adding this compound to a refluxing mixture of 0.5 g. of 5% palladinized charcoal in 25 ml. of *p*-cymene. After refluxing two hours, as much *p*-cymene as possible was removed by distillation. A small amount of benzene (30 ml.) was added to the residue, the mixture was filtered, and the volume of solution reduced to about 15 ml. Approximately twice this volume of alcohol was added and the desired 1-(2-xenyl)-3-(4-xenyl)-benzene crystallized on cooling. The compound was recrystallized twice from a solution of alcohol and benzene. Analytical and physical data are given in Table II.

Preparation of 3-Tolyl-Δ^2-cyclohexenone.—An ethereal solution of the monoethyl ether of dihydroresorcinol was added to an ethereal solution containing an excess of the appropriate tolylmagnesium bromide. The Grignard addition complex was decomposed in the usual manner with dilute sulfuric acid and the whole subjected to steam distillation in order to remove unreacted bromotoluene and any Wurtz reaction product. Actually some loss by steam distillation of the ketone occurs in this step. The residue in the steam pot was extracted with ether, washed with water and dried over magnesium sulfate. After removal of the ether the residue was distilled under reduced pressure.

The *p*-tolyl-Δ^2-cyclohexenone is a solid and need not be distilled but may be easily crystallized from the ether solution after concentration. White crystals result on recrystallization from petroleum ether (30–60°). The analytical and physical data for the 3-tolyl-Δ^2-cyclohexenones are collected in Table III.

The 2,4-dinitrophenylhydrazones (red) of these ketones were prepared in the usual manner. See Table III for analytical and physical data.

Preparation of the Dimethylbiphenyls.—An ethereal solution of the 3-tolyl-Δ^2-cyclohexenone was added to an excess of methylmagnesium bromide in ether. The Grignard complex solution was hydrolyzed with dilute sulfuric acid. The ether layer was washed with water and dried over magnesium sulfate. After removal of the ether, the residue was distilled under reduced pressure.

cyclohexadiene-1,3	Yield, %	B. p. °C.	Mm.	$n^{25}\mathrm{D}$
1-(*o*-Tolyl)-3-methyl-	83.3	85	0.06	1.5661
1-(*m*-Tolyl)-3-methyl-	87.2	100–101	.5	1.5885
1-(*p*-Tolyl)-3-methyl-	88.9	115–116	.2	1.5900

Aromatization to the dimethylbiphenyls was accomplished by refluxing the 1-tolyl-3-methylcyclohexadienes with palladium charcoal (5%) for three hours in the absence of a solvent. The aromatized product was distilled directly from the palladium–charcoal residue.

The dienes tend to polymerize; therefore, it is advantageous to aromatize as quickly as possible. It is interesting to note that these dienes and their aromatized products possess a very pleasing odor, especially *p*-tolyl-methylcyclohexadiene-1,3 and 3,4-dimethylbiphenyl. See Table IV for the analytical and physical data pertaining to the dimethylbiphenyls.

Preparation of the Dicarboxybiphenyls.—The dimethylbiphenyl was refluxed with 2% alkaline potassium permanganate solution. Mechanical stirring was used. The manganese dioxide sludge was removed by filtration, the filtrate heated to nearly boiling, and then acidified with sulfuric acid. On cooling crystalline dicarboxybiphenyl was obtained which was recrystallized from glacial acetic acid. For analytical and physical data, see Table V.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined using a Beckman spectrophotometer. The solvent used was cyclohexane purified by successive extensive treatments with chlorosulfonic acid, concentrated sulfuric acid, alkaline permanganate solution, and final distillation from sodium.

Summary

1. 3-Phenyl-1-(2-xenyl)-benzene, 3-(4-xenyl)-1-(2-xenyl)-benzene, 3-(3-xenyl)-1-(2-xenyl)-benzene and 1,3-di-(2-xenyl)-benzene have been prepared.

2. The ultraviolet absorption spectra of a series of *m*-diaryl benzenes have been determined.

3. The 3,2′-, 3,3′- and 3,4′-dimethylbiphenyls and dicarboxybiphenyls have been synthesized from the monethyl ether of dihydroresorcinol. The ultraviolet absorption spectra of the above dimethylbiphenyls have been determined.

