

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments and Structures of Certain Nitro Compounds and Amines

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The dipole moments of trinitromethane or nitroform, tetranitromethane and nitrogen pentoxide have been determined with the object of studying the molecular structures and the interactions of immediately adjacent nitro groups. A brief account is included in this paper of the determination and interpretation of the moments of cyclohexylamine and morpholine. The moments were obtained with the apparatus and methods previously described.^{1,2}

Preparation of Materials

Benzene.—Benzene was purified as in the work previously described.¹

Carbon Tetrachloride.—Carbon tetrachloride was purified as in the work previously described.²

Tetranitromethane.—Tetranitromethane, prepared according to the method of Chattaway³ by the action of virtually dry nitric acid on acetic anhydride, was dried over anhydrous sodium sulfate and distilled in an all-glass apparatus under reduced pressure at 35°; n_D^{25} 1.43822; d_4^{25} 1.62294.

Nitroform.—This compound was prepared according to the method of Hantzsch and Rickenberger⁴ by the acidification with concentrated sulfuric acid of $\text{KC}(\text{NO}_2)_3$, which was formed by the action of alcoholic potash upon tetranitromethane; m. p. 19°.

Nitrogen Pentoxide.—The method of preparation was essentially that of Russ and Pokorny.⁵ Fuming nitric acid was mixed with an equal volume of concentrated sulfuric acid and distilled from it into phosphorus pentoxide, which was kept at about -20° and stirred until the mixture had the consistency of a paste. The resulting nitrogen pentoxide was sublimed in a stream of ozonized oxygen and collected along with oxygen and ozone in a tube immersed in liquid air. Upon warming after removal from the liquid air, the oxygen and ozone evaporated, leaving the white solid.

Cyclohexylamine.—Material from Merck and Company was distilled, dried over calcium chloride and then sodium, distilled onto fresh sodium in an atmosphere of nitrogen, and redistilled; b. p. 133.8°; d_4^{25} 0.86253.

Morpholine.—Material very kindly given us by the Carbide and Carbon Chemical Corporation was dried over calcium chloride and then over sodium, distilled onto fresh sodium in an atmosphere of nitrogen, and redistilled. The middle fraction was retained and measured without further purification; b. p. 128.7°; n_D^{25} 1.45227; d_4^{25} 0.99619.

Experimental Results

The dielectric constants ϵ and densities d of the

solutions containing mole fraction c_2 of the polar solute and the polarizations P_2 of the polar solute are given in Table I, while the molar refractions MR_D , the polarizations P_∞ obtained by extrapolating the P_2 - c_2 curves to infinite dilution, and the dipole moments μ are listed in Table II.

TABLE I
DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS
AT 25°

c_2	ϵ	d	P_2
Carbon Tetrachloride-Tetranitromethane			
0.00000	2.227	1.58431	($P_1 = 28.18$)
.04039	2.240	1.58241	42.0
.08421	2.251	1.58160	41.2
.14291	2.264	1.58268	40.5
.18437	2.275	1.58364	40.4
.26079	2.295	1.58527	40.3
.30898	2.317	1.58639	40.7
1.00000	2.521	1.62294	40.62
Carbon Tetrachloride-Nitroform			
0.00969	2.308	1.57998	169.8
.01350	2.339	1.57888	167.0
.02944	2.466	1.57345	160.3
.03994	2.546	1.56703	157.7
Carbon Tetrachloride-Nitrogen Pentoxide			
0.00000	2.223	1.5844	($P_1 = 28.11$)
.05934	2.368	1.5813	58.6
.08624	2.435	1.5800	57.9
.09361	2.452	1.5793	57.6
.10243	2.473	1.5790	57.3
Benzene-Cyclohexylamine			
0.00000	2.276	0.87344	($P_1 = 26.67$)
.12935	2.559	.87084	65.7
.20884	2.743	.86946	65.8
.27445	2.892	.86815	65.6
Benzene-Morpholine			
0.08588	2.574	0.88422	73.4
.18193	2.934	.89684	71.6
.22967	3.128	.90295	70.7
.27621	3.316	.90875	69.9
.35608	3.665	.91851	68.7
1.00000	7.33	.99619	59.3

TABLE II
MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE
MOMENTS

Substance	MR_D	P_∞	$\mu \times 10^{18}$
$\text{C}(\text{NO}_2)_4$	31.72	41.7	(0.71)
$\text{CH}(\text{NO}_2)_3$	25.01	177	2.71
N_2O_5	20	60	1.39
$\text{C}_6\text{H}_{11}\text{NH}_2$	30.5	65.7	1.32
$\text{OC}_4\text{H}_8\text{NH}$	23.59	75.3	1.58

(1) Lewis and Smyth, *J. Chem. Phys.*, **7**, Nov. (1939).(2) Lewis and Smyth, *THIS JOURNAL*, **61**, 3063 (1939).(3) Chattaway, *J. Chem. Soc.*, **97**, 2099 (1910).(4) Hantzsch and Rickenberger, *Ber.*, **32**, 628 (1899).(5) Russ and Pokorny, *Monatsh.*, **34**, 1027 (1913).

