Origin of the Additive Relationship for ^{13}C NMR Chemical Shifts of Alkanes as Studied by *ab initio* GIAO Calculations

Fumio Imashiro, Yuji Masuda, Masaru Honda and Shigeru Obara
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606-01, Japan

^{13}C NMR chemical shifts for conformers of alkanes from methane to heptane were calculated by the *ab initio* GIAO method. Conformationally averaged calculated chemical shifts were satisfactorily correlated with the corresponding experimental chemical shifts measured in solutions, yielding an additive relationship by using the additive shift parameters as defined for the experimental additive relationship. For the individual calculated ^{13}C chemical shifts of the alkane conformers, a new additive relationship was successfully constructed by employing four substituent and eight conformation additive shift parameters. It is elucidated that the mere presence of the $\gamma(C_{k\pm3})$-carbon brings about an upfield shift for the C_k carbon despite the conformation of the $2(C_{k\pm1}-C_{k\pm2})$-bond, and that the presence of the $1(C_k-C_{k\pm1})$-, 2-, and/or successive $2,3(C_{k\pm1}-C_{k\pm2}-C_{k\pm3})$-*gauche* bonds results in notable upfield shifts for the C_k carbon: the former two effects are related with the so-called vicinal- and γ-*gauche* effects, respectively. Additive relationships for the anisotropy and the symmetry parameter of the ^{13}C chemical shift tensors were also examined.

Thirty years ago Paul and Grant[1] proposed an additive rule for ^{13}C NMR chemical shifts of alkanes [eqn. (1)], where $\overline{\delta C}_k$ is the

$$\overline{\delta C}_k = \bar{B} + \sum_l \bar{A}_l n_{kl} \qquad (1)$$

chemical shift of the k-th carbon, $\bar{A}_l$ values are additive shift parameters ($l = \alpha, \beta, \gamma, \ldots$), $\bar{B}$ is a constant corresponding to the chemical shift of the methane carbon, which we can regard as one of the additive shift parameters, and n_{kl} is the number of carbon atoms in position l with respect to the C_k carbon. Since various conformers of alkanes larger than propane should be equilibrating in the isotropic phase such as gas, liquid, and solution states, we add bars to the chemical shifts and the parameters in eqn. (1). Among $\bar{A}_l$ values, only $\bar{A}_\gamma$, which represents the presence of the $\gamma(C_{k\pm3})$-carbon, is negative and brings about an upfield shift for the C_k carbon. This is explained by the so-called γ-*gauche* effect[2,3] which appears when the conformation of the 2-bond, connecting the $\alpha(C_{k\pm1})$- and $\beta(C_{k\pm2})$-carbons, is *gauche*. In the isotropic phase, the *gauche* contents of the carbon–carbon bonds in alkane molecules amount to about 30% for every bond. In the solid state or in the urea inclusion compounds the *gauche* contents are, however, considered to decrease, resulting in reduction of the $\bar{A}_\gamma$ values, though the values determined experimentally are still negative.[4] These results suggest that the presence of the γ-carbon yields always an upfield shift for the C_k carbon in spite of the conformation of the 2-bond. In addition to the γ-*gauche* effect, the 'vicinal-*gauche*' effect, resulting from the *gauche* comformation of the 1-bond, connecting the C_k and α-carbons, was proposed to explain the ^{13}C chemical shifts of solid cyclo-alkanes.[5] Recently, Barfield and Yamamura[3] pointed out that parameters A_α–A_γ are strongly conformationally dependent on the basis of the ^{13}C chemical shifts for propane and butane calculated by the *ab initio* IGLO (individual-gauge for localized molecular orbitals) method.[6]

In order to examine the experimental additive relationship, we calculate ^{13}C chemical shifts for conformers of alkanes from methane 1 to heptane 7 (we hereafter denote alkanes with the numbers of the carbons in the molecules) by *ab initio* GIAO (gauge-invariant atomic orbital) calculations[7] and construct the additive relationship based on the conformationally averaged calculated chemical shifts. In the equilibration among

alkane conformers, contributions of those involving successive *gauche* bonds with dihedral angles in the opposite sign, designated as $g^{\pm}$–$g^{\mp}$ bonds, should be very small because of their high energies relative to the corresponding most stable all-*anti* conformers. We, therefore, omit these conformers from consideration. Thus, numbers of the conformers treated in the present calculations are 2, 3, 7 and 13 for 4–7, respectively. We further investigate a new additive relationship which governs all of the ^{13}C chemical shifts of the calculated conformers to elucidate the origin of the additive shift parameters for the conformationally averaged chemical shifts. Additive relationships for anisotropic parameters derived from the ^{13}C chemical shift tensors, the anisotropy $\Delta\sigma$ and the asymmetry parameter η, are also examined. According to the usual definition,[8] the former is discontinuous at $\eta = 1$. In the present work, to avoid the discontinuity we use new definitions for the anisotropy $\Delta\sigma$ given by eqn. (2), where the three principal values of the

$$\Delta\sigma = \sigma_{33} - \sigma_{11} \qquad \Delta\sigma \geq 0 \qquad (2)$$

chemical shift tensors are defined as $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$[9] and the 'symmetry' parameter η' by eqn. (3), where the chemical shift

$$\eta' = 3(\delta C - \sigma_{22})/\Delta\sigma \qquad -1 \leq \eta' \leq 1 \qquad (3)$$

δC is equal to the isotropic value $\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$ of the chemical shift tensor, so $\eta' = 0$ corresponds to the most asymmetric state for the chemical shift tensor. It is noted that the present calculated chemical shifts are obtained as the shielding constants in ppm; therefore, positively large values correspond to upfield chemical shifts, opposite to the conventional definition for the experimental chemical shifts.

