TABLE III

CONVERSION OF REARRANGED TOLYL IODIDE TO TOLUIC ACID

| | | | |
|---|---|---|---|
| $CH_3C_6H_4I$ | g......... | 14.38[a] | 15.32[b] |
| | mole...... | 0.066 | 0.070 |
| Magnesium | g........ | 1.8 | 2.2 |
| | mole..... | 0.074 | 0.090 |
| Ether, ml................. | | 70[c] | 110[c] |
| Time, hours | Addition... | 3 | 6 |
| | Stirring.... | 3 | 12 |
| Toluic acid | g......... | 5.75 | 6.05 |
| | %...... | 64.0 | 63.4 |
| | m. p...... | 102.4–103.0 | 103.3–103.7 |
| Residue | g........... | 1.55 | 1.50 |
| | %......... | 25 | 22.5 |

[a] Plus 15 ml. of anhydrous ether.   [b] Plus 60 ml. of anhydrous ether.   [c] Plus 0.90 ml. of methyl iodide.

tive index 1.607 is higher than the value of 1.603 for o-iodotoluene, and for that reason the main impurity is not likely to be m-iodotoluene, the refractive index of which is 1.601; likewise, it is not likely to be bitolyl, for the refractive index of a 10% solution of crude bitolyl (from the Grignard reaction) in o-iodotoluene is 1.592; the presence of the dissolved iodine does not compensate for the influence of any dissolved material because 0.5% of dissolved iodine does not change the refractive index; second, the small percentage of free iodine in the decomposition product (0.46%) shows that less than 1% of the iodonium compound decomposed into iodine and bitolyl; third, the crude toluic acid obtained from the decomposition product is pure o-toluic acid, uncontaminated by methylphthalic acid or by any m- or p-toluic acid, as shown by (a) the equivalent weight (136.7 against theoretical of 136.1), (b) the high melting point of the crude acid, 103.3–103.7°, a value

practically identical with the best value of recrystallized o-toluic acid obtained in this work, viz., 103.5–103.7°; (c) the mixed melting point of the crude with the purest o-toluic acid, viz., 103.4–103.7°; and (d) the lowering of the melting point of the crude acid by its admixture with the isomeric acids, 5% of which gave these values, meta, 99.5–101.6°; para, 98.5–100°.

Although the yield of o-toluic acid was 64%, a part of the reaction product, namely, 22–25%, was accounted for as bitolyl. The molecular weight of the crude bitolyl, as determined by the camphor method,[10] was found to be 204, whereas that of bitolyl is 182.

Since the yield of toluic acid was 64% and that of bitolyl 22–25%, 86–89% of the original material is accounted for. The presence of water in traces, during the preparation of the Grignard reagent, would lead to the formation of some toluene, which would be lost.

## Summary

Di-o-tolyliodonium iodide decomposes at 155° into o-iodotoluene and not into a mixture of iodotoluenes. The nature of the reaction product indicates that the ditolyliodonium ion splits into o-iodotoluene and positively charged o-tolyl ion by a scission of the C–I bond. The combining of this ion with the negative iodide ion produces o-iodotoluene.

In the formation of di-o-tolyliodonium iodate from o-iodosotoluene and o-iodoxytoluene, silver oxide acts catalytically.

(10) Smith and Young, J. Biol. Chem., 75, 289 (1927).

---

# The Parachor and Molecular Refraction of Hydrazine and Some Aliphatic Derivatives

BY L. D. BARRICK, G. W. DRAKE AND H. L. LOCHTE

Since aliphatic hydrazines and related compounds were until recently relatively rare, little work has been done on their physical constants. The determination of their parachor values seemed especially desirable in view of the variety of nitrogen linkages available. The data on these compounds furnish an opportunity to compare the atomic constants of Sugden[1] with those reported later by Mumford and Phillips.[2]

With the highly purified materials available the molecular refraction and dispersion were also redetermined.

**Preparation and Purification of Materials.**—Anhydrous hydrazine was prepared according to the method of Hale

and Shetterly.[3] Final drying was carried out by high vacuum distillation over freshly prepared calcium oxide; b. p. (corr.) 113° at 760 mm.[4]

Dimethylketazine was prepared according to the directions of Curtius[5] and dried over pellets of potassium hydroxide. The vapor of the fraction boiling at 132–133° was then passed, under vacuum, over fresh potassium hydroxide; m. p. −12.5°.

