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**Carbon-13 Magnetic Resonance. II. Chemical Shift Data for the Alkanes**

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Carbon-13 chemical shift data for the linear alkanes up to *n*-decane and all the branched paraffins through the hexanes are given. Systematic trends in the chemical shift parameter were observed and empirical relationships are given which allow one to estimate with considerable accuracy unknown chemical shift values. Deviation from a very simple additivity relationship based upon the number of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -carbon atoms present in a molecule is correlated with the degree of branching noted in the compound. A sizable  $\gamma$ -substituent effect of opposite sign from the remaining substituent parameters constitutes an interesting and anomalous finding. Coiling in aliphatic chains of four carbon atoms or more appears to offer the best explanation of this anomaly.

**I. Introduction**

As parent compounds for a multitudinous number of alkyl derivatives, the paraffin hydrocarbons form a model class of compounds upon which a study of carbon-13 chemical shift data can be based. These data for the alkanes can be used as reference values in the study of substituent contributions in the corresponding series of derivatives. In addition, the alkanes are an important group to consider theoretically because of their relatively simple characteristics when compared with other organic compounds. Minimal charge polarization resulting from similar electronegativities of hydrogen and carbon is an assumption which should simplify greatly the theoretical assessment of the chemical shift data. This is especially true if one also assumes negligible deviations of the bond angles from tetrahedral symmetry.

Spiesecke and Schneider<sup>1</sup> have given carbon-13 chemical shift data for several of the simpler alkanes, whereas data on the linear alkanes through *n*-decane were communicated earlier by Paul and Grant.<sup>2</sup> In both of these publications additivity relationships were found which argue for a simplified theoretical explanation of the data. The data presented in this paper were obtained with the aid of proton decoupling in accordance with the techniques and methods described in the preceding paper in this series.<sup>3</sup>

As a means of correlating the carbon-13 magnetic resonance data for the alkanes, the chemical shift parameter is subdivided into terms proposed by Saika and Slichter<sup>4</sup> and presented as follows in the formalism used by Pople<sup>5</sup>

$$\sigma^A = \sigma_d^{AA} + \sigma_p^{AA} + \sum_{B(\neq A)} \sigma^{AB} + \sum_{\text{ring}} \sigma^{A, \text{ring}} \quad (1)$$

The value of  $\sigma^{A, \text{ring}}$ , a screening term important in molecules with sizable ring currents, is expected to be negligible for the alkanes. The terms  $\sigma_d^{AA}$  and  $\sigma_p^{AA}$ , respectively, apply to diamagnetic and paramagnetic electron currents on atom A. An expression for  $\sum_B \sigma^{AB}$ , an anisotropic screening term, has been given by Pople<sup>6</sup> and McConnell<sup>7</sup> for neighboring cylindrical bonds as

$$\sum_B \sigma^{AB} = \Sigma(\Delta\chi^B)(1 - 3 \cos^2 \theta_B)/3R_B^3 \quad (2)$$

where  $\Delta\chi^B = (\chi_{\parallel}^B - \chi_{\perp}^B)$  is the anisotropy of the magnetic susceptibility of the Bth bond. The distance from atom A to bond B is  $R_B$ , and  $\theta_B$  is the angle between the bond and the vector from A to B.

Several workers<sup>1,8-13</sup> have analyzed chemical shift data in terms of the anisotropies of nonadjacent bonds in the molecules. Assuming that the anisotropy of the C-H bond is negligible, values for  $\Delta\chi_{CC}$ <sup>14</sup> are 3.3,<sup>8</sup> 4.1,<sup>9</sup> 5.0,<sup>11</sup> 2.0,<sup>12</sup> and 4.2.<sup>13</sup> While these values are considerably larger than the value of 1.21 obtained theoretically by Guy and Tillieu,<sup>15</sup> they do agree with the approximate value of 4.0 proposed by Davies<sup>16</sup> for  $\Delta\chi_{CC}$  from crystal diamagnetic susceptibilities and Cotton-Mouton constants. Davies, however, also estimated that  $\Delta\chi_{CH} \approx 3.0$  which would invalidate the assumption that this term is small when compared with  $\Delta\chi_{CC}$ . A C-C bond shift not directly of the form predicted by eq. 2 has been proposed by Cavanaugh and Dailey<sup>10</sup> and Neikam and Dailey<sup>17</sup> to account for anomalous shifts in alkyl derivatives. This proposal has met with success although it is of an empirical nature.

When long range effects are investigated in flexible chain systems such as the alkanes studied in this work, it is necessary to average these effects over the various rotameric conformations weighted with the appropriate Boltzmann factor. Staggered structures in which 1,4-atoms can be either *trans* (180°) or *gauche* (60°) are assumed to be the only conformations which need be considered. It is useful to use the nomenclature that G and G' represent right-handed and left-handed *gauche* arrangements of carbon atoms and T stands for the *trans* form. The difference in *gauche-trans* energies for butane has been found, within limits of experimental error, to be 800 cal./mole by several workers.<sup>18</sup> For pentane only two rotameric forms were found to exist and the energy difference was determined to be 530<sup>19</sup> and 450 ± 60 cal./mole.<sup>20</sup> It was argued that

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TABLE I  
PROTON AND CARBON-13 CHEMICAL SHIFT DATA FOR  
SELECTED ALKANES