The molar refractions were calculated for tetranitromethane and morpholine from the refractive indices and densities herein reported and that for nitrogen pentoxide as the refraction of N_2O_4 plus half that of O_2 obtained from data in Landolt-Börnstein. The molar refraction of cyclohexylamine was calculated from similar data in Landolt-Börnstein and that of nitroform was the value of von Auwers and Harres.⁶

Discussion of Results

Tetranitromethane was measured because, although two previous investigators had found moments for it in solution so small as to be indistinguishable from zero, absorption measurements⁷ and X-ray analysis of the crystal⁸ had been interpreted as indicating that it was not a symmetrical molecule but actually trinitromethyl nitrite. Mark and Noethling assumed a linear nitrite structure, which now seems highly improbable. After the measurements in the present paper had been carried out, a determination in the vapor state was published indicating a moment indistinguishable from zero. The results of these measurements are summarized in Table III.

TABLE III
DATA ON TETRANITROMETHANE

Investigators	Temp., °C.	M_{RD}	P_{∞}	$(\mu \times 10^{18})$	Solvent
Williams ⁹	25	31	32.5	0.2	C_6H_6
Weissberger and Sängewald ¹⁰	25	35.3	36.2	.19	CCl_4
Coop and Sutton ¹¹	81.8	36.0	38.6	.39	Gas
Lewis and Smyth	25	31.72	41.7	.71	CCl_4

As Coop and Sutton say that the polarization may be "somewhat greater than the above value, but not by more than 3 cc.," and, as our value may be as much as 1 cc. high, the agreement is satisfactory. The value of Weissberger and Sängewald is also low by probably no more than the experimental error. Coop and Sutton's value of the molar refraction was taken as the average of the value of Weissberger and Sängewald, which may have a considerable error because of being determined in dilute solution, and of a value privately communicated to them by M. W. Lister. The value 31.72 determined in the present work agrees closely with that of von Auwers

and Ottens¹² 31.44 and is higher than the sum 29.4 of the refractions of four alkyl nitro groups and one carbon atom taken from Landolt-Börnstein. The value 31.7 is, therefore, to be regarded as the molar refraction. This leaves a difference between the polarization and the refraction of about 10 cc., which would give a moment 0.7.

The moment of the symmetrical tetranitromethane molecule should, of course, be zero, while that of trinitromethyl nitrite would depend upon rotation around the single O-N bond of the nitrite group and would vary from 3.4 to 0 with variation in the position around this bond. Complete freedom of rotation would give a moment 2.4, but repulsion within the molecule should make the general region of the zero moment position more probable, which would mean an average moment possibly less than 1.0. The possibility that the tetranitromethane is really trinitromethyl nitrite is not wholly excluded if the moment is as large as 0.7. However, measurements on nitrobenzene in the vapor state¹³ gave an atomic polarization 6 for nitrobenzene as compared to 1.0 for fluorobenzene and 1.8 for chlorobenzene, and similar measurements on nitromethane¹⁴ gave an atomic polarization 6.1 as compared to 1.2 for phosgene and 0 for hydrogen cyanide obtained at the same time and small values for the alkyl halides obtained at other times. The large errors which commonly accumulate in atomic polarization values make any discussion of it necessarily approximate, but it would appear that a large atomic polarization may be associated with the nitro group. If the atomic polarization of two mononitro compounds is 6, it would not be surprising for a molecule containing four nitro groups to have an atomic polarization of 10. It seems reasonable, therefore, to attribute the difference between the polarization and the refraction to atomic polarization and report the moment as zero and the molecule, therefore, as the symmetrical tetranitromethane and not trinitromethyl nitrite. A determination of structure by the electron diffraction method just published¹⁵ obtains the interatomic distances to be expected on the assumption of a symmetrical tetranitromethane. Before leaving the subject of tetranitromethane, attention should be directed to the somewhat unusual

(6) Von Auwers and Harres, *Ber.*, **62B**, 2287 (1929).
 (7) Harper and Macbeth, *J. Chem. Soc.*, **107**, 87 (1915).
 (8) Mark and Noethling, *Z. Krist.*, **65**, 435 (1927).
 (9) Williams, *Physik. Z.*, **29**, 27 (1928).
 (10) Weissberger and Sängewald, *Ber.*, **65**, 701 (1932).
 (11) Coop and Sutton, *J. Chem. Soc.*, 1269 (1938).