4. The theoretical significance of the ultraviolet absorption spectrum in relation to molecular structure is discussed.

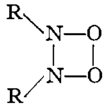
COLLEGE PARK, MARYLAND RECEIVED JUNE 18, 1949

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Crystal Structure of Dimeric Tribromonitrosobenzene

BY CHARLES P. FENIMORE

The problem of the structure of the C-nitroso dimers has not been completely solved. The presence of an N–N bond in the molecule is indicated because the N–N group occurs among the reduction products of one of the dimeric nitroso compounds (dimeric methyl-α-nitroso isopropyl ketone).[1] With this restriction, the only formulation of the molecule is[2]



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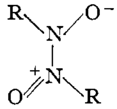
or



II

and other resonance forms. It has been found that some nitroso dimers possess a permanent dipole moment in solution[3] and this observation has been offered as evidence against II under the assumption that II should be centro-symmetric; but since bulky R groups might forbid a center of symmetry in II, this evidence is inconclusive.

The principal cause of failure of a sure discrimination between these structures by classical chemical methods, particularly when R is aromatic, is the ready depolymerization of the dimers in solution. In their colorless crystals, however, C-nitroso compounds are always polymerized and therefore it has been possible to reach a decision by X-ray crystallography: the correct structure is II.

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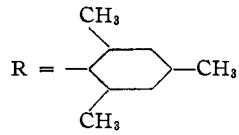
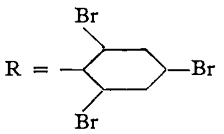
(1) Aston, Menard and Mayberry, THIS JOURNAL, **54**, 1530 (1932).

(2) For a discussion of the C-nitroso dimers, see Sidgwick's "Organic Chemistry of Nitrogen," Oxford University Press, 1942, p. 213.

(3) Hammick, New and Williams, *J. Chem. Soc.*, 29 (1934).

Work was begun on nitrosomesitylene[4] and on tribromonitrosobenzene[5]





These compounds were prepared by methods in the literature cited. They were found to be orthorhombic. They are not isostructural, however, and so the original intent to establish the dominant structural features with the bromine compound and the finer details with the methyl analog had to be abandoned. The data obtained with copper X-radiation filtered through nickel are presented in Table I.

TABLE I

CRYSTAL DATA FOR TWO NITROSO DIMERS

		Nitrosomesitylene	Tribromonitrosobenzene
Unit cell	*a*	10.82 Å.	9.32 Å.
	b	35.1	23.5
	c	8.82	8.59
Dimers/unit cell		8	4
Specific gravity	calcd.	1.18	2.43
	obsd.	...	2.40
Space group		D_{2h}^{15}-Pbca	D_{2h}^{14}-Pbna

Further work was limited to the bromine compound since the only possible degree of polymerization is dimerization in this case and the dimer must either be centro-symmetric or possess a twofold axis (in Pbna, the general position is of multiplicity 8, the only special positions are of multiplicity 4, and the special positions possess either symmetry $\bar{1}$ or 2). In choosing this compound, however, the price for an easy determination is that one must forego precise determination of the coördinates of the light atoms because two-thirds of the scattering power of the crystal resides in the bromine atoms alone. On the other hand, a very approximate determination of the positions of the light atoms is sufficient to determine the configuration of the dimer.

In general the crystals were tabular with the short dimension parallel to the *b* axis. A few were found whose dimensions perpendicular to *a* were roughly equal, and using one of these (dimensions parallel to *b* and *c*, 0.1 mm.; the crystal completely immersed in the X-ray beam) multiple film Weissenberg pictures were taken of the zero and the first five layers about the *a* axis. Intensities were estimated visually on a scale of 1–1200, and Lorentz and polarization corrections were applied. No account was taken of absorption. In subsequent calculations, the atomic scattering factors listed in the International Tables were used,[6] and a temperature correction of the form $e^{-B(\sin\theta/\lambda)^2}$ was employed in which B was chosen as 2×10^{-16}.

The independent coördinates to be determined were those of three bromine atoms, of the six carbon atoms in the benzene ring, and of one nitrogen and one carbon atom. The construction of Patterson–Harker sections suggested a limited number of positions for the bromine atoms. The foreknowledge that these atoms must lie about the benzene ring near the vertices of an equilateral triangle of 5–6 Å. on the side was helpful in resolving ambiguities and a small number of electron density sections (with the signs of the F's determined from the positions of the bromine atoms alone) fixed their coördinates close to the final values reported.

