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Theoretical Determination of the Principal Axes of ^{13}C Chemical Shielding Tensors and their Relationship to the Anisotropies in Some Organic Compounds

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The principal axes and values for the ^{13}C chemical shielding tensors of carbonyl compounds (formaldehyde, acetaldehyde, acetone, and formic acid), methanol, and *n*-paraffins (propane and *n*-butane) have been determined theoretically by the LCGI–MO theory using the MINDO/2 method. Further, their anisotropies have been estimated. These results have then been discussed by comparing them with the observation of Pines *et al.* and in part compared with the anisotropies in the literature calculated by using other theoretical methods.

The chemical shielding constant of a molecule in NMR is a symmetric second-rank tensor quantity with nine components. In gases and liquids one can observe only the isotropic value of the chemical shielding tensor, that is, the average of the three diagonal components resulting from the rapid molecular reorientation. On the other hand, in solid states the molecular motion is greatly reduced. Thus, in principle, it is possible to determine the six independent components of the tensor; in practice, however, it is normally difficult. To know the full tensor would be extremely valuable for, especially, the theoretical study of the chemical shielding constant. In the last several years significant progress has been achieved in experimental techniques and also in the calculation of the ^{13}C chemical shift.[1] The present authors[2] recently concerned themselves with a theoretical study of the anisotropy of the ^{13}C chemical shielding constant in several organic compounds in order to interpret the experimental data measured by Pines *et al.*[3] Although it is very important to know the exact directions of the principal axes of the ^{13}C shielding tensor for each carbon atom in any molecule, we have not enough information about them at present.

Recently Waugh *et al.*[4] and others[5] have determined experimentally the relative orientation of the principal axes of the ^{13}C shielding tensors using single crystals of several organic compounds, and have shown that such information is more easily obtained from NMR than from X-ray diffraction. In this work we will be concerned with the theoretical determination of the principal axes of the ^{13}C shielding tensors and their relations to the shielding tensor in several compounds, such as formaldehyde, acetaldehyde, acetone, formic acid, methanol, propane, and *n*-butane(*n*-paraffins are known to be planar in the solid state).

There are two theoretical approaches to the determination of the principal axes and values. In one, the six independent shielding elements of the tensor are calculated, the principal values are obtained by diagonalizing the complete tensor, and then, from these, the corresponding axes are determined. In the other, the dependence of the diagonal elements of the tensor on the rotation of the coordinate system chosen is calculated, and then, from this, the principal axes and the principal values are determined. In this work the latter method was used because of its simplicity and its applicability to our case.

Theoretical

The shielding tensor, $\boldsymbol{\sigma}'$, is expressed as follows:

$$\sigma' = \begin{pmatrix} \sigma'_{xx} & \sigma'_{yx} & \sigma'_{zx} \\ \sigma'_{xy} & \sigma'_{yy} & \sigma'_{zy} \\ \sigma'_{xz} & \sigma'_{yz} & \sigma'_{zz} \end{pmatrix} \tag{1}$$

The value of each element in the shielding tensor depends upon the coordinate system chosen in any specific molecule. Therefore, in order to determine the principal axes and values, the dependence of the values of the diagonal terms upon the rotation of the coordinate system chosen must be known.

Now, a coordinate system, $\mathbf{X}$ (x,y,z) for the inherent principal axes is defined for $\boldsymbol{\sigma}$ (diagonalized shielding tensor). The transformation of an arbitrary coordinate system, $\mathbf{X}'$ (x′,y′,z′), into the coordinate system, $\mathbf{X}$-(x,y,z), by rotation is as follows:

$$\mathbf{X} = \mathbf{T}\cdot\mathbf{X}' \tag{2}$$

where $\mathbf{T}$ is the transformation matrix. All the molecules concerned are planar. Thus, one of the three principal axes is along the direction perpendicular to the molecular plane due to their symmetry; this axis is defined as the z axis. The rotation of the right-handed coordinate system is about the z axis. Thus, $\mathbf{T}$ is defined as:

$$\mathbf{T} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3}$$

The coordinate system rotates counterclockwise about the z axis. As $\mathbf{T}$ is an unitary matrix, the inverse matrix, $\mathbf{T}^{-1}$, is identical to the transposed matrix, $\tilde{\mathbf{T}}$. From the character of a tensor, we can write the following relation by choosing an appropriate value of θ:

$$\begin{aligned} \sigma &= \mathbf{T}^{-1}\cdot\sigma'\cdot\mathbf{T} \\ &= \tilde{\mathbf{T}}\cdot\sigma'\cdot\mathbf{T} \end{aligned} \tag{4}$$

