Calculation of the Carbon-13 NMR Chemical Shifts of Linear and Branched Paraffins and Saturated Cyclic Hydrocarbons

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The carbon-13 NMR chemical shifts of linear and branched paraffins have been calculated by means of Pople's theory, particularly using the averaged excitation energy method. The calculation was carried out based on the CNDO/2 molecular orbital method. The values calculated by means of the averaged excitation energy method deviate extremely from the experimental ones; therefore, the energies most suitable for giving good agreement are investigated and determined for linear and branched paraffins. The suitable energies are expressed by an empirical formula, correlated to the molecular structure. The results obtained may be briefly expressed by;

$$\Delta E = 11.30 \times 1.015^a \times 0.958^b \times 1.010^c \times S$$

$$S = 1.011^d \times 1.009^e \times 1.029^f \times 1.009^g \times 1.030^h \times 1.031^i$$

(see Results and Discussion for the notations used).

This empirical averaged excitation energy expression is applied to cyclic hydrocarbons, such as cyclohexane, methylcyclohexane, and dimethylcyclohexane. Further, the γ-effect is estimated on the basis of these results.

The carbon-13 (C-13) NMR chemical shifts of saturated hydrocarbons have been studied systematically by Grant *et al.*1–5)

Pople *et al.*6–8) have developed a theory of the C-13 chemical shift and have calculated the C-13 shielding constants of simple hydrocarbons using an averaged excitation energy method (AEE method). It is very convenient to use the AEE method for the calculation of the C-13 shielding constants with the Pople expression. Since the AEE method is, however, a severe approximation, its use makes it difficult to obtain a suitable value for the averaged excitation energy (ΔE), and the calculated chemical shifts are not in good agreement with the experimental values. For example, when the value of 10 eV is used for the ΔE of linear and branched hydrocarbons, the calculated chemical shifts deviate from the experimental values by about 10 or 20 ppm. The C-13 chemical shifts depend on the electronic states of molecules which are influenced by their molecular structures, and the ΔE which largely contributes to the C-13 chemical shifts should be correlated to the molecular structures; *i.e.*, the values of ΔE are not equal to each other for various carbons in a molecule.

Okada *et al.*9) proposed an empirical expression for ΔE in which ΔE was influenced by adjacent carbons until γ-carbon and by the difference in the molecule. This expression is very simple and convenient; however, it is theoretically limited because it uses an extended Hückel theory (EHT) method. The idea that one tries to determine the values of ΔE unified for various molecular structures is based on the fact that the C-13 chemical shifts depend on the molecular structure, though this is ambiguous theoretically. Nevertheless, the empirical ΔE expression is a useful method for calculating the chemical shifts of many molecules. In order to improve this method and to obtain a wider adoptability, a new empirical expression for ΔE will be proposed. This expression is based on the idea of Okada *et al.*, but the method of computation is a CNDO/2 MO one10,11) instead of an EHT one. The expression obtained is parameterized for linear and branched paraffins, and then is applied to saturated cyclic compounds, such as cyclohexane and its derivatives. Further, the γ-effect will be estimated on the basis of these results.

Theory

The C-13 shielding constants of any specified carbon atom, A, in a molecule may be approximated as follows;6,12,13)

$$\sigma^{\mathrm{A}} = \sigma_{\mathrm{d}}{}^{\mathrm{A}} + \sigma_{\mathrm{p}}{}^{\mathrm{A}} + \sum_{\mathrm{B}(\neq \mathrm{A})} \sigma^{\mathrm{A}} + \sigma^{\mathrm{A}}_{\mathrm{ring}} \tag{1}$$