Compound	Carbon number	$f_1^a$	$\delta_H^b$	$\delta_C^c$	$\delta_C^{lit.}$
Benzene		59,985.014	0	0	
1 Methane					130.8 <sup>d,e</sup>
2 Ethane					122.8 <sup>e</sup>
3 Propane	C-1	59,991,423	6.27 <sup>f</sup>	113.10	111.3 <sup>e</sup>
4	C-2	59,991,420	5.84 <sup>f</sup>	112.62	110.9 <sup>e</sup>
5 <i>n</i> -Butane	C-1	59,991,566	6.27 <sup>e</sup>	115.48	
6	C-2	59,990,880	5.90 <sup>e</sup>	103.68	
7 <i>n</i> -Pentane	C-1	59,991,534	6.28	114.97	
8	C-2	59,991,027	5.90	106.13	
9	C-3	59,990,309	5.90	94.17	
10 <i>n</i> -Hexane	C-1	59,991,525	6.28	114.82	
11	C-2	59,991,006	5.90	105.78	
12	C-3	59,990,459	5.90	96.66	
13 <i>n</i> -Heptane	C-1	59,991,521	6.28	114.75	
14	C-2	59,991,002	5.89	105.70	
15	C-3	59,990,438	5.89	96.30	
16	C-4	59,990,614	5.89	99.23	
17 <i>n</i> -Octane	C-1	59,991,515	6.28	114.65	
18	C-2	59,991,000	5.89	105.67	
19	C-3	59,990,439	5.89	96.32	
20	C-4	59,990,601	5.89	99.02	
21 <i>n</i> -Nonane	C-1	59,991,516	6.29	114.67	
22	C-2	59,990,997	5.89	105.62	
23	C-3	59,990,435	5.89	96.25	
24	C-4	59,990,591	5.89	98.85	
25	C-5	59,990,575	5.89	98.58	
26 <i>n</i> -Decane	C-1	59,991,509	6.29	114.55	
27	C-2	59,991,003	5.89	105.72	
28	C-3	59,990,436	5.89	96.26	
29	C-4	59,990,587	5.89	98.78	
30	C-5	59,990,566	5.89	98.43	
31 Isobutane	C-1	59,990,898	6.27 <sup>g</sup>	104.35	103.9 <sup>e</sup>
32	C-2	59,990,898	5.43 <sup>g</sup>	103.52	103.9 <sup>e</sup>
33 2-Methyl- butane	C-1	59,991,036	6.28	106.67	
34	C-2	59,990,591	5.8	98.80	
35	C-3	59,990,466	6.00	96.88	
36	C-4	59,991,667	6.29	117.18	
37 2-Methyl- pentane	C-1	59,991,006	6.29	106.17	
38	C-2	59,990,717	5.8	100.9	
39	C-3	59,989,869	6.0	86.9	
40	C-4	59,991,334	6.0	108.0	
41	C-5	59,991,509	6.30	114.57	
42 Neopentane	C-1	59,990,472	6.25	97.23	97.1, <sup>e</sup> 97 <sup>h</sup>
43	C-2			100.8 <sup>i</sup>	101.1, <sup>e</sup> 101 <sup>h</sup>
44 2,2-Dimethyl- butane	C-1	59,990,620	6.32	99.77	
45	C-2	59,990,536		98.26 <sup>j</sup>	
46	C-3	59,990,178	5.93	92.02	
47	C-4	59,991,835	6.33	120.03	
48 3-Methyl- pentane	C-1	59,991,682	6.29	117.43	
49	C-2	59,990,616	6.0	99.4	
50	C-3	59,990,183	5.8	92.0	
51	C-3a	59,991,242	6.29	110.10	
52 2,3-Dimethyl- butane	C-1	59,991,195	6.32	109.35	
53	C-2	59,990,341	5.8	94.6	

<sup>a</sup> These values of  $f_1$  were corrected to an oscillator frequency,  $\nu_1$ , of 15,085,070 c.p.s. in order to obtain average value where multiple determinations were made. <sup>b</sup> In p.p.m. relative to neat benzene, using first-order splittings. <sup>c</sup> In p.p.m. relative to neat benzene. <sup>d</sup> Determined as a 5 mole % solution in cyclohexane of methane enriched to 70% C<sup>13</sup>. <sup>e</sup> Reference 1. <sup>f</sup>  $\delta_{CH_3-CH_2}$  determined by J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961), to be 0.43 p.p.m., and by D. Whitman, *et al.*, *ibid.*, **32**, 67 (1960), to be 0.44 p.p.m. <sup>g</sup>  $\delta_{CH_3-CH}$  determined by J. S. Waugh and F. W. Dobbs, *ibid.*, **31**, 1235 (1959), to be 0.85 p.p.m. <sup>h</sup> P. C. Lauterbur, *ibid.*, **26**, 217 (1957). <sup>i</sup> Obtained from sweep data. The C-2 in 2,2-dimethylbutane did enhance under decoupling and was observed in this manner.

the two forms were the TT and the equivalent TG, TG', GT, and G'T conformations. Respective values of  $520 \pm 70$  and  $470 \pm 60$  cal./mole were found<sup>20</sup> for the two equivalent sets of conformations (TGT, TG'T, and TTG, TTG', GTT, G'TT) in hexane as compared with the most stable TTT conformer. Once again these workers assumed that forms having more than one *gauche* arrangement have low statistical populations and contribute little to a sum over states. In 2-methylbutane and 2,3-dimethylbutane the energy

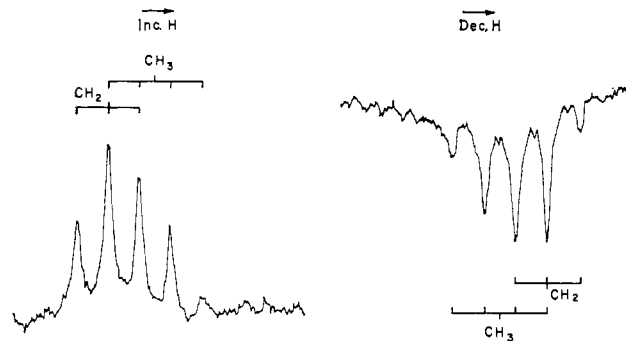


Fig. 1.—The rapid passage carbon-13 magnetic resonance spectrum of *n*-butane is not readily interpreted at 15.1 Mc.p.s. because the chemical shift and coupling parameters are such that considerable overlapping obscures the analysis. Based on the decoupled spectrum, however, the above assignment of lines is made possible.

difference between distinguishable rotamers was found,<sup>21</sup> respectively, to be  $100 \pm 50$  and 0 cal./mole (within experimental error).