3,5,5'-Trimethylpyrazoline was prepared according to the method of Frey and Hoffmann[6] using oxalic acid as rearranging agent. The oxalate of the base was recrystallized from alcohol and the pyrazoline liberated by potassium hydroxide and dried like ketazine; b. p. 165–170° at 750 mm.

(1) Sugden, J. Chem. Soc., 125, 1177 (1924).
(2) Mumford and Phillips, ibid., 2112 (1929).
(3) Hale and Shetterly, THIS JOURNAL, 33, 1071 (1911).
(4) This portion of the work was done under the direction of Prof. W. A. Felsing of this Laboratory.
(5) Curtius, J. prakt. Chem., [2] 44, 164 (1891).
(6) Frey and Hoffmann, Monatsh., 22, 760 (1901).

Methylethylketazine[5] was prepared and purified in the same manner as the dimethyl compound. The yield can be increased to about 70% if a 50% excess of methyl ethyl ketone is refluxed with an excess of sodium carbonate, 1 molecular weight of hydrazine sulfate, and 200 cc. of water, the azine layer separated and 10% of the aqueous layer distilled off. The azine in the distillate can then be separated by means of stick potassium hydroxide and added to the original azine layer which is then dried and fractionated; b. p. 168–170° at 750 mm.

### TABLE I

| Compound | Density $d\,t/4$ (vac.) | Surface tension dyne/cm. | $n_C$ | $n_D$ | $n_F$ |
|---|---|---|---|---|---|
| Hydrazine | 0.9955 | 62.32 | 1.46207 | 1.46444 | 1.47108 |
| Dimethylketazine | .8380 | 26.02 | 1.44721 | 1.45067 | 1.45970 |
| 3,5,5-Trimethyl-pyrazoline | .8960 | 28.19 | 1.44682 | 1.45147 | 1.45919 |
| Methylethylketazine | .8341 | 26.11 | 1.44802 | 1.45127 | 1.45976 |
| Sym-di-isopropyl hydrazine | .7851 | 23.91 | 1.40998 | 1.41211 | 1.41773 |
| Sym-di-s-butyl-hydrazine | .8005 | 24.52 | 1.42235 | 1.42463 | 1.43053 |
| 2,2'-Azobispropane | .7431 | 18.46 | 1.38317 | 1.38633 | 1.39112 |
| 2,2'-Azobisbutane | .7689 | 21.01 | 1.40421 | 1.40643 | 1.41244 |
| Acetone isopropyl-hydrazone | .8184 | 25.60 | 1.43423 | 1.43722 | 1.44487 |
| Methylethyl ketone s-butylhydrazone | .8229 | 25.33 | 1.43958 | 1.44235 | 1.45033 |

Acetone isopropylhydrazone and methyl ethyl ketone secondary-butylhydrazone were prepared by the absolute alcohol method of Lochte, Noyes and Bailey;[7] b. p. 132 and 168–169.5°, respectively.

**Apparatus and Methods.**—All liquids were dried and distilled under high vacuum in the usual vacuum bench all glass apparatus.

A 2.5-cc. pycnometer, directly connected to the vacuum line by means of a ground glass joint, was used for density determinations. Surface tension measurements were made with a Cassel precision capillarimeter[8] calibrated with purified acetone, ethyl acetate, benzene, acetophenone and water. The slope of the plotted curve was found to be constant at 2.80. A Pulfrich refractometer was used for all refractive index determinations. Temperatures were determined to within 0.1° and were kept constant within this amount. As practically all the compounds are very easily oxidized or rearranged, higher refinements in method and technique were not considered essential.

The results are given in Table I. Measurements were made at 25° in all cases, except hydrazine, on which results were obtained at 35°.

Previously reported constants on some of these compounds are listed in Table II.

### TABLE II

| Compound | Ref. | $t$, °C. | Density $d\,t/4$ | $n_C$ | $n_D$ | $n_F$ |
|---|---|---|---|---|---|---|
| Hydrazine | 10 | 22.3 | 1.0065 | 1.46624 | 1.46979 | 1.47715 |
| Dimethylketazine | 10 | 24.5 | 0.8381 | 1.44746 | 1.45105 | 1.46008 |
| 3,5,5-Trimethylpyrazoline | 11 | 16.8 | .9147 | 1.44997 | | 1.46051 |
| Methylethylketazine | 10 | 26.6 | .8338 | 1.44826 | 1.45160 | 1.46000 |
| Sym-di-isopropyl hydrazine | 7 | 27.0 | .7844 | | 1.4125 | |
| Sym-di-isopropyl hydrazine | 12 | 20.0 | .7899 | 1.41516 | 1.41728 | 1.42379 |
| 2,2'-Azobispropane | 7 | 23.0 | .7408 | | 1.3890 | |
| 2,2'-Azobispropane | 12 | 20.0 | .7399–0.7414 | | 1.3889–1.39052 | |
| Isopropyl-azo-s-butane | 9 | 32.0 | .7495 | | 1.3945 | |
| Acetone isopropylhydrazone | 7 | 26.5 | .8225 | | 1.4360 | |
| Methyl ethyl ketone isopropylhydrazone | 9 | 28.0 | .8188 | | 1.4376 | |
| Acetone s-butylhydrazone | 9 | 28.0 | .8248 | | 1.4417 | |

