Theoretical Calculation of the Carbon-13 Chemical Shifts of Some Normal Alkanes by the Linear Combination of Gauge Invariant Atomic Orbitals-Molecular Orbital Theory Using INDO and MINDO/2 Methods

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The ^{13}C chemical shifts of several *n*-alkanes (CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, and C_7H_{16}) were calculated using a linear combination of the gauge invariant atomic orbitals-molecular orbital theory of Pople and the INDO and MINDO/2 methods, and the results were compared with the experimental data reported by Grant *et al.* The calculated chemical-shift differences among the carbons in these molecules were found to agree with the observed data except in some cases, whereas the observed order of the chemical shift of the carbons in *n*-alkanes, which have more than two magnetically nonequivalent carbons, cannot be interpreted by means of the average excitation energy (ΔE) approximation. Histograms showing the distribution of the excitation energies from the occupied to unoccupied orbitals were obtained and compared with ΔE.

The carbon-13(^{13}C) NMR spectra of normal(*n*-) and branched alkanes were at first studied in detail by Paul and Grant.[1] These data were summarized by the so-called "Grant's empirical additivity rule". An early attempt to interpret these data theoretically was reported by Yonezawa *et al.* using the average excitation energy(ΔE) approximation for the paramagnetic term governing the ^{13}C chemical shift(σ) of *n*- and branched alkanes,[2] but their results agree only roughly with the observed data. Recently they have tried to use various values of ΔE among the individual carbons in alkanes and have suggested that the experimental data were better explained by their method than by the usual method of using a common value of ΔE for all the carbons in an alkane molecule.[3] Although the practical utility is large, this method has an ambiguity in its theoretical basis from the point of view of molecular orbital theory. Therefore it is important to consider the ΔE approximation by means of another method without this approximation. In this paper we attempt to calculate precisely the ^{13}C chemical shifts of *n*-alkanes (CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, and C_7H_{16}) in which the large molecules still have not been treated except for CH_4 and C_2H_6, by a method based on molecular orbital theory considering only the valence-electron system, in place of the ΔE approximation, and attempt to interpret theoretically the observed ^{13}C chemical shifts of large *n*-alkanes, which have not been interpreted by the ΔE approximation. For this purpose, we use Pople's consideration[4] that σ may be estimated as the sum of three terms—the diamagnetic and paramagnetic contributions, and the contribution from electrons on the other atoms in the molecule. The ^{13}C chemical shift is predominantly contributed, by the second term.[4] Pople[5] has derived the so-called linear combination of gauge invariant atomic orbitals-molecular orbital (LCGI-MO) theory for Ramsey's paramagnetic shielding tensor[6] based on a series of approximations, commonly in linear combination of atomic orbitals (LCAO-MO) theory. This approach enables us to calculate the σ values approximately for large molecules. Our calculations have been done using two different parametric self-consistent field (SCF) MO theories, that is, the MINDO/2[7] and INDO methods[8] modified for calculating the electronic excitation energies of organic compounds by Yamaguchi *et al.*[9] The major difference between these two methods is in the separation in orbital energies, which have a large effect on the ^{13}C chemical shift. As for the two MO theories, the MINDO/2 method is said to interpret better the excitation energy for π-system molecules without taking the configuration interaction (CI) into account, but for the electron density distribution, the latter may give better results than the former. Thus, in this paper the results of the two methods will be compared with each other.

Theoretical

According to Pople,[4] the chemical shielding, σ_A, of the nucleus, A, is written as;

$$\sigma_A = \sigma_d + \sigma_p + \sum_{B \neq A} \sigma_{AB} \quad (1)$$

where σ_d is the diamagnetic term, σ_p, the paramagnetic term, and σ_{AB}, the neighbour anisotropy term. The dominant factor usually governing ^{13}C chemical shielding is the paramagnetic term, whereas σ_d does not contribute predominantly. The neighbour anisotropy term can be neglected because it is unlikely to exceed a few ppm, as has been described by Pople.[10]

The diamagnetic term was calculated as:[2]

$$\sigma_d = 4.45(3.25 - 0.35(q_A - 4.0))q_A \quad (2)$$

in which q_A is the σ-electron density on the carbon, A.

According to Pople's LCGI-MO theory,[5] the paramagnetic shielding is written as:

$$\sigma_p = -2N^{-1}\chi_p^A \langle r^{-3} \rangle_{2p} \quad (3)$$

where χ_p^A is the paramagnetic contribution of the A atom to the susceptibility tensor; *N*, the Avogadro number, and $\langle r^{-3} \rangle_{2p}$, the mean value of r^{-3} with respect to the 2p orbital (*r*: the distance between the electron and nucleus). χ_p^A is written by averaging over the diagonal elements of the tensor as;

$$\chi_p^A = \frac{1}{3}\{(\chi_p^A)_{xx} + (\chi_p^A)_{yy} + (\chi_p^A)_{zz}\} \quad (4)$$

where;

