

496. *The Parachors of the Alkanes.*

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A statistical comparison has been made between the parachors of branched-chain and normal alkanes in order to evaluate parachor increments attributable to various interactions between non-bonded atoms. This is shown to lead to a simple and accurate method of correlating the parachors of these compounds. Comments are made upon the significance of the parachor and upon its dependence upon molecular structure.

THE effects of interactions between non-bonded atoms upon the parachors of the alkanes have been studied by making an *ad hoc* statistical comparison of the observed parachors of normal and of branched-chain isomerides. For this purpose, it has been assumed that the parachor of a given alkane is the sum of atomic constants and of increments due to the interactions associated with certain molecular structural factors. Thus :

$$[P] \text{ for } C_nH_{2n+2} = n[P]_C + (2n + 2)[P]_H + n_a p_a + n_b p_b + \dots \quad (1)$$

where the structural factor,  $a$ , giving rise to a parachor increment  $p_a$ , occurs  $n_a$  times within the molecule, and so on. Subtraction of the parachors of a set of branched-chain, isomeric alkanes from the parachor of the normal isomeride provides a set of differences, each one of which may be represented.

$$\Delta[P] = (n_a^n - n_a^b) p_a + (n_b^n - n_b^b) p_b + \dots \quad (2)$$

where the superscripts indicate "normal" and "branched."

Although each difference is comparatively small, and correspondingly sensitive to experimental error, a sufficient number of them can be used statistically to determine values for the structural increments,  $p_a$ ,  $p_b$ , etc., with some reliability. This has been done by applying the method of least squares, the required values of the increments being taken as those which minimised the over-all sum of the squares of the residual deviations between calculated and observed values of  $\Delta[P]$ . Data from the literature,<sup>1</sup> recalculated where necessary, have been used to provide a set of 28 parachor differences, to which this treatment has been applied.

<sup>1</sup> Coffin and Maass, *J. Amer. Chem. Soc.*, 1928, **50**, 1427; Timmermans, Hennaut-Roland, *et al.*, *J. Chim. phys.*, 1926, **23**, 733; 1928, **25**, 411; 1932, **29**, 529; 1935, **32**, 501; *Bull. Soc. chim. belges*, 1931, **40**, 177; Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg, *Rec. Trav. chim.*, 1939, **58**, 329; Quayle, Day, and Brown, *J. Amer. Chem. Soc.*, 1944, **66**, 938; Edgar and Calingaert, *ibid.*, 1929, **51**, 1540; Richards, Speyers, and Carver, *ibid.*, 1924, **46**, 1196; Vogel, *J.*, 1946, 133.

Since the parachor increments to be evaluated are hypothetically attributed to interactions between atoms not directly bound to each other by valency bonds, it was considered that no interactions between atoms outside a "three-carbon group" could be significant. That is to say, only those interactions occurring between any pair of non-bonded atoms in a chain of three carbon atoms, with their attached hydrogen atoms, were taken into account. Some of these were found by trial not to be significant. The method may be illustrated in terms of the interactions listed in Table 1.

TABLE 1.

Interactions between :

Next-but-one carbon atoms, $\begin{array}{c}   &   &   \\ \text{C} & - & \text{C} & - & \text{C} \\   &   &   \end{array}$ .....	Symbol $c_1$
H atoms linked to the same C, $\begin{array}{c}   \\ \text{H} - \text{C} - \text{H} \\   \end{array}$ .....	$h_1$
Methyl H atoms and H on adjacent C, $\begin{array}{c}   &   \\ \text{H} - \text{C} - \text{CH}_3 \\   \end{array}$ .....	$h_{2a}$
H atoms on adjacent methylenes, $-\text{CH}_2 - \text{CH}_2-$ .....	$h_{2b}$
H atoms of adjacent methylene and methine, $-\text{CH}_2 - \text{CH}$ .....	$h_{2c}$
H atoms of adjacent methines, $\begin{array}{c}   &   \\ \text{CH} & - & \text{CH} \\   &   \end{array}$ .....	$h_{2d}$
H atoms on adjacent C atoms, undifferentiated ( $\Sigma[h_{2a}/3, h_{2b}/4, h_{2c}/2, h_{2d}]$ ) .....	$h_2$
H atoms on C atoms once removed, $\begin{array}{c}   &   &   \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\   &   &   \end{array}$ .....	$h_3$
C atom and H on adjacent C, $\begin{array}{c}   &   \\ \text{H} - \text{C} - \text{C} - \\   &   \end{array}$ .....	$ch_1$
C atom and H on C atom once removed, $\begin{array}{c}   &   &   \\ \text{H} - \text{C} - \text{C} - \text{C} - \\   &   &   \end{array}$ .....	$ch_2$

The number of times a structural factor which gives rise to a particular kind of interaction occurs in a branched-chain alkane is subtracted from the number of times it occurs in the corresponding normal isomeride, giving a coefficient of one of the parachor increments in equation (2). All of these coefficients, for the alkanes indicated, are collected in Table 2, together with the values of  $\Delta[P]$  adopted for the calculations.

