PARACHORS OF TRIALKYLMETHYLSILANES

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In the course of the use of Gibling's group-value method for the calculation of theoretical values of the parachor and the comparison of these values with the experimentally determined values of organic compounds of various types, it has been found necessary to introduce corrections into the theoretical values, these being required—according to Gibling—in order to take account of the interaction of hydrocarbon chains (corrections for parallelism) [1]. Corrections of this sort were found to be necessary for ethers [1, 2], amines [3], and arsines [4], which contain either a polar group (C = O, P = O, S = O), or atoms having unshared electrons, which can cause the bending of ether or hydrocarbon chains in the direction of the central polar group or the atom with the unshared electron pair. After being bent, the chains are arranged parallel to one another, so that a correction for parallelism is required. It would be of interest to determine whether not only compounds of this type, but also compounds of hydrocarbon character—not containing polar groups or atoms having unshared electron pairs—can require parallelism corrections.

Much attention has been given recently to the study of the parachors of hydrocarbons [5]. The value of the parachor has been found to be very sensitive with respect to the structure of a hydrocarbon molecule. Effects due to the presence of side chains and their positions in the hydrocarbon molecule are particularly notable ("strain constant") [6]. All of the experimental results, however, refer to hydrocarbons having short side chains (methyl, ethyl), and for these it is impossible to determine whether the hydrocarbon chains interact and become parallel [5]. In order to resolve the question of corrections for parallelism, instead of hydrocarbons having long chains such as trialkyl- and tetraalkyl-methanes, we selected the more accessible silanes of analogous structure for investigation. As the parallelism correction is more clearly manifested when three chains rather than four (when paired interactions are possible) are present in the molecule, we prepared a series of trialkylmethylsilanes for the investigation.

Table 1 gives the constants of the compounds that we prepared, the method of preparation being based on that already described for triethylmethylsilane [8]—reaction of triethoxymethylsilane with the corresponding organomagnesium compounds.

In the literature there are data on the preparation of compounds No. 1, 2, and 3 of Table 1, but their properties have not been described fully. Compounds No. 1 and 2 were prepared by reaction of the corresponding trialkylfluorosilanes with methylmagnesium iodide the only constant given for No. 1 is b.p. 126.8° (760 mm) [9], No. 2 is stated to have b.p. 183° (765 mm) and nD20 1.4290, the analytical data being: found % C 69.5; H 14.1; Calculated: C 69.7; H 14.05 [9]. Tributylmethylsilane (No. 3) was prepared by the action of C4H9Li on triethylmethylsilane, and its boiling point is given as 101-104° (93 mm) [10].

Data in the literature on the calculation of the parachors of aliphatic hydrocarbons indicate the necessity of making corrections to the values of the molecular parachor for the interaction of side chains, but different corrections are proposed by different investigators. The "strain constant" of Mumford and Phillips is about 3 units for each side chain, and it varies according to the structure of the molecule and the length of the side chain. Gibling finds a correction of −1.7 units for 2,3-dimethylpentane and for 3,4-dimethylhexane and a correction of −1.2 units for 3-ethylpentane [11]. Quayle finds corrections varying from −2.1 to −6.5 units for 17 octane isomers, and in calculations he assumes an average value of −3.7 units for each branching [5].

Table 2 gives values of parachors determined by us for a series of trialkylmethylsilanes, beginning from triethylmethylsilane and continuing to tridecylmethylsilane, in which the branching chains are much longer.

The atomic parachors of silicon given in the literature were calculated from the parachors of tetraalkylsilanes [12] and compounds of other classes, and they have nonidentical values ranging from 25.8 to 38.2 units [13]. From the parachor of triethylmethylsilane we have calculated the parachor of the group \((C)\) to be 33.38 units.

\[
\text{(C)} \quad \text{Si} \quad \text{(C)}
\]

The theoretical values of the parachors were calculated by the "group-value method" both with allowance for the possibility of side-chain interaction (I-between three chains, II-between two chains), and also without such
allowance. In the latter case the discrepancy between observed and calculated parachors exceeded experimental error (it varied from $-0.3\%$ to $-1.5\%$), which indicates the necessity for corrections to the value of molecular parachor to take into account the parallelism of the chains after the bend at the $\gamma$-carbon atom (the correction for the $\gamma$-carbon of each chain is $-1.4$ units) [14].