$$(\chi_p^A)_{xx} = (Ne^2\hbar^2/m^2c^2)\sum_i^{occ}\sum_{k(\neq i)}^{unocc}(\Delta E_{k-i})^{-1}(c_{iy_A}c_{kz_A} - c_{iz_A}c_{ky_A}) \times \sum_B(c_{iy_B}c_{kz_B} - c_{iz_B}c_{ky_B}) \quad (5\text{-}1)$$

$$(\chi_p^A)_{yy} = (Ne^2\hbar^2/m^2c^2)\sum_i^{occ}\sum_{k(\neq i)}^{unocc}(\Delta E_{k-i})^{-1}(c_{iz_A}c_{kx_A} - c_{ix_A}c_{kz_A}) \times \sum_B(c_{iz_B}c_{kx_B} - c_{ix_B}c_{kz_B}) \quad (5\text{-}2)$$

$$(\chi_p^A)_{zz} = (Ne^2\hbar^2/m^2c^2)\sum_i^{occ}\sum_{k(\neq i)}^{unocc}(\Delta E_{k-i})^{-1}(c_{ix_A}c_{ky_A} - c_{iy_A}c_{kx_A}) \times \sum_B(c_{ix_B}c_{ky_B} - c_{iy_B}c_{kx_B}) \quad (5\text{-}3)$$

Here, c_{ixA} is the coefficient of the $2p_x$ atomic orbital on the atom of the i-th molecular orbital in the LCAO-MO theory; $\sum_i^{occ}$ and $\sum_{k(\neq i)}^{unocc}$ are the summations over the occupied and unoccoupied orbitals; $\sum_B$ runs over all the atoms in the molecule (including A), and ΔE_{k-i} is the singlet-singlet excitation energy between the i-th occupied orbital and the k-th unoccupied one. ΔE_{k-i} is expressed as follows:

$$\Delta E_{k-i} = \varepsilon_k - \varepsilon_i - J_{ki} + 2K_{ki} \quad (6)$$

where ε_k and ε_i are the unoccupied and occupied orbital energies and where J_{ki} and K_{ki} are the two-electron Coulomb and exchange integrals. $\langle r^{-3}\rangle_{2p}$ in Eq. (3) for the Slater 2p orbital of the A atom depends primarily on the local electron density on the carbon atom ($-q'_A$ e is the net charge) and is given as;[10]

$$\langle r^{-3}\rangle_{2p} = 34.33a_0^{-3}(1-0.323q_A')/24 \quad (7)$$

where a_0 is the Bohr radius. From the expressions described above, the ^{13}C chemical shieldings of n-alkanes were estimated by the INDO and MINDO/2 methods for the valence-electron system.

Here, the C–C and C–H bond lengths used are set at 1.54 and 1.10 Å respectively, and all the C–C–C, C–C–H, and H–C–H bond angles are set at 109°28′.[11]

The calculations were carried out by means of the HITAC-8800 computer of the Computer Centre of the University of Tokyo.

Results and Discussion

Before calculating the ^{13}C chemical shift of n-alkanes, it would be helpful in understanding it to discuss the electron density distributions, the orbital energies, the excitation energies, and the ionization potentials as calculated by the INDO and MINDO/2 methods. Here, although n-alkane molecules with more than three carbon atoms can take conformations containing the *gauche* form other than the *trans* form in the liquid state, only the *trans* form, which is the major conformation among the possible conformations, is involved except for n-butane and n-pentane. The total electron density and 2p electron density distributions in seven kinds of n-alkanes, as calculated by the INDO and MINDO/2 methods, are shown in Fig. 1, where the latter is given in brakets. The total and 2p electron densities on the carbon atoms as calculated by the INDO method were found to give slightly larger values than those calculated by the MINDO/2 method. Because $\langle r^{-3}\rangle_{2p}$ decreases with an increase in the total electron density, the MINDO/2 method is found to lead to a somewhat larger contribution of the paramagnetic shielding than does the INDO method. Next, let us examine the orbital energies of n-alkanes. The values calculated by both methods are shown in Fig. 2. It is found that the separations between the occupied and unoccupied orbital energies calculated by the MINDO/2 method are smaller than between those calculated by the INDO method. Therefore, the MINDO/2 method will give somewhat larger contribution to the paramagnetic shielding than will the INDO method. Further, it will become a measure of the magnitude of the paramagnetic contribution to show the histograms of the singlet-singlet transitions from occupied to unoccupied orbitals in alkanes. Therefore, they are shown in Fig. 3, where the vertical axis of the histogram indicates the number of transitions from occupied to unoccupied orbitals and where the interval of the excitation energy is 1 eV. (Such histograms for molecules with π-electrons—for example, ethylene and benzene, may not be appropriate, since the π-π^* transition of the transitions from occupied to unoccupied orbitals does not contribute to the paramagnetic shielding because of the orbital symmetry; therefore, the vertical axis of the histogram should include the weight of each transition in computing the contribution to the chemical shift. However, in the molecules considered here, a σ-electron system, such histograms may be useful in seeing the tendency of the distribution of the excitation energy of n-alkanes without the weight.) As is shown in Fig. 3, the excitation energies giving maximum values in the histograms of the transitions calculated by the MINDO/2 and INDO methods shift to higher energies with an increase in the number of carbon atoms; their exicitation energies are about 9—10 and 14—15 eV respectively, except for CH_4 and C_2H_6. Thus, the MINDO/2 method gives a value about 5 eV lower than does the INDO method. The former may be therefore expected to make a larger paramagnetic contribution than the latter.