It will be noticed that the coefficients of the factors  $c_1$ ,  $h_1$ , and  $ch_1$  are invariably in the ratio 1 : 1 : -2. This is a necessary relation similar to that noted by Gibling<sup>2</sup> which compels the use of a composite structural factor,  $(c_1 + h_1 - 2ch_1)$ .

In order to determine which of the factors were significant, the least-squares calculation was performed a number of times. In the first calculation, none of the factors was considered; in the second,  $(c_1 + h_1 - 2ch_1)$  alone was taken into account; in subsequent trials of this kind, the other factors were introduced progressively and, where reasonable, alternatively. In each case, the root mean square deviation between observed and calculated values of  $\Delta[P]$  gave a measure of closeness of fit. Those interactions whose introduction improved the closeness of fit were considered to be significant; those which gave no improvement were discarded as insignificant. A selection of the results of these trials is shown in Table 3.

It appears that differentiation of interactions between hydrogen atoms on adjacent carbon atoms (*i.e.*, subdivision of  $h_2$  into  $h_{2a} \dots h_{2d}$ ) is warranted, notwithstanding that

<sup>2</sup> Gibling, *J.*, 1945, 236.

the corresponding increments stand nearly in proportion to the number of combinations in pairs of hydrogen atoms which are involved. The inclusion of an interaction between hydrogen atoms attached to carbon atoms once removed ( $h_3$ ) is justified, but its subdivision is not. The increment is small, but its coefficients are large. The zero increment for  $ch_2$  which has been found is to be expected. It will be noticed that all the increments are negative and fall away rapidly with increasing distance between the interacting atoms. The values shown in the last line of Table 3 have been adopted.

TABLE 2.

Alkane	Coefficients										$\Delta[P]$
	$c_1$	$h_1$	$h_2$	$h_{2a}$	$h_{2b}$	$h_{2c}$	$h_{2d}$	$h_3$	$ch_1$	$ch_2$	
isoButane .....	1	1	-7	-1	-1	0	0	15	-2	8	-0.1
isoPentane .....	1	1	-6	0	-2	1	0	8	-2	6	-1.15
2-Methylpentane .....	1	1	-6	0	-2	1	0	9	-2	6	-1.5
3-Methylpentane .....	1	1	-5	1	-3	2	0	2	-2	4	-3.0
2:2-Dimethylbutane .....	3	3	-18	-2	-3	0	0	25	-6	18	-4.3
2:3-Dimethylbutane .....	2	2	-11	0	-3	0	1	10	-4	10	-4.5
2-Methylhexane .....	1	1	-6	0	-2	1	0	9	-2	6	-1.7
3-Methylhexane .....	1	1	-5	1	-3	2	0	3	-2	4	-4.3
3-Ethylpentane .....	1	1	-4	2	-4	3	0	-3	-2	2	-7.1
2:2-Dimethylpentane .....	3	3	-18	-2	-3	0	0	27	-6	18	-4.95
2:3-Dimethylpentane .....	2	2	-10	1	-4	1	1	5	-4	8	-7.15
2:4-Dimethylpentane .....	2	2	-12	0	-4	2	0	19	-4	12	-4.45
3:3-Dimethylpentane .....	3	3	-16	0	-4	0	0	13	-6	14	-7.15
2:2:3-Trimethylbutane ...	4	4	-22	-2	-4	0	0	21	-8	20	-8.8
2-Methylheptane .....	1	1	-6	0	-2	1	0	9	-2	6	-1.85
3-Methylheptane .....	1	1	-5	1	-3	2	0	3	-2	4	-3.3
4-Methylheptane .....	1	1	-5	1	-3	2	0	4	-2	4	-3.5
3-Ethylhexane .....	1	1	-4	2	-4	3	0	-2	-2	2	-6.1
2:3-Dimethylhexane .....	2	2	-10	1	-4	1	1	6	-4	8	-6.6
2:5-Dimethylhexane .....	2	2	-12	0	-4	2	0	18	-4	12	-4.0
3:4-Dimethylhexane .....	2	2	-9	2	-5	2	1	0	-4	6	-8.2
2:2:3-Trimethylpentane ...	4	4	-21	-1	-5	1	0	17	-8	18	-10.2
2:2:4-Trimethylpentane ...	4	4	-24	-2	-5	1	0	38	-8	24	-6.9
3-Ethyl-3-methylpentane ...	3	3	-14	2	-5	0	0	2	-6	10	-10.6
2:6-Dimethylheptane .....	2	2	-12	0	-4	2	0	18	-4	12	-4.2
2:7-Dimethyloctane .....	2	2	-12	0	-4	2	0	18	-4	12	-4.3
4:5-Dimethyloctane .....	2	2	-9	2	-5	2	1	2	-4	6	-10.5
3:4-Diethylhexane .....	2	2	-7	4	-7	4	1	-8	-4	2	-12.9

TABLE 3.

