Theoretical Calculation of ^{13}C Chemical Shielding Anisotropy in Some Organic Compounds. II.

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(Received September 18, 1974)

The ^{13}C chemical shielding anisotropies of acetic acid and its related compounds were calculated theoretically by the LCGI-MO theory, using the MINDO/2 method; the results were found to agree with the experimental data measured by Pines *et al.* As for acetic acid, a dimer structure was suggested to be preferable to the monomer structure on the basis of the calculated and experimental results.

In our previous paper[1] we calculated theoretically the ^{13}C chemical shielding anisotropies of benzene and its derivatives, and of acetone with a linear combination of the gauge invariant atomic orbitals-molecular orbital (LCGI-MO) theory of Pople,[2] using the MINDO/2 method;[3] we thus obtained good agreement with the experimental data measured by Pines *et al.*[4] In the same way, we will now calculate the ^{13}C chemical shielding anisotropies of acetic acid, taking into account the monomer and dimer structures, and compare our results with Pines' results in order to obtain information on its molecular structure. Further, we will discuss the ^{13}C shielding parameters of its related compounds containing the carbonyl group, acetic anhydride, methyl formate, and acetaldehyde.

Calculation

The ^{13}C chemical shielding is dominated by the paramagnetic terms, σ_{xx}, σ_{yy}, σ_{zz}, which are estimated by the use of the LCGI-MO theory using 2p orbitals, as follows (*e.g.*, σ^p_{xx}):

TABLE 1. THE CALCULATED AND EXPERIMENTAL[4] ^{13}C CHEMICAL SHIELDING PARAMETERS IN ACETIC ACID, ACETIC ANHYDRIDE, METHYL FORMATE, AND ACETALDEHYDE

Compound		Calculated (ppm)				Experimental (ppm)				
		σ^p_{xx}	σ^p_{yy}	σ^p_{zz}	$\Delta\sigma_{calc}$ [a]		σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma_{obs}$ [a]
Acetic acid										
Case I	CO	−445.8	−278.5	−223.2	138.9					
Case II	CO	−439.9	−262.8	−238.2	113.2	CO	−140±6	−55±6	19±6	116.5±6
Case III	CO	−413.8	−285.2	−229.4	120.1					
Acetic anhydride	CO	−367.9	−196.2	−215.9	95.7		−152±6	13±6	13±6	82.5±6
Methyl formate	CO	−443.0	−276.5	−228.9	130.8		−124±6	−7±7	22±7	87.5±7
Acetaldehyde	CO	−447.1	−381.8	−221.6	192.8		−147±7	−105±6	42±6	168±6

a) $\Delta\sigma_{calc}$ and $\Delta\sigma_{obs}$ are the calculated and observed shielding anisotropies, respectively.

$$\sigma^{p}_{xx} = -(2e^2\hbar^2/m^2c^2)\langle r^{-3}\rangle_{2p}\sum_{i}^{occ}\sum_{k(\neq i)}^{unocc}\Delta E^{-1}_{k-i} \times (C_{i_{y_A}}C_{k_{z_A}} - C_{i_{z_A}}C_{k_{y_A}})\sum_{B}(C_{i_{y_B}}C_{k_{z_B}} - C_{i_{z_B}}C_{k_{y_B}}) \quad (1)$$

where $C_{i_{x_A}}$ 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 $\sum_{i}^{occ}$ and $\sum_{k(\neq i)}^{unocc}$ are the summations over occupied and unoccupied orbitals respectively, where $\sum_{B}$ runs over all atomic orbitals 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:[5]

$$\langle r^{-3}\rangle_{2p} = 34.33a_0^{-3}(1.0-0.323q_A')/24 \quad (2)$$

where a_0 is the Bohr radius and where $-q_Ae$ is the net charge. The MINDO/2 method was used as the molecular orbital method, because the excitation energy for the molecule with π-electrons is said to be interpreted well by this method without taking the configuration interaction into account.

The bond lengths and bond angles used were set at standard values.[6] In the dimer of acetic acid, the distance between the oxygen atoms in the hydrogen bond (C–O–H···O=C) used was 2.76 Å.[7]

The calculations were carried out by means of the HITAC-8800/8700 computer of the Computer Center of the University of Tokyo.

Results and Discussion

First, let us examine the acetic acid molecule. Generally, carboxylic acids are well-known to form hydrogen bonding in the liquid and solid states.[8] Thus, as the molecular structure of acetic acid, we consider the cyclic dimer structure, together with the two monomer structures, as is shown in Table 1. In calculating each component of the chemical shielding, it is necessary to know the direction of the principal axis of the molecule. We assume that the principal axis is along the C=O bond. This seems appropriate approximately for the carbonyl carbon. The principal values, σ^{p}_{xx}, σ^{p}_{yy}, and σ^{p}_{zz}, calculated for the carbonyl carbons are shown in Table 1, together with the experimental values, σ_{11}, σ_{22}, and σ_{33}, measured by Pines *et al.*; the latter are the components of the shielding tensor. The experimental chemical shielding anisotropy is defined as $\Delta\sigma_{obs}=\sigma_{33}-(\sigma_{11}+\sigma_{22})/2$, in which σ_{33} is the most shielded component ($\sigma_{11}<\sigma_{22}<\sigma_{33}$); on the other hand, the calculated anisotropy, $\Delta\sigma_{calc}$, is estimated by taking the most shielded component as the component corresponding to σ_{33} in the experimental results (here, in acetic acid σ^{p}_{yy} is taken as its component). As for the carbonyl carbon, the $\Delta\sigma_{cal}$ values of Cases II and III are found to agree with the experimental ones better than that of Case I. For a more detailed comparison between these, the stick spectra of each shielding tensor are shown in Fig. 1. From this figure the results of Case III are found to agree well with the observed values and also with the results obtained by another method.[8]

