

The writer has found no previous determinations for comparison. The activity coefficients for potassium chlorate determined in this Laboratory<sup>3</sup> are entered in Table II for comparison.

(3) Jones and Froning, *THIS JOURNAL*, **66**, 1672 (1944).

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## Tetrahedral Interactions and Diamagnetic Susceptibilities

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Recently French and Trew<sup>1</sup> have summarized the molar susceptibilities of the polyhalogen derivatives of methane. These compounds are anomalous in the sense that they deviate seriously from Pascal's additivity rule. It is desired here to show that the data can be interpreted empirically by assuming that the molar susceptibility is the sum of the atomic susceptibilities and six interaction terms directed along the edges of a tetrahedron. The geometry of a tetrahedron is useful in the interpretation of diamagnetic susceptibilities as well as the heats of disproportionation reactions.<sup>2</sup> The compounds under consideration together with the experimental molar susceptibilities<sup>1</sup> are given in Table I columns one and two. The susceptibilities calculated by summing Pascal's atomic susceptibilities are in column three. The necessary data are from the "International Critical Tables"<sup>3</sup> and the constitutive correction factor for a single halogen bonded to carbon was not used. These calculated values are all higher than the experimental ones and the deviations increase with increasing number of halogens on the same carbon. In case of tetrahalogen compounds, the difference is close to 30%.

TABLE I

EXPERIMENTAL AND CALCULATED DIAMAGNETIC SUSCEPTIBILITIES

Compound	$\chi_M$ exp $\times 10^6$	$\chi_A$ Pascal $\times 10^6$	$\chi_M$ calcd. $\times 10^6$
CH <sub>4</sub>	16	17.7	17.7
CH <sub>3</sub> Cl	32.0	34.9	33.3
CH <sub>2</sub> Cl <sub>2</sub>	46.6	51.2	46.3
CHCl <sub>3</sub>	58.6	69.2	56.6
CCl <sub>4</sub>	66.8	86.4	64.8
CH <sub>3</sub> Br	42.8	45.4	44.3
CH <sub>2</sub> Br <sub>2</sub>	65.9	73.1	65.8
CHBr <sub>3</sub>	82.2	100.7	82.1
CBr <sub>4</sub>	93.7	128.4	93.4
CH <sub>3</sub> I	57.2	59.4	58.5
CH <sub>2</sub> I <sub>2</sub>	93.5	101.1	91.7
CHI <sub>3</sub>	117.3	142.7	117.2
CI <sub>4</sub>	135.6	184.4	135.2

The molar susceptibilities listed in the last column of the table were calculated on the assumption

- (1) French and Trew, *Trans. Faraday Soc.*, **41**, 439 (1945).  
(2) J. R. Lacher, *THIS JOURNAL*, **68**, 526 (1946).  
(3) "International Critical Tables," Vol. VI, p. 349.

that they could be represented as the sum of atomic susceptibilities plus six appropriate interaction terms. The equations used are

$$\text{CH}_4: \chi_M = \chi_C + 4\chi_H$$

$$\text{CH}_3\text{X}: \chi_M = \chi_C + 3\chi_H + (\chi_X + 3\text{H}\cdot\text{X})$$

$$\text{CH}_2\text{X}_2: \chi_M = \chi_C + 2\chi_H + 2(\chi_X + 3\text{H}\cdot\text{X}) - (2\text{H}\cdot\text{X} - \text{X}\cdot\text{X})$$

$$\text{CHX}_3: \chi_M = \chi_C + \chi_H + 3(\chi_X + 3\text{H}\cdot\text{X} - 3(2\text{H}\cdot\text{X} - \text{X}\cdot\text{X}))$$

$$\text{CX}_4: \chi_M = \chi_C + 4(\chi_X + 3\text{H}\cdot\text{X}) - 6(2\text{H}\cdot\text{X} - \text{X}\cdot\text{X})$$

The atomic susceptibilities for carbon and hydrogen,  $\chi_C$  and  $\chi_H$ , are from Pascal.<sup>3</sup> The constitutive correction due to a hydrogen-hydrogen interaction, H·H, was arbitrarily placed equal to zero. The susceptibility due to a halogen and three hydrogen-halogen interactions,  $\chi_X + 3\text{H}\cdot\text{X}$ , was calculated to give the best fit for the data of French and Trew.<sup>1</sup> The difference between two hydrogen-halogen and a halogen-halogen interaction,  $2\text{H}\cdot\text{X} - \text{X}\cdot\text{X}$ , was also calculated from the experimental data. The numerical values of all these quantities are summarized in Table II. The susceptibilities due to  $\text{X} + 3\text{H}\cdot\text{X}$  are close to the values of Pascal's constants for chlorine, bromine and iodine. The latter are 20.1, 30.6 and 44.6, respectively.

