

correction of 2-triazoethanol at 25°, expressed as a percentage of the calculated parachor, is 2.8.

The group values obtained from triazoacetone are somewhat higher than the mean values calculated by the systems of Sugden and Samuel. The value calculated by Gibling's method has been corrected for the influence of the carbonyl group and agrees quite well with the values obtained for the aromatic triazo compounds.

The mean parachor values calculated from the experimental results agree well with those predicted by the different systems. The mean value previously reported for both Sugden's and Samuel's systems is 77.3 compared to our values for these systems of 77.26 and 77.17, respectively. Gibling's value for the triazo group is 79.9 compared with our value of 79.38.

NEW ORLEANS, LOUISIANA

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[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

The Physical Properties of Some Triazo Compounds. II. Dipole Moments¹

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In Part I³ of this investigation, molar refractions and parachors were reported for twelve triazo compounds. The dipole moments of these and three additional triazo compounds have been determined to obtain further information which may be correlated with the structure of the triazo group.

Experimental

Preparation of Compounds.—*o*-, *m*- and *p*-derivatives of chloro-, bromo- and methyltriazobenzene, triazoethane, 2-triazoethanol and triazoacetone were prepared and purified as reported in Part I³ of this series. *o*-, *m*- and *p*-nitrotriazobenzene were prepared by the method of Noelting and Michel.⁴ The products were recrystallized twice from 60% alcohol solution, partially dried on a Büchner funnel and finally over phosphorus pentoxide in a desiccator. The melting ranges of the *o*-, *m*- and *p*-nitrotriazobenzenes are 50.8–51.2°, 51.9–52.0° and 70.3–70.5°, respectively.⁵

Benzene.—J. T. Baker C.P. benzene was purified as described previously⁶ and distilled immediately before its use.

Density.—The densities of the benzene solutions were measured at 25.00 ± 0.02° with a calibrated 15-ml. specific gravity bottle.

Dielectric Constants.—The dielectric constants of the benzene solutions of the triazo compounds were determined at 25.00 ± 0.05° with the heterodyne beat apparatus and the cell previously described.⁶ Measurements were made on at least four solutions of each compound in which the mole fractions of the solute, N_2 , varied between the limits of 0.002 and 0.0380. The dielectric constant for each solution was measured at three different frequencies, the mean value being used in the subsequent calculations.

Results and Calculations

The calculation of the polarization, P_{20} , of a compound was made by the method of Halverstadt and Kumler,⁷ using their equation

$$P_{20} = (E_1 - 1)/(E_1 + 2)(M_2v_1 + M_1B) + 3Av_1M_1/(E_1 + 2)^2$$

in which E_1 and v_1 are the dielectric constant and the specific volume of the pure solvent, respectively; M_1 and M_2 are the molecular weights of the solvent and solute, respectively. The constants, A and B , E_1 and v_1 in the empirical equations,

$E_{12} = E_1 + AN_2$ and $v_{12} = v_1 + BN_2$, were evaluated by the method of least squares. These values as well as the polarization of the solute at infinite dilution, P_{20} , the sum of the electronic and atomic polarizations, P_{e+a} , and the dipole moment, μ , are given in Table I. For all compounds, the atomic polarization was assigned a value equal to 5% of the electronic polarization contribution.

The molar refractions for all compounds except the nitrotriazobenzenes were previously reported.³ For the nitro derivatives, the molar refractions are calculated from refraction equivalents since these compounds are solids at ordinary temperatures. The value for the "aromatic" triazo group used in these calculations, 10.38, is the mean experimental value calculated from the molar refractions of the chloro, bromo and methyltriazobenzenes.

Discussion

The dipole moments of the disubstituted benzene compounds have been calculated assuming the substituted groups to be colinear and to lie in the plane of the benzene ring. The general equation employed in these calculations is

$$\mu = (m_1^2 + m_2^2 + 2m_1m_2 \cos \theta)^{1/2}$$

where m_1 and m_2 are the individual group moments and θ is the angle between the group vectors. The group moments employed are 1.56 (chloro),⁸ 1.53 (bromo),⁸ 0.41 (methyl),⁸ 4.23 (nitro)⁹ and 1.55 (triazolo).^{10,11} The results of these calculations, presented in Table I, are compared with our experimental values and those previously reported in the literature. It should be noted that moments calculated by the above equation represent theoretical values which assume there is no interaction between the substituted groups.

The small moment of toluene, 0.41,⁸ indicates the methyl group is the least polar of the various substituents. This group would be expected to have little effect on the triazo group when both occur in the same compound. This conclusion is substantiated by the excellent agreement between the experimental and calculated dipole moments found for the methyltriazobenzenes.