where $\sigma_{\mathrm{d}}{}^{\mathrm{A}}$ and $\sigma_{\mathrm{p}}{}^{\mathrm{A}}$ are the diamagnetic and paramagnetic contributions on the specified carbon atom, A, respectively, where $\sum_{\mathrm{B}(\neq \mathrm{A})} \sigma^{\mathrm{B}}$ is sum of the contributions from the neighbouring atoms bonded to the A atom and where $\sigma^{\mathrm{A}}_{\mathrm{ring}}$ is the contribution from the ring current. Usually the effects of $\sum \sigma^{\mathrm{B}}$ and $\sigma^{\mathrm{A}}_{\mathrm{ring}}$ in the C-13 chemical shifts are known to be very small and contribute less than a few parts per million (ppm). With Slater atomic orbitals, the increase in $\sigma_{\mathrm{d}}{}^{\mathrm{A}}$ when a 2p electron is added is 14 ppm, only about 10% of the entire observed range of the C-13 chemical shifts. The differences in C-13 chemical shifts among various carbon atoms are mostly due to the difference in $\sigma_{\mathrm{p}}{}^{\mathrm{A}}$. In this paper, in order to discuss the C-13 chemical shifts in detail we will take $\sigma_{\mathrm{d}}{}^{\mathrm{A}}$ and $\sigma_{\mathrm{p}}{}^{\mathrm{A}}$ into account and will neglect the contributions from $\sum \sigma^{\mathrm{B}}$ and $\sigma^{\mathrm{A}}_{\mathrm{ring}}$. The value of $\sigma_{\mathrm{d}}{}^{\mathrm{A}}$ is given by the following formula:

$$\sigma_{\mathrm{d}}{}^{\mathrm{A}} = \frac{e^2}{3mc^2} \sum_i \left\langle \frac{1}{r_i} \right\rangle \tag{2}$$

where $\langle r_i^{-1} \rangle$ is the mean inverse distance of the i-th electron from a nucleus, m is its mass, e is its charge, and c is the light velocity, and where the sum is taken over all the electrons on the atoms being considered.

According to the Pople theory, $\sigma_{\mathrm{p}}{}^{\mathrm{A}}$ is given by the following equations:

$$\sigma_{\mathrm{p}}{}^{\mathrm{A}} = -2N^{-1} \langle r^{-3} \rangle_{\mathrm{A}} \chi_{\mathrm{p}}{}^{\mathrm{A}} \tag{3}$$

$$(\chi_{\mathrm{p}}{}^{\mathrm{A}})_{\mathrm{zz}} = \frac{Ne^2\hbar^2}{m^2c^2} \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{unocc}} (E_j - E_i)^{-1} (C_{i\mathrm{xA}} C_{j\mathrm{yA}} - C_{i\mathrm{yA}} C_{j\mathrm{xA}}$$
$$\times \sum (C_{i\mathrm{xB}} C_{j\mathrm{yB}} - C_{i\mathrm{yB}} C_{j\mathrm{xB}}) \tag{4}$$

In order to calculate these equations, some approximations are introduced; therefore,[12)]

$$\sigma_d{}^A = 4.45z^*q \tag{5}$$

where:

$$z^* = 3.25-0.35(q-4) \tag{6}$$

in which q is the total electron density around the particular carbon atom and in z^* which is the "effective nuclear charge" estimated according to Slater's rules.

$$\sigma_p{}^A = -\frac{e^2\hbar^2}{2m^2c^2\Delta E}\left\langle\frac{1}{r^3}\right\rangle_{2p}\sum_B Q_{AB} \tag{7}$$

where;

$$\begin{aligned} Q_{AB} = {} & \frac{4}{3}\delta_{AB}(P_{X_AX_B}+P_{Y_AY_B}+P_{Z_AZ_B}) \\ & -\frac{2}{3}(P_{Y_AY_B}P_{Z_AZ_B}+P_{Z_AZ_B}P_{X_AX_B}+P_{X_AX_B}P_{Y_AY_B}) \\ & +\frac{2}{3}(P_{Y_AZ_B}P_{Z_AY_B}+P_{Z_AX_B}P_{X_AZ_B}+P_{X_AY_B}P_{Y_AX_B}) \end{aligned} \tag{8}$$

$$\left\langle\frac{1}{r^3}\right\rangle_{2p} = \frac{1}{24a_0{}^3}\{3.25-0.35(q_{2p}-3)\}^3 \tag{9}$$

$$q_{2p} = P_{X_AX_A} + P_{Y_AY_A} + P_{Z_AZ_A} \tag{10}$$

In these formulae, ΔE is an averaged excitation energy, $<r^{-3}>_{2p}$ is the mean inverse cube radius for carbon 2p orbitals and depends on the local electron density on the particular carbon atom, $\sum$ is a sum over all the atoms, δ_{AB} is a Kronecker symbol, and a_0 is a Bohr radius.