The coördinates of the six carbon atoms were obtained as follows. It was found possible to place an hexagonal benzene ring (1.38 Å. on a side) in the plane of the three bromine atoms so that the three C–Br bonds were of equal length (1.90 Å.) and so that the C–C–Br angle was (in the case of greatest departure from 120°) within 15 to 120°. Electron density maps confirmed the general location of the benzene ring but never gave enough resolution to improve on this assumption.

The coördinates of the nitrogen and oxygen atoms were determined approximately from electron density projections of slices through the cell

$$\int_{-1/6}^{1/6} \rho dz$$

which includes all atoms of one molecule except, perhaps, part of the oxygen (Fig. 1) and

$$\int_{1/4-1/6}^{1/4+1/6} \rho dx$$

which includes all atoms of one molecule except the bromine atoms ortho to the nitroso group (Fig. 2). Due to the overlap of different molecules, projections of the entire cell contents were not useful in locating the atoms.

The *z* coördinates of the bromine atoms were further checked by calculating one dimensional electron density sections at values of (*x*, *y*) given for the bromine positions by the first of these projected slices.

TABLE II

COÖRDINATES OF ATOMS OF TRIBROMONITROSOBENZENE

Atom	*x*	*y*	*z*
Br	0.225	−0.023	0.123
Br	−.053	.183	.133
Br	.550	.178	−1.25
O	.250	.240	−2.00
N	.252	.230	−.046
C	.258	.061	.064
C	.133	.096	.099
C	.135	.153	.068
C	.255	.172	.006
C	.375	.139	−.028
C	.376	.084	.001

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(4) Ingold and Piggott, *J. Chem. Soc.*, **125**, 173 (1924).

(5) Pechmann and Nold, *Ber.*, **31**, 562 (1898).

(6) "International Tables for the Determination of Crystal Structures," Vol. II, reprinted by Edwards Bros., Ann Arbor, Michigan, 1944, p. 571.

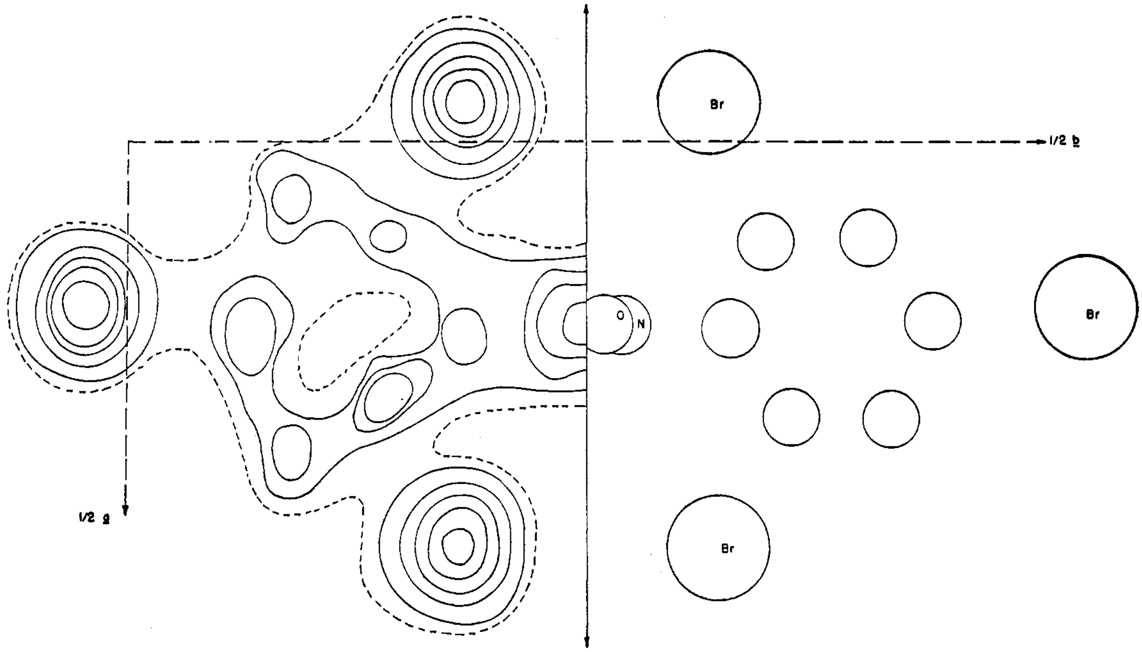


Fig. 1.—Projected electron density of the slice $\int_{-1/6}^{1/6} P\,dz$. Contour spacing for Br atom is four times that for other atoms. Atomic positions to the right of the two axis (at $y = {}^1/_4$, $z = 0$) serve as key to the density distribution to the left of this axis.