Symmetrical di-isopropylhydrazine was prepared by the procedure of Lochte, Noyes and Bailey[7] by catalytic hydrogenation of the azine. The vapor of the fraction boiling at 124–125.5° at 750 mm. was passed over solid potassium hydroxide under vacuum, condensed over aluminum amalgam, and redistilled, b. p. 124.5–125° at 750 mm.

Symmetrical di-secondary-butylhydrazine was prepared and purified in analogous manner. The hydrochloride melted at 154° and the pure base boiled, like the azine, at 168–170° which was also practically the boiling point range of the corresponding hydrazone of s-butylhydrazine.

2,2'-Azobispropane was obtained from the hydrazo compound by the copper oxide oxidation method of Lochte, Noyes and Bailey[7] and dried by passing the vapor over calcium chloride; b. p. 89–89.5° at 747 mm.

2,2'-Azobisbutane was prepared in the same way except that it was found necessary to decompose the copper complex under vacuum or to oxidize by means of ammoniacal copper acetate from which the azo compound may be distilled easily by steam; b. p. 141–142° at 747 mm.

(7) Lochte, Noyes and Bailey, THIS JOURNAL, 44, 2556 (1922).

**Discussion of Results.**—Table III shows parachor values ($P$) observed in this study, those

### TABLE III

| Compound | $P$ | $P_1$ | $P_2$ |
|---|---|---|---|
| Hydrazine | 90.7 | 93.4 | 85.0 |
| Dimethylketazine | 302.2 | 305.4 | 313.0 |
| 3,5,5-Trimethylpyrazoline | 288.4 | 291.5 | 294.5 |
| Methylethylketazine | 379.8 | 383.4 | 393.0 |
| Sym-di-isopropyl hydrazine | 327.1 | 327.3 | 330.0 |
| Sym-di-s-butyl hydrazine | 400.8 | 405.4 | 410.0 |
| 2,2'-Azobispropane | 318.4 | 316.4 | 318.3 |
| 2,2'-Azobisbutane | 395.5 | 394.4 | 398.3 |
| Acetone isopropylhydrazone | 313.7 | 316.4 | 321.9 |
| Methyl ethyl ketone s-butyl hydrazone | 387.6 | 394.4 | 401.9 |

(8) Cassel, Chem.-Ztg., 53, 479 (1929).

(9) George Decherd, unpublished Master's Thesis, University of Texas, 1926.

(10) Brühl, Z. physik. Chem., 22, 373 (1897); 79, 30 (1912).

(11) Von Auwers and Heimke, Ann., 458, 175 (1927).

(12) Taipale, C. A., 18, 3049 (1924).

($P_1$) calculated from Sugden's constants[1] and those ($P_2$) calculated from the constants of Mumford and Phillips.[2]

While the values calculated according to Sugden agree fairly well with the observed ones, those obtained according to Mumford and Phillips generally show much poorer agreement so that we must conclude that special "strain constants" would have to be introduced to make the values of Mumford and Phillips of use. Since the values of Sugden agree as well as can be expected no such complications seem to be called for. In fact the constants of Sugden seem to be as well adapted for calculating the parachor of aliphatic hydrazines and related compounds as for the various other classes of compounds which have been investigated.