$P_{X_AX_B}$ is the matrix element for the $2p_X$ atomic orbitals on the A and B atoms. When A=B, it is the electron density in $2p_X$ on the A atom and when A$\neq$B, it is the bond-order between the two atomic orbitals.

To estimate the bond-order matrix, as the molecular orbital method the CNDO/2 MO method was used.

Results and Discussion

The carbon-13 chemical shifts were calculated for linear and branched paraffins, using the Pople theory for the shielding constants by means of the AEE method and the CNDO/2 MO method.

As a result of using the value of 10 eV for ΔE, the calculated chemical shifts were found to deviate from the experimental values by more than 10 ppm for paraffins. In an *n*-pentane, for example, the experimental carbon-13 chemical shifts of two secondary carbons differ from each other by about 12 ppm, while the calculated values are almost indistinguishable from each other. The total electron densities of the two secondary carbons are nearly identical when calculated by the CNDO/2 MO method. In molecules which have π-electrons and/or lone pair electrons, such as aromatic and azine compounds, it has been reported that there is a correlation between the C-13 chemical shifts and the charge distributions.[14)] Sichel *et al.*[15)] have reported empirically on the apparent correlation between the C-13 chemical shifts and the electron-charge densities on the carbon atoms in hydrocarbons; they worked on the basis of the extended Hückel method. On the other hand, if the calculation is carried out by the CNDO/2 MO method, there is no obvious correlation between the C-13 chemical shifts and the electron densities for the same compounds.

In the calculation of the C-13 chemical shift of saturated hydrocarbons, one of the most important factors is the averaged excitation energy. Various values have been proposed for ΔE.[7,8,14,16)] It should be noted that, in the vacuum UV spectra of *n*-paraffins the wavelengths at the most intense absorption peak become larger as the chain length increases. This suggests that the averaged excitation energies depend on the molecular structures. The tendency for the C-13 chemical shifts to increase as the carbon numbers of hydrocarbons decrease can be barely explained, using the excitation energy values from the UV spectra as ΔE.

Okada *et al.*[9)] obtained an empirical averaged excitation energy expression for linear and branched paraffins using the extended Hückel method:

$$\Delta E = 10.0 \times \alpha^a \times \beta^b \times \gamma^c \times c^d \tag{9}$$

where α, β, and γ are the parameters showing the effects of α, β, and γ-carbons respectively, where a, b, and c are the numbers of α, β, and γ-carbons respectively, where c is the parameter showing the conformational effect, and where d is the number of the possible gauche conformation. The numerical values for the α, β, γ, and c parameters are 0.974, 0.960, 1.009, and 1.009 respectively. The value of 10.0 is adopted as the ΔE coefficient for all the carbons. Using this expression, the calculated C-13 chemical shifts are considerably improved. However, this expression is based on an extended Hückel method, so there is a substantial limitation. Nevertheless, this method is important because it is convenient for calculating ΔE from the structural parameters. In order to improve this expression, we proposed the new empirical one with a similar form and more structural parameters, using the CNDO/2 MO method. The new ΔE expression has the following form:

$$\Delta E = K \times \alpha^a \times \beta^b \times \gamma^c \times S \tag{10}$$

$$\begin{aligned} S = {} & [1^\circ(4^\circ)]^d \times [2^\circ(3)^\circ]^e \times [2^\circ(4^\circ)]^f \times [3^\circ(2^\circ)]^g \\ & \times [3^\circ(3^\circ)]^h \times [4^\circ(2^\circ)]^i \end{aligned} \tag{11}$$

where K is a coefficient and would be a ΔE of methane when there are no α, β, and γ-carbons, where S is a structural parameter [1°(4°)] showing the effect of the primary carbon adjacent to the quaternary carbon, and where d is the number of [1°(4°)] carbons. These parameters were determined for linear and branched paraffins by the least-squares multiple method.

Contrary to the modified ΔE expression given above, there is another method which represents ΔE by means of the sum of the contributions from all the carbons. Considering that these are all empirical expressions, we must choose a simplified formula.

