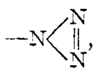
[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

The Physical Properties of Some Triazo Compounds. I. Molar Refractions and Parachors[1]

BY HANS O. SPAUSCHUS AND JOHN M. SCOTT

The molar refractions and parachors have been determined for nine aromatic and three aliphatic triazo compounds and are discussed with respect to the structure of the triazo group. The experimental values are consistent with a resonating linear structure for the group. The vapor pressure of triazoethane between 23.9 and 46.6° is described by the equation, $\log P_{mm} = -1644.4/T + 8.0135$, and its heat of vaporization is 7525 calories per mole.

The structure of the triazo group has been a problem of interest for many years. The results of chemical structural studies[2-4] have not been conclusive and structural evidences obtained from the measurement of physical properties[5-11] were often contradictory. The more favored of the proposed structures include the ring, , the covalent linear chain, $-\mathrm{N}{=}\mathrm{N}{\equiv}\mathrm{N}$, and the resonating linear chain postulated to exist as a hybrid of the two extreme structures, $-\mathrm{N}{=}\mathrm{N}\underline{\rightarrow}\mathrm{N}$ and $-\mathrm{N}{\leftarrow}\mathrm{N}{\equiv}\mathrm{N}$. Results of the application of electron diffraction data to triazomethane by Pauling and Brockway[12] indicated the resonating linear structure to be correct.

This investigation was undertaken to determine the physical properties of both aliphatic and aromatic triazo compounds and their relation to the proposed structures.

Experimental

Preparation and Purification of Materials.—*o*-, *m*- and *p*-derivatives of chloro-, bromo- and methyltriazobenzene were prepared from the corresponding aniline compounds by a method similar to that of Noelting and Michel.[13] The aniline derivatives were diazotized and the diazonium salts (hydrochlorides) were allowed to react with a slight excess of an aqueous solution of sodium azide added dropwise while stirring vigorously. The products were brown liquids, only slightly miscible with the aqueous layer, and could be removed readily from the latter with a separatory funnel. The triazo compounds were dried over calcium chloride, distilled through a short column under reduced pressure and the fractions collected in a receiving flask immersed in a Dry Ice–acetone-bath. Only constant boiling fractions were retained for the determination of the physical constants. A nearly constant refractive index(±0.0001) for successive constant boiling fractions was considered sufficient evidence for the purity of the compounds.

All of the freshly distilled products were clear, straw-yellow liquids which darkened on prolonged exposure to light. The yield of product in all cases was greater than 80% of the theoretical amount calculated for the weight of aniline compound used.

Triazoethane,[14] 2-triazoethanol[15] and triazoacetone[16] were prepared and purified by methods previously described.

Refractive Indices.—The refractive indices were determined at 25.0 ± 0.1° with an Abbe refractometer and a sodium vapor lamp light source.

Densities.—The density determinations were made at 25.00 ± 0.05° with specific gravity bottles. A 2-ml. bottle was used for the less volatile liquids, a 10-ml. bottle for those liquids having appreciable vapor pressures at room temperature.

Surface Tensions.—The surface tensions were measured at 25.00 ± 0.05° by the capillary rise method previously described.[17]

Vapor Pressure.—Vapor pressure measurements on triazoethane were made from 23.9 to 46.6° with a slightly modified Smith and Menzies isoteniscope.[18]

The boiling point ranges, densities, refractive indices and surface tensions of the compounds are listed in Table I.

TABLE I

Triazobenzenes	B.p., °C.	$P_{mm.}$	$d^{25}{}_4$	$n^{25}{}_D$	S.T.,[a] dynes/cm. 25°
o-Chloro	58-60	1.2	1.2808	1.5855	40.80
m-Chloro	49–51	0.7	1.2643	1.5787	39.02
p-Chloro	44–46	1.0	1.2634	1.5823	39.17
o-Bromo	69–71	0.45	1.5961	1.6117	43.11
m-Bromo	63–65	0.7	1.5840	1.6057	41.45
p-Bromo	58-60	0.9	1.5827	1.6106	41.68
o-Methyl	43–45	0.3	1.0648	1.5520	34.87[b]
m-Methyl	60–62	2.0	1.0554	1.5497	34.05
p-Methyl	38–40	0.65	1.0538	1.5504	34.66[c]
Aliphatic compounds					
Triazoethane	48.8–50.0[d]	766	0.8765	1.3928	22.83
2-Triazoethanol	52–54[e]	5.0	1.1454	1.4588[f]	41.38
Triazoacetone	33–35[g]	1.0	1.1132	1.4515	38.97[h]

[a] Maximum probable error of these values is 0.085. [b] 35.73 at 22.2°.[7] [c] 34.78 at 22.5°.[7] [d] 49° at 755 mm.[14] [e] 60° at 8 mm.[15] [f] 1.45778 at 24.9°.[5] [g] 54° at 2 mm.[16] [h] 39.33 at 18.5°.[7]

The vapor pressure data for triazoethane are listed in Table II.