Interactions considered	Parachor increments								Residual deviation, r.m.s.
	$c_1 + h_1$ $-2ch_1$	$h_2$	$h_{2a}$	$h_{2b}$	$h_{2c}$	$h_{2d}$	$h_3$	$ch_2$	
No interactions .....	—	—	—	—	—	—	—	—	6.31
$(c_1 + h_1 - 2ch_1)$ only .....	-2.6	—	—	—	—	—	—	—	2.66
$(c_1 + h_1 - 2ch_1), h_2$ .....	-12.4	-1.8	—	—	—	—	—	—	0.90
$(c_1 + h_1 - 2ch_1), h_{2a}, h_{2b}, h_{2c}, h_{2d}$ .....	-9.8	—	-4.3	-5.5	-3.2	-1.9	—	—	0.56
$(c_1 + h_1 - 2ch_1), h_2, h_3$ .....	-23.9	-4.4	—	—	—	—	-0.45	—	0.69
$(c_1 + h_1 - 2ch_1), h_{2a}, h_{2b}, h_{2c}, h_{2d}, h_3$ .....	-15.9	—	-8.3	-10.8	-5.7	-3.1	-0.2	—	0.50
$(c_1 + h_1 - 2ch_1), h_{2a}, h_{2b}, h_{2c}, h_{2d}, h_2, ch_2$ .....	-15.9	—	-8.3	-10.8	-5.7	-3.1	-0.2	0	0.50

Once the parachor increments have been determined in this way, they can be applied to individual compounds to eliminate the effects of all interactions which are not common to a set of isomerides. Thus, a corrected parachor,  $[P]'$ , may be obtained by subtracting the appropriate numbers of structural increments from the observed parachor of a compound. This gives, not a summation of atomic parachors alone, but the parachor of a hypothetical alkane in which all the hydrogen-hydrogen interactions are removed except

those which are present in methane, and all the carbon-hydrogen interactions except those of the kind which occur in ethane. This may be expressed as

$$[P]' = n[P]_0 + (2n + 2)[P]_{\text{H}} + 6h_1 + 6(n - 1)ch_1 \quad . \quad . \quad . \quad (3)$$

This quantity is found in fact to be linear with  $n$ ; the least-squares line for the 28 branched-chain alkanes and their 7 normal isomerides passes through the origin with negligible error and is represented by :

$$[P]' = 67.34n \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

All alkanes with the same value of  $n$  should have the same value of  $[P]'$ . This requirement has been tested, for all the original 35 alkanes and all the additional members of the series for which Quayle<sup>3</sup> has collected data. The results of this test are shown in Table 4, together with the predictions of equation (4).

For 60 hydrocarbons from ethane to hexadecane, the mean deviation between observed and calculated values of  $[P]'$  is 0.07% and for 53 of these it is 0.04%. One C<sub>8</sub> hydrocarbon (3-ethyl-2-methylpentane) and five C<sub>9</sub> hydrocarbons (2:2:4:4-tetramethylpentane,

TABLE 4.

$n$	No. of isomers	Obs. or mean of obs. $[P]'$	Mean deviatn. from mean (%)	Calc. $[P]'$ eqn. (4)	Obs. - calc. $[P]'$ (%)
1	1	72.6	—	67.3	+7.30
2	1	135.4	—	134.7	+0.52
3	1	199.9	—	202.0	-1.10
4	2	268.95	0.56	269.4	-0.17
5	2	337.0	0.06	336.7	+0.09
6	5	404.0	0.12	404.0	0.00
7	9	471.4	0.08	471.4	0.00
8	16	539.1	0.07	538.7	+0.07
9	12	605.9	0.06	606.1	-0.03
10	5	673.1	0.11	673.4	-0.04
11	2	740.7	0.05	740.7	0.00
12	1	808.5	—	808.1	+0.05
13	1	876.2	—	875.4	+0.09
14	1	944.6	—	942.8	+0.19
15	1	1012	—	1010	+0.20
16	1	1079	—	1078	+0.09
26	1	1765	—	1751	+0.79
32	1	2170	—	2155	+0.69
60	1	4114	—	4040	+2.04

TABLE 5.