The coefficient of this expression, K, has an important influence on the improvement of the calculated values. Instead of the value of 10 eV, we tried to adopt 9.705 eV,[17)] which was obtained from a vacuum UV spectrum, for the averaged excitation energy of methane, but we did not get any improvement in the calculated values. Strong[18)] got the value of 11.30 eV for the ΔE of methane by statistically averaging the excitation energies between the ground states and the excited states.

It has been found that the deviation of the calculated values from the experimental values is considerably influenced by varying the K, *i.e.*, the coefficient of the ΔE expression. Therefore, we can expect at least to get the most preferable K which makes the difference between the calculated and experimental values. The equation representing the relation between the experimental chemical shifts and the calculated ones is as follows:

$$\delta_i = \delta_c + \delta_{di} - \frac{K_i}{\Delta E_i} \tag{12}$$

where δ_i is the experimental chemical shift of the i-th carbon, δ_{di} is a calculated diamagnetic contribution from the i-th carbon, $K_i/\Delta E_i$ is a paramagnetic one, and δ_c is a constant that is common to all the carbons. Then, the ΔE of each n-paraffin can be determined from this equation because δ_c and δ_i are known and δ_{di} and K_i can be calculated. We plotted such ΔE's for various n-paraffin's carbons against the number of carbon atoms in n-paraffins in Fig. 1. In this figure, three kinds of ΔE values are adopted as follows: (a) 10.0, (b) 9.705, and (c) 11.30eV. Comparing the curves in Fig. 1, we can conclude that the value of 11.30 eV is the most suitable for the calculation by using an empirical expression, because in Curve (c) the slopes between the nearest and second nearest carbons from an end are all equal to one another, irrespective of the increase in n, and because the ΔE's of the nearest and second nearest carbons are equal to each other when n is larger than 4. Using the above-determined ΔE, we can determine the parameters for n-paraffins having the carbons of from 1 to 7.

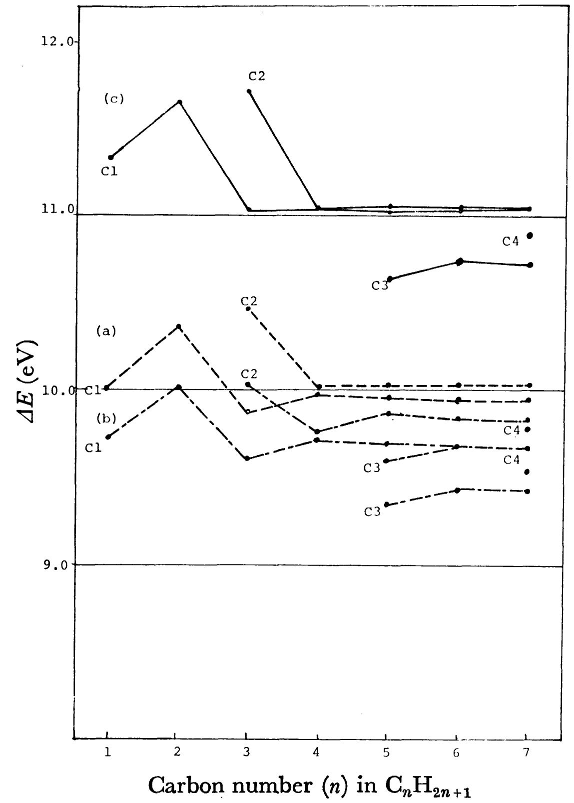

Fig. 1. The averaged excitation energies of linear paraffins when (a) 10.0, (b) 9.705, and (c) 11.30 eV are adopted as the reference values for methane.

Table 1. Calculated values of C-13 chemical shifts in linear and branched paraffins