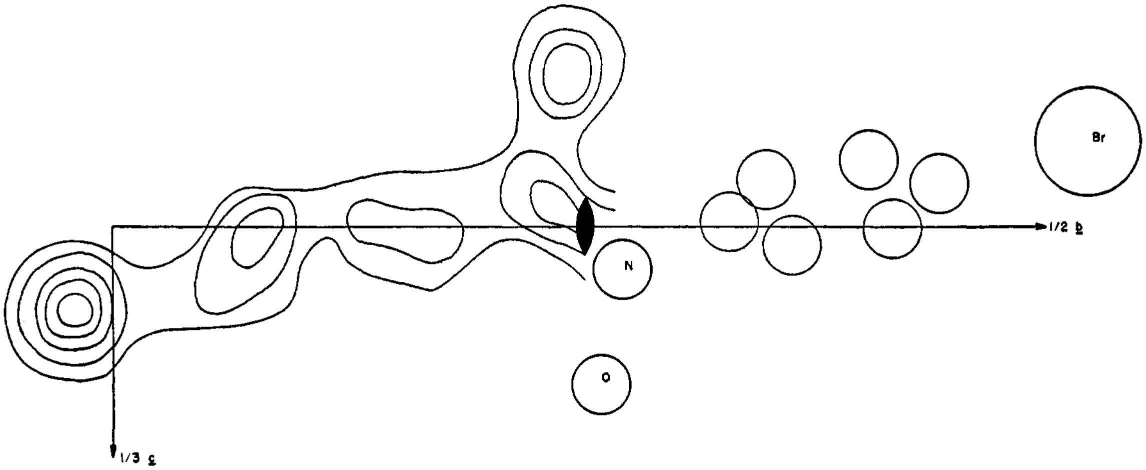


Fig. 2.—Projected electron density of the slice $\int_{1/4 - 1/6}^{1/4 + 1/6} P\,dx$. Contour intervals as in Fig. 1. Two axis relates density distribution (on left) to key (on right of two axis).

With the coördinates found as stated, a final calculation gave

$$\Sigma||F_{\text{obs.}}| - |F_{\text{calcd.}}||/\Sigma|F_{\text{obs.}}| = 0.21$$

Unobserved or immeasurably weak reflections (indicated in Table III by vw) were omitted in computing this deviation. The atomic coördinates used in the calculation are listed (Table II) and a comparison of calculated and observed amplitudes is presented (Table III).

A glance at the electron density maps shows that all atoms except the bromines are somewhat indeterminate. It would be unjustified to state more about the monomer than that the positions listed in Table II describe it as possessing customary bond lengths (within 0.1 Å.). The three bromine and the six carbon atoms are coplanar by assumption, the two ortho bromines appear to be bent away from the carbon bearing the nitroso group, and the nitroso group itself