Then, as $\tilde{\mathbf{T}}\cdot\mathbf{T}=\mathbf{E}$ ($\mathbf{E}$: unit matrix),

$$\sigma' = \mathbf{T}\cdot\sigma\cdot\tilde{\mathbf{T}} \tag{5}$$

As has been described above, one of the three principal axes is the z axis perpendicular to the molecular plane. In obtaining the remaining principal axes, we first calculate the angle (relative to the principal axes) at which the value of σ'_{xx} and σ'_{yy} are equal to each other:

$$\sigma'_{xx} = \sigma'_{yy} \tag{6-1}$$

then

$$\sigma_{xx} + (\sigma_{yy} - \sigma_{xx})\sin^2\theta$$
$$= \sigma_{yy} - (\sigma_{yy} - \sigma_{xx})\sin^2\theta \qquad (6\text{-}2)$$
$$(\sigma_{yy} - \sigma_{xx})(2\sin^2\theta - 1) = 0 \qquad (6\text{-}3)$$

From this equation, the value of θ is found to be 45 degrees when $\sigma_{yy} \neq \sigma_{xx}$. This result may be true only in this case. Therefore, the position where $\sigma'_{xx} = \sigma'_{yy}$ is found to deviate by 45 degrees from the principal axis. This shows that, in the principal axis systems, the values of σ'_{xx} and σ'_{yy} take the maximum or minimum value. Thus, we can find the principal axes and values by calculating the dependence of the values of σ'_{xx}, σ'_{yy} and σ'_{zz} upon the rotation of the coordinate system chosen.

The paramagnetic term governing predominatly the ^{13}C chemical shielding constant is estimated using the LCGI-MO theory of Pople[6] according to a previous paper[2] as follows (*e.g.*, σ'^{p}_{xx}):

$$\sigma'^{p}_{xx} = -(2e^2\hbar^2/m^2c^2)\langle r^{-3}\rangle_{2p}\sum_{i}^{\text{occ}}\sum_{k(\neq i)}^{\text{unocc}}\Delta E_{k-i}^{-1}$$
$$\times (C_{iy_A}C_{kz_A} - C_{iz_A}C_{ky_A})\sum_{B}(C_{iy_B}C_{kz_B} - C_{iz_B}C_{ky_B}) \qquad (7)$$

where C_{ix_A} is the coefficient of the 2p$_x$ atomic orbital on the A atom of the i-th molecular orbital in the LCAO MO theory, where $\sum\limits_{i}^{\text{occ}}$ and $\sum\limits_{k(\neq i)}^{\text{unocc}}$ are the summations over occupied and unoccupied orbitals, respectively, where $\sum\limits_{B}$ runs over all the atoms in the molecule, and where ΔE_{k-i} is the singlet-singlet excitation energy between the i-th occupied and the k-th unoccupied orbitals. $\langle r^{-3}\rangle_{2p}$ represents the atomic 2p orbital dimension given by:[7]

$$\langle r^{-3}\rangle_{2p} = 34.33a_0^{-3}(1-0.323q_A')/24 \qquad (8)$$

where a_0 is the Bohr radius and where $-q_A'e$ is the net charge. The MINDO/2 method[8] was used as the molecular orbital method.

The bond lengths and bond angles used were as follows:[9] Bond length (the notation of Xn is used for an atom, X, with an elemental symbol being bonded to n neighbours. For example, the carbon atoms in propane and formaldehyde will be described as C4 and C3, respectively):

$$l_{\text{C4-H}} = 1.09,\quad l_{\text{C3-H}} = 1.08,\quad l_{\text{C4-C4}} = 1.54,$$
$$l_{\text{C4-C3}} = 1.52,\quad l_{\text{C3-O1}} = 1.22,\quad l_{\text{C4-O2}} = 1.43,$$
$$l_{\text{C3-O2}} = 1.36,\quad l_{\text{O2-H}} = 0.96\ (\text{Å})$$