(12) Von Auwers and Ottens, *Ber.*, **57B**, 446 (1924).
 (13) McAlpine and Smyth, *J. Chem. Phys.*, **3**, 55 (1935).
 (14) Smyth and McAlpine, *THIS JOURNAL*, **56**, 1697 (1934).
 (15) Stosick, *THIS JOURNAL*, **61**, 1127 (1939).

occurrence of a minimum in the density-concentration curves in the very dilute region of its solutions in carbon tetrachloride.

No account of atomic polarization has been taken in the calculation of the moment of nitroform in Table II. The addition of 8 cc. to the refraction, a maximum value for atomic polarization, would lower the moment by only 0.07. The solvent effect has presumably already lowered it by more than this from its true gas value. The ratio of the value 2.71 to the solution value of nitromethane is 0.85, while the ratio of the chloroform moment to that of methyl chloride is 0.56. If there were no inductive action between neighboring dipoles, the moments of the mono- and the tri-substituted molecules should be equal as required by their tetrahedral structures. The lowering of the moment by induction is much less in nitroform than in chloroform, for not only is the ratio of the tri- to the mono-substituted compound 0.85 as compared to 0.56, but the absolute lowering is only 0.5 as compared to 0.8. The total polarizability of the nitro group is slightly greater than that of chlorine as shown by its refraction of 6.7 as compared to 5.97, but its polarizability per atom and per displaceable electron is only a little more than a third of that of chlorine and that for the chlorine electrons. In some positions of the nitro groups as they rotate around the C-N bonds, an oxygen of one nitro group may come very close to that of another with a considerable resultant lowering of the N-O dipole moments, but if, as it was found necessary to assume in the electron diffraction investigation of tetranitromethane¹⁵ and as should be equally probable here, the nitro groups are undergoing rotatory oscillation about the C-N bonds in such a way as to keep the oxygen-oxygen repulsions minimized as far as possible, the oxygens are somewhat removed from neighboring dipoles and the inductive effects should be smaller than those in chloroform. The smaller reduction in dipole moment is thus accounted for.

The nitrogen pentoxide molecule should consist of two nitro groups attached to a central oxygen. A rather early electron diffraction investigation¹⁶ indicated a symmetrical molecule with a 180° valence angle for the central oxygen. As this structure would have zero moment, the considerable moment 1.39 given in Table II shows it to be impossible. Evidently, the molecule is

bent and a very rough value of the oxygen valence angle may be calculated from the group and bond moments involved. If from the solution value of nitromethane 3.2, the approximate moment of the H-C bond 0.3 is subtracted, a moment 2.9 is obtained for the nitro group. If induction reduces this by 10% as compared to the 15% reduction in nitroform, the group moment is 2.6. This moment in each half of the molecule is opposed by the N-O bond moment, which is about 0.3.¹⁷ The moment of each half of the molecule is, therefore, 2.3, acting approximately in the direction of the oxygen valence bonds. The moment of the molecule as a whole should, therefore, be $2 \times 2.3 \cos (\theta/2) = 1.39$, where θ is the oxygen valence angle. This gives $\theta = 145^\circ$, which seems rather large. However, electron diffraction¹⁸ gives an oxygen valence angle 100° in OF₂ and 115° in OCl₂, in which latter molecule the repulsion between the two attached atoms should be larger. Calculation of the dimensions of the OCl₂ and O(NO₂)₂ molecules shows that, for a given oxygen valence angle, steric repulsion between the two nitro groups must be much greater for certain positions in the rotation of the groups about their bonds to the central oxygen than the repulsion between the two chlorine atoms. Thermal oscillation around these bonds should, therefore, tend to widen the oxygen valence angle and may be sufficient to account for the large value 145° estimated approximately. It should be remarked that the bond moment calculated from the moment and valence angle of the OCl₂ molecule was consistent with other indications of its size.¹⁹ Neglect of atomic polarization in calculating the moment of nitrogen pentoxide presumably raises its value somewhat, but the presence of impurity due to decomposition of the unstable substance tends to compensate for this. It is thus clearly established that the molecule is bent, but the angle of bending is only very approximately estimated.

The moment of cyclohexylamine 1.32 is 0.2-0.3 higher than those of secondary alkyl amines, about the same size as those of the primary alkyl amines, and smaller than those of the aryl primary amines as would be expected. Its behavior is thus normal.

The moment of morpholine 1.58 in Table II is slightly higher than the value 1.48 recently pub-

(17) Smyth, *THIS JOURNAL*, **60**, 183 (1938).