TABLE III

COMPARISON OF CALCULATED AND OBSERVED STRUCTURE AMPLITUDES

k index	F_{hkl} Obs.	F_{hkl} Calc.
h_0, l_0		
4	12	13
6	50	57
8	45	-35
10	20	10
12	30	22
14	43	-35
16	vw	9
18	9	-9
20	18	-19
h_0, l_1		
2	4	3
4	6	7
6	12	13
8	15	14
10	16	18
12	10	6
14	14	17
16	4	2
h_0, l_2		
0	35	15
2	6	5
4	12	-10
6	5	2
8	6	-4
10	4	-1
12	4	1
14	5	4
h_0, l_3		
2	vw	3
4	3	3
6	11	11
8	11	16
10	11	12
12	9	11
14	10	10
16	6	4
h_0, l_4		
0	49	-51
2	vw	2
4	7	-8
6	35	-41
8	20	23
10	vw	-14
12	7	-7
14	23	24
h_0, l_5		
2	6	-2
4	6	-11
6	vw	-4
8	13	-11
10	vw	-5
12	6	-5
14	7	-7
h_0, l_6		
0	6	0
2	4	-2
h_1, l_1		
1	3	-2
2	vw	1
3	vw	2
4	4	5
5	4	3
6	vw	1
7	25	26
8	vw	1
9	7	9
10	vw	4
11	18	17
12	vw	-3
13	18	15
h_1, l_2		
1	31	-30
2	46	-44
3	30	-26
4	40	43
5	9	-13
6	15	-17
7	8	-13
8	12	-11
9	vw	-1
10	34	35
11	8	-2
12	23	-23
13	6	5
14	2	4
15	4	7
16	10	14
17	12	8
18	14	-14
h_1, l_3		
0	3	-8
1	13	-16
2	4	-2
3	8	-6
4	vw	-2
5	2	-1
6	3	1
7	18	-23
8	vw	2
9	4	-3
10	3	-5
11	10	-8
12	vw	2
13	10	-13
14	vw	0
15	4	-2
h_1, l_4		
1	vw	-3
2	8	-1
3	2	-2
4	6	-2
5	vw	1
6	4	4
7	vw	1
h_1, l_4		
8	vw	-1
9	5	2
10	3	2
11	3	-3
h_1, l_5		
0	vw	-2
1	9	-9
2	4	-4
3	3	-2
h_1, l_0		
1	8	11
2	12	14
3	2	8
4	19	-19
h_2, l_0		
4	38	-44
5	12	8
6	32	27
7	16	7
8	45	-43
9	8	4
10	15	13
11	vw	8
12	20	14
13	3	0
14	10	-14
15	3	3
16	10	17
h_2, l_1		
3	18	-27
4	10	-5
5	14	-5
5	14	16
6	15	-17
7	vw	-5
8	7	-7
9	10	-14
10	19	-17
11	14	15
12	11	-10
13	7	-7
14	8	-8
15	4	-1
16	6	-6
h_2, l_2		
0	4	-3
1	3	1
2	4	-2
3	vw	4
4	vw	1
5	vw	1
6	4	-4
7	vw	-2
8	6	8
9	vw	1
10	vw	-3
11	vw	-1
12	3	2
13	2	-2
h_2, l_3		
1	3	-1
2	vw	-3
3	18	-17
4	8	-6
5	10	12
6	8	-9
7	5	-5
8	8	-9
9	8	-10
10	12	-10
11	9	10
12	8	-11
13	vw	-6
14	7	-7
15	vw	0
16	8	-7
17	8	8
h_2, l_4		
0	15	-15
1	2	2
2	36	39
3	3	2
4	15	16
5	4	-5
6	12	11
7	6	-6
8	20	26
9	4	-4
10	5	-5
11	7	-7
12	15	-14
13	3	-1
14	10	13
15	vw	0
16	16	-16
h_2, l_5		
1	4	-5
2	vw	2
3	18	18
4	7	6
5	6	-8
6	7	7
7	vw	1
8	6	6
h_2, l_6		
0	7	5
1	vw	3
2	3	-1
h_3, l_1		
0	12	-4
1	20	25
2	9	-8
3	17	-17
4	6	-8
5	16	-18
6	7	-5
7	12	14
8	8	-3
h_3, l_1		
9	25	-25
10	vw	-1
11	16	-12
12	8	-1
13	6	3
14	10	4
15	22	-22
16	4	3
h_3, l_2		
1	20	19
2	17	-22
3	vw	21
4	19	19
5	17	15
6	15	-19
7	6	7
8	7	-15
9	8	3
10	10	10
11	4	0
12	17	-19
13	12	-9
14	6	-6
15	10	2
16	8	4
17	7	-7
18	8	-10
19	8	-8
h_3, l_3		
0	8	12
1	10	-21
2	6	7
3	8	9
4	vw	2
5	14	20
6	vw	4
7	9	-10
8	vw	3
9	15	20
10	vw	-2
11	10	11
12	3	2
13	4	-4
14	4	-1
15	13	14
h_3, l_4		
1	vw	0
2	3	1
3	vw	5
4	vw	-2
5	vw	-3
6	vw	0
7	vw	1
8	vw	0
h_3, l_5		
0	10	7
1	8	-9
2	vw	3
3	vw	5
4	3	2
5	9	11
6	4	4
7	5	-5
h_3, l_6		
1	7	-8
2	5	5
3	vw	-7
4	4	-3
5	9	-9
h_4, l_0		
3	7	-7
4	19	20
5	4	-4
6	18	16
7	11	-10
8	5	-3
9	10	-13
h_4, l_1		
1	18	19
2	6	5
3	14	-19
4	4	4
5	19	28
6	6	9
7	vw	1
8	4	6
9	15	-13
10	9	10
11	8	19
12	6	6
h_4, l_2		
1	vw	-3
2	vw	1
3	3	0
4	2	2
5	vw	2
6	vw	4
7	3	-3
8	4	-4
h_4, l_3		
1	12	14
2	12	3
3	12	-12
4	6	3
5	18	22
6	vw	7
7	vw	1
8	8	6
9	8	-10
10	6	6
11	12	14
12	9	9
h_4, l_4		
0	17	-17
1	4	1
2	8	-9
3	vw	6
4	5	-6
5	4	4
6	12	-12
7	6	5
8	5	3
9	6	8
h_5, l_1		
1	18	18
2	9	9
3	4	-1
4	3	6
5	8	-9
6	4	4
7	20	22
8	6	3
9	8	-7
h_5, l_2		
1	13	-13
2	6	7
3	10	-10
4	vw	5
5	vw	5
6	vw	7
7	10	-10
8	7	8
h_5, l_3		
0	5	-4
1	18	-21
2	4	-6
3	vw	3
4	vw	-7
5	6	8
6	6	-5
7	15	-25
h_5, l_4		
0	vw	0
1	vw	6
2	vw	-2
3	vw	2
4	vw	3
5	vw	-4
6	vw	1
7	vw	2
h_5, l_5		
0	4	-4
1	12	-11
2	vw	-5
3	vw	2
4	vw	-5
5	4	8
6	8	-4
7	12	-14