Experimental

NMR Measurements.—The ^{13}C chemical shifts of alkanes 5–7 in $CDCl_3$ solutions at 298 K were measured on a JEOL GX-400 spectrometer operating at 100.5 MHz. Chemical shifts were referenced to $CDCl_3$ (76.85 ppm from Me_4Si) as a secondary standard.

Calculations.—Geometries of all the alkane conformers in the present work were fully optimized by *ab initio* closed-shell

Table 1 [13]C Chemical shifts (δC) for conformers of alkanes 1–7 calculated by the *ab initio* GIAO method with their fractional populations p at 298 K[a]

Conformer	p	δC C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
1	1.000	207.16						
2	1.000	199.38	199.38					
3	1.000	191.28	192.59	191.28				
4 *a*	0.695	192.12	184.34	184.34	192.12			
g	0.305	194.60	186.37	186.37	194.60			
5 *aa*	0.522	192.11	185.28	175.95	185.28	192.11		
ga	0.425	194.07	186.79	177.89	187.87	192.10		
gg	0.053	195.20	191.17	180.38	191.17	195.20		
6 *aaa*	0.392	192.10	185.26	176.90	176.90	185.26	192.10	
gaa	0.318	194.00	186.85	178.88	179.57	185.26	192.04	
aga	0.148	192.03	187.37	178.38	178.38	187.37	192.03	
gga	0.072	195.15	190.68	180.77	182.80	188.53	192.12	
gag	0.033	194.07	186.53	181.19	181.19	186.53	194.07	
gag'	0.028	194.15	187.10	181.77	181.78	187.10	194.15	
ggg	0.009	195.02	191.58	185.15	185.15	191.58	195.02	
7 *aaaa*	0.293	192.10	185.27	176.89	177.84	176.89	185.27	192.10
gaaa	0.238	194.05	186.84	178.85	180.49	176.88	185.27	192.11
agaa	0.223	192.04	187.33	178.36	179.29	179.00	185.16	192.11
ggaa	0.054	195.17	190.65	180.74	183.74	180.13	185.24	192.07
agga	0.024	192.11	188.52	182.31	181.14	182.31	188.52	192.11
gaag	0.025	194.03	186.72	178.84	182.97	178.84	186.72	194.03
gaag'	0.024	193.97	186.77	178.74	183.15	178.74	186.76	193.97
gaga	0.047	194.07	186.40	180.65	181.60	178.06	187.37	192.01
gag'a	0.038	194.09	187.07	181.18	182.16	178.69	187.35	192.00
ggga	0.012	195.02	191.54	184.68	185.56	183.17	188.38	192.10
ggag	0.012	195.24	190.71	180.56	186.07	181.87	186.54	194.04
ggag'	0.009	195.16	190.83	180.97	186.86	182.40	187.19	194.08
gggg	0.001	195.02	191.38	185.53	189.93	185.53	191.38	195.03

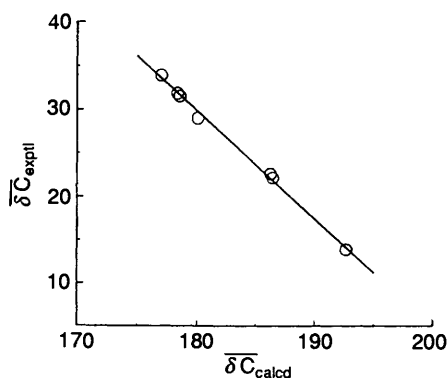[a] *a*, *g* and *g'* denote *anti*, (+)-*gauche* and (−)-*gauche* bonds, respectively.

Fig. 1 Correlation between the experimental ^{13}C chemical shifts $\overline{\delta C}_{expt}$ measured in CDCl₃ solution and the conformationally averaged calculated ^{13}C chemical shifts $\overline{\delta C}_{calcd}$ for alkanes from pentane (5) to heptane (7). The least-squares fitted line is solid.

restricted Hartree–Fock (RHF) calculations. The ^{13}C chemical shift tensors were calculated by the analytical second derivative method[10] of RHF energies with respect to the external magnetic field and the nuclear magnetic moment. The basis function we employed is the 4-31G GIAO function which is actually the 4-31G function multiplied by a phase factor which originates from the gauge invariance of one-electron eigenstates with respect to the choice of gauge of the external magnetic field. The existence of the phase factor in the expression of the RHF energies provides us with quite satisfactory chemical shift tensors[7] comparable with those

obtained by the more elaborated methods.[6] Since what we need is the relative differences of chemical shift tensors between distinct conformers rather than their exact absolute values, we consider the present valence double-zeta quality set to be reasonably pertinent to the present purpose. On comparison with experimental values, fractional populations were taken into account with the assumption of the Boltzmann distribution at 298 K on the basis of the calculated RHF energies and the geometrical multiplicities of the conformers.

All the molecular orbital calculations were performed with the *ab initio* calculation program KOTO[11] on a SONY NEWS-3260.