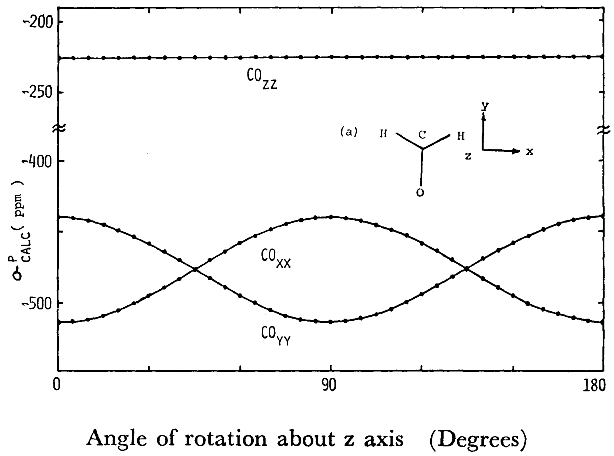
Bond angle:

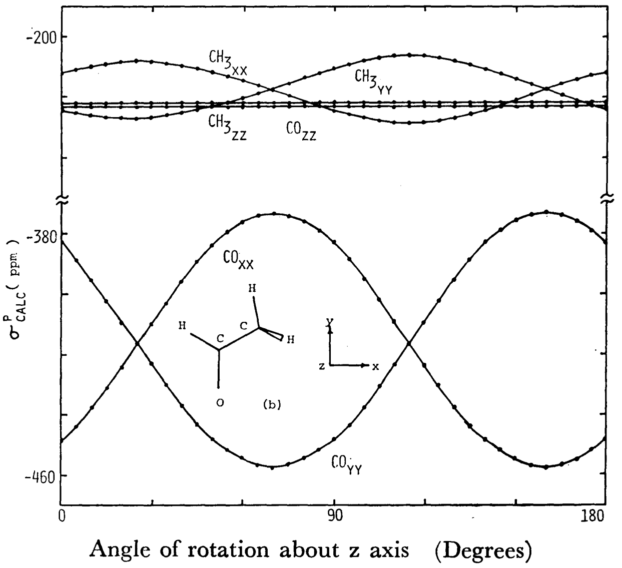
$$\angle\text{C-C-C} = \angle\text{C-C-H} = \angle\text{H-C-H} = \angle\text{H-O-C}$$
$$= \angle\text{O-C-H} = 109°28'$$
$$\angle\text{C-C=O} = \angle\text{H-C=O} = \angle\text{O-C=O} = 120°$$

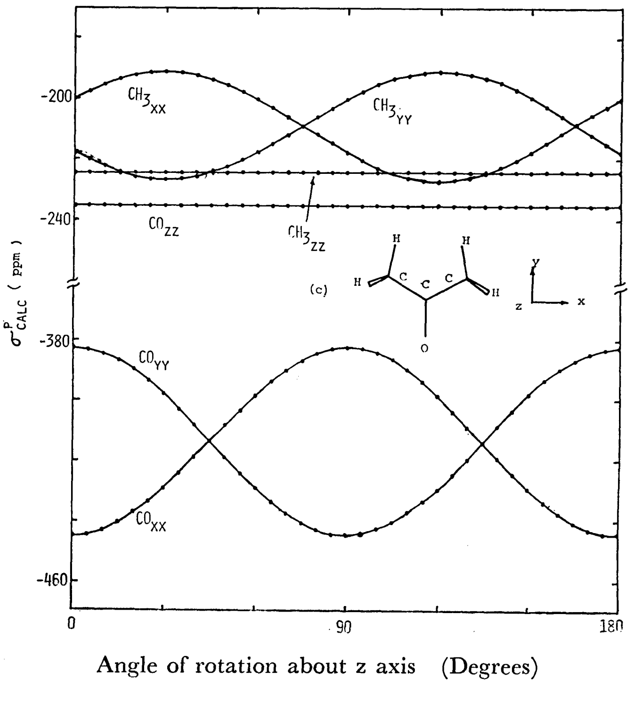
All the calculations were carried out by means of the HITAC-8800 computer of the Computer Center of the University of Tokyo.

