The melting point was lowered by the further addition of either phenol or trimethylamine oxide. The addition compound was extremely soluble in benzene. On treatment with water it immediately broke up, forming trimethylamine oxide dihydrate and phenol.

**The Addition Compound between Trimethylamine Oxide and Aniline.**—Upon heating one mole of aniline with one mole of trimethylamine oxide, an addition compound is formed (m. p. 78°). Treatment of one mole of trimethylamine oxide with two moles of aniline resulted in the formation of a compound melting at 51.4°. The addition of either trimethylamine oxide or aniline to the above compounds lowered their melting points. They were soluble in boiling benzene, from which they separated in long thin plates melting at 45–46°. This product dissociated easily into its components. The analysis agreed best with the formula  $(\text{CH}_3)_3\text{NO} \cdot \frac{1}{2}\text{C}_6\text{H}_5\text{NH}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ .

**The Addition Compound  $(\text{CH}_3)_3\text{NO} \cdot \text{C}_6\text{H}_5\text{NH}_2 \cdot \text{C}_6\text{H}_5\text{OH}$ .**—To 100 cc. of dry benzene were added 2.3 g. of anhydrous trimethylamine oxide, 2.9 cc. of aniline (freshly distilled from zinc dust), and 3.0 g. of phenol. The mixture was heated on a steam-bath until solution was complete; 90 cc. of benzene was then removed by distillation. Diamond-shaped plates separated upon cooling—yield, 6.3 g., m. p. 71° after recrystallization from benzene. This addition compound gave a carbylamine reaction and was dissociated by water from which phenol and trimethylamine oxide dihydrate were isolated and identified.

*Anal.* N, 10.68, 10.55. Calcd. for  $\text{C}_{15}\text{H}_{22}\text{O}_2\text{N}_2$ ; N, 10.68.

### Summary

The space group,  $Pbnm$  ( $V_h^{16}$ ) and the unit of structure of *m*-dinitrobenzene,  $a = 13.27 \text{ \AA}$ .,  $b = 14.06 \text{ \AA}$ .,  $c = 3.820 \text{ \AA}$ ., were determined from monochromatic x-ray diffraction photographs. The unit of structure contains four molecules. The minimum molecular symmetry is a plane of symmetry which contains the nitrogen, carbon and hydrogen atoms of a molecule. The compound is associated along the *c* axis.

The observed crystallographic equivalence of the oxygen atoms of a nitro group is indicative of quinquevalent nitrogen. Nitrogen is probably quinquevalent in a number of compounds in which it is joined to at least two oxygen atoms. Nitrogen is probably trivalent in the nitrones, nitrenes, azoxy and nitroso compounds, which are free radicals chemically similar to some aldehydes and ketones. Evidence is given in support of the inner ammonium salt structure of trimethylamine oxide.

WASHINGTON, D. C.