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The Carbon-13 Chemical Shift of *n*-Butane

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The temperature dependence of the carbon-13 chemical shift of *n*-butane was calculated using the CNDO/2 method, taking into account the rotational isomers and assuming the Boltzmann distribution among them. The observed results could be well interpreted by assuming *ca.* 11.15 eV as the average excitation energy.

The chemical shifts of carbon-13 nuclei in saturated hydrocarbons have been studied systematically by the experiment of Grant *et al.*[1] Pople[2] has given a theory of the carbon-13 chemical shift, and has caluclated the shifts of ethane and other simple molecules. His approach is not convenient for calculating the carbon-13 chemical shift of a large molecule because of the tedious work involved. Then Sichel *et al.*[3] have reported empirically on an apparent correlation between the carbon-13 chemical shifts and the electron charge densities on the carbon atoms of hydrocarbons, as calculated by the extended Hückel method.[4] Yonezawa *et al.*[5] have interpreted theoretically the carbon-13 chemical shifts of various hydrocarbons by approximating Pople's theory[2] for the paramagnetic shielding of the carbon-13 nucleus, but the agreement between the calculated and observed chemical shifts is not good. This disagreement may be due mainly to the approximation, assuming the constancy of terms containing the bond orders between neighbouring atoms, the ambiguity of the value of the average excitation energy, and the neglect of the rotational isomers.

In this paper we will calculate the paramagnetic shielding constants of carbon atoms in *n*-butane based on Pople's theory, and will interpret the temperature dependence of the carbon-13 chemical shifts by estimating the diamagnetic shielding constant in addition to

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[1] E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1701 (1963), D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964).

[2] J. A. Pople, *Mol. Phys.*, **7**, 301 (1964).

[3] J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta*, **5**, 35 (1966).

[4] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[5] T. Yonezawa, I. Morishima, and H. Kato, This Bulletin, **39**, 1398 (1966).

its paramagnetic shielding constant, taking the rotational isomers into account also.

Experimental

The proton-decoupled carbon-13 NMR spectra of *n*-butane in neat liquid were measured at temperatures from −60 to 0°C at 25.25 MHz in the external-locked mode, using a Japan Electron Optics Laboratory, JEOL PS-100-type, spectrometer. The sample (purity: 99.9%) was obtained from the Tokyo Kasei Co., Ltd.

Calculation

The magnetic shielding constant of any specified carbon atom, A, in a molecule, σ_A, may be approximated by a sum of the following terms:[2)]

$$\sigma_A = \sigma_{AA}^{dia} + \sigma_{AA}^{para} + \sigma' \tag{1}$$

where σ_{AA}^{dia} and σ_{AA}^{para} are the diamagnetic and paramagnetic contributions to the specified carbon atom, A, respectively, and σ', the contribution from the neighbouring atoms bonded to the A atom. Usually the effect of σ' on the carbon-13 chemical shift is known to be very small,[2)] contributing less than a few parts per million. With Slater atomic orbitals, σ_{AA}^{dia} increases 14 ppm if a 2p electron is added, only about 10% of the width of the observed range of the carbon-13 chemical shifts. However, in this paper in order to discuss the carbon-13 chemical shift in detail we will take into account the terms of both the diamagnetic and paramagnetic shielding effects.

The value of σ_{AA}^{dia} is given by the formula:[6)]

$$\sigma_{AA}^{dia} = (e^2/3mc^2)\sum_i \langle r_i^{-1} \rangle \tag{2}$$

where $\langle r_i^{-1} \rangle$ is the mean inverse distance of an electron from a nucleus; *m*, its mass; *e*, its charge and *c*, the velocity of light; the summation is over all the electrons on the atom being considered. The approximate value of σ_{AA}^{dia} for the carbon atom **is** given as:

$$\sigma_{AA}^{dia} = 4.45Z^*q \tag{3}$$

where:

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

in which *q* is the total electron density around the carbon atom, and *Z**, the "effective nuclear charge" estimated according to Slater's rules.[7)]