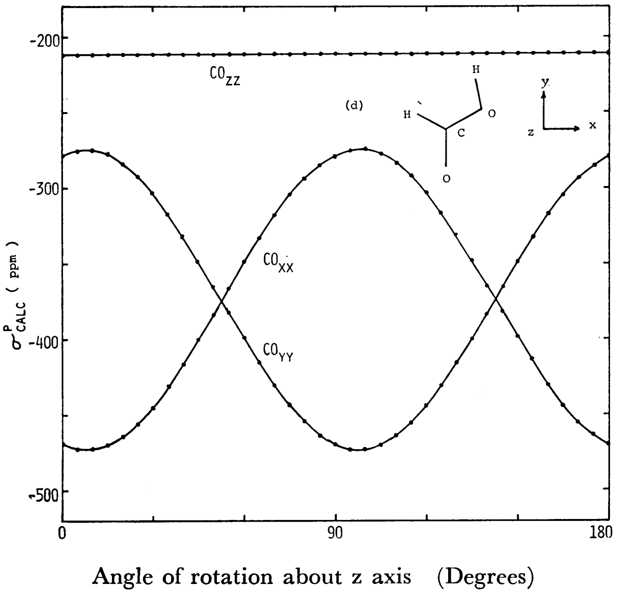
Results and Discussion

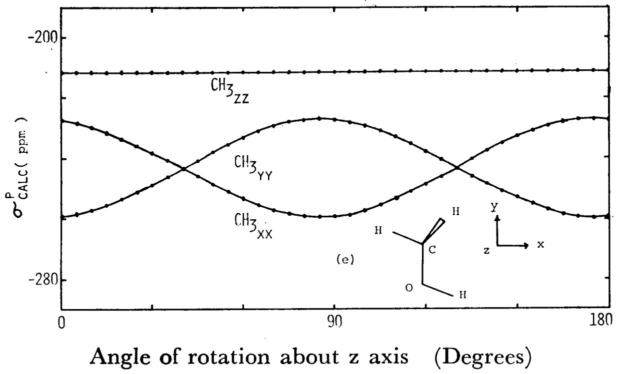
The calculated dependences of the σ'^{p}_{xx}, σ'^{p}_{yy}, and σ'^{p}_{zz} of the molecules concerned here upon the rotation of the coordinate system chosen are shown in Fig. 1, where the coordinate system of each carbon rotates

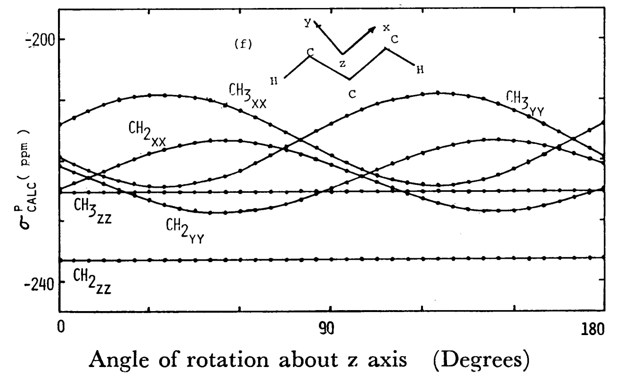












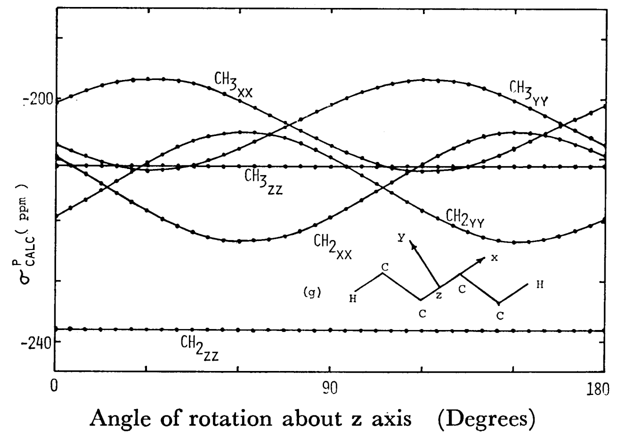


Fig. 1. Dependence of the calculated ^{13}C shielding tensor components σ^{P}_{calc} upon the rotation of the coordinate system for (a) formaldehyde, (b) acetaldehyde, (c) acetone, (d) formic acid, (e) methanol, (f) propane, (g) *n*-butane. For example, CH_{3xx} denotes the xx component of the shielding tensor for the methyl carbon.

counterclockwise from the position shown in the figure; the interval of the plots of the calculated value is 5 degrees, and the conformations of *n*-paraffins are taken as of the *trans* zig-zag form.