These surprisingly low values are supposedly due to chain branching, and it must be concluded that the effect of a tertiary carbon atom on a bond axis of rotation is to reduce the preference of one rotamer over another.

## II. Results

Chemical shift data for the linear alkanes, propane through decane, are given in Table I along with the values for the branched paraffins up through the hexanes. The literature values<sup>1</sup> for methane and ethane are added to complete the table. The assignment of the chemical shift parameter to a given carbon atom can be made on the basis of peak intensities in several instances. The middle carbon in the odd-numbered linear alkanes (*i.e.*, propane, pentane, heptane, nonane) has a spectral intensity ratio of 1:2 when compared with the remaining peaks. In each of these cases a transition was found which was  $1/2$  the intensity of the remaining peaks. Thus, observations 4, 9, 16, and 25 in Table I have been assigned on this basis. In propane the remaining peak with double intensity must be due to carbon 1 (entry 3).

All remaining data for the linear alkanes are obtained from decoupled spectra in which the peaks have equal intensities. The assignment of values for *n*-butane, however, is made possible by observing the rapid passage spectra of this compound without proton decoupling. Figure 1 contains the rapid passage carbon-13 spectra of *n*-butane in which carbon 1 exhibits the characteristic quartet due to the three terminal methyl hydrogens, whereas the resonance of carbon 2 is split into a triplet due to the two directly bonded methylene hydrogens.

Confirmation of this assignment is obtained from the partially decoupled spectra which are shown in Fig. 2. When the proton splitting in the lower field multiplet is decoupled, a distorted quartet remains evident at higher field. Likewise, a distorted triplet remains upon decoupling the higher field, proton-induced multiplet. When taken together, these data

(21) G. J. Szasz and N. Sheppard, *J. Chem. Phys.*, **17**, 93 (1949).

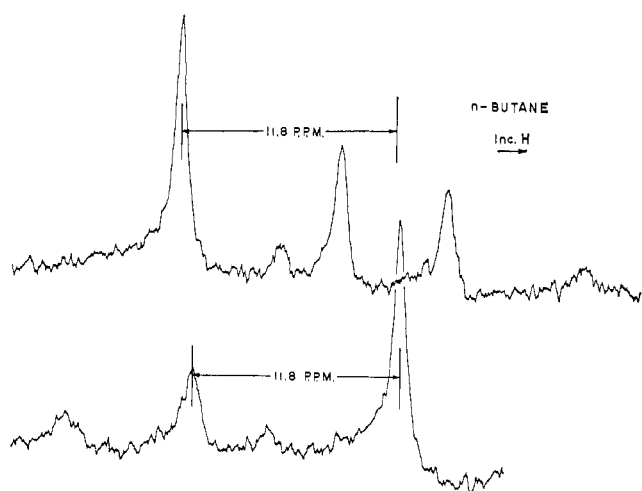


Fig. 2.—Decoupling in the lower field triplet in the spectrum of *n*-butane leaves a distorted quartet, whereas decoupling in the higher field multiplet clearly confirms that the triplet is down field. These spectra were required to assign unequivocally the interlaced multiplets of *n*-butane in Fig. 1.

establish that the chemical shift of the C-1 position comes at a higher field than the value for the second carbon.

The rapid passage and decoupled spectra for *n*-pentane and *n*-hexane are presented in Fig. 3 and 4, respectively. The decoupled spectra in both cases were obtained during the course of a single sweep by successively resetting the decoupler to the frequency of the next peak to be observed. In the instance of *n*-pentane the third carbon can be assigned on the basis of intensities for the decoupled spectrum as indicated above. The remaining peaks for *n*-pentane and the three *n*-hexane peaks are assigned by comparing the rapid passage and decoupled spectra. The over-all lower intensity of the quartet and the coincidents of the central line of a triplet with the decoupled transition are sufficient to make the assignment given in Fig. 3 and 4. In this manner C-1 and C-2 in *n*-pentane and C-1 in *n*-hexane are assigned unequivocally. The assignment of C-2 and C-3 in *n*-hexane, both triplets in the rapid passage spectrum, is made on the basis of similarity to corresponding peaks in *n*-pentane.

The data for methane through hexane provide sufficient information to indicate that regular trends exist for the chemical shift values in the linear alkanes. The remaining screening values for *n*-heptane through *n*-decane are assigned with considerable confidence, as they conform very well with the trends established by earlier members of the series where ambiguity did not exist in the spectral assignment. Figure 5 exhibits graphically the variation in chemical shift values for a first, second, third, fourth, and fifth carbon atom in a linear paraffin. The ordinate in Fig. 5 gives the chemical shift parameter, while the abscissa is the number of carbon atoms in the compound exceeding the position number of the carbon in question (*e.g.*, the number of carbon atoms attached to carbon 3 in *n*-heptane would be four for the purpose of constructing Fig. 5). The almost parallel solid lines link together values which correspond to the same carbon atom in the various species. The dashed lines indicate relationships between the chemical shift values for nonequivalent carbons in a given compound. A brief consideration of

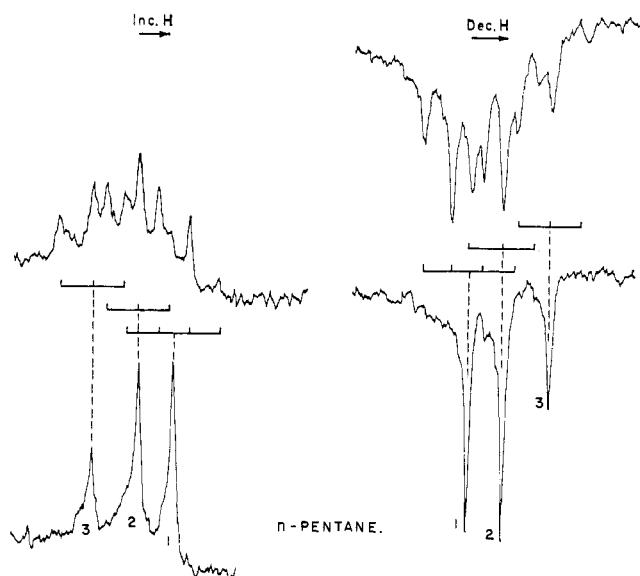


Fig. 3.—When considered together, the rapid passage and decoupled spectra of *n*-pentane allow the spectral lines to be sorted and assigned in the manner indicated. The two triplets corresponding to the second and third carbon atoms are assigned on the basis of the 2:1 intensity ratios, respectively.