According to Pople's theory,[2)] σ_{AA}^{para} is given as:

$$\sigma_{AA}^{para} = -(e^2\hbar^2/2m^2c^2\varDelta E)\langle r^{-3}\rangle_{2p}\sum\nolimits_{B(=A)} Q_{AB} \tag{5}$$

where:

$$\begin{aligned} Q_{AB} = {} & \frac{4}{3}\delta_{AB}(P_{x_Ax_B}+P_{y_Ay_B}+P_{z_Az_B}) \\ & -\frac{2}{3}(P_{y_Ay_B}P_{z_Az_B}+P_{z_Az_B}P_{x_Ax_B}+P_{x_Ax_B}P_{y_Ay_B}) \\ & +\frac{2}{3}(P_{y_Az_B}P_{z_Ay_B}+P_{z_Ax_B}P_{x_Az_B}+P_{x_Ay_B}P_{y_Ax_B}) \end{aligned} \tag{6}$$

$$\langle r^{-3}\rangle_{2p} = \frac{1}{24a_0^3}(3.25-0.35(q_{2p}-3))^3 \tag{7}$$

$$q_{2p} = P_{x_Ax_B}+P_{y_Ay_A}+P_{z_Az_A} \tag{8}$$

In these formulae, $\varDelta E$ is an averaged electronic excitation energy; $\sum_{B(=A)}$, a summation over all the atoms; $\langle r^{-3}\rangle_{2p}$, the mean inverse cube radius for carbon 2p orbitals; q_{2p}, the electron density of the 2p electrons; δ_{AB}, the Kronecker symbol, and a_0, the Bohr radius. $P_{x_Ax_B}$ is the element of the matrix for the $2p_x$ atom 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.

σ_{AA}^{para} and σ_{AA}^{dia} were estimated by the CNDO/2 (Complete Neglect of Differential Overlap) molecular orbital method.[8)]

In the *n*-butane molecule, three conformations are possible as the rotational isomerism (*trans*(T) and *gauche* (G or G′) with respect to the central bond). T, G, and G′ are defined as occuring at the rotational angles about 0, 120, and 240° respectively, by the clockwise rotation around the C–C bond, as expressed in the Newman projection. One of the three methyl protons was assumed to take the *trans* position in relation to the third carbon atom from the methyl carbon atom.

Then, obtaining the chemical shift of *n*-butane, we must average the calculated chemical shifts of the three possible isomers. For the averaging of the chemical shifts of the isomers, the following formula was used:[9)]

$$\sigma_{AV} = \sum_{i=1}^{3} X_i \sigma_{A_i} \tag{9}$$

where σ_{AV} is the averaged chemical shift; σ_{A_i}, the chemical shift of the *i*-th isomer, and X_i, its fraction. X_i is expressed as:

$$X_i = e^{-\varDelta E_i/RT} / \sum_{i=1}^{3} e^{-\varDelta E_i/RT} \tag{10}$$

where *R* is the gas constant; *T*, the absolute temperature, and $\varDelta E_i$, the energy difference between the reference isomer (*trans*) and the *i*-th isomer. From the equations presented above, we can calculate the carbon-13 chemical shift and the temperature dependence of *n*-butane.

Here, the C–C and C–H bond lengths are set at 1.54 and 1.10 Å respectively, and both the C–C–C and the C–C–H bond angles are set at 109°28′.[10)]

The numerical calculation was carried out by means of the HITAC-5020E computer of the Computer Center of the University of Tokyo.

Results and Discussion

n-Butane can take three rotational isomers, of one *trans* and two *gauche* forms; the total electron densities of the *trans* and *gauche* isomers are shown in Fig. 1. The electron densities and bond orders of the 2p electrons of the carbon atoms in these isomers are shown in Table 1. There is not much differences in the electronic states between the *trans* and *gauche* forms. Therefore, the large temperature dependence of the chemical shift of *n*-butane cannot be explained in terms of these

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6) W. E. Lamb, *Phys. Rev.*, **60**, 817 (1941).
7) J. C. Slater, *ibid.*, **36**, 57 (1930).
8) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S 136 (1965).
9) H. S. Gutowsky, *ibid.*, **37**, 2196 (1962).
10) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press (1960).

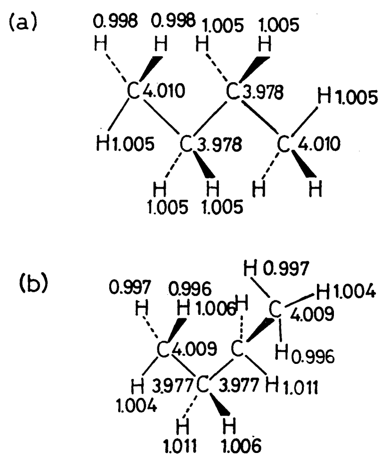

Fig. 1. The total electron density distribution of *n*-butane. (a): *trans* isomer, (b): *gauche* isomer.

total densities.