Table 1. The calculated and observed ionization potentials of n-alkanes (eV)

	Calculated		Observed[a]
	INDO method	MINDO/2 method	
CH_4	16.71	13.15	12.95
C_2H_6	14.15	11.48	11.65
C_3H_8	12.91	10.88	11.08
C_4H_{10}	12.09	10.32	10.65
C_5H_{12}	11.52	9.96	10.33
C_6H_{14}	11.20	9.73	10.17
C_7H_{16}	10.94	9.55	10.06

a) From Ref. 12.

Before concerning with the present purpose, we will concern with the average excitation energy approximation. Our calculated results of the excitation energies showing maximum values in the histograms by the

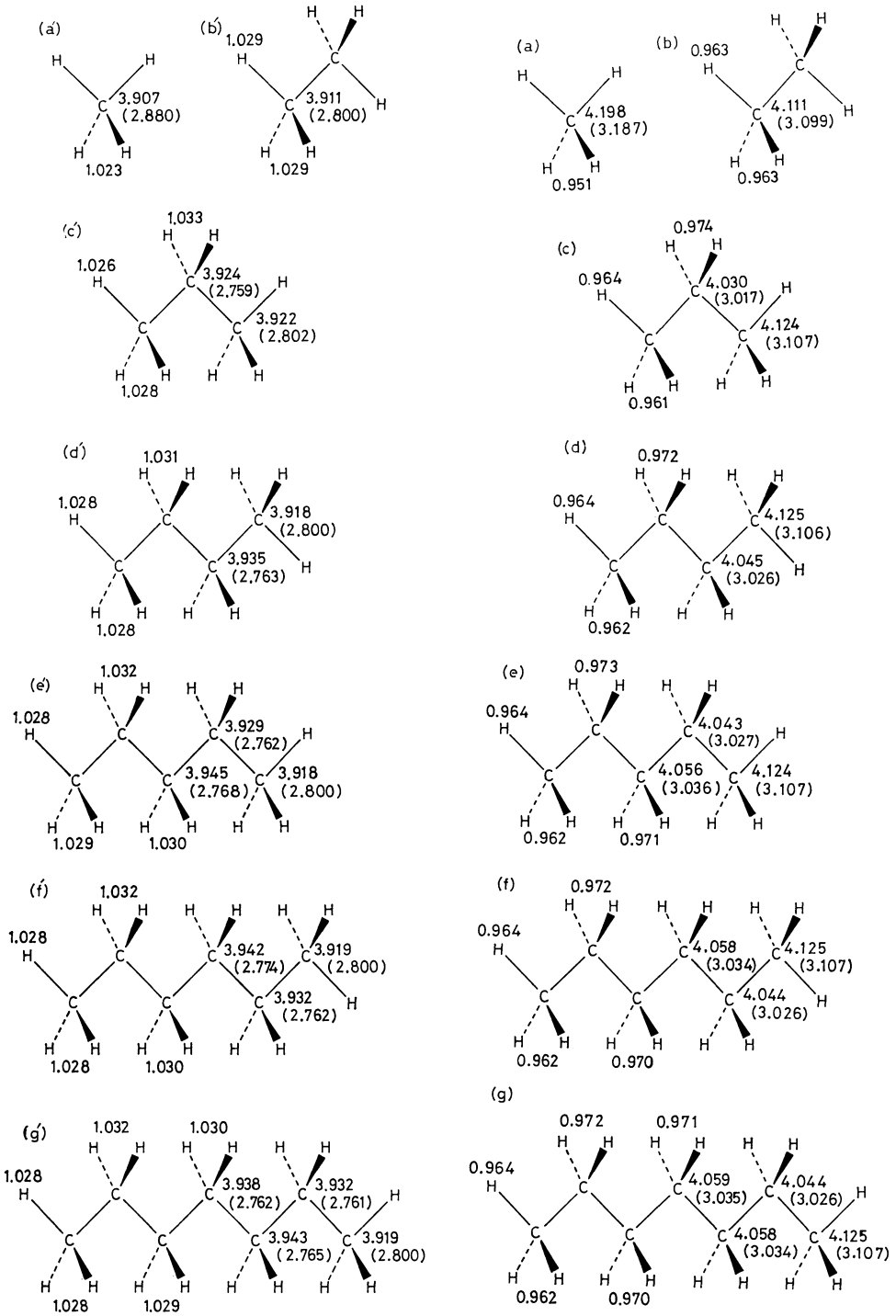

Fig. 1. Total electron density and 2p electron density (with brackets) distributions of *n*-alkanes calculated by INDO and MINDO/2 methods
a), a') CH_4; b), b') C_2H_6; c), c') C_3H_8; d), d') C_4H_{10}. e), e') C_5H_{12}; f), f') C_6H_{14}; g), g') C_7H_{16}. The prime indicates the electron density by MINDO method and other by INDO method. All the conformations are *trans* form.