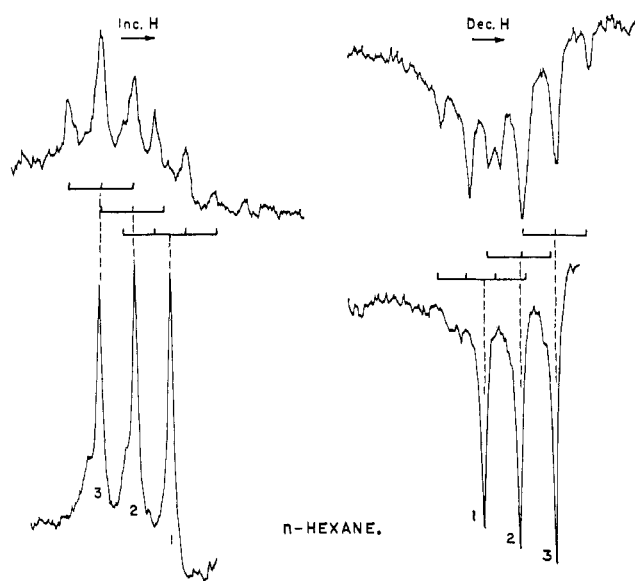


Fig. 4.—The assignment of peaks in the rapid passage and decoupled spectra of *n*-hexane rests on the identification of the quartet corresponding to the first carbon, and the comparable chemical shifts of the second and third carbon atoms found in both *n*-hexane and *n*-pentane. The equal intensities of all peaks in the decoupled spectrum for *n*-hexane otherwise prevent the assignment of the two triplets.

Fig. 5 would indicate that any other assignment of the data in Table I would have scrambled the values in such a manner that the systematic trends in Fig. 5 would not have been preserved. The only possible alternate assignment which would not disturb greatly the trends in Fig. 5 is an exchange of the assignment of C-4 and C-5 in *n*-decane. This seems unlikely, however, as the fifth carbon in *n*-nonane is downfield from the fourth and, as will be shown in the next section, a linear regression with only five independent variables corroborates the assignment in *n*-decane.

For the branched hydrocarbons seven entries in Table I (33, 37, 42, 43, 44, 52, 53) can be assigned

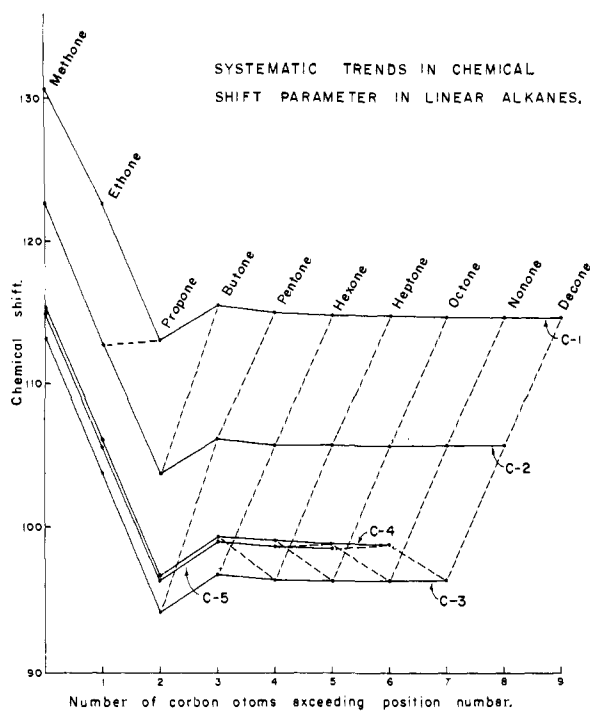


Fig. 5.—The chemical shift data for all the linear alkanes up to *n*-decane conform to a systematic pattern when plotted vs. the number of carbon atoms exceeding the position number in the molecule. Dotted lines link together the data obtained on a given compound, whereas the solid lines show the relationship existing for the carbon in the same position in each molecule.

directly on the basis of intensity comparisons. Furthermore, the two peaks corresponding to positions 1 and 2 with a relative intensity of two can be separated from peaks of unit intensity resulting from positions 3 and 3a in 3-methylpentane. In isobutane the decoupled spectra contained only a single resonance peak which could not be resolved into its component parts. The chemical shift difference between the two carbons in isobutane therefore is the same as exists between the two sets of protons. Work by Spiess and Schneider<sup>1</sup> agrees within experimental error with this conclusion.

The remaining spectral assignments depend upon arguments which find their origin in the systematic trends noted in the linear alkanes. In Fig. 5, it can be seen that  $\alpha$ - and  $\beta$ -carbon atoms shift the resonance position downfield by approximately 9 p.p.m., whereas a  $\gamma$ -carbon shifts the spectral peak upfield by about 2.5 p.p.m. The  $\delta$  contribution is downfield and relatively quite small, being about 0.4 p.p.m.