Compound		ΔE (eV)	Error[a)]	Chem. shift[b)] (ppm)	Error[c)]
Methane		11.30	0.0	130.8	0.0
Ethane		11.46	−0.17	119.94	−2.86
Propane	1	10.98	−0.05	112.18	−0.92
	2	11.63	−0.05	111.69	−0.93
n-Butane	1	11.09	−0.07	114.24	−1.24
	2	11.14	0.0	103.76	0.08
n-Pentane	1	11.09	−0.05	114.08	−0.89
	2	11.25	−0.02	105.70	−0.43
	3	10.67	0.05	95.29	1.12
n-Hexane	1	11.09	−0.03	114.22	−0.60
	2	11.25	0.0	105.86	0.08
	3	10.78	0.05	97.71	1.05
n-Heptane	1	11.09	−0.03	114.22	−0.53
	2	11.25	0.01	105.84	0.14
	3	10.78	0.07	97.69	1.39
	4	10.89	0.03	99.68	0.45
Isobutane	1	10.51	−0.03	103.84	−0.51
	2	11.80	0.10	105.y4	1.82
2,2-Dimethylbutane	1	10.28	0.01	99.62	−0.15
	2	11.82	0.0	98.17	−0.09
	3	10.51	0.0	92.09	0.07
	4	11.32	0.10	118.38	−1.65
Neopentane	1	10.18	0.01	97.47	0.24
	2	11.97	−0.02	100.52	−0.28
Isopentane	1	10.62	−0.03	106.0	−0.67
	2	11.40	0.0	98.78	−0.02
	3	10.-6	0.0	96.83	−0.05
	4	11.20	−0.05	116.23	−0.95
2,3-Dimethylbutane	1	10.73	−0.06	108.15	−1.20
	2	11.15	0.0	94.57	−0.03

a) (Error) = − (ΔE when calculated chemical shift coincide with observed one) + (ΔE calculated by the empirical formula) b) From benzene c) (Error) = (calculated value) − (observed value)

Next, using the above empirical expression, we obtain:

$$\Delta E = 11.30 \times 1.015^a \times 0.958^b \times 1.010^c \times S \tag{13}$$

$$S = 1.011^d \times 1.009^e \times 1.029^f \times 1.009^g \times 1.030^h \times 1.031^i \tag{14}$$

as the most suitable empirical formula for the estimation of the C-13 chemical shift in n-paraffin. We tried to calculate inversely the C-13 chemical shifts in the compounds which were used for parameterization. These results are listed in Table 1. The differences between the experimental and calculated values are extremely small for most paraffins. A considerable discrepancy was seen in ethane, isobutane, 2,2-dimethylbutane, *etc.* In the case of ethane, there is only an α-effect; it is, therefore, difficult to estimate the absolute value of the α-effect instead of a relative value. The discrepancy in ethane may be due to this circumstance. For isobutane and 2,2-dimethylbutane, the principal source for the discrepancy is probably due to their steric hindrances.

TABLE 2. CALCULATED VALUES OF C-13 CHEMICAL SHIFTS IN CYCLOHEXANE DERIVATIVES

Compound		ΔE (eV)	Chem. shift[a] (ppm)	Error[b]
Cyclohexane		10.78	96.91	−4.09
Methylcyclohexane	1	11.12	93.89	−1.11
	2,6	10.41	89.90	−2.48
	3,5	10.89	99.13	−2.17
	4	10.78	96.88	−4.54
	Me	10.73	108.07	2.89
1,1-Dimethylcyclohexane	1	11.78	98.17	0.28
	2,6	10.46	91.37	3.30
	3,5	11.00	101.29	−4.03
	4	10.78	96.90	−4.33
	Me	10.28	99.57	0.50
cis-1,2-Dimethylcyclohexane	1,2	10.88	89.54	−3.96
	3,6	10.51	92.01	−4.52
	4,5	10.89	99.14	−5.28
	Me	10.84	110.20	−2.23
trans-1,2-Dimethylcyclohexane	1,2	10.88	89.65	1.00
	3,6	10.51	92.07	0.22
	4,5	10.89	99.10	−1.85
	Me	10.84	110.18	2.25
cis-1,3-Dimethylcyclohexane	1,3	11.24	96.y6	1.47
	2	10.06	82.89	−0.04
	4,6	10.41	89.90	−2.74
	5	11.00	101.32	−0.12
	Me	10.73	108.02	2.82
trans-1,3-Dimethylcyclohexane	1,3	11.24	96.16	−4.43
	2	10.06	82.63	−4.03
	4,6	10.41	89.75	−4.23
	5	11.00	101.20	−6.00
	Me	10.73	107.99	0.48
cis-1,4-Dimethylcyclohexane	1,4	11.12	93.81	−3.93
	2,3 5,6	10.51	92.03	−5.04
	Me	10.73	108.08	0.09
trans-1,4-Dimethylcyclohexane	1,4	11.12	93.89	−1.30
	2,3 5,6	10.51	92.07	−0.21
	Me	10.73	108.07	2.63

a) From benzene. b) (Error) = (calculated value) − (observed value).