MINDO/2 method are found to be near to the value of ΔE in the average excitation energy approximation, proposed by Pople[10] for the σ-system carbon atom. These may become roughly one of the measures of the value of ΔE, when the distribution of the histograms is not broad. (According to this viewpoint, the ionization potential may also become a measure of it. As for the ionization potential, the results calculated by the MINDO/2 method are somewhat lower values than those calculated by the INDO method as shown in Table 1. This corresponds to the above-obtained result for the maximum value in the histogram.) Now, let us particularly consider the large *n*-alkanes, and, as an example, let us consider *n*-pentane by the following ΔE approximation, with three magnetically non-equivalent carbon atoms:

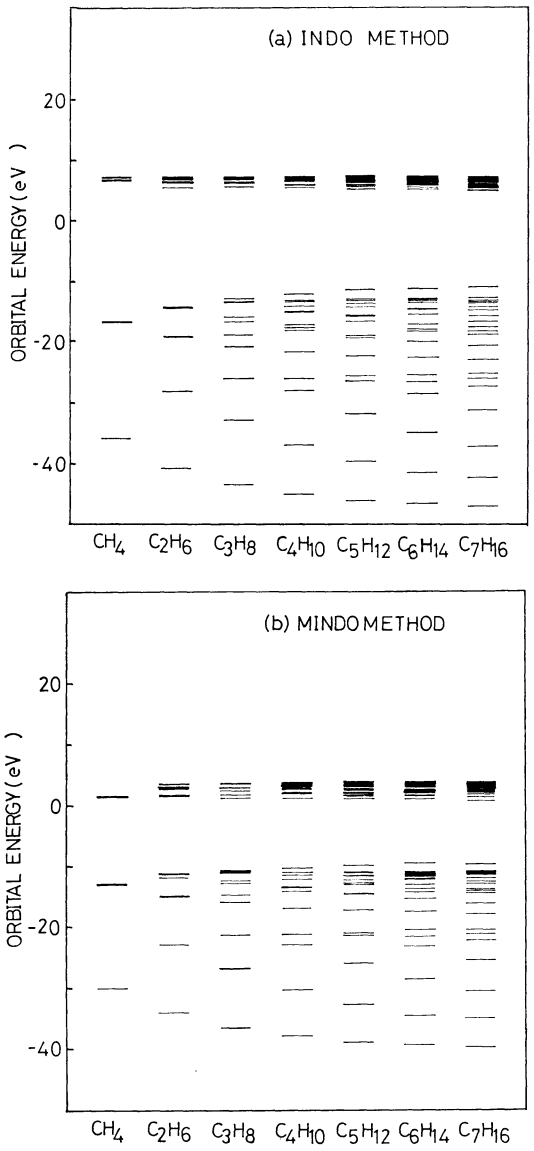

Fig. 2. Orbital energies of *n*-alkanes calculated by INDO (a) and MINDO/2 (b) methods.

$$\sigma_p = -(e^2\hbar^2/2m^2c^2\Delta E)\langle r^{-3}\rangle_{2p}\sum_{B(=A)} Q_{AB} \tag{8}$$

where;

$$Q_{AB} = \frac{3}{4}\delta_{AB}(p_{x_Ax_B}+p_{y_Ay_B}+p_{z_Az_B}) - \frac{2}{3}(p_{y_Ay_B}p_{z_Az_B}+p_{z_Az_B}p_{x_Ax_B}+p_{x_Ax_B}p_{y_Ay_B}) + \frac{2}{3}(p_{y_Az_B}p_{z_Ay_B}+p_{z_Ax_B}p_{x_Az_B}+p_{x_Ay_B}p_{y_Ax_B}) \tag{9}$$

In these formulas, $\sum_{B(=A)}$ is a summation over all the atoms; δ_{AB}, the Kronecker symbol, and p_{XAXB}, the element of the matrix for the $2p_x$ atomic orbitals on the A and B atoms. When A=B, it is the charge density in $2p_x$ on the A atom, and when A≠B, it is the bond order between the two atomic orbitals. The ^{13}C chemical shifts of *n*-pentane, as calculated by the use of the ΔE approximation using the INDO and MINDO/2 methods, are shown in Table 2, where 10 eV is used as the value of ΔE. It is shown that