Use is made of Fig. 6 in which the chemical shift data are portrayed schematically for the remaining unassigned hydrocarbons along with the values for *n*-butane, *n*-pentane, and neopentane. Compounds with adjacent spectra differ by only one carbon atom, and the tie lines between spectra relate carbons which hold the same position in the smaller compound and in the moiety of the larger molecule that corresponds directly with the smaller compound. The Greek letter represents the orientation of the additional carbon atom relative to the carbon atom in question. In every instance the additional carbon atom shifts the peak as assigned in the same direction observed for the linear hydrocarbons. It is readily apparent, however, for nuclei at the center of branching and those

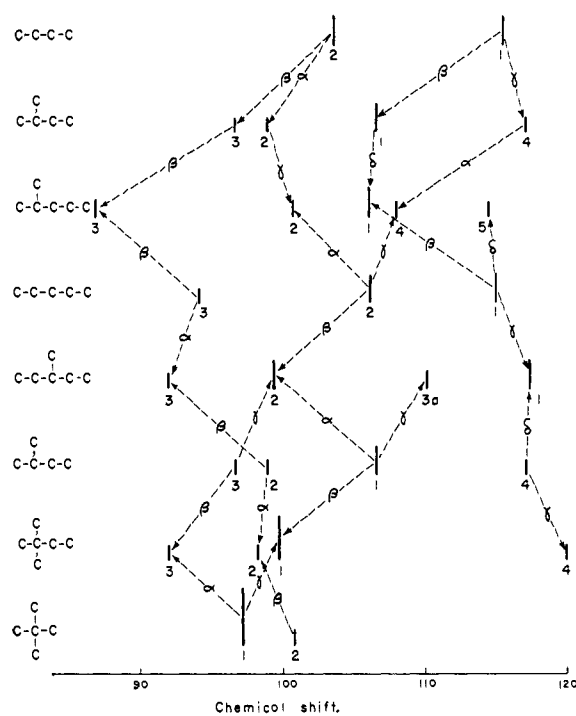


Fig. 6.—The decoupled spectra of several hydrocarbons are shown schematically in this figure to facilitate a discussion of the arguments used in making the spectral assignments. The numerals indicate the carbon to which the spectral line is assigned. Adjacent spectra are for compounds differing by one carbon atom. The Greek letter indicates the spatial relationship of this additional carbon atom to the other nuclei in the moiety of the larger compound which corresponds directly to the adjacent smaller molecule. This allows one to assess quickly at all positions the effect of adding a methyl group to any of the smaller hydrocarbons given in this schematic drawing.

adjacent to these positions that the magnitudes of the shifts do not correspond to the values found for the linear alkanes.

In comparing 3-methylpentane with *n*-pentane, only the given assignment of the double intensity peaks agrees with a negative  $\beta$ -shift and a positive  $\gamma$ -shift. Furthermore, the magnitudes are nearly the same as those found in the linear set. Likewise, a negative  $\alpha$ -shift for carbon 3 is realized only for the 92.0 p.p.m. peak. The remaining peak of unit intensity is relatively far upfield and probably due to the 3a-carbon. This is confirmed by the  $\gamma$ -shift noted between the resonance position for C-1 in 2-methylbutane and C-3a in 3-methylpentane. The effect of substituting a methyl group in position 2 of *n*-pentane is comparable to that noted in 3-methylpentane. In comparing 2-methylpentane with *n*-pentane, only one peak is found downfield of the resonance position of C-2 in *n*-pentane which could be due to an  $\alpha$ -shift. Again this  $\alpha$ -shift at a center of branching is considerably less than for the linear paraffins. The  $\beta$ -shift between the two third carbons has the proper sign and magnitude to confirm this assignment. Peaks four and five exhibit the proper  $\gamma$ - and  $\delta$ -shifts, and the peak at 106.36 p.p.m. with double intensity is unambiguously assigned to C-1.

Only the  $\gamma$ -shift between C-1 in neopentane and C-1 in 2,2-dimethylbutane has the proper sign and magnitude. This corroborates the intensity data which established the assignment of these two peaks and further vindicates the validity of the other arguments

which are based upon a positive  $\gamma$ -shift in highly branched compounds of this type. The remaining two peaks can be assigned either on the basis of small but negative  $\alpha$ - and  $\beta$ -shifts or in terms of a larger negative  $\beta$ -shift and a positive  $\alpha$ -shift of about 1 p.p.m. As all other  $\alpha$ -shifts were found to be negative, it seems likely that the first assignment would be better. Furthermore, as the proton decoupler was varied from the setting required to decouple the 92.02 peak, broadening typical of a proton multiplet occurred in this transition before the peak disappeared in the electronic noise. Under the same conditions, the peak assigned to C-2 exhibited less broadening, as might be expected for a quaternary carbon. The remaining high field peak is assigned to the fourth carbon.

As mentioned above, C-1 in 2-methylbutane can be assigned on the basis of intensity arguments. The fourth position in this compound is intermediate between the values for C-4 in *n*-butane and for C-4 in 2,2-dimethylbutane. Exhibiting a regular positive  $\gamma$ -shift as methyl groups are added in position two, this systematic trend lends validity to the assignment of C-4 in both of the substituted butanes. Furthermore,  $\alpha$ - and  $\delta$ -shifts of the proper sign and magnitudes are found between C-4 in 2-methylbutane and the corresponding carbon atoms in 2-methylpentane and 3-methylpentane, respectively. The assignment of the remaining two peaks to C-2 and C-3 depends primarily on the  $\gamma$ -shift found for these two carbons when compared with C-2 in 2-methylpentane and C-2 in 3-methylpentane, respectively. In addition, all the  $\alpha$ - and  $\beta$ -relationships noted in Fig. 6 for C-2 and C-3 in 2-methylbutane are negative and have magnitudes which are in line with the other values found for the branched systems. As a final confirmation of the assignment of C-2 and C-3 in 2-methylbutane the 2-deuterio-2-methylbutane was synthesized from 2-chloro-2-methylbutane by treating the corresponding Grignard reagent with  $D_2O$ . The 96.88 resonance peak enhanced with proton decoupling as before, whereas the 98.80 peak assigned to C-2 could not be enhanced because of the deuterium splittings.