Further, we calculated the C-13 chemical shifts of cyclohexane and its methyl derivatives, using the above empirical expression. The cyclohexane system has the least steric hindrance among the cyclic hydrocarbons. The calculated values are listed in Table 2 and are illustrated by the schematic stick spectrum models in Fig. 2. The stick spectra calculated by Grant's additive rule are also shown in Fig. 2 for purposes of comparison. In cyclohexane, the calculated value is lower than the experimental one by 4.09 ppm. In various kinds of dimethylcyclohexane, *trans*-1,2-, *cis*-1,3-, and *trans*-1,4-dimethylcyclohexanes deviate a little from the experimental values. On the other hand, 1,1-, *cis*-1,2-, *trans*-1,3-, and *cis*-1,4-dimethylcyclohexane deviate from the experimental values by more than about 3 to 4 ppm (see Table 2). By comparing the values calculated by Pople's method using the ΔE expression and the values

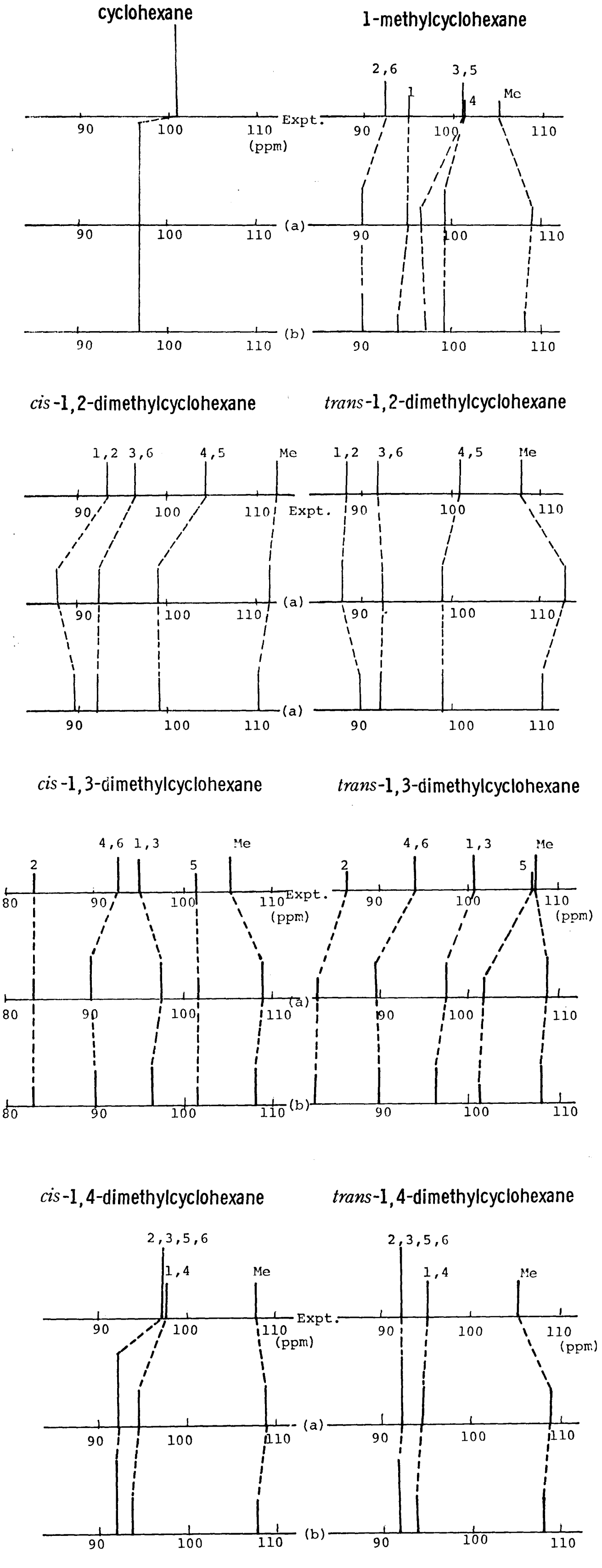

Fig. 2. Experimental and calculated C-13 chemical shifts of cyclohexane derivatives. Expt. shows the experimental values. (a) and (b) are calculated ones by Grant's additive rule and the empirical ΔE formula, respectively.