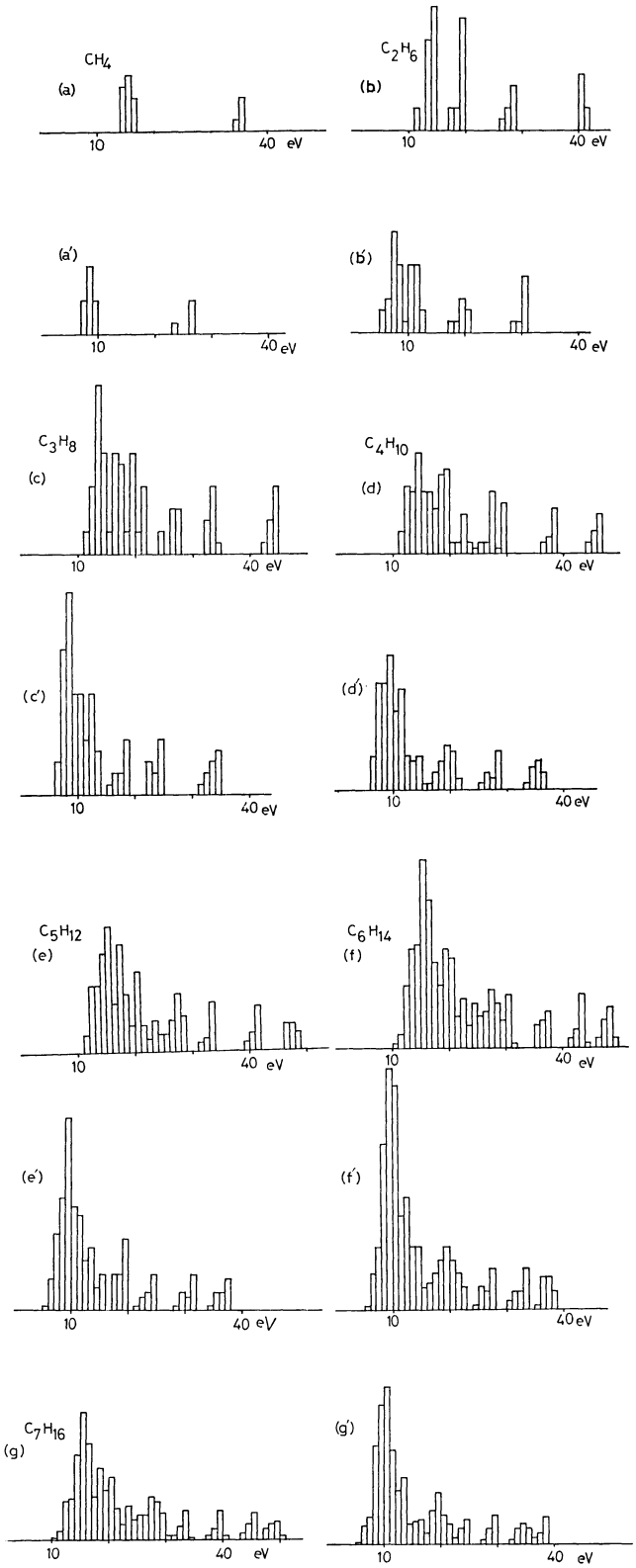

Fig. 3. Histograms of number of the excitation from occupied to unoccupied orbitals against the singlet–singlet excitation energies of *n*-alkanes calculated by INDO and MINDO/2 methods.
a), a') CH_4; b), b') C_2H_6; c), c') C_3H_8; d), d') C_4H_{10}; e), e') C_5H_{12}; f), f') C_6H_{14}; g), g') C_7H_{16}. The prime indicates the electron density by MINDO/2 method and other by INDO method. All the conformations are *trans* form.

Table 2. The ^{13}C chemical shifts of *n*-pentane calculated by the ΔE approximation using the INDO and MINDO/2 methods[a] and the observed ones (ppm)

	INDO method				MINDO/2 method				Observed[d]	
	σ_d	σ_p	σ	$\Delta\sigma$[b]	σ_d	σ_p	σ	$\Delta\sigma$	σ[c]	$\Delta\sigma$[b]
CH_3(1)	58.85	−206.68	−147.83	0	57.17	−225.75	−168.58	0	114.97	0
CH_2(2)	58.20	−222.21	−164.01	−16.18	57.26	−238.42	−181.16	−12.58	106.13	−8.84
CH_2(3)	58.31	−221.74	−163.43	−15.60	57.39	−239.57	−182.18	−13.60	94.17	−20.80

a) The conformation is the TT form. b) The CH carbon is the reference. c) The reference is benzene.
d) From Ref. 1.