The carbon-13 chemical shifts of the *trans* and *gauche* isomers, and those averaged over these isomers, were calculated using Eqs. (1), (3), (5), and (9); they are shown in Table 2. The calculated and observed chemical-shift differences between the methyl and methylene carbons at 300K are also shown. Since there is no definite value for the average excitation energy (ΔE) published for *n*-butane, we first tried to use 10 eV for ΔE; this value was originally used by Pople[2] in the case of ethane.

As expected, and as Table 2 shows, σ_{AA}^{para} contributes mainly to the chemical-shift difference between the methyl and methylene carbons. The calculated chemical shifts of both methyl carbons in the *trans* and *gauche* isomers are nearly equal to each other, but those of the methylene carbon in the former appear at a slightly higher field than in the latter. This is due to the change in the electronic state of the methylene atom for the rotation around the central bond. Therefore, the chemical shift of the methylene carbon may be expected to depend upon the population of the rotational isomers, which is itself governed by the energy difference (ΔE_g) between the *trans* and *gauche* forms. It is known from spectroscopic studies that extensive results for liquid *n*-hydrocarbons confirm a value of 500±100 cal/mol for ΔE_g.[11] Recently, on the basis of a laser-Raman spectroscopic study,[12] it has been reported that 600 cal/mol is more reasonable as

Table 1. The charge densities and bond orders of $2p_x$, $2p_y$, and $2p_z$ electrons on the carbon atoms of *n*-butane

(a) *Trans* form.

	$2p_x$				$2p_y$	
	$CH_3(1)$	$CH_2(2)$	$CH_2(3)$	$CH_3(4)$	$CH_3(1)$	$CH_2(2)$
$2p_x$ CH_3 (1)	1.0327	−0.6144	0.0053	−0.0525	0.0000	0.0000
CH_2 (2)	−0.6144	1.0146	0.1340	0.0053	0.0000	0.0000
CH_2 (3)	0.0053	0.1340	1.0148	−0.6144	0.0000	0.0000
CH_3 (4)	−0.0525	0.0053	−0.6144	1.0325	0.0000	0.0000
$2p_y$ CH_3 (1)	0.0000	0.0000	0.0000	0.0000	0.9765	0.1683
CH_2 (2)	0.0000	0.0000	0.0000	0.0000	0.1683	0.9600
CH_2 (3)	0.0000	0.0000	0.0000	0.0000	−0.0044	0.1641
CH_3 (4)	0.0000	0.0000	0.0000	0.0000	−0.0063	−0.0044
$2p_z$ CH_3 (1)	0.0177	−0.2707	−0.0380	−0.0209	0.0000	0.0000
CH_2 (2)	−0.2875	0.0061	−0.0139	−0.0110	0.0000	0.0000
CH_2 (3)	−0.0111	−0.0136	0.0062	−0.2873	0.0000	0.0000
CH_3 (4)	−0.0209	−0.0380	−0.2709	0.0177	0.0000	0.0000

	$2p_y$		$2p_z$			
	$CH_2(3)$	$CH_3(4)$	$CH_3(1)$	$CH_2(2)$	$CH_2(3)$	$CH_3(4)$
$2p_x$ CH_3 (1)	0.0000	0.0000	0.0177	−0.2875	−0.0111	−0.0209
CH_2 (2)	0.0000	0.0000	−0.2707	0.0061	−0.0036	−0.0380
CH_2 (3)	0.0000	0.0000	−0.0380	−0.0139	0.0062	−0.2709
CH_3 (4)	0.0000	0.0000	−0.0209	−0.0110	−0.2873	0.0177
$3p_y$ CH_3 (1)	−0.0044	−0.0063	0.0000	0.0000	0.0000	0.0000
CH_2 (2)	0.1641	−0.0044	0.0000	0.0000	0.0000	0.0000
CH_2 (3)	0.9600	0.1683	0.0000	0.0000	0.0000	0.0000
CH_3 (4)	0.1683	0.9764	0.0000	0.0000	0.0000	0.0000
$2p_z$ CH_3 (1)	0.0000	0.0000	0.9771	0.0544	−0.0300	−0.0011
CH_2 (2)	0.0000	0.0000	0.0544	1.0194	−0.7085	−0.0300
CH_2 (3)	0.0000	0.0000	−0.0300	−0.7085	1.0192	0.0544
CH_3 (4)	0.0000	0.0000	−0.0011	−0.0300	0.0544	0.9773

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11) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press (1954).