Results and Discussion

Table 1 collects the calculated values of the ^{13}C chemical shifts for the individual conformers of alkanes 1–7 with the fractional populations of the conformers, and Tables 2 and 3 list the calculated values for the corresponding anisotropic parameters of the ^{13}C chemical shift tensors.

Additive Relationship for Conformationally Averaged [13]C *Chemical Shifts.*—From Table 1 conformationally averaged calculated ^{13}C chemical shifts $\overline{\delta C}_{calcd}$ for alkanes 1–7 can readily be obtained. The chemical shift values for unique carbons in the molecules are listed in Table 4. In order to confirm the accuracy of the present calculations, we compared $\overline{\delta C}_{calcd}$ for 5–7 with the corresponding experimental chemical shifts $\overline{\delta C}_{expt}$ measured in CDCl₃ solutions at 298 K listed in Table 5, where the experi-

Table 2 Anisotropies of the ^{13}C chemical shift tensors $\Delta\sigma$ for conformers of alkanes 1–7 calculated by the *ab initio* GIAO method[a]

Conformer	$\Delta\sigma$/ppm C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
1	0.00						
2	10.41	10.41					
3	26.30	11.47	26.30				
4 *a*	25.81	28.25	28.25	25.81			
g	24.73	17.29	17.29	24.73			
5 *aa*	26.07	27.39	44.66	27.39	26.07		
ga	25.00	17.03	28.73	24.70	25.95		
gg	24.02	17.47	14.31	17.47	24.02		
6 *aaa*	26.27	27.75	43.68	43.68	27.75	26.27	
gaa	24.81	17.06	27.76	40.13	27.66	26.35	
aga	26.40	25.01	29.51	29.51	25.01	26.40	
gga	23.72	16.94	14.35	34.54	23.91	26.15	
gag	24.93	17.67	28.64	28.64	17.67	24.93	
gag'	25.36	17.53	26.97	26.97	17.54	25.36	
ggg	24.20	17.61	21.45	21.45	17.61	24.20	
7 *aaaa*	26.38	27.93	44.07	42.79	44.07	27.93	26.38
gaaa	24.76	17.26	28.08	39.17	43.90	27.99	26.47
agaa	26.51	25.00	29.63	28.55	40.83	28.04	26.37
ggaa	23.64	16.82	14.53	33.57	39.64	27.83	26.44
agga	26.22	23.64	33.71	14.46	33.71	23.63	26.22
gaag	24.71	17.40	27.78	29.90	27.76	17.40	24.70
gaag'	24.73	17.38	27.98	39.25	27.98	17.38	24.73
gaga	24.94	18.14	28.88	29.37	29.76	25.37	26.64
gag'a	25.47	17.71	27.38	27.05	29.94	25.68	26.52
ggga	24.21	17.34	20.45	21.45	34.69	24.07	26.33
ggag	23.21	16.92	14.53	32.40	28.12	18.01	25.04
ggag'	23.68	17.36	14.89	26.81	26.65	17.75	25.62
gggg	24.35	17.87	22.05	21.57	22.05	17.87	24.35

[a] *a*, *g* and *g'* denote *anti*, (+)-*gauche* and (−)-*gauche* bonds, respectively.

mental shifts for **8–12** are also collected. As shown in Fig. 1 the correlation between them is linear as expressed by eqn. (4), with

$$\overline{\delta C}_{exptl} = -1.25\overline{\delta C}_{calcd} + 255.36 \qquad (4)$$

a satisfactory correlation coefficient r of 0.9987. We consider that this result shows the validity of the present calculations, though the $\overline{\delta C}_{exptl}$ values are systematically larger by a factor of 1.25 than the corresponding $\overline{\delta C}_{calcd}$ ones.

First, we determined the experimental additive shift parameters by the least-squares fit of the experimental ^{13}C chemical shifts for **5–12** to eqn. (1), and found that not six[1] but five parameters listed in Table 6 are enough for the relevant additive relationship: standard and maximum errors are only 0.03 and 0.12 ppm, respectively, with $r = 0.99998$.

The five additive shift parameters were also applied to the additive relationship for the conformationally averaged calculated ^{13}C chemical shifts of **1–7**. A rather good relationship was found to hold with $r = 0.9994$, but the standard and maximum errors (0.24 and 1.00 ppm, respectively) were larger than the corresponding values for the experimental shifts. When we took off the value for **1** from the least-squares fit, these errors decreased notably to 0.07 and 0.28 ppm, respectively. We therefore omitted **1** hereafter from the determination of additive shift parameters. The calculated additive shift parameters thus obtained are also listed in Table 6. Characteristic features of the four additive shift parameters $\overline{A}_\alpha$–$\overline{A}_\delta$ for the calculated chemical shifts are similar to the corresponding experimental additive shift parameters: $\overline{A}_\alpha$, $\overline{A}_\beta$ and $\overline{A}_\delta$ contribute to the downfield shift for the C_k carbon, whereas only $\overline{A}_\gamma$ contributes to the upfield

shift. The good correlations between the calculated and the experimental values for both the chemical shifts and the additive shift parameters enable the following investigation of the origin of the additive relationship on the basis of the calculated ^{13}C chemical shifts for the individual alkane conformers.