(8) Fieser and Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 568.

(9) Glasstone, "Textbook of Physical Chemistry," second edition, D. Van Nostrand Co., New York, N. Y., 1946, p. 595.

(10) Bergmann and Schütz, *Z. physik. Chem.*, **19B**, 389 (1932).

(11) Sidgwick, Sutton and Thomas, *J. Chem. Soc.*, 406 (1933).

(1) Taken from a portion of the dissertation submitted by Hans O. Spauschus to the Graduate School of Tulane University in partial fulfillment of the requirements for the Ph.D. degree.

(2) TAP Laboratory, General Electric Co., Pittsfield, Mass.

(3) Spauschus and Scott, *THIS JOURNAL*, **73**, 208 (1951).

(4) Noelting and Michel, *Ber.*, **26**, 86 (1893).

(5) The melting point ranges reported by Noelting and Michel, reference 4, for these compounds are 51–53° (ortho-), 52–55° (meta-) and 71–73° (para-).

(6) Spauschus, Mills, Scott and MacKenzie, *THIS JOURNAL*, **72**, 1377 (1950).

(7) Halverstadt and Kumler, *ibid.*, **64**, 2988 (1942).

TABLE I

Compound	A	B	E ₁	ν_1 , ml./g.	P ₂₀	P _{0+∞}	Detd. $\mu \times 10^{18}$	Calcd.
<i>o</i> -NO ₂ C ₆ H ₄ N ₃	28.19	-0.8360	2.2733	1.1448	450.59	43.88	4.46	5.18
<i>m</i> -NO ₂ C ₆ H ₄ N ₃	18.14	-.8273	2.2736	1.1445	303.12	43.88	3.56	3.70
<i>p</i> -NO ₂ C ₆ H ₄ N ₃	12.26	-.8412	2.2753	1.1452	216.50	43.88	2.90 ^a	2.68
<i>o</i> -ClC ₆ H ₄ N ₃	8.239	-.7039	2.2739	1.1461	157.21	42.22	2.37	2.69
<i>m</i> -ClC ₆ H ₄ N ₃	3.300	-.6615	2.2750	1.1455	85.52	42.37	1.45	1.55
<i>p</i> -ClC ₆ H ₄ N ₃	0.3771	-.6670	2.2722	1.1453	42.41	42.61	0.01 ^{a,b}	0.01
<i>o</i> -BrC ₆ H ₄ N ₃	7.508	-1.240	2.2748	1.1453	149.01	45.27	2.25	2.67
<i>m</i> -BrC ₆ H ₄ N ₃	3.049	-1.161	2.2772	1.1444	85.29	45.26	1.40	1.54
<i>p</i> -BrC ₆ H ₄ N ₃	0.4601	-1.236	2.2727	1.1452	45.57	45.58	0.02 ^a	0.02
<i>o</i> -CH ₃ C ₆ H ₄ N ₃	2.977	-0.3232	2.2752	1.1449	81.54	41.96	1.39	1.39
<i>m</i> -CH ₃ C ₆ H ₄ N ₃	4.526	-.3024	2.2726	1.1444	104.84	42.18	1.75	1.79
<i>p</i> -CH ₃ C ₆ H ₄ N ₃	5.333	-.3091	2.2738	1.1450	116.59	42.28	1.90 ^b	1.96
C ₂ H ₅ N ₃	5.979	.0140	2.2717	1.1454	112.52	20.32	2.12	..
2-N ₃ C ₂ H ₄ OH	8.491	-.2784	2.2730	1.1451	148.01	21.82	2.48	2.79
CH ₃ COCH ₂ N ₃	18.32	-.2583	2.2721	1.1452	297.07	25.19	3.64	3.59

^a Bergmann and Schütz, ref. 10, give 2.96 for *p*-NO₂C₆H₄N₃, 0.47 for *p*-ClC₆H₄N₃, and 0.64 for *p*-BrC₆H₄N₃. ^b Sidgwick, Sutton and Thomas, ref. 11, give 0.33 for *p*-ClC₆H₄N₃ and 1.96 for *p*-CH₃C₆H₄N₃.

For the para substituted halogen triazobenzene compounds, the moments 0.10 and 0.02 *D* are indistinguishable from zero and thus agree well with the theoretically derived values. The moments found for the meta compounds are somewhat smaller than those calculated assuming no interaction. A similar but larger discrepancy is observed for the ortho derivatives where the two polar groups are much closer together. The observed diminution of the dipole moment can be explained by either a separation of the groups resulting in an increase in the angle θ or a mutual induction effect. The latter of the two possible explanations is preferred since electron diffraction data indicate only a slight change of θ regardless of the type of groups present.¹² The magnitude of the differences between calculated and observed moments found in the chloro and bromo derivatives is nearly the same. This is to be expected since the chloro and bromo group moments are almost equal.