Next, let us discuss the $\Delta\sigma$ value of the carbonyl carbon in acetic anhydride. The calculated $\Delta\sigma_{calc}$ value is 95.7 ppm. If the values of σ^{p}_{yy} and σ^{p}_{zz} are averaged with each other by taking into account the observed fact that $\sigma_{22}=\sigma_{33}$, the calculated $\Delta\sigma_{calc}$ value is obtained as 80.9 ppm. This agrees well with the observed value, 82.5 ppm. The stick spectra are shown in Fig. 1. In acetic anhydride, the most shielded component is σ^{p}_{yy}, which is slightly more shielded than σ^{p}_{zz}. This is different from the case of acetic acid, in

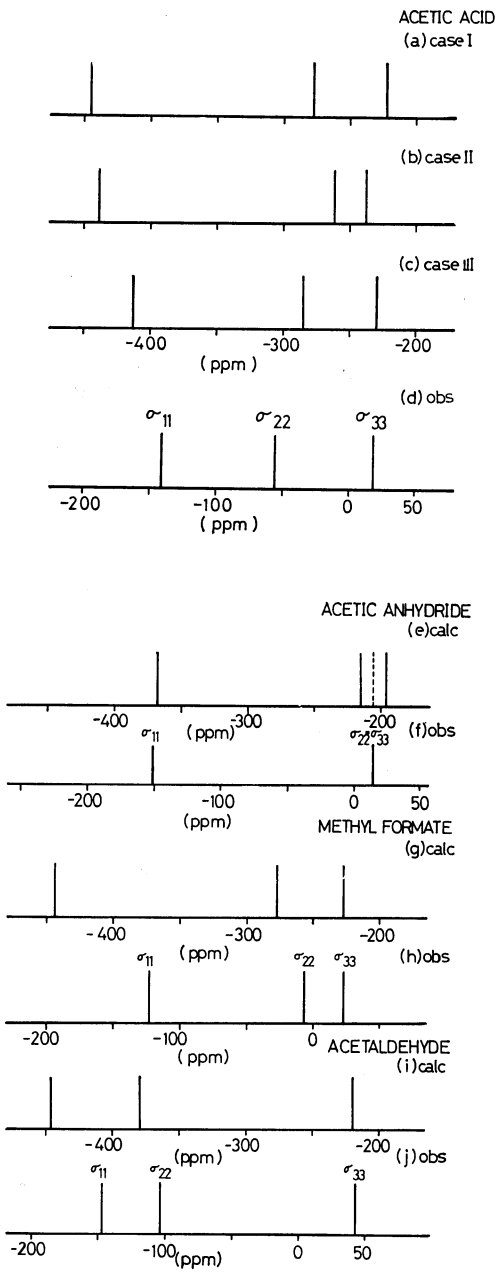

Fig. 1. The calculated and observed[4] stick spectra of acetic acid, acetic anhydride, methyl formate, and acetaldehyde.
acetic acid: calculated, (a)—(c), observed, (d), acetic anhydride: calc, (e). The dash-line is one averaged over σ^{p}_{yy} and σ^{p}_{zz}. observed, (f).
methyl formate: calculated, (g), observed, (h).
acetaldehyde: calculated, (i), observed, (j).

which the most shielded component is σ^{p}_{zz}.

The calculated $\Delta\sigma_{calc}$ values of the carbonyl carbons of methyl formate and acetaldehyde molecules are also shown in Table 1. The calculated results are somewhat larger than the observed ones, but the tendency of the shielding tensors of these carbons is plausible, as is shown in Fig. 1.

If the calculated $\Delta\sigma_{calc}$ values of the carbonyl carbons in all of the molecules are seen as a whole, the order of their magnitutes is found to be; acetaldehyde> methyl formate>acetic acid>acetic anhydride. This order agrees with the observed one. Moreover, we notice the tendency of each shielding tensor through all the compounds. The σ^{p}_{yy} value is found to be especially sensitive to the substituent in the calculated results. This sensitivity is also displayed by the observed results.

Only the most shielded component in acetic anhydride is σ^{p}_{yy}; the other compounds are σ^{p}_{zz}. This may be because the π-electrons of the carbonyl group in acetic anhydride are more delocalized than in the others; therefore, the shielding of the yy component increases in comparison with the other compounds. In acetic anhydride the magnitudes of σ^{p}_{yy} and σ^{p}_{zz} are near to each other, but in other compounds they are not. This would also be qualitatively interpreted by the above reason.

Our theoretical approach to the ^{13}C chemical shielding anisotropy will contribute to obtaining valuable information on the molecular structure in the solid state and to determining the principal axis of the molecule concerned.

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