Additive Relationship for ^{13}C Chemical Shifts of Alkane Conformers.—The five additive shift parameters were again applied to the additive relationship for the ^{13}C chemical shifts of **2**, **3**, and only the all-*anti* conformers of **4–7**. Their values are included in the right column of Table 6, where the bars, representing conformationally averaged values, should be removed from these parameters. The additive relationship holds excellently with $r = 0.99997$. It should be noted that A_δ is unnecessary, and that A_γ is still positive, though the value for A_γ is smaller than that for $\overline{A}_\gamma$. The latter result suggests that the mere presence of the γ-carbon results in an upfield shift for the C_k carbon.

We then separated the additive shift parameters into two parameter sets: one consists of substituent additive shift parameters B, A_α, A_β and A_γ, the latter three parameters representing the mere presence of the carbon atoms in positions α, β and γ with respect to the C_k carbon, respectively, and the other consists of conformation additive shift parameters G_1, G_2 and G_3 involving corrective shift parameters. The 14 conformation additive shift parameters appearing in the present conformers are schematically illustrated in Fig. 2. The three parameters G_1, G_2 and G_3 represent that conformations of the 1-, 2- and 3-bonds to the C_k carbon are *gauche*, respectively;

Table 3 Symmetry parameters of the ^{13}C chemical shift tensors η' for conformers of alkanes 1-7 calculated by the *ab initio* GIAO method[a]

| Conformer | η' | | | | | | |
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
1	1.000						
2	1.000	1.000					
3	0.602	−0.150	0.602				
4 *a*	0.589	0.273	0.273	0.589			
g	−0.055	0.681	0.681	−0.055			
5 *aa*	0.591	0.245	0.325	0.245	0.591		
ga	0.008	0.779	0.430	−0.412	0.624		
gg	−0.042	−0.145	0.100	−0.145	−0.042		
6 *aaa*	0.594	0.256	0.304	0.304	0.256	0.594	
gaa	0.021	0.807	0.400	0.017	0.268	0.588	
aga	0.618	−0.299	0.421	0.421	−0.299	0.618	
gga	−0.030	−0.108	0.155	0.158	−0.360	0.637	
gag	−0.001	0.768	0.043	0.043	0.768	−0.001	
gag'	−0.019	0.675	−0.156	−0.156	0.675	−0.019	
ggg	0.014	−0.179	0.177	0.177	−0.179	0.014	
7 *aaaa*	0.595	0.263	0.315	0.287	0.315	0.263	0.595
gaaa	0.019	0.803	0.416	−0.010	0.319	0.260	0.595
agaa	0.620	−0.289	0.414	0.400	0.069	0.275	0.590
ggaa	−0.022	−0.091	0.144	0.133	0.060	0.289	0.594
agga	0.641	−0.347	0.150	0.215	0.151	−0.346	0.641
gaag	0.030	0.784	0.425	0.127	0.425	0.785	0.029
gaag'	0.019	0.786	0.417	−0.630	0.417	0.785	0.019
gaga	−0.002	0.765	0.084	−0.021	0.442	−0.293	0.623
gag'a	−0.033	0.687	−0.059	−0.091	0.400	−0.335	0.619
ggga	0.020	−0.160	0.106	0.245	0.141	−0.301	0.646
ggag	−0.023	−0.116	0.118	−0.503	0.109	0.752	−0.024
ggag'	−0.026	−0.114	0.122	−0.035	−0.125	0.656	−0.017
gggg	0.021	−0.127	0.141	0.101	0.141	−0.127	0.021

[a] *a*, *g* and *g'* denote *anti*, (+)-*gauche* and (−)-*gauche* bonds, respectively.

Table 4 Conformationally averaged calculated ^{13}C chemical shifts $\overline{\delta C}_{calcd}$ for alkanes 1-7 at 298 K[a]

| | $\overline{\delta C}_{calcd}$ | | | |
	C(1)	C(2)	C(3)	C(4)
1	207.16			
2	199.38			
3	191.28	192.59	·	
4	192.88	184.96		
5	192.69	186.46	177.02	
6	192.64	186.29	178.56	
7	192.66	186.26	178.36	180.07

[a] Values are given only for unique carbons in molecules.

parameters G_1 and G_2 are directly related to the vicinal- and the γ-*gauche* effects, respectively. The corrective shift parameters are necessary for conformers with two *gauche* bonds in a molecule, and are distinguished with a prime if the two *gauche* bonds are located in the opposite direction to the C_k carbon atom and with a sign ' + ' or ' − ' corresponding to the case that the sign of the dihedral angles of the two *gauche* bonds are the same or different, respectively.

Employing all the 18 parameters (set-18: the four substituent and the 14 conformation additive shift parameters) we fit the 161 calculated ^{13}C chemical shifts for the conformers of 2-7 to eqn. (5), where m_{kj} stands for the number of the G_j terms

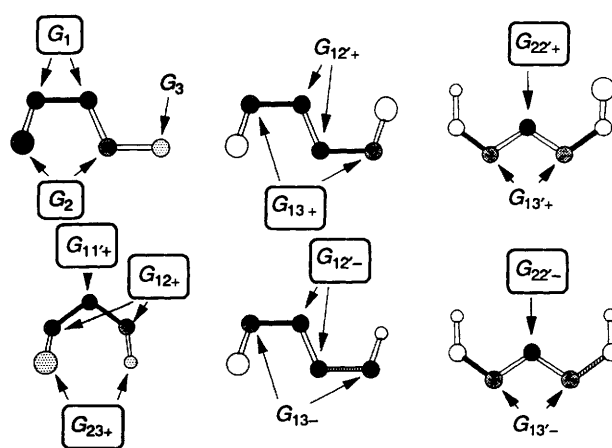$$\delta C_k = B + \sum_i A_i \times n_{ki} + \sum_j G_j \times m_{kj} \quad (5)$$