(18) Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(19) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

(16) Maxwell, Mosley and Deming, *J. Chem. Phys.*, **2**, 331 (1934).

lished by Partington and Coomber,²⁰ which does not affect its interpretation. The dioxane molecule, which has two possible forms, a Z-shape and a U-shape, has been shown by its moment^{21,22} to exist almost wholly in the Z-form. Similarly, the moment found for morpholine, which has two possible Z-forms and four possible U-forms, agrees well with the identical values calculated for the two Z-forms. Our reasoning has agreed with that of Partington and Coomber in leading to the conclusion that the morpholine molecule exists primarily in its Z-forms, although the presence of U-forms is not entirely excluded.

Summary

The dipole moments of tetranitromethane, nitroform and nitrogen pentoxide have been de-

(20) Partington and Coomber, *Nature*, **141**, 918 (1938).

(21) Hunter and Partington, *J. Chem. Soc.*, 87 (1933).

(22) Smyth and Walls, *THIS JOURNAL*, **53**, 2115 (1931).

termined in carbon tetrachloride solution and those of cyclohexylamine and morpholine have been measured in benzene solution. Tetranitromethane is concluded to have a large atomic polarization but zero dipole moment, which means that it is not trinitromethyl nitrite as sometimes suggested. The moment of nitroform is consistent with its tetrahedral structure, inductive effects in the molecule being smaller than those in chloroform, probably because of the lower polarizability of the atoms and of a staggering of the nitro groups in their rotation around their bonds to the central carbon atom. The moment of cyclohexylamine is of the same size as those of the primary alkyl amines, as it should be. The moment of morpholine shows that it exists primarily in the Z- or chair-shaped forms of the molecule.

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Allylic Rearrangements. IX. The Isolation and Rearrangement of Primary and Secondary Pentenyl, Hexenyl and Heptenyl Bromides^{1,2}

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In the first paper³ of this series it was recognized for the first time that the so-called crotyl bromide was actually a mixture of primary and secondary butenyl bromides which were far more mobile than previously suspected. Although they could be separated by low-temperature fractional distillation, they rearranged even at room temperature to an equilibrium mixture. Later papers⁴ have pointed out that studies involving the formation or reaction of these butenyl bromides must take into consideration the possibility of an allylic rearrangement during the reaction, and also a thermal rearrangement after the products are formed. Since other alkenyl bromides have been

prepared and used in the synthesis of many types of compounds without recognition by investigators of the need for carefully controlled conditions, there exists, therefore, a need for a careful and extended study of the alkenyl bromides, their equilibria and reactions.

It is the purpose of this paper to discuss the separation and thermal rearrangement of the primary and secondary pentenyl, hexenyl and heptenyl bromides. A separation of the hexenyl bromides^{5a} and the synthesis of several pure primary alkenyl bromides^{5b} have been reported, but it will be shown that sufficient precautions were not used in the isolation of the pure compounds.

(1) This work was accomplished with the aid of a grant from the Board of Research of the University of California.

(2) The terms primary alkenyl and secondary alkenyl bromides are used to designate the two allylic isomers, $R-CH=CHCH_2Br$ and $R-CHBrCH=CH_2$ respectively. Accordingly, the terms primary pentenyl, hexenyl and heptenyl bromides refer to 1-bromo-2-pentene, 1-bromo-2-hexene, and 1-bromo-2-heptene, respectively. Similarly, secondary pentenyl, hexenyl and heptenyl bromides refer to 3-bromo-1-pentene, 3-bromo-1-hexene, and 3-bromo-1-heptene, respectively.

(3) Winstein and Young, *THIS JOURNAL*, **58**, 104 (1936).

(4) (a) Young, Winstein and Prater, *ibid.*, **58**, 289 (1936); (b) Young and Winstein, *ibid.*, **58**, 441 (1936); (c) Young and Lane, *ibid.*, **59**, 2051 (1937); (d) **60**, 347 (1938); (e) Young, Lane, Loshokoff and Winstein, *ibid.*, **59**, 2441 (1937); (f) Young, Kaufman, Loshokoff and Pressman, *ibid.*, **60**, 900 (1938).

Experimental Part

Preparation of Materials

Alkylvinylcarbinols.—The ethyl, propyl and butylvinylcarbinols used as a source of the desired vinyl bromides were prepared in 60% yields by the action of the appropriate Grignard reagent on acrolein according to the method of Delaby⁶ as modified by Prévost.⁷

(5) (a) Van Risseghem and Gredy, *Compt. rend.*, **302**, 489 (1936); (b) Delaby and Lecomte, *Bull. soc. chim.*, [5] **4**, 749 (1937).

(6) Delaby, *Compt. rend.*, **175**, 967 (1922).

(7) Prévost, *Ann. chim.*, [10] **10**, 113, 147 (1928).