

from a straight line over the region investigated by 1% (the total change in the parachor in this range being 11%).

Sugden<sup>1</sup> had obtained 457.6 as the parachor of molten aluminum bromide, assuming the same formula  $Al_2Br_6$ . The value obtained here deviates by 3% from Sugden's value. If Sugden had used the formulas  $AlBr_3$  or  $Al_3Br_9$ , he would have obtained parachors of 228.8 and 686.4, respectively; in this work the same formulas give values of 232.9 and 703.2 after extrapolation, which represent deviations of a little less than 3%.

Our extrapolation is over a large range, so that any errors made at low concentrations will magnify greatly the error in the final value of the parachor. For this reason, it is somewhat surprising that the extrapolated values for the solution fall so near the values for the molten salt.

Owing to the above uncertainty, we can say only that the results obtained here tend to indicate that the formula of aluminum bromide dissolved in benzene is the same as that for the molten compound.

DEPARTMENT OF CHEMISTRY  
COLLEGE OF THE CITY OF NEW YORK  
NEW YORK, N. Y.

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### Preparation of Di-*o*-tolylchloromethane

BY EUGENE B. REID

Incidental to a program of measurement of physical properties, di-*o*-tolylchloromethane was prepared. It has not been described previously in the literature.

*o,o'*-Dimethylbenzohydrol was prepared by reducing *o,o'*-dimethylbenzophenone with 2% sodium amalgam; m. p. 120.5–121.5°. Boyd and Hatt<sup>1</sup> found 119–119.5°. A benzene solution of the carbinol was kept in contact with a concentrated aqueous hydrochloric acid solution for two days; the two layers were separated, and the benzene solvent evaporated. The di-*o*-tolylchloromethane crystallized from petroleum ether as long prisms; m. p. 70–71°; yield 90%.

*Anal.* Calcd. for  $C_{15}H_{15}Cl$ : Cl, 15.37. Found: Cl, 15.44.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF MICHIGAN  
ANN ARBOR, MICHIGAN

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(1) Boyd and Hatt, *J. Chem. Soc.*, 898 (1927).

### The Dipole Moment of the Amino Benzoic Acids in Dioxane

BY LLOYD VAN BLARICOM AND E. C. GILBERT

The dipole moments of *o*-, *m*- and *p*-aminobenzoic acid have been determined in water solution<sup>1</sup> in which solvent they occur partially in the zwitter-ion form. In non-polar solvents they should exist in ordinary molecular form but their low solubility has precluded measurements of their moment in such solvents. However, their solubility in dioxane proved upon examination to be sufficiently high to allow satisfactory measurements, which are reported in this paper. Dioxane has an additional advantage in that it does not cause association, in general, and it has therefore been used in the determination of the moments of many acids which associate in the ordinary non-polar solvents.<sup>2</sup>

**Apparatus and Method.**—The apparatus has been described previously.<sup>3</sup> It is based upon the heterodyne beat method and has been demonstrated to give correct results on substances of known dielectric constant. Refractive index was measured with a Bausch and Lomb dipping refractometer. Densities were determined with a pycnometer designed to avoid evaporation losses.<sup>4</sup> All weights were reduced to vacuum.

**Materials.**—Eastman Kodak Co. dioxane was refluxed with sodium hydroxide for ten hours and fractionated, discarding the first and last portions. It was then refluxed over sodium metal for another ten hours, and again distilled. That used for the measurements had the following constants: m. p. 11.7°;  $n_D^{25}$  1.41990;  $e^{25}$  2.2266;  $d_4^{25}$  1.02681.

The amino acids were Eastman best grade, further recrystallized three times. They were boiled with charcoal when necessary to improve the color and fractionally crystallized. They had the melting points: ortho, 144.5–145°; meta, 173–174°; para, 187–188° (all corrected for emergent stem).

### Results

The results are shown in Table I, and summarized in Table II. It is frequently assumed that the dipole moments of acids will be similar to those of their methyl esters. Estermann has determined the moments of the three methyl esters of these acids and they are included in the tables for comparison.<sup>5</sup> In each case the moment of the free acid is greater than that of the ester by a considerable percentage.

Dielectric studies of these acids in aqueous solu-

(1) (a) Hedestrand, *Z. physik. Chem.*, **135A**, 36 (1928); (b) Devoto, *Gazz. chim. ital.*, **63**, 247 (1933).

(2) Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

(3) Frey and Gilbert, *This Journal*, **59**, 1344 (1937).

(4) Gilbert and Stark, *ibid.*, **59**, 1818 (1937).

(5) Estermann, *Z. physik. Chem.*, **1B**, 134 (1928).