TABLE II

T, Å.	$P_{mm.}$	T, Å.	$P_{mm.}$	T, Å.	$P_{mm.}$
319.8	766	309.8	524	302.8	388
315.9	664	307.6	478	299.2	328
314.1	622	305.3	432	297.1	300
312.2	576				

Results and Calculations

The molar refractions of the triazo compounds have been calculated by the Lorentz–Lorenz equa-

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[1] A part of the dissertation submitted by H. O. Spauschus to the Graduate School of Tulane University in partial fulfillment of the requirements for the Ph.D. degree. TAP Laboratory, General Electric Co., Pittsfield, Mass.

[2] E. Fischer, *Ann.*, **137**, 67 (1878).

[3] J. Thiele, *Ber.*, **44**, 2522 (1911).

[4] M. O. Forster, *J. Chem. Soc.*, **107**, 260 (1915).

[5] J. C. Philip, *ibid.*, **93**, 918 (1908); **101**, 1866 (1912).

[6] L. Pauling and S. B. Hendricks, THIS JOURNAL, **47**, 2904 (1925).

[7] H. Lindemann and H. Thiele, *Ber.*, **61**, 1529 (1928).

[8] L. E. Sutton, *Nature*, **128**, 639 (1931).

[9] E. Bergmann and W. Schütz, *ibid.*, **128**, 1077 (1931).

[10] N. V. Sidgwick, *Trans. Faraday Soc.*, **30**, 801 (1934).

[11] R. Samuel, *J. Chem. Phys.*, **12**, 167 (1944).

[12] L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 13 (1937).

[13] E. Noelting and O. Michel, *Ber.*, **26**, 86 (1893).

[14] O. Oliveri-Mandalá and G. Carrona, *Gazz. chim. ital.*, **71**, 182 (1941).

[15] M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 1865 (1908).

[16] M. O. Forster and H. E. Fierz, *ibid.*, **93**, 72 (1908).

[17] C. A. MacKenzie, A. P. Mills and J. M. Scott, THIS JOURNAL, **72**, 2032 (1950).

[18] A. Smith and A. W. C. Menzies, *ibid.*, **32**, 1412 (1910).

tion. The accepted refraction values used in these calculations are 31.05 (chlorobenzene),[19] 33.88 (bromobenzene),[19] 30.96 (toluene),[20] 12.78 (ethanol),[20] 23.99 (acetone),[21] 1.100 (hydrogen)[22] and 2.418 (carbon).[22]

For all compounds except triazoethane the density of the vapor was considered negligible in comparison with that of the liquid.

For triazoethane, the density of the vapor at 25° was obtained from the data in Table II. A plot of $1/T$ *versus* log P indicated a linear relationship between these functions described by the equation, $\log P_{\text{mm.}} = -1644.4/T + 8.0135$. Use of this equation gives 315 mm. for the vapor pressure of triazoethane at 25° and a corresponding vapor density of 0.0012 g./ml. A calculation of the heat of vaporization of triazoethane gives a value of 7525 calories per mole.

The contributions of the triazo group to the parachors of these compounds have been calculated using the systems of parachlor equivalents developed by Sugden,[23] Samuel[11] and Gibling.[24] These values as well as the refraction data are listed in Table III.