### III. Discussion

The relationships portrayed in Fig. 5 suggest that chemical shift values for the normal alkanes might be described with a linear equation

$$\delta_C(k) = B + \sum_l A_l n_{kl} \quad (3)$$

where  $\delta_C(k)$  is the carbon-13 chemical shift value of the  $k$ th carbon,  $B$  is a constant which will be about equal to the chemical shift of methane,  $n_{kl}$  is the number of carbon atoms in the  $l$ th position relative to the  $k$ th carbon, and  $A_l$  is the additive chemical shift parameter assigned to the  $l$ th carbon atom. The values for  $A_l$  obtained from a linear regression analysis of the 30 chemical shift observations in the normal alkanes is contained in Table II along with the appropriate statistical summary. It is apparent from the multiple correlation coefficient and the student  $T$  ratios that the five variables (corresponding to the  $\alpha$  through  $\epsilon$  carbons) are excellent predictors of the chemical shift parameter. Furthermore, the standard deviation of the fit does not greatly exceed the estimated experimental error of  $\pm 0.07$  p.p.m. When compared with

TABLE II

REGRESSION ANALYSIS OF CHEMICAL SHIFT PARAMETERS IN THE LINEAR ALKANES UP TO *n*-DECANE

Number of observations: 30  
 Number of independent variables: 5  
 Multiple correlation coefficient  $R$  squared: 0.9996  
 Standard deviation in predicted chemical shift:  $\pm 0.21$  p.p.m.  
 Constant term: 131.26 p.p.m.

Carbon position $l$	$A_l$ in p.p.m.	Student $T$ ratio
$\alpha$	$-9.12 \pm 0.09$	105.1
$\beta$	$-9.38 \pm .09$	103.2
$\gamma$	$2.53 \pm .10$	26.4
$\delta$	$-0.37 \pm .10$	3.6
$\epsilon$	$-0.17 \pm .09$	1.8

the 37 p.p.m. range noted for this set of compounds, the error between predicted and observed values is minimal. Figure 7 contains a graphic comparison of the predicted and observed chemical shift values for both the linear and branched alkanes. The predicted values were calculated with eq. 3 from the additive parameters contained in Table II. The solid circles representing the linear alkanes fall very nicely upon a straight line, as also do several of the values obtained from the branched systems. Carbon atoms adjacent to or at the position of branching fail to follow the simple parameters given in Table II. These values, however, fall in sets which are parallel to the fitted line as shown by dashed lines in Fig. 7 and suggest that further additive parameters are required to bring the predicted values into agreement with the experimentally determined chemical shifts.

For highly branched systems, sizable terms are required to correct data for tertiary and quaternary carbons and for carbon atoms directly bonded to these centers. Thirteen independent variables which were required to obtain an analysis with a high correlation index are given in Table III with the accompanying

TABLE III

REGRESSION ANALYSIS OF CHEMICAL SHIFT PARAMETERS IN SELECTED LINEAR AND BRANCHED ALKANES

Number of observations: 53  
 Number of independent variables: 13  
 Multiple correlation coefficient  $R$  squared: 0.9992  
 Standard deviation in predicted chemical shifts:  $\pm 0.30$  p.p.m.  
 Constant term: 131.18 p.p.m.

Variable and coefficients	$A_l$ in p.p.m.	Observations affected by variable, no.	Student $T$ ratio
Carbon position			
$\alpha$	$-9.09 \pm 0.11$	52	79.8
$\beta$	$-9.40 \pm .11$	48	84.6
$\gamma$	$2.49 \pm .07$	36	35.5
$\delta$	$-0.31 \pm .10$	23	3.2
$\epsilon$	$-0.11 \pm .12$	15	0.9
Corrective term	Coefficient in p.p.m.		
$1^\circ(3^\circ)$	$1.12 \pm 0.21$	5	5.5
$1^\circ(4^\circ)$	$3.37 \pm .35$	2	9.7
$2^\circ(3^\circ)$	$2.50 \pm .24$	3	10.5
$2^\circ(4^\circ)$	7.23	1	<i>a</i>
$3^\circ(2^\circ)$	$3.65 \pm 0.17$	3	21.9
$3^\circ(3^\circ)$	9.47	1	<i>a</i>
$4^\circ(1^\circ)$	$1.50 \pm 0.12$	2	12.6
$4^\circ(2^\circ)$	8.36	1	<i>a</i>

<sup>a</sup> Only a single observation was available for each of these and therefore statistical analysis of experimental deviations for these terms presently is unavailable.

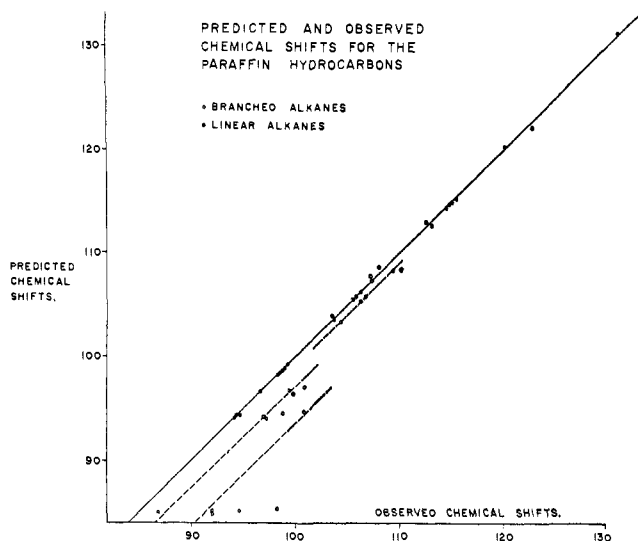


Fig. 7.—The experimental chemical shifts given in Table I are compared with the values predicted on the basis of the six parameters given in Table II. The solid circles corresponding to the linear alkanes fall on the line, whereas some of the data of the branched systems (open circles) are not correlated very well with this simple treatment. Nevertheless, the data which do not fall on the line exhibit further systematic trends suggesting the need for parameters which correct the predicted chemical shifts at or near centers of branching.