TABLE I

POLARIZATION DATA FOR DIOXANE SOLUTIONS OF AMINO-BENZOIC ACIDS

| Mole fraction | $n_D^{25}$ | $d_D^{25}$ | $n_D^{20}$ | $P_2$ |
|---------------|------------|------------|------------|-------|
| Ortho         |            |            |            |       |
| 0.0000        | 2.23025    | 1.02689    | 1.41990    |       |
| .00510        | 2.24795    | 1.02857    | 1.42143    | 90.0  |
| .012868       | 2.26766    | 1.03134    | 1.42356    | 82.7  |
| .020991       | 2.28782    | 1.03406    | 1.42581    | 80.3  |
| Meta          |            |            |            |       |
| 0.0000        | 2.22661    | 1.02681    | 1.41990    |       |
| .002963       | 2.26603    | 1.02817    | 1.42101    | 188.8 |
| .006905       | 2.30146    | 1.02933    | 1.42181    | 183.5 |
| .009591       | 2.32697    | 1.03029    | 1.42256    | 177.6 |
| Para          |            |            |            |       |
| 0.0000        | 2.22661    | 1.02681    | 1.41990    |       |
| .006280       | 2.33950    | 1.02933    | 1.42190    | 291.2 |
| .014378       | 2.47570    | 1.03234    | 1.42487    | 280.1 |
| .019724       | 2.55689    | 1.03436    | 1.42624    | 267.4 |

tion have indicated<sup>1,6</sup> that they differ considerably in the extent to which they exist in the polar amphoteric form, the meta acid being the only one which is predominantly of the zwitter-ion type, its solutions showing characteristically different behavior from the others.

(6) Devoto, *Z. Elektrochem.*, **40**, 490 (1934); Halbedel, *Z. physik. Chem.*, **33B**, 83 (1936).

TABLE II

DIPOLE MOMENTS OF AMINO-BENZOIC ACIDS (DEBYE UNITS)

| Acid  | $\infty P_2$ | $R_2$ | $\frac{P_E + P_A}{P_A}$ | $\mu$ , obsd. | $\mu$ , calcd. | $\mu$ , ester |
|-------|--------------|-------|-------------------------|---------------|----------------|---------------|
| Ortho | 91.5         | 39.7  | 43.7                    | 1.51          | 1.73           | 1.00          |
| Meta  | 194.5        | 39.0  | 42.9                    | 2.70          | 2.95           | 2.40          |
| Para  | 301.5        | 40.6  | 44.7                    | 3.51          | 3.40           | 3.30          |

In the non-polar solvent dioxane, on the other hand, it assumes the expected intermediary position between the para- and ortho-. This may be shown by a rough calculation of the moment by the method of Williams involving vector addition,<sup>7</sup> the results of which are shown in Table II, column 4. In making them a value of  $-1.9$  is assigned to the carboxyl group and  $+1.5$  to the amino group. Such simple assumptions cannot be applied quantitatively to structures as complicated as these molecules since they neglect the effects of valency angles, rotation, resonance, etc. Qualitatively, however, they are useful in illustrating the effect of polarity of the solvent upon the behavior of the meta acid.

(7) Williams, *THIS JOURNAL*, **80**, 2350 (1928).

DEPARTMENT OF CHEMISTRY  
OREGON STATE COLLEGE  
CORVALLIS, OREGON

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## NEW BOOKS

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**Organic Syntheses.** An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. XIX. By JOHN R. JOHNSON, *Editor-in-Chief*, HOMER ADKINS, C. F. H. ALLEN, W. E. BACHMANN, N. L. DRAKE, R. L. SHRINER, LEE IRVIN SMITH and A. H. BLATT, *Secretary*. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y., 1939. vi + 105 pp. 15.5 × 23.5 cm. Price, \$1.75.

The present volume, like the preceding one, is in harmony with the contemporary interest in biochemistry. As a reviewer of this volume (G. Bryant Bachman) recorded in a recent number of our News Edition, "it is interesting to note that 17 of the 30 preparations described are of nitrogen compounds." The methods of preparation have all been carefully tested. In a few instances—as in preparations IX, XXII, XXV, and XXX—a brief statement is given concerning the specific usefulness of the compound. Some of us, I am sure, would be glad to see an extension of this desirable feature.

The list of the new preparations is as follows:  $\alpha$ -acetaminocinnamic acid, acetylglycine, acridone, 2-amino-4-methylthiazole, benzimidazole, benzohydroxamic

acid,  $\epsilon$ -benzoylamino- $\alpha$ -bromocaproic acid,  $\epsilon$ -benzoylamino-caproic acid,  $\omega$ -bromoacetophenone, *n*-butyl sulfate, *n*-butyl sulfite, copper chromite catalyst, cyclohexylbenzene, dichloroacetic acid, *p*-dinitrobenzene, ethyl benzoyl-dimethylacetate, ethyl hydrogen sebacate, hexamethylene glycol, 5-iodoanthranilic acid, iodobenzene, *m*-iodobenzoic acid, *dl*-lysine hydrochlorides, methyl nitrate, *dl*- $\beta$ -phenylalanine, *o*-phenylenediamine, phenylnitromethane, phenylpyruvic acid, *p*-thiocyanodimethylaniline, 1,2,3-triiodo-5-nitrobenzene, triphenylmethylsodium.

M. GOMBERG

**Chemie der Zucker und Polysaccharide.** (Chemistry of Sugars and Polysaccharides.) By FRITZ MICHEEL, Professor of Organic Chemistry at the University of Münster (Westfalen). Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig C 1, Germany, 1939. xvi + 399 pp. 16 × 23.5 cm. Price, RM. 26.80; bound, RM. 28.40.

The author, whose important carbohydrate researches are well known, has now published one of the best treatises dealing with this field. The chemistry of the sugars, with