Table 3. The ^{13}C chemical shifts of *n*-alkanes calculated by the LCGI-MO theory using the INDO and MINDO/2 methods and the observed ones[a] (ppm)

	INDO method[d]				MINDO/2 method[d]				Observed	
	σ_d	σ_p	σ	$\Delta\sigma$[b]	σ_d	σ_p	σ	$\Delta\sigma$[b]	σ[c]	$\Delta\sigma$[b]
CH_4	59.42	−129.24	−69.82		57.07	−248.63	−191.56		130.8	
CH_3CH_3	58.74	−132.24	−73.50		57.12	−234.05	−176.93		122.8	
$CH_3CH_2CH_3$										
CH_3(1)	58.85	−125.60	−66.75	0	57.20	−219.57	−162.37	0	113.10	0
CH_2(2)	58.10	−137.32	−79.22	−12.47	57.21	−227.31	−170.10	−7.73	112.62	−0.48
$CH_3CH_2CH_2CH_3$										
CH_3(1)	58.86	−120.69	−61.83	0	57.17	−206.55	−149.38	0	115.48	0
CH_2(2)	58.21	−133.73	−75.52	−13.69	57.31	−222.36	−165.05	−15.67	103.68	−11.80
$CH_3CH_2CH_2CH_2CH_3$										
CH_3(1)	58.85	−117.31	−58.46	0	57.17	−198.94	−141.77	0	114.97	0
CH_2(2)	58.20	−129.27	−71.07	−12.51	57.26	−211.42	−154.16	−12.39	106.13	−8.84
CH_2(3)	58.31	−130.87	−72.56	−14.10	57.39	−218.61	−161.22	−19.45	94.17	−20.80
$CH_3CH_2CH_2CH_2CH_2CH_3$										
CH_3(1)	58.85	−114.50	−55.65	0	57.18	−191.53	−134.35	0	114.82	0
CH_2(2)	58.21	−125.86	−67.65	−12.00	57.28	−203.94	−146.66	−12.31	105.78	−9.04
CH_2(3)	58.32	−128.03	−69.71	−14.06	57.37	−210.50	−153.13	−18.78	96.66	−18.16
$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$										
CH_3(1)	58.85	−112.31	−53.46	0	57.18	−186.06	−128.88	0	114.75	0
CH_2(2)	58.21	−123.38	−65.17	−11.71	57.28	−196.33	−139.05	−10.17	105.70	−9.05
CH_2(3)	58.32	−124.83	−66.51	−13.05	57.37	−203.71	−146.34	−17.46	96.30	−18.45
CH_2(4)	58.33	−125.26	−66.93	−13.47	57.37	−204.77	−147.40	−18.52	99.23	−15.52

a) From Ref. 1. b) The CH_3 carbon in a molecule is the reference. c) The reference is benzene.
d) The conformation is the TT form.

the chemical-shift difference between the CH_3(1) and CH_2(2) carbons* agrees roughly with the experimental value, but that between the CH_2(2) and central CH_2(3) carbons does not agree with the experimental value (in the INDO method the order of the CH_2(2) and CH_2(3) carbons is opposite to that in the experimental results.) Therefore, it is difficult to interpret the ^{13}C chemical shift of long *n*-alkane by means of the ΔE approximation. When *n*-alkanes have a broad distribution of the exicitation energy, as is shown in Fig. 3, it may be seen not to be plausible to estimate the ^{13}C chemical shifts using a definite common value of ΔE.

Next, let us discuss the ^{13}C chemical shift of the *n*-alkanes calculated by means of the LCGI-MO theory using the INDO and MINDO/2 methods. The calculated results are shown in Table 3. As has been described above, the magnitudes of the paramagnetic contribution as calculated by means of the MINDO/2 method are found to give larger values than those calculated by means of the INDO method. We will first discuss the chemical shifts of the carbons in each *n*-alkane having more than two magnetically non-equivalent carbon atoms. In the case of *n*-propane calculated by the INDO and MINDO/2 methods, the order of the CH_3 and CH_2 carbons in their chemical shifts agrees qualitatively with the observed order, but for the difference between the two carbons the calculated value are too much larger than the observed value. In the case of *n*-butane, the INDO method gives a fairly good agreement with the observed results, better than the MINDO/2 method. In the case of *n*-pentane, although, as has been mentioned above, we could not interpret the observed chemical-shift difference between the CH_2(2) and CH_2(3) carbons when we used the ΔE approximation, the LCGI-MO theory using the MINDO/2 method gives good agreement between the calculated and observed results, while the INDO method does not give good results quantita-

* The representation of *n*-pentane is as follows; CH_3(1)–CH_2(2)–CH_2(3)–CH_2(2)–CH_3(1). The representations of the other *n*-alkanes are the same as this.

tively, for the chemical-shift difference between the $CH_2(2)$ and $CH_2(3)$ carbons, although the qualitative orders of the carbons agree with each other. In the case of *n*-hexane, the MINDO/2's calculation agrees well with the observed results, but the INDO's calculation does not give good results for the chemical-shift difference between the $CH_2(2)$ and $CH_2(3)$ carbons as well as in the case of *n*-pentane. In the case of *n*-heptane, the observed four signals of the carbon atoms are assigned in order of the $CH_3(1)$, $CH_2(2)$, $CH_2(4)$, and $CH_2(3)$ carbons from the high field (the chemical-shift difference between the $CH_2(3)$ and $CH_2(4)$ is small). In the MINDO/2 method, the chemical shifts of the $CH_3(1)$, $CH_2(2)$, and $CH_2(3)$ carbons agree with the observed ones, but the $CH_2(4)$ carbon appears at a slightly lower field than the $CH_2(3)$ carbon. In the INDO method the chemical shifts of the other carbons except for the chemical-shift difference between the $CH_3(1)$ and $CH_2(2)$ carbons disagree with the observed results.