TABLE IV

| Compound | $M_C$ | $M_D$ | $M_F$ | $M_F - M_C$ |
|---|---|---|---|---|
| Hydrazine | 8.8522 | 8.892 | 9.000 | 0.148 |
| Dimethylketazine | 35.732 | 36.00 | 36.607 | .875 |
| 3,5,5-Trimethylpyrazoline | 33.54 | 33.72 | 34.22 | .680 |
| Methylethylketazine | 44.98 | 45.26 | 46.00 | 1.02 |
| Sym-di-isopropylhydrazine | 36.65 | 36.823 | 37.26 | 0.61 |
| Sym-di-s-butylhydrazine | 45.80 | 46.12 | 46.58 | .78 |
| 2,2'-Azobispropane | 35.835 | 36.107 | 36.5025 | .668 |
| 2,2'-Azobisbutane | 45.240 | 45.456 | 46.044 | .804 |
| Acetone isopropylhydrazone | 36.334 | 36.552 | 37.112 | .778 |
| Methyl ethyl ketone s-butyl-hydrazone | 45.490 | 45.735 | 46.457 | .967 |

Inspection of Table V shows that the constants used are all accepted ones but in the case of nitrogen they are used in some cases in a manner not heretofore attempted. As has been observed by Brühl, the nitrogens of hydrazines should be considered as primary amine nitrogens so that, in those compounds, the N–N linkage is equivalent to the N–H bond. With this as a starting point, we find that this holds even for the N=N of aliphatic azo compounds in which each of the nitrogens has the primary amine value. The C=N linkage of hydrazones and ketazines is equivalent to two C–N bonds and the nitrogens show secondary amine constants. The value of the double bonds is kept constant at that accepted for the C=C linkage. Previous workers have not used the double bond value for any but the C=C grouping and have simply added the double bond increment observed to the special constant for nitrogen, or other element concerned. Since a preliminary study of the extensive data reported by Brühl and others indicates that the simple scheme used above is not generally applicable, we refrain from discussion of any theoretical implications in regard to the linkages involved, but intend to continue the study of the regularities observed.

TABLE V

| Compound | C | H | Pri. amine | Sec. amine | Double bond | $M_D$ Calcd. | $M_D$ Found |
|---|---|---|---|---|---|---|---|
| (CH₃)₂CH—NH—NH—CH(CH₃)₂ | 6 | 16 | 2 | 0 | 0 | 36.75 | 36.82 |
| (CH₃)(C₂H₅)CH—NH—NH—CH(C₂H₅)(CH₃) | 8 | 20 | 2 | 0 | 0 | 45.99 | 46.12 |
| (CH₃)₂CH—NH—N=C(CH₃)₂ | 6 | 14 | 1 | 1 | 1 | 36.46 | 36.55 |
| (CH₃)(C₂H₅)CH—NH—N=C(C₂H₅)(CH₃) | 8 | 18 | 1 | 1 | 1 | 45.70 | 45.73 |
| (CH₃)(C₂H₅)CH—NH—N=C(CH₃)₂ | 7 | 16 | 1 | 1 | 1 | 41.08 | 41.25 |
| (CH₃)₂CH—NH—N=C(C₂H₅)(CH₃) | 7 | 16 | 1 | 1 | 1 | 41.08 | 41.10 |
| (CH₃)₂C=N—N=C(CH₃)₂ | 6 | 12 | 0 | 2 | 2 | 36.18 | 36.00 |
| (CH₃)(C₂H₅)C=N—N=C(C₂H₅)(CH₃) | 8 | 16 | 0 | 2 | 2 | 45.41 | 45.26 |
| (CH₃)₂CH—N=N—CH(CH₃)₂ | 6 | 14 | 2 | 0 | 1 | 36.28 | 36.11 |
| (CH₃)(C₂H₅)CH—N=N—CH(C₂H₅)(CH₃) | 8 | 18 | 2 | 0 | 1 | 45.52 | 45.46 |
| (CH₃)(C₂H₅)CH—N=N—CH(CH₃)₂ | 7 | 16 | 2 | 0 | 1 | 40.90 | 40.90 |
| 3,5,5'-Trimethylpyrazoline | 6 | 12 | 1 | 1 | 1 | 34.26 | 33.72 |

The molecular refraction and dispersion values of this series are given in Table IV.

Agreement between $M_D$ found and $M_D$ calculated, using the constants of Eisenlohr,[13] shows that molecular refraction can be used in this series in structure determinations provided certain arbitrary but accepted values for nitrogen are used. Table V shows the satisfactory agreement obtained if the various atoms are assigned the constants indicated.

(13) Eisenlohr, Z. physik. Chem., 75, 585 (1910); 79, 129 (1912).

**Summary**

The parachors of a series of aliphatic hydrazine derivatives are determined and calculated. The utility of Sugden's constants is demonstrated for these compounds.

The molecular refraction of these compounds was determined and calculated. Satisfactory agreement is obtained provided certain unusual atomic constants for nitrogen are consistently employed.