The rather large difference between the calculated and the observed value for *o*-nitrotriazobenzene may also be accounted for by mutual induction. However, it is necessary to consider other factors to explain the surprisingly large moment found for the *p*-nitro derivative. Many of the properties of nitrobenzene are best explained on the basis of resonating structures having electron deficiencies in the ortho and para positions. The triazo group may exist as a hybrid of the two resonating structures, $-\text{N}=\text{N} \rightleftharpoons \text{N}$ and $-\text{N} \leftarrow \text{N} \equiv \text{N}$. Then, in *p*-nitrotriazobenzene, resonance of the electrons in the nitro group with the benzene ring will induce a negative charge in the triazo group nitrogen atom adjacent to the ring. The contribution of this polar hybrid could readily account for the observed exalted dipole moment.

The dipole moment of triazoethane should be representative of alkyl triazo compounds since a moment induced in a carbon chain is seldom transmitted through more than two carbon atoms. Furthermore, this compound is void of distortions produced by strongly polar groups. The magnitude of the experimental dipole moment is in agreement with these observations.

(12) Reference 9, p. 555.

The difference in the dipole moments of triazoethane (2.12 *D*) and triazobenzene (1.55 *D*) can be explained on the basis of the relative polarities of the ethyl and phenyl groups. The dipole moment of ethylbenzene, approximately 0.5 *D*,¹³ is at least partially a result of the difference of electronegativities of the ethyl and phenyl groups, the phenyl group being the more negative. It must be emphasized that these observations offer a plausible explanation for the observed difference and are not to be interpreted quantitatively.

In 2-triazoethanol, free rotation may occur about several bonds and in calculating a theoretical dipole moment all possible positions around these bonds must be taken into consideration. This calculation can be made employing the equation suggested by Eyring.¹⁴ The molecule is considered to contain two opposing dipoles in the directions of the triazo and hydroxy groups. The moments of these dipoles are 2.12 *D* (triazoethane) and 1.70 *D* (ethyl alcohol),¹⁵ respectively. The valence angle for carbon is 110° and the C-N-N bonds form an angle of 120°. Employing these values, the calculated dipole moment of the molecule is 2.79 *D*. This value is considerably larger than the observed dipole moment, 2.48 *D*, suggesting the possibility of a restricted rotation favoring those structures in which the group moments oppose each other.

It is interesting to compare the dipole moment of triazoethanol (2.48 *D*) with that of 2-chloroethanol (2.0 *D*).¹⁷ The difference can be explained on the basis of a linear structure for the triazo group. The centers of polarity in the hydroxy and a linear triazo group should be farther apart than if the group had a cyclic structure. If the cyclic structure were correct, little difference would be ex-

(13) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), New York, N.Y., 1931, p. 108.

(14) Eyring, *Phys. Rev.*, **39**, 746 (1932). The calculation is based on the statement that the mean square of *n* vectors is equal to the sum of the squares of the lengths of the separate vectors plus twice all the possible products of the lengths of two vectors multiplied by the product of the cosines of the angles made by the directed lines connecting the pair.

(15) Reference 13, p. 193.

(16) Pauling and Brockway, *THIS JOURNAL*, **59**, 13 (1937).

(17) Reference 13, p. 202.

pected between the dipole moments of the chloro and triazoethanols.

It should also be noted that the terminal nitrogen of a linear triazo group is separated by four atoms from the hydroxy group. The chlorine is separated from the hydroxy group by only two atoms, making it more susceptible to the inductive effect which tends to decrease the resultant moment.

The dipole moment of triazoacetone, 3.64 *D*, is the resultant of the moments of the carbonyl and the triazo groups. A theoretical dipole moment has been calculated for this molecule using the method applied to 2-triazoethanol. This calculation is based on the assumptions that: (a) The acetone molecule is Y shaped. The two branches of the Y, making an angle of 110°, represent the positions of the methyl groups. The C-C-O bond angle is 125°. (b) The carbonyl group moment is 2.7 *D*.¹⁸ (c) The C-N-N angle of the triazo group is 120°¹⁶ and the group moment is 2.12 *D*. (d) Free rotation occurs about the carbonyl carbon to triazo group carbon and C-N bonds with an equal probability for all possible positions. (e) Mutual induction effects in the triazo and carbonyl groups are negligible.

(18) Smyth, ref. 13, p. 90.