As may seen be from Table 3, the observed values of the ^{13}C chemical shifts in a molecule could be better explained by the MINDO/2 method than by the INDO method, although one of the causes of some discrepancies may be the simple *trans* planar form.

Next, with respect to *n*-butane and *n*-pentane, we will discuss the effect of possible rotational isomers on the chemical shift. Here the MINDO/2 method was used, because it gives better results than the INDO method in the TT form of *n*-pentane. The electron-density distributions and the orbital energies of the G form in *n*-butane and of the TG and GG forms in *n*-pentane are shown in Figs. 4 and 5 respectively. The latter is shown together with the *trans* forms. Histograms of the number of the excitation against

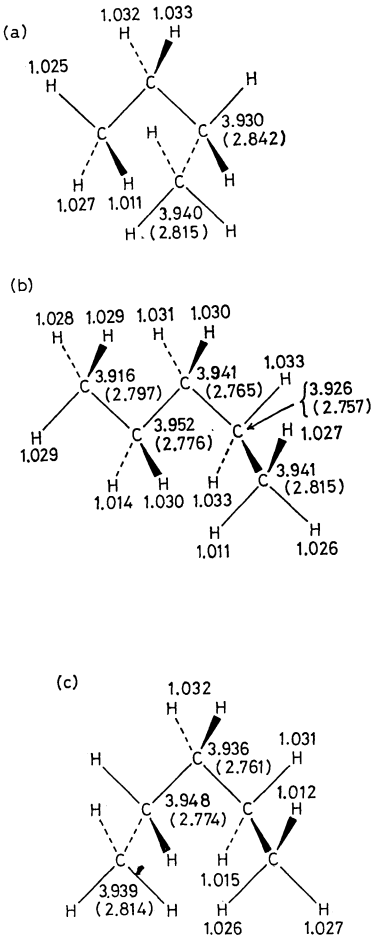

Fig. 4. Total electron density and 2p electron density distributions of the G form in *n*-butane (a), and of the TG (b) and GG (c) forms in *n*-pentane calculated by MINDO/2 method.

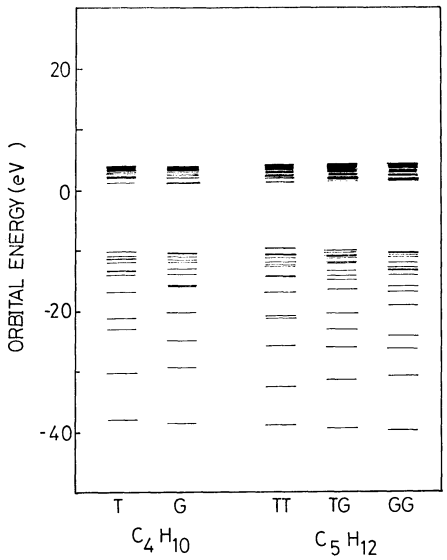

Fig. 5. Orbital energies of the T and G forms in *n*-butane and of the TT, TG and GG forms in *n*-pentane calculated by MINDO/2 method.

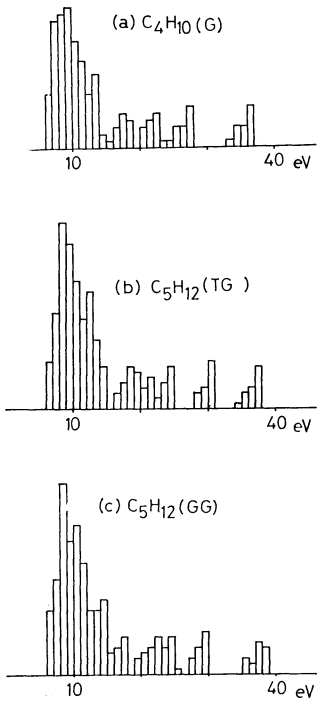

Fig. 6. Histograms of number of the excitation from occupied to unoccupied orbitals against the singlet–singlet excitation energies of the G form in *n*-butane (a), and of the TG, GG forms in *n*-pentane calculated by MINDO/2 method.