The best agreement between observed and calculated parachors was obtained when it was assumed that interaction occurred between two chains of the molecule rather than three, for which considerable discrepancies were observed (from $+0.3\%$ to $+2.1\%$) (Table 2). The data in Table 2 enable us to conclude that for trialkylmethyisilanes molecules the most probable structure is an extended one in which two chains are parallel, which is in accord with data on parachors obtained previously for esters of orthopropionic and various other acids [15], in which the central atom is not polar.

Quayle [5] has recently proposed that the calculation be based on atomic parachors, and he calculated the parachor of the CH$_2$ group to be 40.0 units for $n \leq 12$ and 40.3 units for $n \leq 12$. The parachors of trialkylmethyisilanes calculated from Quayle's atomic parachors with a correction for two branchings in the molecule ($-3.7 \times 2 = -7.4$ units) differ appreciably from the observed values, the difference being $+2.5\%$ for triethylmethyisilane, $+1.3\%$ for methyltripropylsilane, still less at $+0.1\%$ for tributylmethyisilane, and then becoming negative until it attains $-0.9$ unit for tridecylmethyisilane. Better agreement is therefore obtained between observed and calculated parachors when these are calculated by the group-value method rather than by Quayle's method of atomic parachors.

**EXPERIMENTAL**

Trialkylmethyisilanes were prepared by the general method of reaction of trichloromethyisilane with the corresponding organomagnesium bromides.

**Ethylethylmethyisilane.** Ethylmagnesium bromide was prepared from 16.5 g of magnesium and 75 g of ethyl bromide (added dropwise) in 250 ml of dry ether. The solution so obtained was stirred, and 20 g of trichloromethyisilane, b.p. 66°, was added gradually. Reaction was very vigorous. When the whole of the trichloromethyisilane had been added, the mixture was heated under reflux in a water bath for three hours. Ether was distilled off, and the residue was heated for a further three hours and then decomposed with 10% hydrochloric acid. The acid was added dropwise with the reflux condenser still in place. A little ether was added to the reaction product, and the resulting ethereal solution was washed, first with water, then with sodium carbonate solution, and finally with water again; it was dried over calcium chloride. The ether was distilled off, and the distillation of the residue yielded 6 g of ethylethylmethyisilane, b.p. 123.0 - 124.0° (760 mm). After distillation over metallic sodium, the ethylethylmethyisilane had b.p. 123.0 - 124° (760 mm); $n_D^20$ 1.4130; $d_4^20$ 0.7420; Found MR 43.78; Calculated MR 44.17; $\delta^2$ 20.82.

**Methyltripropylmethyisilane.** This was prepared similarly to ethylethylmethyisilane. Propylmagnesium bromide was prepared in 250 ml of dry ether from 13 g of magnesium and 65 g of propyl bromide, and 20 g of trichloromethyisilane was added immediately to the resulting solution. Reaction began when the mixture was heated in a water bath. The mixture was heated for three hours, and the residue remaining after removal of ether was heated for six hours. Dilute hydrochloric acid was added under ice cooling. The washed and dried product distilled completely (7 g) through a Widmer column at 177-181° (760 mm). After distillation over sodium the methyltripropylmethyisilane had b.p. 182.5 - 183.5° (765 mm); $n_D^20$ 1.4280; $d_4^20$ 0.7660; Found MR 57.88; Calculated MR 58.06; $\delta^2$ 22.90.

In view of their high stabilities, the trialkylmethyisilanes were analyzed by the combustion method. The weighed sample in the boat was covered with a finely ground mixture of cupric oxide and lead chromate, and part of the cupric oxide in the combustion tube was replaced by lead chromate, which was contained in a cartridge of copper gauze. Combustion of trialkylmethyisilanes without the use of lead chromate evidently led to the formation of carbides that could not be broken down by heat [16], and the carbon results for methyltripropylmethyisilane, methyltrioctylmethyisilane, and tridecylmethyisilane were low by 1.5-3.5%, in all analyses, whereas, good agreement was obtained for hydrogen.

Found %: C 69.73; H 14.11  
Calculated%: C 69.72; H 14.04

**Tributylmethyisilane.** This was prepared in a similar way. The organomagnesium compound was prepared from 10.7 g of magnesium and 60 g of butyl bromide in 180 ml of dry ether, and it was stirred while 20 g of trichloromethyisilane was added rapidly. Reaction occurred with evolution of heat, and when the mixture was heated a precipitate formed. Ether was distilled off, and the residue was heated for five hours in a water bath. The solid precipitate was decomposed with 10% hydrochloric acid, snow cooling being applied. The product was washed with water and sodium carbonate solution, a little ether was added, and the ethereal solution was washed with water and dried with calcium.