Fig. 2 Definition of the 14 conformation additive shift parameters. Filled and hatched bonds stand for the (+)-, and (−)-*gauche* bonds, respectively. The set-12 parameters are enclosed with open squares.

appearing in the conformers. For example, the ^{13}C chemical shifts of the C(3) and C(4) carbons in the $g^+-g^+-a-g^-$ conformer of 7 are evaluated by eqns. (6) and (7), respectively. The

$$\delta C_3 = B + 2A_\alpha + 2A_\beta + A_\gamma + 2G_1 + G_3 + G_{11'+} + G_{13-} + G_{13'-} \quad (6)$$

$$\delta C_4 = B + 2A_\alpha + 2A_\beta + 2A_\gamma + G_1 + 2G_2 + G_{12+} + G_{12'-} + G_{22'-} \quad (7)$$

Table 5 Experimental ^{13}C chemical shifts ($\overline{\delta C}_{\text{exptl}}$) for alkanes 5–12 in CDCl$_3$ solutions at 298 K [a]

	$\overline{\delta C}_{\text{exptl}}$					
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
5	13.89	22.21	34.00			
6	13.94	22.62	31.59			
7	13.94	22.68	31.91	29.06		
8	13.96	22.67	31.94	29.35		
9	13.97	22.68	31.94	29.39	29.65	
10	13.97	22.67	31.94	29.38	29.68	
11	13.99	22.67	31.94	29.38	29.68	29.73
12	13.99	22.67	31.93	29.36	29.67	29.71

[a] Values are given only for unique carbons in molecules.

Table 6 Least-squares fitted values for the additive shift parameters for the experimental and the calculated ^{13}C chemical shifts of alkanes[a]

		Calcd.[c]	
Parameter	Exptl.[b]	Average[d]	All-*anti*[e]
$\bar{B}$	−1.80 ± 0.02	205.68 ± 0.06	206.35 ± 0.04
$\bar{A}_\alpha$	8.70 ± 0.01	−6.44 ± 0.04	−6.88 ± 0.02
$\bar{A}_\beta$	9.26 ± 0.01	−7.89 ± 0.04	−8.29 ± 0.02
$\bar{A}_\gamma$	−2.55 ± 0.01	1.54 ± 0.04	0.93 ± 0.03
$\bar{A}_\delta$	0.35 ± 0.01	−0.20 ± 0.04	0.00 ± 0.02
Std. error[f]	0.03	0.07	0.05
Max. error[g]	0.12	0.28	0.10

[a] Values are given in ppm. [b] For alkanes 5–12. [c] For alkanes 2–7. [d] For conformationally averaged shifts. [e] For chemical shifts of the all-*anti* conformers. [f] Standard error. [g] Maximum error.
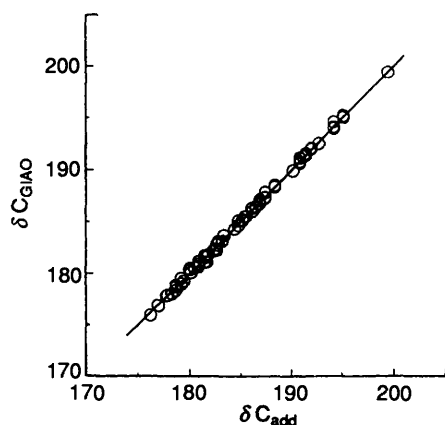
Fig. 3 Correlation between the calculated ^{13}C chemical shifts δC_{GIAO} and the ^{13}C chemical shifts δC_{add} evaluated from the additive relationship with the set-12 parameters in Table 7 for conformers of alkanes from ethane (2) to heptane (7). The least-squares fitted line is solid.

additive relationship holds successfully with $r = 0.9995$. The least-squares fitted values for the set-18 parameters are listed in the left column of Table 7. Omitting the parameters less than 0.2 ppm and unifying $G_{22'+}$ and $G_{22'-}$ to $G_{22'}$, we can reduce the number of the parameters from 18 to 12 (set-12: the eight conformation additive shift parameters in this set are enclosed with open squares in Fig. 2). With this new practical, set-12 parameters, the additive relationship also holds with $r = 0.9995$ as shown in Fig. 3, and the least-squares fitted values are listed in the right column of Table 7.

The values for the substituent additive shift parameters are close to those for the corresponding additive shift parameters for the all-*anti* conformers (the right column of Table 6), but different from those for the corresponding ones for the

Table 7 Least-squares fitted values for substituent and conformation additive shift parameters for the calculated ^{13}C chemical shifts of conformers of alkanes 2–7[a]