calculated by Grant's method, we find that the former are more improved than the latter in methylcyclohexane and *cis*-1,2-, *trans*-1,2-, *cis*-1,3-, and *trans*-1,4-dimethylcyclohexanes. On the other hand, the former are nearly equal to the latter in *trans*-1,3- and *cis*-1,4-dimethylcyclohexanes. In cyclohexane their values are equal to each other. Consequently, it can be said that Pople theory, in which ΔE is calculated by the empirical ΔE expression, can predict the most exact C-13 chemical shift of non-constrained cyclic saturated hydrocarbons, such as cyclohexane and its methyl derivatives.

In cyclohexane, however, the deviation of about 4 ppm suggests that the ΔE expression cannot include the steric factor. The C-13 chemical shift of cyclohexane is higher than the value of the central carbon of *n*-hexane by 4.3 ppm. Furthermore, the calculated values agree fairly with the experimental ones when both methyl groups are in equatorial positions, while the agreement is not so good when the methyl groups are in axial positions. However, if about 4 ppm is added to the values of dimethylcyclohexane of which the methyl groups are in axial positions, the results are excellently improved. We can conclude that about 4 ppm is the contribution from the steric effect in the cyclohexane system.

In the carbons of methyl groups, the deviations are about 2 to 3 ppm. This is due to the steric influence of the cyclohexane ring. This steric effect is almost thought to equal the γ effect. In a cyclohexane system, all the ring carbons are in a *gauche* conformation, the axial methyl groups are *gauche* to the γ-carbons of the cyclohexane ring. γ-Effects in *gauche* conformations are estimated by comparison with various hydrocarbons, such as norbornane,[19] its methyl derivatives, and methylcyclohexane. The correlation between the γ-effect and a dihedral angle between C_1 and C_4 carbons is illustrated in Fig. 3.

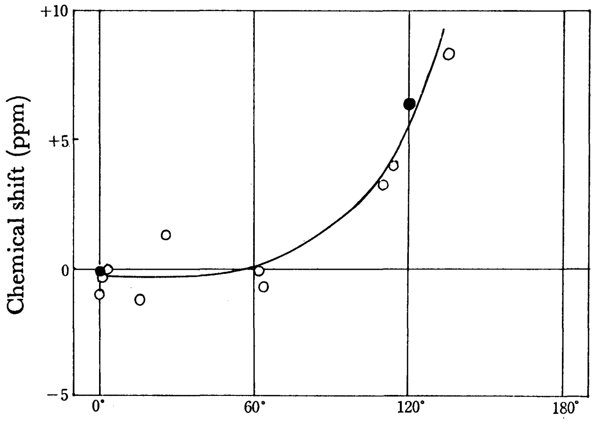

Fig. 3. Correlation between γ-effect and dihedral angle. ○ and ● correspond to the values obtained from norbornane and a methyl derivatives of cyclohexane, respectively.

As is shown in Fig. 3, the γ effect in a *trans* conformation is −0.4 ppm, and the γ-effect in which a dihedral angle is 60° is nearly zero and the γ-effect in which a dihedral angle is 120° (*gauche* conformation) is almost 6 ppm. These results show that, in equatorial methyl groups, the γ-effect are very small, while in axial methyl groups the cyclohexane ring's influence about comprises the γ-effects.

Since the ΔE expression includes the averaged γ-effect, there is no difference in the calculated C-13 chemical shifts between compounds with the same framework, such as *cis*-1,3- and *trans*-1,3-dimethylcyclohexane. By showing the improved calculated value of the C-13 chemical shift in cyclohexane and its derivatives it is proved that the empirical ΔE expression is useful for cyclics and that the C-13 chemical shift of saturated hydrocarbons may be explained with regard only to the influence of α-, β-, and γ-carbons. In the future, it will be interesting to apply this method to the cyclic strained hydrocarbons and to examine the steric effects.

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