TABLE III

Triazobenzenes	$MR_{\text{Exp.}}$	R Equiv. N_3 group	$P_{\text{Exp.}}$	P Equiv. N_3 group Sugden	Samuel	Gibling
o-Chloro	40.21	10.26	303.0	75.8	75.8	81.0
m-Chloro	40.35	10.40	303.6	76.4	76.4	78.6
p-Chloro	40.58	10.63	304.1	76.9	76.9	79.6
o-Bromo	43.11	10.33	317.9	77.0	77.0	81.9
m-Bromo	43.10	10.32	317.2	76.3	76.3	78.2
p-Bromo	43.41	10.63	317.9	77.0	77.0	79.4
o-Methyl	39.96	10.10	303.9	74.9	74.9	80.3
m-Methyl	40.17	10.31	304.8	75.8	75.8	78.2
p-Methyl	40.27	10.41	306.6	77.6	77.6	80.5
Aliphatic compounds						
Triazoethane	19.35	9.01	177.5	82.4	82.4	82.4
2-Triazoethanol	20.78	9.10	192.8	77.7	77.2	74.3
Triazoacetone	23.99	8.93	222.4	79.3	78.8	78.2
			Mean	77.26	77.17	79.38

Discussion

While triazo compounds might be expected to be unstable like the heavy metal azides, the organic triazo compounds studied, particularly the aromatic derivatives, exhibit a surprising stability.[25]

The mean triazo group refraction value is 9.01 cc. for aliphatic compounds and 10.38 cc. for aromatic compounds because of an exaltation[5] common in conjugated systems. This exaltation is considered as evidence for a loose electronic system in the triazo group which is stabilized by resonance. The data for the substituted aromatic compounds indicate that chlorine and bromine produce about the same distortion in the electrons of the triazo group and that this distortion is greater than the one caused by the methyl group. This might be predicted from the electric moments for aromatic Cl, Br and CH_3 of 1.56, 1.53 and 0.41 D,[26] respectively. It must be kept in mind, however, that the substituents distort each other mutually, as shown by the lack of strict additivity, although the triazo group as the substituent with the least rigid electronic system is likely to be affected most.

Theoretical parachor values have been calculated[11,23,24] for the three structures proposed for the triazo group. These values are:

Structure	Cyclic		Covalent linear		Resonating linear	
System	Sugden	Samuel	Sugden	Samuel	Sugden	Gibling
Parachor	77.4	84.1	107.3	77.3	82.4	79.9

The large range of predicted values shows the weakness of the parachor as a tool for certain structural determinations.

The experimental parachor values calculated for the triazo group by applying the three systems are quite consistent. The systems of Sugden and Samuel yield the same group equivalents for the aromatic compounds. For these two systems, in general, the data indicate that the effective volume of the triazo group increases in passing from the ortho to the meta to the para positions in the ring. This variation is a function of the distance between the two polar groups. In the method of Gibling, a correction term has been introduced to compensate for the effect of position. The lack of consistency in the values calculated with his system could be attributed to the application of erroneous corrections. The large values obtained for the ortho compounds indicate that the normal ortho correction, −2.7, is preferable to the ortho augmented value, −4.7, although the latter was postulated to apply to those ortho compounds in which one of the substituent groups consisted of two or more atoms joined by a multiple bond.

The triazo group equivalent in triazoethane, 82.4, is the largest obtained for the group in any of the three systems. This value should be representative of the "normal" triazo group in absence of conjugation and other polar groups. It agrees exactly with one calculated for the structures of Pauling and Brockway using the parachor equivalents of Sugden.

The group value in 2-triazoethanol agrees well with the mean value calculated by the systems of Sugden and Samuel. The low value found by Gibling's method may be a result of association through the hydroxy groups. Gibling suggests the calculation of a "packing correction" which is the difference between the calculated and the experimental parachors of hydroxy compounds and is a function of the temperature. The packing

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(19) K. Seubert, *Ber.*, **22**, 2519 (1889).

(20) A. Weissberger, Editor, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, pp. 666–669.

(21) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 35.

(22) F. Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911).

(23) S. Sugden, "The Parachor and Valency," G. Routledge and Sons, London, 1930.

(24) T. W. Gibling, *J. Chem. Soc.*, 229 (1941); 661 (1942); 146 (1943).

(25) After approximately 6 months storage in a darkened cabinet about 15 ml. of triazoacetone decomposed spontaneously with enough violence to break the glass-stoppered flask and left a hard carbonaceous residue.

(26) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 568.

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.

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The Physical Properties of Some Triazo Compounds. II. Dipole Moments[1]

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In Part I[3] 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 I[3] 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 previously[6] 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_{2_0}, of a compound was made by the method of Halverstadt and Kumler,[7] using their equation

$$P_{2_0} = (E_1 - 1)/(E_1 + 2)(M_2v_1 + M_1B) + 3Av_1M_1/(E_1 + 2)^2$$

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_{2_0}, 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 (triazo).[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.

(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).

(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).