TABLE II

ATOMIC AND CONSTITUTIVE SUSCEPTIBILITIES			
Element or interaction	$\chi \times 10^{18}$	Element or interaction	$\chi \times 10^{18}$
C	6.0	Br + 3H·Br	29.5
H	2.93	I + 3H·I	43.7
H·H	0.0	2H·Cl-Cl·Cl	2.6
Cl + 3H·Cl	18.5	2H·Br-Br·Br	5.1
		2H·I-I·I	7.6

The molar susceptibilities calculated from the above equations and the data in Table II are given in the fourth column of Table I. The agreement between the experimental ones and those calculated in this way is quite satisfactory. Experimental studies on mixed halogen derivatives of methane would be interesting.

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## Halogenated Sulfonanilides

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In a previous contribution<sup>1</sup> from these laboratories, there was described a series of N<sup>1</sup>-phenyl sulfanilamides in which the N<sup>1</sup>-phenyl group was variously substituted with chlorine and bromine atoms. Since substituents in the 3,5-positions were found most effective as far as antibacterial activity is concerned, more compounds of this general type have now been prepared for study. Not only have chlorinated and brominated compounds been prepared and studied further, but also the iodinated and trifluoromethylated deriva-

- (1) Kaplan and Leubner, *THIS JOURNAL*, **67**, 1076 (1945).

TABLE I  
 SULFONANILIDES

Compound	Yield, <sup>a</sup> %	M. p., °C.	Analyses, %			
			Nitrogen		Sulfur	
			Calcd.	Found	Calcd.	Found
3',5'-bis-(Trifluoromethyl)-sulfanilaniide <sup>b</sup>	85	162-164	7.29	7.29	8.32	8.35
3'-Trifluoromethyl-sulfanilaniide <sup>b</sup>	87	115-117	8.85	8.83	10.12	10.20
3',5'-Diiodosulfanilaniide	81	191-192	5.60	5.55	6.40	6.06
3'-Bromo-5'-chlorosulfanilaniide	76	142-143	7.75	7.12	8.86	8.77
3',5'-Dibromo-4'-hydroxybenzenesulfonaniide	36	161-163	3.44	3.21		
3',5'-Dibromo-4'-hydroxysulfanilaniide	80	199-200	6.64	6.94		
3'-Bromo-5'-chloro-4'-hydroxysulfanilaniide	55	207-208	7.41	7.30	8.48	8.10
3',5'-Diiodo-4'-hydroxysulfanilaniide	45	192-194	5.43	5.43	6.19	6.09
3',5'-Dibromo- <i>o</i> -aminobenzenesulfonaniide	62	158-160	6.90	6.91	39.3 <sup>c</sup>	39.10 <sup>c</sup>
3',5'-Dibromo- <i>m</i> -aminobenzenesulfonaniide	61	173-175	6.90	6.95	39.3 <sup>c</sup>	39.31 <sup>c</sup>
N <sup>4</sup> -Succinyl-3',5'-dibromosulfanilaniide		217-218 (dec.)	5.61	5.79	253.1 <sup>d</sup>	247 <sup>d</sup>

<sup>a</sup> The yield is based on the amount of substituted aniline originally used. <sup>b</sup> L. H. Schmidt and C. L. Sesler, *J. Pharmacol.*, **87**, 313 (1946), makes reference to the preparation of this compound in other laboratories also. <sup>c</sup> % Bromine. <sup>d</sup> Acid number.

tives have been synthesized. The effect of a phenolic hydroxyl in the molecule has also been investigated. Further a pair of isomers of 3',5'-dibromosulfanilamide has been prepared in which the para amino group has been shifted to the ortho and meta positions. This was done to complete the partly finished picture presented by the high antibacterial activity of 3',5'-dibromobenzenesulfonaniide as compared to 3',5'-dibromosulfanilaniide.