is bent out of the plane of the three bromine atoms.

The aim of the paper, however, is to establish the structure of the dimer and the X-ray result is clear on this point. The two monomers of a dimer are related to each other by the twofold axis at $y = {}^1/_4$, $z = 0$; not by the center of symmetry (at $x = y = z = 0$ or at $x = {}^1/_2$, $y = z = 0$) because the electron density function possesses maxima athwart the twofold axis but does not possess them near the centers of symmetry. Furthermore, it is clear that the nitrogen atoms (the atoms nearest the benzene ring) are

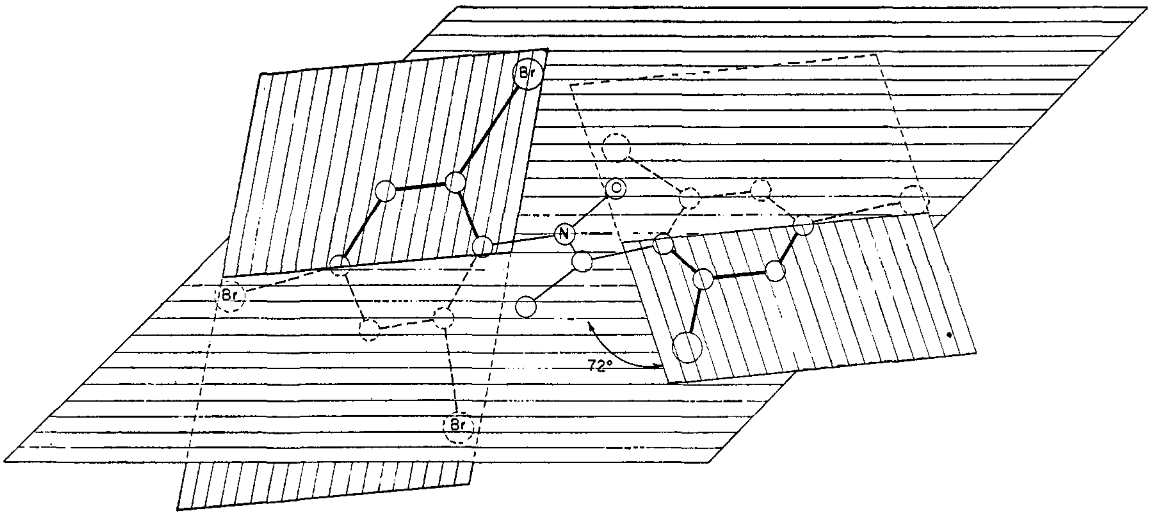


Fig. 3.—Tribromonitrosobenzene dimer: Nitrogen and oxygen atoms nearly coplanar, the two benzene rings with attached bromine atoms twisted in opposite directions, the angle between the planes of the benzene rings and the plane of the nitroso groups equals 72°.