Parameter	Set-18	Set-12
B	206.17 ± 0.07	206.20 ± 0.07
A_α	−6.74 ± 0.04	−6.75 ± 0.04
A_β	−8.23 ± 0.04	−8.23 ± 0.04
A_γ	0.77 ± 0.04	0.78 ± 0.04
G_1	1.62 ± 0.05	1.66 ± 0.05
G_2	2.22 ± 0.04	2.20 ± 0.04
G_3	0.04 ± 0.05	
$G_{11'+}$	0.55 ± 0.08	0.55 ± 0.08
G_{12+}	1.78 ± 0.06	1.75 ± 0.06
$G_{12'+}$	0.07 ± 0.07	
$G_{12'-}$	0.64 ± 0.09	0.63 ± 0.09
G_{13+}	−0.38 ± 0.07	−0.37 ± 0.06
G_{13-}	0.17 ± 0.09	
$G_{13'+}$	0.12 ± 0.09	
$G_{13'-}$	0.03 ± 0.10	
G_{22}[b]		0.64 ± 0.10
$G_{22'+}$	0.47 ± 0.13	
$G_{22'-}$	0.78 ± 0.15	
G_{23+}	0.91 ± 0.06	0.96 ± 0.05
Std. error[c]	0.17	0.17
Max. error[d]	0.50	0.52

[a] Values are given in ppm. [b] $G_{22} = G_{22'+} = G_{22'-}$. [c] Standard error. [d] Maximum error.

conformationally averaged shifts (the middle column of Table 6). This indicates that not only $\bar{A}_\gamma$ but also all of the other additive shift parameters (including $\bar{B}$) should be influenced by the conformation effects.[3] Since A_δ and G_3 are neglected in the set-12 parameters, the contribution of the 3-*gauche* bond to $\bar{A}_\delta$ is not explicit, but it should be brought about from the corrective shift parameters such as G_{23} and G_{13}

When we consider only G_1, G_2 and G_{23+} as the conformation additive shift parameters, we still found the validity of the additive relationship with $r = 0.998$, though the errors amount to about twice (0.36 and 1.00 ppm for the standard and maximum errors, respectively), representing that the conformation effects can mainly be ascribed to the 1-, 2-, and successive 2,3-*gauche* bonds. It is worthy of note that all the *gauche* bonds bring about upfield shifts for carbons nearby the bonds. The negative value for G_{13+} reduces only the magnitude of the upfield shift due to G_1. Although geometrical environment of conformers involving $g^\pm$–a–$g^\pm$ bonds seems to be similar to that of conformers with $g^\pm$–a–$g^\mp$, actions of the corrective shift parameters are quite different: the $g^\pm$–a–$g^\pm$ bond decreases the magnitude of the upfield shift for the outer carbons (G_{13+}), whereas the $g^\pm$–a–$g^\mp$ bond brings about an additional upfield shift to the inner carbons ($G_{12'-}$).

Additive Relationships for Anisotropic Parameters.—With the same parameter set employed for the ^{13}C chemical shift additive relationship, those for the anisotropic parameters of the ^{13}C chemical shift tensors $\Delta\sigma$ (Table 2) and η' (Table 3) of the alkane conformers were examined. By using the set-18 parameters an additive relationship for $\Delta\sigma$ was found to be valid with $r = 0.987$. The least-squares fitted values are listed in the left column of Table 8. A similar correlation was obtained when the number of the parameters was limited to 13 ($r = 0.987$) listed in the middle column of Table 8, as shown in Fig. 4. The most significant factors controlling $\Delta\sigma$ are the presence of the β-carbon and the 1-*gauche* bond, leading to nearly constant $\Delta\sigma$ values (25 ± 2 ppm) for the methyl carbons of alkanes longer than 2.

Even by employing the set-18 parameters it seems that no additive relationship holds for the η' values of all the conformers as plotted in Fig. 5 ($r = 0.905$): the least-squares fitted

Table 8 Least-squares fitted values for substituent and conformation additive parameters for the anisotropy $\Delta\sigma$ and the symmetry parameter η' of the ^{13}C chemical shift tensors of conformers of alkanes 2–7[a]

| Parameter | $\Delta\sigma$ | | η' |
	Set-18	Set-13	Set-18
B	11.0 ± 0.5	10.9 ± 0.4	0.91 ± 0.06
A_α	1.1 ± 0.3	1.2 ± 0.3	−0.29 ± 0.04
A_β	14.7 ± 0.3	14.6 ± 0.3	−0.02 ± 0.04
A_γ	−0.1 ± 0.3		0.00 ± 0.04
G_1	−12.5 ± 0.3	12.5 ± 0.3	0.22 ± 0.04
G_2	−2.3 ± 0.3	−2.7 ± 0.2	−0.59 ± 0.04
G_3	−0.2 ± 0.3		0.02 ± 0.04
$G_{11'+}$	−2.4 ± 0.5	−2.3 ± 0.5	−0.42 ± 0.07
G_{12+}	5.0 ± 0.4	5.1 ± 0.4	0.04 ± 0.05
$G_{12'+}$	3.0 ± 0.4	3.1 ± 0.4	0.22 ± 0.06
$G_{12'-}$	−0.7 ± 0.6		0.01 ± 0.08
G_{13+}	1.7 ± 0.4	1.2 ± 0.4	0.04 ± 0.06
G_{13-}	2.0 ± 0.6	1.7 ± 0.5	0.04 ± 0.08
$G_{13'+}$	−1.1 ± 0.6	−1.4 ± 0.5	−0.04 ± 0.08
$G_{13'-}$	−1.2 ± 0.7	−1.7 ± 0.6	−0.14 ± 0.09
$G_{22'+}$	−4.6 ± 0.8	−4.2 ± 0.8	0.43 ± 0.11
$G_{22'-}$	−0.7 ± 0.9		0.40 ± 0.12
G_{23+}	−0.6 ± 0.4		−0.05 ± 0.05
Std. error[b]	1.1	1.1	0.14
Max. error[c]	3.7	3.7	0.56

[a] Values for $\Delta\sigma$ are given in ppm. [b] Standard error. [c] Maximum error.