statistical summary. The terms were the five used in the linear alkanes for the number of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ - and  $\epsilon$ -carbons plus eight corrective terms which adjust the chemical shift data obtained for branched systems. Among the eight required correction factors are terms for a methyl group adjacent to either a tertiary or quaternary carbon which is represented by  $1^\circ(3^\circ)$  and  $1^\circ(4^\circ)$ , respectively. The remaining terms and their symbols are: secondary carbons adjacent to a tertiary center,  $2^\circ(3^\circ)$ , or quaternary carbon,  $2^\circ(4^\circ)$ ; tertiary carbon attached to a secondary carbon,  $3^\circ(2^\circ)$ , or tertiary carbon,  $3^\circ(3^\circ)$ ; and finally, the  $4^\circ(1^\circ)$  and  $4^\circ(2^\circ)$  terms describing quaternary carbons next to methyl radicals or methylene groups, respectively.

In three terms,  $2^\circ(4^\circ)$ ,  $3^\circ(3^\circ)$ ,  $4^\circ(2^\circ)$ , only a single observation was available to calculate the required corrections due to chain branching, thereby decreasing the degrees of freedom of the statistical analysis. Thus far, other attempts to explain these trends due to branching have not been successful. The magnitude of the effects would suggest that substituent values for  $\sigma_p^{AA}$  given in eq. 1 are not negligible but conversely are probably quite large. Deviations from tetrahedral symmetry as a result of steric strain may change the hybridization of the carbon atom which in turn would make  $\sigma_p^{AA}$  significant. The large  $\alpha$ - and  $\beta$ -carbon effects upon the chemical shift probably require a similar explanation.

Using energy values given in the introduction for *gauche-trans* isomerism,<sup>18-21</sup> the population of the various rotameric forms were calculated using the Boltzmann equation. The *gauche* and *trans* statistical populations were calculated for the  $\gamma$ -carbons where applicable for items in Table I, and a new regression analysis then was undertaken to determine the effect of  $\gamma_T$  and  $\gamma_{G \text{ or } G'}$  carbon atoms. This gave  $A_i$  values of  $2.38 \pm 0.39$  and  $2.32 \pm 0.27$  p.p.m., respectively,

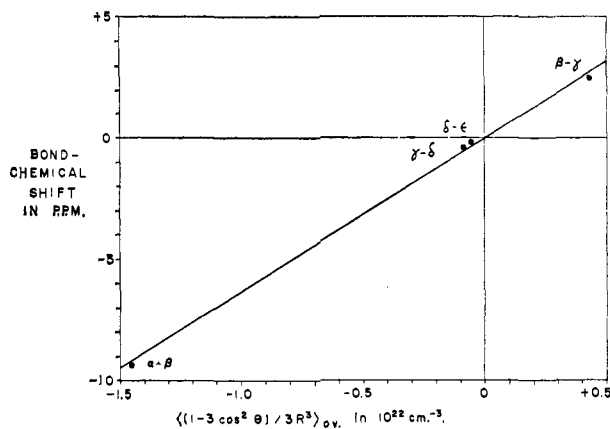


Fig. 8.—The substituent chemical shifts are compared with the value of  $(1 - 3 \cos^2 \theta) / 3R^3$  averaged over all allowed conformations. The slope of  $416 \times 10^{-6}$  cm.<sup>3</sup>/mole for this plot is much larger than values found for  $\Delta\chi_{C-C}$  in other work. The correlation presented here is therefore empirical because of the inconsistencies encountered in the application of eq. 2.

for  $\gamma$ -carbon atoms which are *trans* and *gauche*. Differing by considerably less than the standard deviation of the errors, the  $A_i$ 's for  $\gamma_T$  and  $\gamma_{G \text{ or } G'}$  are indistinguishable from the single coefficient for  $\gamma$ , and without additional data there is no reason for making a distinction. Assuming that the correct *gauche-trans* energies<sup>18-21</sup> were used to calculate the population differences, it would appear from this study that conformational terms are not directly affecting the chemical shift data. This would suggest that a term such as  $\sum_B \sigma^{AB}$  given by eq. 2 may be of minor importance because the contribution from this source is very dependent upon the geometry of the molecule. In addition, values used by other workers<sup>8-13</sup> for  $\Delta\chi_{C-C}$  and  $\Delta\chi_{C-H}$  to calculate long-range shielding parameters would only account for chemical shifts of a few tenths p.p.m. at the carbon and not the 2.5 p.p.m. found in this study.

While acknowledging the difficulties confronting the application of eq. 2 to long-range chemical shift effects, it is interesting to note that the anomalous +2.5 p.p.m. shift due to  $\gamma$ -carbons can be rationalized with eq. 2 with the one simplifying assumption that all allowed conformations are equally probable (*i.e.*,  $E_T = E_G$ ). Those configurations which require that two atoms occupy the same position in space are eliminated from consideration. The  $\beta$  through  $\epsilon$  substituent parameters recorded in Tables II and III then correlate well with the expression,  $(1 - 3 \cos^2 \theta_B) / 3R_B^3$ , properly averaged over the allowed conformations as can be observed in Fig. 8. It is assumed that a substituent contribution is not due merely to the designated atom but is due to the C-C bond connecting this atom to the preceding carbon in the chain, and they are so labeled in Fig. 8. The number of conformations included in the average for each C-C bond is given in parentheses as:  $\alpha$ - $\beta$ (1),  $\beta$ - $\gamma$ (3),  $\gamma$ - $\delta$ (7), and  $\delta$ - $\epsilon$ (17). The slope of this line yields a value of  $416 \times 10^{-6}$  cm.<sup>3</sup>/mole which is about two orders of magnitude larger than the values given by other workers<sup>8-13</sup> for  $\Delta\chi_{C-C}$ . For convenience, the values of  $(1 - 3 \cos^2 \theta) / 3R^3$  used in the sum over conformations are given in Table IV. These values were calculated on the basis of the staggered diamond lattice with all angles taken to be tetrahedral and the