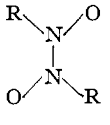
linked to each other (N–N = 1.4 Å. approximately) but that the oxygen atoms cannot be linked to each other, and so the dimer does not possess a four-membered ring.

The conclusion that the dimer does not possess a four-membered ring could have been reached by considering the positions of the bromine atoms only. Thus if the dimer contained a four-membered ring lying on the twofold axis, surely one ortho bromine atom would be considerably more distant from its equivalent in the other half of the dimer, generated by the twofold axis, than the other ortho bromine atom from its equivalent. However, these distances are approximately equal (3.9 and 4.0 Å.). Consequently, no such ring exists.

The structure of the dimer is pictured in Fig. 3. The nitrogen and oxygen atoms lie roughly in the plane x = constant, the two benzene rings with their attached bromine atoms are twisted in opposite directions, and the angle between the planes of the benzene rings and the plane of the nitroso groups is about 72°.

In the crystal, the interatomic Br...Br distances between different dimers are all greater than 4 Å. A discussion of other interatomic distances is unprofitable in view of the uncertainty of the coördinates of the light atoms. Conservatively, any one or all of them could be changed by 0.1 Å. with inappreciable effect on the agreement of calculated and observed structure amplitudes.

Hammick, New and Williams[3] found the dimer of nitrosomesitylene to possess a dipole moment of 1.4 D in solution, and that of 2-nitroso-2,5-dimethylhexane 1.0 D.; and this finding has been used to question the atomic arrangement

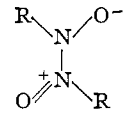


assuming a center of symmetry to be diagnostic for such a structure. But if the R groups are large, as they are in both these cases, a non-centro-symmetric configuration of this arrangement would be energetically more economical. In tribromonitrosobenzene, the observed distance between a bromine atom ortho to the nitroso group and its equivalent in the other half of the dimer (3.9 and 4.0 Å. in the two cases) is equal to twice the van der Waals radius for bromine (1.95 Å.), but if the two halves of the dimer were related by a center of symmetry the distance would be only about 3.3 Å. Consequently, the molecule should not be centro-symmetric and a permanent dipole moment is compatible with the atomic arrangement. Since the van der Waals radii of bromine and methyl are about the same, one should expect a permanent dipole moment in nitrosomesitylene as well. It might be supposed that the two N–O bond moments would be the greatest bond moments in either molecule and, since these approximately cancel in the structure just determined, that the dipole moments of the nitroso dimers would be relatively small, as is observed. While the approximate planarity of the nitrogen and oxygen atoms in tribromonitrosobenzene may result from other factors as well, it is probably required for resonance of the dimer among the different possible valence structures and in general the resultant of the two N–O bond moments should be small.

Summary

In an X-ray determination of the crystal structure of dimeric tribromonitrosobenzene (space group, Pbna; a, b, c = 9.32, 23.5, 8.59 Å.; four dimers/unit cell) atoms other than bromine atoms cannot be located accurately. An approximate determination of the coördinates of the light atoms suffices to show that the dimer possesses

a twofold axis but not a center of symmetry and can be represented



plus other resonance forms. The absence of a center of symmetry agrees with the observation that the methyl analog, presumably of the same structure, possesses a permanent dipole moment.

The space group of the crystalline methyl analog, nitrosomesitylene, has been determined (Pbca; *a*, *b*, *c* = 10.82, 35.1, 8.82; eight dimers/unit cell).

ABERDEEN PROVING GROUND, MD.

RECEIVED MARCH 2, 1949

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Reaction Heats of Organic Fluorine Compounds. III. The Vapor Phase Heats of Hydrobromination of Some Simple Fluoroölefins[1]

BY J. R. LACHER, K. R. LEA, C. H. WALDEN,[2] G. G. OLSON AND J. D. PARK

The first two papers[3,4] of this series described the calorimeter and its performance, and presented the vapor phase heats of chlorination of tetrafluoroethylene, trifluorochloroethylene, 1,1-dichloro-2,2-difluoroethylene, perfluoropropene and perfluorocyclobutene. The present paper deals with the vapor phase heats of hydrobromination of the first three olefins listed above.