The resultant moment, 3.59 *D*, is in excellent agreement with the experimentally determined value, 3.64 *D*. Hence there is little evidence for restricted rotation or interaction between the polar groups in triazoacetone.

Summary

1. The dipole moments have been determined for a series of organic triazo compounds in benzene solution at 25°. The moments, in debye units, for the triazobenzene derivatives are: *o*-nitro, 4.46; *m*-nitro, 3.56; *p*-nitro, 2.90; *o*-chloro, 2.37; *m*-chloro, 1.45; *p*-chloro, 0.30; *o*-bromo, 2.25; *m*-bromo, 1.40; *p*-bromo, 0.32; *o*-methyl, 1.39; *m*-methyl, 1.75; *p*-methyl, 1.90. For the aliphatic compounds the dipole moments are: triazoethane, 2.12; 2-triazoethanol, 2.48; and triazoacetone, 3.64 *D*.

2. The aromatic and aliphatic triazo group moments are 1.55 and 2.12 *D*, respectively.

3. The results of the determinations are evidence in favor of a linear resonating structure for the triazo group in both aromatic and aliphatic compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

I-Strain as a Factor in the Chemistry of Ring Compounds^{1,2}

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The chemistry of the cycloalkane derivatives exhibits a number of highly unusual phenomena for which no general explanation has yet been advanced. For example, both chlorocyclopropane⁶ and chlorocyclobutane⁷ are far less reactive in typical displacement reactions than are simple secondary aliphatic halides. Again, chlorocyclohexane is extraordinarily inert toward the usual nucleophilic displacements reagents,⁸ although the corresponding derivatives of cyclopentane and cycloheptane are quite reactive.⁹

On the other hand, the six-membered ring derivative, cyclohexanone, is highly reactive toward carbonyl reagents, such as cyanide ion¹⁰ and semicarbazide,¹¹ whereas cyclopentanone and cycloheptanone are surprisingly inert toward these reagents. Similarly, the reaction of perbenzoic acid with the three cyclic ketones gives the same order of reactivity.¹²

(1) Chemical Effects of Steric Strains. IV.

(2) Much of the material discussed in this paper was included in two papers presented to the Division of Organic Chemistry at Meetings of the American Chemical Society on April 10, 1946, and September 15, 1947.

(3) Department of Chemistry, Purdue University.

(4) Parke, Davis and Company Fellow at Wayne University, 1945-1947.

(5) United States Rubber Company Fellow at Wayne University, 1947-1948.

(6) Gustavson, *J. prakt. Chem.*, [2] **43**, 396 (1891).

(7) Perkin, *J. Chem. Soc.*, **65**, 950 (1894).

(8) Conant and Hussey, *This Journal*, **47**, 476 (1925).

(9) Loevenich, Utsch, Moldrickx and Schaefer, *Ber.*, **62**, 3084 (1929).

(10) (a) Lapworth and Manske, *J. Chem. Soc.*, 2533 (1928); 1976 (1930); (b) Prelog and Kobelt, *Helv. Chem. Acta*, **32**, 1187 (1949).

(11) Price and Hammett, *This Journal*, **63**, 2387 (1941).

(12) Friess, *ibid.*, **71**, 2571 (1949).

The differences in reactivity between five- and seven-membered ring compounds on the one hand and the six-membered ring compounds on the other, are quite large and involve factors of the order of 100. There can be little doubt, therefore, that these differences in reactivity point to an important effect of ring size on chemical behavior.

In the case of the 3- and 4-membered rings the concept of I-strain¹³ furnishes a satisfactory explanation of the inertness of chlorocyclopropane and chlorocyclobutane in bimolecular displacement reactions as well as the inertness of 1-chloro-1-methylcyclopropane and -butane in unimolecular solvolysis reactions. It is not immediately obvious that I-strain should also be an important factor in the reactions of 5-, 6- and 7-membered ring compounds. However, the I-strain hypothesis would predict that the rate of unimolecular hydrolysis of tertiary chlorides derived from these cycloalkanes should be altered by the internal strain in the ring in a manner very similar to that in which the rates of the bimolecular displacement reactions of the chlorocycloalkanes are affected. To obtain evidence on this point the rates of hydrolysis of 1-chloro-1-methylcyclopentane (I), -hexane (II) and -heptane (III) were determined.

In the course of the investigation it became of interest to observe whether methyl substituents in the cyclohexane ring would have a pronounced steric effect upon the rate of hydrolysis of the tertiary chloride (II). Accordingly, 1-chloro-1,2-(IV), 1-

(13) Brown and Gerstein, *ibid.*, **72**, 2926 (1950), and unpublished work with Mr. M. Borkowski.