Let us first discuss the position of the principal axes by dividing the compounds concerned into two groups, carbonyl compounds and methanol, and *n*-paraffins. In the former group, if the carbonyl carbon is involved, we can expect that one of the principal axes in formaldehyde and acetone is along the C=O bond axis, as is predicted by the molecular symmetry, but the axes for acetaldehyde and formic acid are not always along the C=O bond axis (*cf.* Fig. 1). As for acetaldehyde and formic acid, the corresponding axes deviate by 20 degrees clockwise and by 8 degrees counterclockwise from the C=O bond axis, as is shown in the figure. Therefore, the axis of the former is oriented approximately along the direction bisecting the O–C–C angle, and the deviation of the latter from the C=O bond axis is very slight, contrary to expectations. These results show that the influence of the OH group neighbouring the carbonyl carbon on the position of the principal axes concerned is smaller than that of the CH_3 group. As for the methyl groups of acetaldehyde, acetone, and methanol, it is found that the principal axis corresponding to the C_{3v} axis of the CH_3 group is oriented at the positions of 25 degrees counterclockwise, 30 degrees counterclockwise, and 6 degrees clockwise respectively from the fixed coordinate system defined in the figure; therefore, these corresponding principal axes are found to deviate by 5 degrees clockwise, and about 0 degree and 6 degrees clockwise respectively from the C_{3v} axis of the CH_3 group. In these compounds, one of the principal axes is found to be oriented approximately along the C_{3v} axis, although this axis, speaking strictly, deviates slightly from the C_{3v} axis.

Next, let us discuss the *n*-paraffins. As for the methyl carbons of propane and *n*-butane, it is found that their principal axes corresponding to the above-mentioned axis deviate by 35 and 30 degrees counterclockwise respectively from the fixed coordinate system; therefore, these principal axes are found to deviate by 16 and 10.5 degrees respectively from the C_{3v} axis of the CH_3 group. The deviation of the former is slightly larger than that of the latter. This may be due to the difference between the CH_3 and CH_2 groups in its next nearest-neighbour group. However, it may still be said that these axes are oriented approximately along the C_{3v} axis. As for the CH_3 groups of these molecules, one of the principal axes is found to deviate by 54.7 and 62 degrees counterclockwise respectively from the fixed coordinate system; therefore, in propane this axis bisects the angle formed by the directions of the CH_3–CH_2 and CH_2–CH_3 bonds, and in *n*-butane it deviates slightly by 7.3 degrees counterclockwise from the corresponding axis, probably because of the symmetry.

Next, let us discuss the principal values and the anisotropies of the shielding constants of the compounds concerned. Here, for convenience, we will define the principal values in terms of σ_{11}, σ_{22}, and σ_{33} (the magnitude of shielding is $\sigma_{11}\lesssim\sigma_{22}\lesssim\sigma_{33}$) instead of σ^{p}_{xx}, σ^{p}_{yy}, and