12) T. Fujishima, M. Tashumi, and T. Shimanouchi, Symposium on Polymer, 771 (1970) Kyoto.

(b) *Gauche* form.

	$2p_x$				$2p_y$	
	$CH_3(1)$	$CH_2(2)$	$CH_2(3)$	$CH_3(4)$	$CH_3(1)$	$CH_2(2)$
$2p_x$ CH_3 (1)	1.0301	−0.6124	−0.0087	−0.0143	−0.0001	0.0000
CH_2 (2)	−0.6124	1.0165	0.1495	−0.0056	−0.0003	0.0014
CH_2 (3)	−0.0087	0.1495	0.9704	−0.0272	0.0028	0.0049
CH_3 (4)	−0.0143	−0.0056	−0.0272	0.9910	0.0071	0.0046
$2p_y$ CH_3 (1)	−0.0001	−0.0003	0.0028	0.0071	0.9779	0.1677
CH_2 (2)	0.0000	0.0014	0.0049	0.0046	0.1677	0.9565
CH_2 (3)	−0.0059	0.0039	−0.0253	0.3376	−0.0065	0.1546
CH_3 (4)	0.0228	−0.0042	0.3379	−0.0226	0.0029	−0.0095
$2p_z$ CH_3 (1)	0.0168	−0.2705	−0.0403	−0.0029	−0.0002	−0.0006
CH_2 (2)	−0.2856	0.0099	0.0071	0.0094	0.0012	−0.0027
CH_2 (3)	−0.0155	−0.0136	−0.0073	0.1437	0.0020	0.0002
CH_3 (4)	0.0012	0.0165	0.1348	−0.0086	−0.0027	−0.0370

	$2p_y$		$2p_z$			
	$CH_2(3)$	$CH_3(4)$	$CH_3(1)$	$CH_2(2)$	$CH_2(3)$	$CH_3(4)$
$2p_x$ CH_3 (1)	−0.0059	0.0228	0.0168	−0.2856	−0.0155	0.0012
CH_2 (2)	0.0039	−0.0042	−0.2705	0.0099	−0.0136	0.0165
CH_2 (3)	−0.0253	0.3379	−0.0403	0.0071	−0.0073	0.1348
CH_3 (4)	0.3376	−0.0226	−0.0029	0.0094	0.1437	−0.0086
$2p_y$ CH_3 (1)	−0.0065	0.0029	−0.0002	0.0012	0.0020	−0.0027
CH_2 (2)	0.1546	−0.0095	−0.0006	−0.0027	0.0002	−0.0370
CH_2 (3)	1.0028	−0.4174	−0.0042	−0.0119	0.0073	−0.2348
CH_3 (4)	−0.4174	1.0168	−0.0003	−0.0124	−0.2466	0.0144
$2p_z$ CH_3 (1)	−0.0042	−0.0003	0.9770	0.0545	−0.0305	−0.0064
CH_2 (2)	−0.0119	−0.0124	0.0545	1.0192	−0.7082	−0.0305
CH_2 (3)	0.0073	−0.2466	−0.0305	−0.7082	1.0191	0.0545
CH_3 (4)	−0.2348	0.0144	−0.0064	−0.0305	0.0545	0.9771

Here *n*-butane was numbered like CH_3 (1)–CH_2 (2)–CH_2 (3)–CH_3 (4).

TABLE 2. THE CALCULATED σ_{AA}^{dia}, σ_{AA}^{para}, AND σ_A OF *n*-BUTANE AND ITS OBSERVED CARBON-13 CHEMICAL SHIFT

	trans isomer (ppm)			*gauche* isomer (ppm)			Averaged over the *trans* and *gauche* isomers (at 300K) (ppm)			Obsd a) (at 300K) (ppm)
	σ_{AA}^{dia}	σ_{AA}^{para}	σ_A	σ_{AA}^{dia}	σ_{AA}^{para}	σ_A	σ_{AA}^{dia}	σ_{AA}^{para}	σ_A	
CH_3	57.93	−219.60	−161.67	57.92	−219.57	−161.65	57.93 (57.93)	−219.57 (−219.60)	−161.66 b) (−161.67) c)	11.90
CH_2	57.67	−231.98	−174.31	57.66	−233.23	−175.57	57.67 (57.67)	−232.56 (−232.51)	−174.89 b) (−174.84) c)	0
CH_3–CH_2	0.26	12.38	12.64	0.26	13.66	13.92	0.26 (0.26)	12.99 (12.91)	13.23 b) (13.17) c)	11.90

a) Reference is the signal of the methylene carbon.
b) Calculated using 500 cal/mol as ΔE_g.
c) Calculated using 600 cal/mol as ΔE_g.