Table 4. The ^{13}C chemical shifts of *n*-butane and *n*-pentane calculated by the LCGI–MO theory using the MINDO/2 method for their preferred isomers and statistically averaged states at 300 K, using 570 cal/mol as ΔE_g

		^{13}C chemical shifts (ppm)			
		σ_d	σ_p	σ	$\Delta\sigma$[a]
$CH_3CH_2CH_2CH_3$					
T	$CH_3(1)$	57.17	−206.55	−149.38	0
	$CH_2(2)$	57.31	−222.36	−165.05	−15.67
G	$CH_3(1)$	57.35	−209.37	−152.02	0
	$CH_2(2)$	57.27	−221.11	−163.84	−11.82
$CH_3CH_2CH_2CH_2CH_3$					
TT	$CH_3(1)$	57.17	−198.94	−141.77	0
	$CH_2(2)$	57.26	−211.42	−154.16	−12.39
	$CH_2(3)$	57.39	−218.61	−161.22	−19.45
TG	$CH_3(1)$	57.15	−199.40	−142.25	0
	$CH_2(2)$	57.45	−212.61	−155.16	−12.91
	$CH_2(3)$	57.36	−214.14	−156.78	−14.53
	$CH_2(4)$	57.24	−209.27	−152.03	−9.78
	$CH_3(5)$	57.36	−201.01	−143.65	−1.40
GG	$CH_3(1)$	57.34	−203.36	−146.02	0
	$CH_2(2)$	57.42	−211.31	−153.89	−7.87
	$CH_2(3)$	57.32	−214.32	−157.00	−10.98
Averaged $CH_3CH_2CH_2CH_3$[b]					
	$CH_3(1)$	57.25	−207.77	−150.52	0
	$CH_2(2)$	57.29	−221.82	−164.53	−14.01
$CH_3CH_2CH_2CH_2CH_3$[c]					
	$CH_3(1)$	57.25	−200.17	−142.92	0
	$CH_2(2)$	57.32	−211.14	−153.82	−10.90
	$CH_2(3)$	57.36	−215.72	−158.36	−15.44

a) The $CH_3(1)$ carbon in a molecule is the reference. b) *n*-Butane: averaged over the T, G, and G′ isomers. c) *n*-Pentane: averaged over the TT, TG, TG′, GT, G′T, GG, and G′G′ isomers.

their singlet-singlet excitation energies are also shown in Fig. 6. These results do not differ greatly from those of the *trans* forms shown in Fig. 3. The difference in the electron density among the carbons in the conformation containing the *gauche* form is shown to be smaller than that in the *trans* form. On the other hand, the separation of the occupied and unoccupied orbital energy levels in the conformation containing the *gauche* form is shown to be somewhat larger than that in the *trans* form. Therefore, these results predict that the conformations containing the *gauche* form may give a smaller chemical-shift difference among the carbons than does the *trans* form. These calculated results are tabulated in Table 4. As has been predicted, in the conformations containing the *gauche* form their chemical-shift differences between the $CH_3(1)$ and $CH_2(2)$ carbons in *n*-butane, and between the $CH_2(2)$ and $CH_2(3)$ carbons in *n*-pentane, are somewhat smaller than the corresponding values in the *trans* forms. The observed results should be compared with the calculated results averaged over all the possible conformations (T, G, and G′ for *n*-butane; TT, TG, TG′, GT, G′T, GG, and G′G′ for *n*-pentane) using the following equation:[13]

$$\sigma_{AV} = \sum_i^n X_i \sigma_i \qquad (10)$$

where;

$$X_i = e^{-\Delta E_i/RT} / \sum_i^n e^{-\Delta E_i/RT}$$

in which X_i and σ_i are the fraction and the chemical shift of the *i*-th isomer respectively. R is the gas constant; T, the absolute temperature, and E_i, the energy difference between the *trans* form and the *i*-th isomer. Here, 570 cal/mol[14] is used as the value of the energy difference between the *trans* and *gauche* forms, and 300 K is used as the temperature. These results are also tabulated in Table 4, where the chemical shifts of the carbons in the G and G′ forms of *n*-butane are equal to each other; also, those of the carbons in the TG and TG′, the GT and G′T, and the GG and G′G′ forms of *n*-pentane are equal to each other. These agree relatively well with the observed results. Furthermore, from the results of the chemical-shift difference between the CH_3 and CH_2 carbons in the conformations containing the *gauche* form of *n*-butane and *n*-pentane, the difference is predicted to decrease with an increase in the temperature. However, the observed results of *n*-butane[15] and *n*-pentane[16] in neat liquid are opposite to the calculated ones. The reason for this is that the chemical-shift difference between the CH_3 and CH_2 carbons of the conformation containing the *gauche* form is too small compared with that of the *trans* form.

As has been mentioned above, the LCGI–MO theory was found to interpret well the tendencies of the chemical shift of the carbons in a molecule. However, Table 4 shows that the quantitative agreement between the calculated and observed chemical shifts of the carbons among the molecules is not satisfactory. This discrepancy arises partly from the MO theories, which do not strictly estimate the singlet-singlet excitation energies among the *n*-alkanes considered. Further, some other factors may be pointed out. A molecular orbital approximation cannot give an exact value for the energy of a molecule because it usually neglects the electron correlation due to the mutual Coulomb repulsion of the electrons. Some approximations are made for this in both the INDO and MINDO/2 treatments by the adjustment of the parameter, but there is a limit to this kind of adjustment. Thus, to improve our calculation it will be necessary to take the configuration interaction into account in the future.

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