$67.34n$	$(c_1 + h_1 - 2ch_1)$	$h_{2a}$	$h_{2b}$	$h_{2c}$	$h_{2d}$	$h_3$	$[P]_{\text{calc.}}$	$[P]_{\text{obs.}}$
<i>n-Octane</i>	6	4	5	0	0	28		
538.7	-95.4	-33.2	-54.0	—	—	-5.6	350.5	351.2
2:2:3-Trimethylpentane	10	3	0	1	0	45		
538.7	-159.0	-24.9	—	-5.7	—	-9.0	340.1	340.3
2:3:3-Trimethylpentane	10	4	0	0	0	38		
538.7	-159.0	-33.2	—	—	—	-7.6	338.9	339.0
2:3:4-Trimethylpentane	9	5	0	0	2	37		
538.7	-143.1	-41.5	—	—	-6.2	-7.4	340.5	340.8
2:2:4-Trimethylpentane	10	2	0	1	0	66		
538.7	-159.0	-16.6	—	-5.7	—	-13.2	344.2	343.7

2:2:4-trimethylhexane, 2:3-, 2:4-, and 3:3-dimethylheptane) show much wider deviations, between 0.4% and 2%; four of the discrepant results rest on unsupported observations. Increased deviations occur for extreme values of  $n$  and may be associated

<sup>3</sup> Quayle, *Chem. Rev.*, 1953, **53**, 439.

with "first-term anomalies" and with the "hexadecyl discontinuity" discussed by Mumford.<sup>4</sup>

Equation (4), and the six interaction increments, provide one of the best means of correlating the parachors of the alkanes from C<sub>4</sub> to C<sub>16</sub>. An example is given in Table 5 of the calculation of the parachors of five C<sub>8</sub> hydrocarbons, the results being compared with the observed parachors given by Quayle.<sup>3</sup>

It is clear that, for all four of the trimethylpentanes, the variation of the parachor with the positions of the methyl groups is adequately expressed.

#### DISCUSSION

The correspondence between parachors and molecular volumes has recently been demonstrated.<sup>5</sup> It is probable that close proportionality depends on uniformity of intermolecular forces and on the absence of preferred molecular orientation at the liquid surface. These conditions are likely to be satisfied by non-polar molecules which are not too long and attract each other by means of dispersion forces only. The analysis of the alkane data, and recent applications of the parachor to studies of preferred conformations of alkoxide molecules,<sup>6</sup> support this opinion.

Applications of the parachor depending on its division into additive structural and atomic constants must always be uncertain because of the arbitrary assumptions necessarily involved in such a division.<sup>7</sup> The concept of an atomic constant is difficult to accept, since, for atoms which define the size of the molecular skeleton, covalent radii will be significant parameters, whereas for peripheral atoms van der Waals dimensions will apply. Interactions between non-bonded atoms complicate the task and may arise in different ways. Normally, they are considered in terms of overlap of van der Waals fields and may greatly affect molecular volume in cases such as the perfluoroalkanes, where significant interpenetration is prevented.<sup>8</sup> It is, however, necessary to consider the envelope volumes generated by librational or rotational motion of molecules in the liquid phase. In attempting to divide such a volume into atomic contributions, the difficulty is encountered that one atom may follow the rotational path of another and so require no additional space in which to execute its own motion. Thus, in a hypothetical, freely rotating methyl group, all three hydrogen atoms traverse the same path which could equally well be swept out by one of them. Such coincidences will produce an effective "loss of volume" in a summation of atomic constants, and it is suggested that this effect is of predominant importance.

The alkane data may be examined in the light of these considerations. In equation (3)  $[P]_0$  is a function of the covalent radius of carbon;  $[P]_H$  is a function of the van der Waals radius of hydrogen, and the interaction  $ch_1$  is probably zero in effect. If this is so, equation (3), with  $n = 0$ , requires:

$$2[P]_H + 6h_1 = 0$$

The residual interaction effects,  $6h_1$ , are those present in methane, and the "loss in volume" due to them can be identified with the "volume" of two hydrogen atoms, since a hypothetical, rotating CH<sub>2</sub> molecule would generate the same envelope volume as a rotating methane molecule. Whether this result is coincidental or not, a case has been made that, in the alkane series, the parachor is a very well behaved molecular function of real physical significance.

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<sup>4</sup> Mumford, *J.*, 1952, 4897.

<sup>5</sup> Edward, *Chem. and Ind.*, 1956, 774.

<sup>6</sup> Bradley, Kay, and Wardlaw, *J.*, 1956, 4916.

<sup>7</sup> Samuel, *J. Chem. Phys.*, 1944, 12, 167.

<sup>8</sup> Simons and Dunlap, *ibid.*, 1950, 18, 335; Simons and Hickman, *J. Phys. Chem.*, 1952, 56, 420.