TABLE IV  
VALUES OF  $(1 - 3 \cos^2 \theta)/3R^3$  FOR VARIOUS BOND CONFIGURATIONS  
(STAGGERED DIAMOND LATTICE WITH A C-C BOND OF 1.542 Å.  
ASSUMED)

Bond	Conformation designation <sup>a</sup>	$(1 - 3 \cos^2 \theta)/3R^3$ in $10^{22}$ cm. <sup>-3</sup>	Bond	Conformation designation <sup>a</sup>	$(1 - 3 \cos^2 \theta)/3R^3$ in $10^{22}$ cm. <sup>-3</sup>
$\alpha\beta$		-1.45	$\delta\epsilon$	GTT	-0.02
$\beta\gamma$	T	-1.42		TGG	+ .35
	G	+1.36		TGG'	+ .35 <sup>b</sup>
$\gamma\delta$	TT	-0.27		GTG	+ .35
	TG	+0.35		GTG'	- .02
	GT	-1.05		GGT	- .23
	GG	+0.53		GG'T	-1.42 <sup>b</sup>
	GG'	+1.36 <sup>b</sup>		GGG	-0.23
$\delta\epsilon$	TTT	-0.22		GGG'	+0.53 <sup>b</sup>
	TTG	+ .23		GG'G	-1.45 <sup>b</sup>
	TGT	- .44		GG'G'	+1.36 <sup>b</sup>

<sup>a</sup> Conformations which are mirror images to those given in the table have the same value. <sup>b</sup> These conformations are not allowed between carbon atoms in the paraffin series as two hydrogen atoms would occupy the same lattice position.

C-C bond distance equal to 1.542 Å. The vector  $R$  begins at the carbon for which the chemical shift is determined and terminates at the midpoint of the bond in question.

That the model for magnetic anisotropy of a C-C bond cannot explain the long-range shifts noted here, there can be little doubt; nevertheless, it is interesting

to note that the shifts are correlated in an empirical manner by an expression of the same form. Although no satisfactory explanation of the phenomena is presently available, it seems likely that the effect will only be explained in terms of more direct interactions between remote groups and the electronic structure of the carbon atom under consideration. The possibility of pseudo-six-member ring formation with four carbon atoms in a chain and the two attached hydrogens might well be a better explanation for the  $\gamma$ -carbon effect. This interaction would be very reminiscent of Newman's "rule of six"<sup>22</sup> in which sixth position hydrogen atoms greatly affect reaction rates. The energies associated with such interactions are sufficiently large to change the specific rate constants by several orders of magnitude. An interaction of this nature may well be large enough to modify slightly the electronic structure of the carbon atom. Admixture of higher paramagnetic orbitals or alteration in the degree of bond delocalization at the carbon atom due to this pseudo-six-member ring may be important in changing the chemical shift parameter. Both of these possibilities offer a means of explaining why a carbon atom would be affected by a remote  $\gamma$ -group, whereas no similar shifts of the magnitude discussed here have been observed in proton magnetic resonance spectra.

(22) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 204.

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## Nuclear Magnetic Resonance Studies of Hydrogen Bonding.

### II. Calculation of the Shift upon Complex Formation<sup>1a,b</sup>

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The shift upon hydrogen bond formation for the weak hydrogen bonds formed between chloroform and nitrogen bases was assumed to arise from two contributions: (a) the Buckingham electric field effect and (b) the neighbor anisotropy effect. The magnitudes of these two effects were then obtained as functions of the various parameters entering into the calculation. The electric fields were found by integrating over approximate nitrogen lone-pair electron distributions. The Pople-McConnell dipolar approximation was used to estimate effect (b). The results proved to be insensitive to all the parameters except the hydrogen bond length. Therefore, experimental values of the shifts were used to find these lengths, which proved to be in accord with X-ray crystallographic data, and to increase as the hybridization of the lone pair went from  $sp^3$  to  $sp$ . It was concluded for these weak hydrogen bonds that the above two effects are an adequate explanation for the shift upon hydrogen bond formation, and that this shift is a good criterion of "basicity" for weak hydrogen bonds if magnetic anisotropy effects are small, or if they are approximately constant for a series of electron donors.

#### Introduction

It is now well documented that hydrogen bond formation causes a shift to low field of the n.m.r. signal of the proton involved.<sup>2</sup> The principal contributions to this shift were suggested some time ago<sup>2</sup> and are: 1. A contribution to the proton screening (always negative) due to the distortion of the electronic structure of the chemical bond in which the proton is participating. 2. A contribution (negative or positive) to the proton screening due to any magnetic anisotropy

of the molecule to which the proton is hydrogen-bonded.

Buckingham<sup>3</sup> has suggested how the magnitude of the first effect ( $\Delta_E$ ) might be estimated, if it can be ascribed as solely due to polarization of the H-X bonding electrons by the electric field arising from the proximity of the electron donor molecule. He has derived the relation

$$\Delta_E = k_E \times 10^{-12} E_z - 0.738 \times 10^{-18} E^2 \quad (1)$$

where  $k_E$  is a proportionality constant,  $E_z$  is the magnitude of the field strength along the H-X bond axis, and  $E$  is the total field magnitude. The first term is taken as negative since the lone-pair electrons of the base repel the H-X bonding electrons toward X. Since Buckingham's original paper,<sup>3</sup> values of  $k_E$  from

(1) (a) Supported in part by Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-216-63; (b) presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., January, 1964; (c) Jersey Production Research Co. Fellow, 1962-1964.

(2) J. A. Pople, J. J. Bernstein, and W. G. Schneider, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 15.

(3) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).