the ΔE_g value. Here, we have calculated the chemical shifts of the methyl and methylene carbons for both ΔE_g value, 500 and 600 cal/mol, at 300K. As may be seen from Table 2, the calculated chemical shifts between the methyl and methylene carbons using ΔE_g values of 500 and 600 cal/mol at 300K are 13.23 and 13.17 ppm respectively. There is only a slight difference (about 5%) between them.

The calculated and observed chemical-shift differences between the methyl and methylene carbons are 13.23 and 11.90 ppm respectively at 300 K. The agreement is good; the small difference is considered mainly to be due to the ambiguous estimation of the average excitation energy.

Now let us attempt to estimate an appropriate value of ΔE in order to interpret the observed chemical shift rigorously. As the first approximation, it may be considered that, according to Gutowsky's consideration,9) the observed temperature dependence of the carbon-13 chemical shift of *n*-butane can be interpreted in terms of the temperature dependence of the fraction of rotational isomers. Therefore, if the ΔE_g and the

TABLE 3. THE OBSERVED CHEMICAL SHIFT DIFFERENCES BETWEEN THE METHYL AND METHYLENE CARBONS ($\Delta\sigma_{CH_3-CH_2}$) AND ΔE IN VARIOUS TEMPERATURES

T(K)		212	252	270	294	300
$\Delta\sigma_{CH_3-CH_2}$(ppm)		11.75	11.77	11.84	11.86	11.90
ΔE (eV)	(a)	11.19	11.23	11.16	11.17	11.10
	(b)	11.13	11.15	11.12	11.13	11.17

a) $\Delta E_g = 500$ cal/mol, b) $\Delta E_g = 600$ cal/mol

temperature are determined, all the values of the chemical shifts observed for a wide range of temperatures can be estimated by a single value of ΔE.

The absolute measurement of the temperature dependence of the carbon-13 chemical shifts of the methyl or methylene carbons is very difficult because of some possible temperature drifts of the external or internal reference signal, whereas the temperature dependence of the chemical-shift difference ($\Delta\sigma_{CH_3-CH_2}$) between the methyl and methylene carbons is not affected by the temperature drifts of the reference signal. Thus, the values of $\Delta\sigma_{CH_3-CH_2}$ were measured at temperatures from 212 to 300 K, as is shown in Table 3; the values of ΔE were then calculated to fit the observed $\Delta\sigma$ value (where both 500 and 600 cal/mol were used as ΔE_g values). From the results, it was found that the observed values can be interpreted reasonably using the constant (ΔE) value of 11.16±0.04 and 11.14±0.02 eV in the cases of ΔE_g values of 500 and 600 cal/mol respectively. There is no significant difference between the two cases.

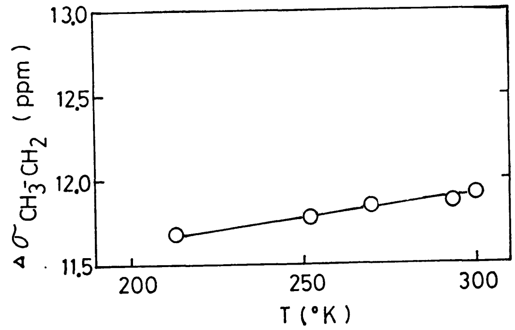

Fig. 2. The calculated and observed temperature dependences of the chemical shift difference between the methyl and methylene carbons of *n*-butane.

Drawn line: calculated using 11.16 eV as ΔE

○: observed

Next, in order to compare clearly the observed and calculated results, they are both shown in Fig. 2; the latter was obtained using 11.16 eV as ΔE and 500 cal/mol as ΔE_g. In this figure the observed data may be found to fit the calculated line better. Therefore, we may conclude that the temperature dependence of the carbon-13 chemical shift of *n*-butane may be interpreted using the rotational isomers and a single value of ΔE