Experimental Details.—The olefins[5] were purified as described in papers I and II.[3,4] A sample of purified tetrafluoroethylene was submitted to Dr. F. L. Mohler of the National Bureau of Standards for mass spectrographic analysis. Aside from traces of mercury and water vapor (due to the method used in preparing the sample for shipment) nothing but the olefin could be detected. Hydrogen bromide obtained from the Matheson Company was used without further purification. The catalyst consisted of "Columbia" activated carbon which was sized to pass a number 6 and be retained on a number 20 screen. It was activated by heating to 250° *in vacuo* for two hours. After being transferred to the reaction chamber of the calorimeter, the catalyst was again evacuated for one hour at 94°. Hydrogen bromide was then passed into the catalyst chamber.

The procedure in making a run was similar to that used for the chlorination reactions described in papers I and II. The hydrogen bromide was mixed in the catalyst chamber with excess olefin. The product gases were then tested for unreacted hydrogen bromide. The reaction was quantitative in the case of tetrafluoroethylene, trifluorochloroethylene and 1,1-dichloro-2,2-difluoroethylene. An attempt was made to measure the heat of addition of hydrogen bromide to perfluorocyclobutene. However, at the temperature of the calorimeter, the reaction was far from quantitative and a steady state could not be attained. The incomplete reaction is presumed to be due to a small heat of reaction leading to an unfavorable equilibrium.

When hydrogen bromide adds to the three simple olefins, the bromine goes to the CF_2– group in accordance with Markownikoff's rule.[6] In order to test the calorimeter product for the presence of substances produced by a possible reverse addition or disproportionation reactions, samples of the effluent gases from the calorimeter were trapped at −80°. They were analyzed by taking infrared spectra in a manner similar to that previously described.[3,4] If any side reactions took place, they were less than 0.2%. Using auxiliary apparatus and a catalyst identical to that in the calorimeter, a considerable quantity of each of the hydrogen bromide adducts was prepared. The products were carefully distilled using a 36-inch Hypercal Podbielniak fractionating column. The distillation was followed by taking infrared spectra of the various fractions and again no evidence for reverse addition was found for the unsymmetrical olefins. The spectra of the carefully purified products are presented in Figs. 1, 2 and 3. A further attempt was made to detect the presence of the reverse addition product in case of the trifluorochloroethylene. The reaction was carried out at 200° with a little air in the hydrogen bromide stream. A careful distillation of the product and infrared analysis again indicated that the reaction takes place quantitatively in accordance with Markownikoff's rule.

TABLE I

VAPOR PHASE HEATS OF HYDROBROMINATION AT 94°

Run	Olefin flow, mole/min. × 10^4	HBr flow, mole/min. × 10^4	Energy input, cal./min.	$-\Delta H_{367°K.}$ cal./mole
		Tetrafluoroethylene		
1	5.0	3.5532	11.6245	32,746
3	6.6	1.9235	6.3442	32,982
4	4.8	1.9230	6.3288	32,910
6	5.1	2.4394	8.0624	33,050
		Average 32, 922 ± 180 cal./mole		
		Trifluorochloroethylene		
2	5.7	1.9766	5.1506	26,057
4	5.9	2.4338	6.2910	25,848
6	5.6	2.1860	5.7430	26,271
7	5.5	2.0996	5.4711	26,057
8	5.6	1.9726	5.1572	26,144
		Average 26,074 ± 226 cal./mole		
		1,1-Dichloro-2,2-difluoroethylene		
1	7.3	1.9241	4.4497	23,126
2	7.1	2.1505	4.9317	22,932
3	9.4	2.1505	4.9583	23,056
4	7.0	2.7239	6.2850	23,073
		Average 23,047 ± 115 cal./mole		

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[1] Presented before the Symposium on Fluorine Chemistry, 116th Meeting of the American Chemical Society, Atlantic City, N. J.

[2] American Cyanamid Fellow, 1948.

[3] J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson and J. D. Park, THIS JOURNAL, **71**, 1330 (1949).

[4] J. R. Lacher, J. J. McKinley, C. H. Walden, K. R. Lea and J. D. Park, *ibid.*, **71**, 1334 (1949).

[5] Samples of tetrafluoroethylene, trifluorochloroethylene and 1,1-dichloro-2,2-difluoroethylene were supplied us through the courtesy of Jackson Laboratory, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

[6] W. B. Markownikoff, *Ann.*, **153**, 256 (1870).