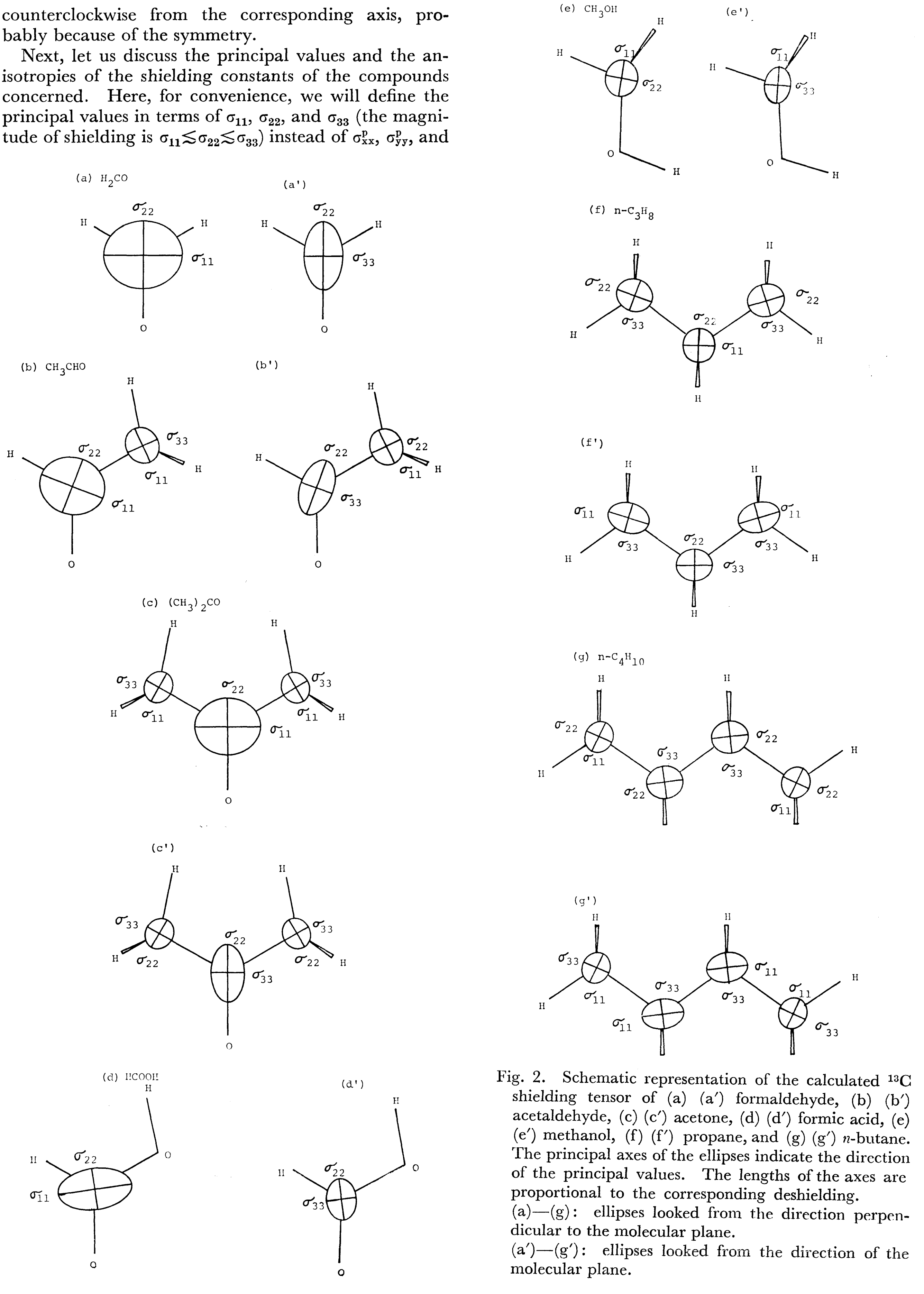


Fig. 2. Schematic representation of the calculated ^{13}C shielding tensor of (a) (a′) formaldehyde, (b) (b′) acetaldehyde, (c) (c′) acetone, (d) (d′) formic acid, (e) (e′) methanol, (f) (f′) propane, and (g) (g′) *n*-butane. The principal axes of the ellipses indicate the direction of the principal values. The lengths of the axes are proportional to the corresponding deshielding.
(a)—(g): ellipses looked from the direction perpendicular to the molecular plane.
(a′)—(g′): ellipses looked from the direction of the molecular plane.

TABLE 1. THE CALCULATED PRINCIPAL VALUES AND ANISOTROPIES OF ^{13}C SHIELDING TENSORS IN SOME ORGANIC COMPOUNDS

(For the comparison, the experimental data in the literature are indicated.)