*In vitro* studies carried out by Dr. C. A. Lawrence and Mr. G. R. Goetchius in these laboratories showed that all the compounds described here have definite antibacterial action upon *Streptococcus pyogenes* C203, *Eberthella typhosa* "Hopkins" strain, *Clostridium perfringens*, *Mycobacterium tuberculosis* var. *hominis* H-37-Rv. Details of these results are being published elsewhere.

#### Experimental

All the necessary aniline intermediates were prepared according to methods recorded in the literature. *m*-Nitrobenzenesulfonyl chloride was prepared by the chlorosulfonation procedure of Hodgson.<sup>2</sup>

*o*-Nitrobenzenesulfonyl chloride was prepared according to the method of Wertheim.<sup>3</sup>

**3',5'-bis-Trifluoromethylsulfanilaniide.**—To 11.45 g. (0.05 mole) of 3,5-bis-trifluoromethylaniline dissolved in 25 cc. of pyridine and 30 cc. of acetone, 12.85 g. (0.0525 mole) of *p*-acetaminobenzenesulfonyl chloride was added. The resulting solution was heated on a steam-bath under reflux for one hour and then poured into ice water. The crystalline product was filtered off, thoroughly washed with water and dried. The crude yield was 21.5 g. (slightly more than theoretical) but no purification was carried out at this point. The crude acetyl derivative was heated under a reflux condenser with 40 cc. of 35% sodium hydroxide on a steam-bath. The reaction mixture was charcoaled and filtered. After acidifying with glacial acetic acid, the precipitated product was filtered off and dried. Recrystallization of 16.2 g. of crude material from aqueous alcohol gave 15.6 g. of pure product, m. p. 162-164°.

All the other *p*-aminobenzenesulfonaniides were made in this way (see Table I).

**3',5'-Dibromo-*o*-aminobenzenesulfonaniide.**—3,5-Dibromoaniline and *o*-nitrobenzenesulfonyl chloride were

(2) H. H. Hodgson and J. S. Whitehurst, *J. Chem. Soc.*, 482 (1944).  
 (3) Wertheim, "Organic Syntheses," Coll. Vol. II, 471 (1943).

condensed in a manner exactly analogous to the procedure described above. The yield of crude 3',5'-dibromo-*o*-nitrobenzenesulfonaniide was 92%. To a solution containing 27 g. of stannous chloride, 45 cc. of concentrated hydrochloric acid and 90 cc. of 95% ethanol was added 21.8 g. (0.05 mole) of the crude product. All were heated together for one hour under reflux. The solution was cooled and precipitated solid was filtered off, dissolved in sodium hydroxide, charcoaled and precipitated with acetic acid. Filtration gave 12.5 g. (62%) of product, m. p. 155-157°. Recrystallization from benzene raised the melting point to 158-160°.

The corresponding *m*-amino compound was prepared similarly.

**N<sup>4</sup>-Succinyl-3',5'-dibromosulfanilaniide.**—3',5'-Dibromosulfanilaniide (30.45 g.) was heated to reflux in 150 cc. of absolute alcohol. To this was added with stirring eight grams of succinic anhydride. After refluxing one and one-half hours, the solution was cooled and filtered giving 28 g. of crude product. This was recrystallized from alcohol to give 20 g. of the succinyl derivative, m. p. 217-218° (dec.).

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#### Heat of Combustion and Formation of 1,3,5,7-Cyclooctatetraene and its Heat of Isomerization to Styrene

BY EDWARD J. PROSEN, WALTER H. JOHNSON AND  
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Using the apparatus and procedures described previously,<sup>1,2,3</sup> determination has been made of the heat of combustion of the hydrocarbon, 1,3,5,7-cyclooctatetraene.

The cyclooctatetraene made available for these measurements was a 15-g. sample submitted with the following description: "The material was prepared by the polymerization of acetylene under pressure in the presence of tetrahydrofuran and nickel cyanide. It was purified by two distillations under reduced pressure in an atmosphere of nitrogen, using a 10-inch column packed with 42-mesh platinum screen spiral at a reflux ratio of

(1) E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **27**, 289 (1941).

(2) E. J. Prosen and F. D. Rossini, *ibid.*, **33**, 255 (1945).

(3) W. H. Johnson, E. J. Prosen and F. D. Rossini, *ibid.*, **36**, 463 (1946).