Table 9 Least-squares fitted values for substituent and conformation additive parameters for the symmetry parameter η' of the ^{13}C chemical shift tensors for the methyl and α-methylene carbons of conformers of alkanes 3–7

Parameter	Methyl	α-Methylene
B'	0.608 ± 0.005	−0.15 ± 0.04
A_β		0.41 ± 0.04
G_1		0.48 ± 0.01
G_2	−0.614 ± 0.007	−0.59 ± 0.02
G_{12+}		−0.29 ± 0.02
Std. error[a]	0.02	0.04
Max. error[b]	0.05	0.09

[a] Standard error. [b] Maximum error.

values are listed in the right column of Table 8. It, however, holds for the η' values of the methyl and the α(terminal)-methylene carbons. From the geometrical reason η' of the methyl carbon of 2 is 1.0, so it can be omitted from the least-squares fit. Values of relevant additive parameters thus obtained are collected in Table 9, where B' stands for the sum of B and A_α, since they are no longer independent of each other. It is of much interest that only two values are allowed for η' of the methyl carbon according to the conformation of the 2-bond ($\eta = 0.6$ or 0.0 for the 2-*anti* or 2-*gauche* bond, respectively). This distinct difference can be applicable to the determination of the conformation of the terminal part of alkyl chains in, for example, solid and liquid-crystalline states. The factors controlling η' of the α-methylene carbon are limited to the presence of the β-carbon and the conformation of the 1- and 2-bonds.

Dihedral-angle Dependence of the Parameters for the ^{13}C *Chemical Shift Tensors.*—As for the three components of the ^{13}C chemical shift tensors δC, $\Delta\sigma$ and η' for the methyl carbons of the present alkane conformers of 3–7, the above calculations suggest that: (*a*) the presence of the γ-carbon always brings about an upfield shift for δC; (*b*) the $\Delta\sigma$ value is restricted within 25 ± 2 ppm; and (*c*) η' depends only on the conformation of the 2-bond. In order to examine these suggestions, we calculated the dihedral-angle dependence of the three components for the C(1) and C(2) carbons of 4 using fully optimized geometries under the
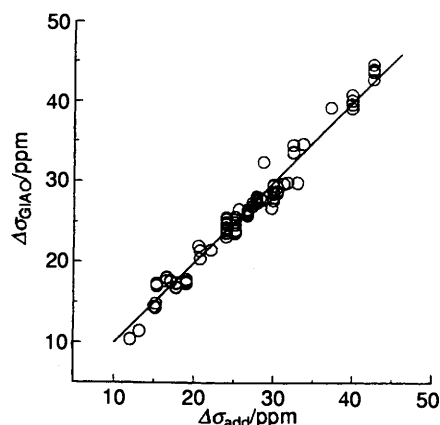
Fig. 4 Correlation between the calculated anisotropies $\Delta\sigma_{GIAO}$ of the ^{13}C chemical shift tensors and the anisotropies $\Delta\sigma_{add}$ evaluated from the additive relationship with the set-13 parameters in Table 9 for conformers of alkanes from ethane (2) to heptane (7). The least-squares fitted line is solid.
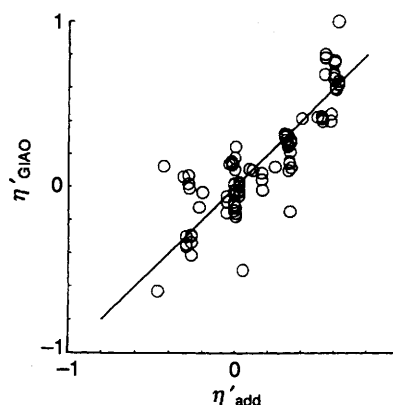
Fig. 5 Correlation between the calculated symmetry parameters η'_{GIAO} of the ^{13}C chemical shift tensors and the symmetry parameters η'_{add} evaluated from the additive relationship with the set-18 parameters in Table 9 for conformers of alkanes from ethane (2) to heptane (7). The least-squares fitted line is solid.

fixed C(1)–C(2)–C(3)–C(4) dihedral angle ω with every 30°. Calculated values are plotted in Fig. 6, The variation of δC is similar to, but smoother than that calculated by the IGLO method,[3,*] probably due to the geometrical optimization: although the δC values for the C(1) and C(2) carbons are the largest in the *syn* conformation ($\omega = 0°$), that for the C(2) carbon is the smallest in the *anti* conformation ($\omega = 180°$), but that for the C(1) carbon is not. The δC value for the C(1) carbon at nearby $\omega = 120°$ and 240° is smaller than that for the C(1) carbon of 3, showing the upfield shift due to the γ-carbon is not valid for these conformers, though they are not stable at least in the isotropic phases. As shown in Fig. 6, ω cannot uniquely be determined from any parameters of δC, $\Delta\sigma$ and η', indicating that the above-mentioned features (*a*)–(*c*) should be valid for the cases where the conformation of the bonds is limited to *anti* or *gauche*.†