Compounds		calculated (ppm)				experimental$^{b)}$ (ppm)			
		σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma^{a)}$	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$
$\begin{smallmatrix}H\diagdown\\ C{=}O\\ H\diagup\end{smallmatrix}$		−514	−439	−226	250.5	—	—	—	—
$\begin{smallmatrix}CH_3\diagdown\\ C{=}O\\ H\diagup\end{smallmatrix}$	CH_3	−227	−223	−208	17	74±6	86±6	126±7	46±7
	CO	−458	−374	−222	194	−147±7	−105±6	42±6	168±7
$\begin{smallmatrix}CH_3\diagdown\\ C{=}O\\ CH_3\diagup\end{smallmatrix}$	CH_3	−227	−225	−191	35	81±6	81±6	131±6	50±6
	CO	−445	−383	−235	179	−150±6	−136±6	50±7	193±7
$\begin{smallmatrix}H\diagdown\\ C{=}O\\ HO\diagup\end{smallmatrix}$		−474	−275	−212	162.5	—	—	—	—
CH_3OH		−260	−227	−212	31.5	55±6	55±6	118±6	63±6
$CH_3CH_2CH_3$	CH_3	−224	−220	−209	13	—	—	—	—
	CH_2	−237	−229	−217	16	—	—	—	—
$CH_3CH_2CH_2CH_3$	CH_3	−212	−211	−197	14.5	—	—	—	—
	CH_2	−238	−224	−206	25	—	—	—	—

a) $\Delta\sigma=\sigma_{33}-(\sigma_{11}+\sigma_{22})/2$ b) Shifts are in ppm relative to benzene liquid.

σ^{p}_{zz}, because the physical meaning for the xx, yy, and zz suffixes sometimes becomes obscure in this case. The calculated results of the principal values and the anisotropies for the compounds concerned are tabulated in Table 1, together with the experimental data in the literature. For further clarification, the principal axes and values are shown by a schematic representation in Fig. 2. In the carbonyl carbons it is found that the principal value of the shielding tensor perpendicular to the molecular plane is the largest one, that the order of the magnitude of their anisotropies ($\Delta\sigma=\sigma_{33}-(\sigma_{11}+\sigma_{22})/2$) is $\begin{smallmatrix}H\\H\end{smallmatrix}\!>C{=}O>\begin{smallmatrix}CH_3\\H\end{smallmatrix}\!>C{=}O>\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!>C{=}O>\begin{smallmatrix}H\\HO\end{smallmatrix}\!>C{=}O$, and that the magnitude of $\Delta\sigma$ is sensitive to the substituents. As for the methyl carbons in all the compounds concerned the axis of the most shielding component is found to be oriented approximately along the C_{3v} axis except for CH_3OH (*cf.* Fig. 2).

Next, we will discuss the individual compounds separately. As for the anisotropy of formaldehyde, Appleman *et al.*[1)] and Tokuhiro *et al.*[10)] have reported values of 250.8 and 294.9 ppm respectively, calculated using the *ab initio* method. Our results agree well with the former. For acetaldehyde, the value of the carbonyl carbon in this work increases slightly compared with the previous case[2b)] ($\Delta\sigma=192.8$ ppm); one of the principal axes is assumed to lie on the C=O bond and is very much smaller than the value of 280 ppm calculated by Appleman *et al.*[1)] On the other hand, for the methyl carbon our value is larger than their value of 2.9 ppm. The experimental values of Pines *et al.*[3)] are found to agree with our results. As for acetone, the value of the methyl carbon in this work increases compared to the previous case;[2a)] one of the principal axes is assumed to lie on the C=O bond.[11)] The value in this work is found to be consistent with the experimental value.[3)] As for formic acid, the value in this work is smaller than that of 198.4 ppm calculated by Appleman *et al.*[1)] In general, their calculated results are larger than our results for carbonyl carbons. As for methanol, the calculated value is somewhat smaller than the experimental data. One of the reasons for this discrepancy may be that it partly arises from the neglect of the hydrogen bonding among the molecules. Further, it should be noted that the most shielded component is not along the C_{3v} axis, but along the direction perpendicular to the fixed molecular plane, contrary to the results for the other methyl groups. As for *n*-paraffins, the value of $\Delta\sigma$ for the methylene carbon in propane is found to be larger than that in *n*-butane. This may be because in the former the neighbouring groups are the methyl groups, while in the latter they are the methyl and methylene groups. The value of $\Delta\sigma$ is found to be very sensitive to the environment of the specified carbon. As for the methyl carbons, it is found that there is a slight difference between the values of $\Delta\sigma$ in the two paraffins; this must also be due to the above-mentioned reason. The observation of these molecules has not yet been done; after it has, we hope to measure $\Delta\sigma$ to get important information for the study of the molecular motion in a solid.

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11) In this calculation l_{C-H} is taken as 1.09 Å. Therefore the shielding components of the carbonyl carbon differ slightly.