Conclusions

^{13}C NMR chemical shifts for conformers of alkanes 1–7,

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* Similar variations of the δC values for central carbons of 8 were calculated by the *ab initio* GIAO method.[12]
† Calculated absolute ω values for the *anti* and *gauche* bonds in the present alkane conformers are 178 ± 3° and 64 ± 3°, respectively.
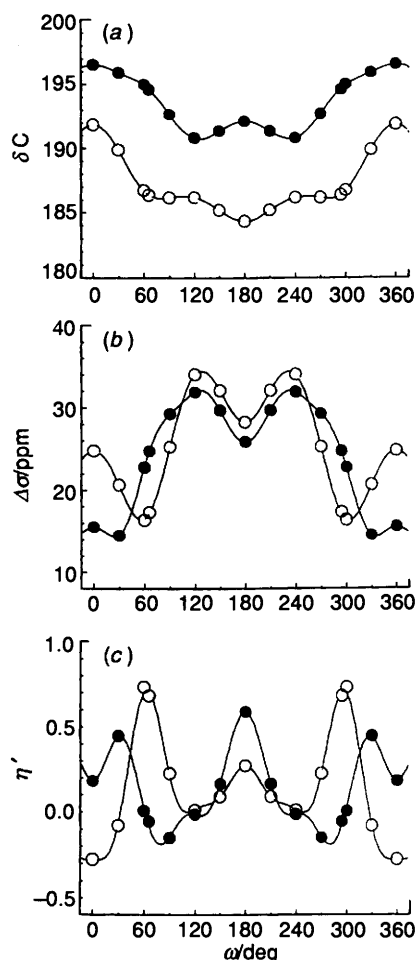
Fig. 6 Variations of the parameters of the ^{13}C chemical shift tensors for the C(1) and C(2) carbons of butane (4) against the C(1)–C(2)–C(3)–C(4) dihedral angle ω. (a) The ^{13}C chemical shifts δC. (b) The anisotropies $\Delta\sigma$. (c) The symmetry parameters η'. Filled and open circles stand for the C(1) and C(2) carbons, respectively. Solid curves through the data points are obtained and the least-squares fit to trigonometric polynomials according to ref. 3.

A new additive relationship for the ^{13}C chemical shifts of the conformers of alkanes 2–7 was successfully constructed with the four substituent and eight conformation additive shift parameters. It is elucidated that the mere presence of the $\gamma(C_{k\pm3})$-carbon gives an upfield shift for the C_k carbon despite the conformation of the $2(C_{k\pm1}-C_{k\pm2})$-bond, and that the conformation effects to the ^{13}C chemical shifts are mainly ascribed to the presence of the 1-, 2-, and/or successive 2,3-gauche bonds: the former two effects are directly related to the vicinal- and the γ-gauche effects, respectively. From comparison of the additive shift parameters for the conformationally averaged chemical shifts with those for the chemical shifts of the individual alkane conformers, all of the former parameters are concluded to be influenced by the conformation effects.

For anisotropic parameters of the ^{13}C chemical-shift tensors of the present alkane conformers, an additive relationship is valid for the anisotropies $\Delta\sigma$, but is not for the symmetry parameter η'.

which contribute significantly to the conformational equilibrium of the individual alkane in the isolated state, were calculated by the *ab initio* GIAO method. The conformationally averaged calculated ^{13}C chemical shifts are satisfactorily correlated with the corresponding experimental chemical shifts, though the latter values are systematically larger by a factor of 1.25 than the former ones. The additive relationship, therefore, holds for the conformationally averaged calculated shifts.

References

1 E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, 1963, **85**, 1701; D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, 1964, **86**, 2984.
2 A. E. Tonell and F. C. Schilling, *Acc. Chem. Res.*, 1981, **14**, 233.
3 M. Barfield and S. H. Yamamura, *J. Am. Chem. Soc.*, 1990, **112**, 4747 and references cited therein.
4 F. Imashiro, T. Maeda, T. Nakai, A. Saika and T. Terao, *J. Phys. Chem.*, 1986, **90**, 5498.
5 M. Möller, W. Gronski, H.-J. Cantow, and H. Höcker, *J. Am. Chem. Soc.*, 1984, **106**, 5093; H. Drotloff, H. Rotter, D. Emeis and M. Möller, *J. Am. Chem. Soc.*, 1987, **109**, 7797.
6 W. Kutzelnigg, *Isr. J. Chem.*, 1980, **19**, 193; M. Schindler and W. Kutzelnigg, *J. Chem. Phys.*, 1982, **76**, 1919; *Mol. Phys.*, 1983, **48**, 781.
7 R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789; C. McMichael, C. Rohlfing, L. C. Allen and R. Ditchfield, *Chem. Phys.*, 1984, **87**, 9; D. B. Chesnut and C. G. Phung, *J. Chem. Phys.*, 1989, **91**, 6238.
8 U. Haeberlen, *High Resolution NMR in Solids*, Academic Press, New York, 1976.
9 H. W. Spiess, in *Dynamic NMR Spectroscopy*, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, Berlin, 1978, p. 55.
10 For recent reviews, see H. Fukui, *Magn. Reson. Rev.*, 1987, **11**, 205; C. J. Jameson, in Nuclear Magnetic Resonance, *Spec. Publ. R. Soc. Chem.*, 1987, No. 16.
11 S. Obara, M. Honda, H. Nakano, F. Sakano, S. Takada, Y. Miyake, K. Sato and T. Nakajima, library program 202 Y4/KOTO91 at the Data Processing Center of Kyoto University, 1991.
12 H. Kurosu, I. Ando and G. A. Webb, *Magn. Reson. Chem.*, 1993, **31**, 399.