Medium Effects on the Molecular Electronic Structure. III. Quantum-Chemical Analysis of Solvent-Induced ^{13}C NMR Chemical Shift Changes of Some Polyene Compounds

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A reaction-field theory (Hoshi et al., *J, Chem. Phys.*, **87**, 1107 (1987)) is applied to the analysis of solvent-induced ^{13}C chemical shift changes of some polyene compounds. The solvent dependence of the ^{13}C chemical shifts is calculated by means of the INDO-finite perturbation method combined with this theory. It is shown that the calculations well reproduce characteristic ^{13}C shift changes observed in aprotic solvents. This indicates the validity of the theory. In addition, the origin of the solvent-induced ^{13}C shifts is discussed on the basis of the electronic distribution obtained.

Theoretical estimation of environmental effects on properties of molecules is essential in understanding a variety of phenomena occurring in condensed phases. Recently, we have developed a self-consistent reaction field theory capable of estimating medium effects in heterogeneous systems,[1] and incorporated it into semi-empirical molecular orbital methods with some examples of numerical calculations.[2] And it has been shown that the calculated results for free energy and dipole moment changes induced by medium effects are in fairly good agreement with ab initio data based on a similar solvation theory.[3] Further extensive studies will be required to extend the applicability and to clarify the limitations of the method.

Second-order properties such as nuclear spin–spin coupling and chemical shifts in NMR are sensitive probes of the electronic structure of molecules in that variations in these quantities often imply subtle electronic changes.[4,5] In particular, ^{13}C NMR chemical shift is a parameter sensitively reflecting the electronic structure related to a given carbon atom.[6–8] Studies on solvent-induced ^{13}C shifts, therefore, provide useful information about the nature of solute–solvent interactions.

The pioneering work by Ando et al.[9] and their subsequent works[4,5] have demonstrated that solvent-induced ^{13}C shift changes are theoretically reproducible by molecular orbital calculations combined with Klopman's solvation model,[10] which is a sort of reaction field model treating solvent as a dielectric. These studies have indicated that the major part of the solvent-induced ^{13}C shifts is originated in dielectric effects from surrounding solvent molecules. Thus, the reliability of the theory considered here can be examined through the analysis of solvent-induced ^{13}C shifts.

In this paper, we describe the results applied for some polyenals. The reason why polyenals are appropriate for the present purpose is as follows: they are expected to be the most sensitive probes of dielectric effects from the medium, because they are highly polar and polarizable. This is supported by our previous study which is concerned with solvent effects on the ^{13}C sheilding of retinal (vitamine A aldehyde).[11] The ^{13}C shielding constants are estimated by the INDO-finite perturbation method[12,13] combined with our reaction-field theory. We show that the calcultation well reproduces the characteristic trends of solvent-induced ^{13}C shift changes observed in aprotic solvents.

Experimental

The polyenals used here are acrolein, crotonaldehyde, 2,4-hexadienal and β-ionone. For comparison, acetaldehyde, and acetone are used as typical carbonyl compounds. These compounds except 2,4-hexadienal were purchased from Toko Kasei Co., Tokyo and 2,4-hexadienal purchased from Aldrich chemical Co., Inc, Wisconsin. The compounds except β-ionone were dried over anhydrous calcium sulfate and distilled before use. Solvents were selected with special

Table 1. List of Solvents and Their Dielectric Constants, ε[a] at 304 K

No.	Solvent	ε	$(\varepsilon-1)/(\varepsilon+1)$
1	Pentane	1.75	0.27
2	Hexane	1.83	0.29
3	Triethylamine	2.36	0.40
4	Dibutyl ether	2.95	0.49
5	Dipropyl ether	3.33	0.54
6	Diisopropyl ether	3.80	0.58
7	Diethyl ether	4.16	0.61
8	Butyl acetate	4.81	0.66
9	Ethyl acetate	5.90	0.71
10	Tetrahydrofuran	7.43	0.76
11	Cyclohexanone	18.5	0.90
12	1-Nitropropane	23.2	0.92
13	Acetonitrile	37.5	0.95
14	DMSO-d_6	46.9	0.96
15	Formamide	107.3	0.98
16	Chloroform	4.61	0.64
17	Water	76.5	0.97

a) Corrected for temperature using $\varepsilon \cdot T \propto$ const.. Then the values of dielectric constants were taken from J. A. Riddick and W. B. Bunger, "Techniques of Chemistry," 3rd ed, Wiley-Interscience, New York (1970).

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care: namely, i) to cover a wider range of dielectric constants, and ii) to exclude solvents forming molecular complexes with the solutes, such as hydrogen bonding and π-charge transfer complexes. Aromatic and halogenated solvents are thus excluded, while a few hydrogen bonding solvents are included for comparison. Solvents and their dielectric constants are listed in Table 1. All the solvents except deuterated compounds were used after purification.

^{13}C-NMR spectra were recorded on a JEOL-PS-100 spectrometer, equipped with a PFT-100 Fourier transform system at 25.14 MHz, EC-100 spectrum computer, deuterium field-frequency lock, and noise-modulated proton decoupling system. ^{13}C NMR spectra of acrolein, crotonaldehyde, acetone and acetaldehyde were observed in all the solvents listed in Table 1, while those of 2,4-hexadienal and β-ionone were done in some of the solvents (solvent No. 1, 3, 5, 10, and 14). Chemical shifts were measured in ppm as downfield shifts from external tetramethylsilane (TMS), and corrected for bulk magnetic susceptibility. All experiments were carried out at 31±1 °C and at concentration of 5% (v/v). ^{13}C NMR signals of the compounds were assigned by reference to the literature.[14]

Theoretical

The solute molecule is embedded into the medium of dielectric constant ε (Fig. 1). The interaction between the solute and the medium is calculated according to the formalism given in Refs. 1 and 2. The Hamiltonian $\mathscr{H}$ of the solute is modified by the coulombic interaction V with a reaction field generated by the polarization of the surrounding dielectric. Then, the Helmholtz free energy H of the solute-dielectric system is given by

$$H = <\psi|\mathscr{H}|\psi> - \frac{1}{2}<\psi|V|\psi> \quad (1)$$

where the second term of the right-hand side indicates the energy required to plarize the medium. The reaction field was determined by solving the Laplace equation numerically with the aid of the boundary element method. The boundary surface, formed between the dielectric and the cavity (Fig. 1), is then divided into a sufficient number of elements. The method of surface division was described in Ref. 2. The perturbed wave function was obtained by solving the following Fock equations:

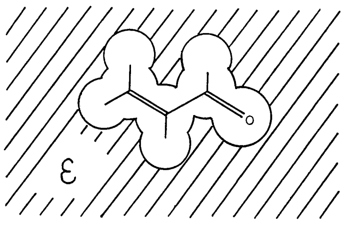

Fig. 1. Schematic representation of a solute-solvent system. Acrolein (solute) is accomodated into the cloud-like shaped cavity generated in the infinitely expanded dielectric (shaded region). In actual calculation, the shape of the cavity was taken to be identical with that of the CPK molecular model.

$$F_{\mu\nu} = F^{\circ}_{\mu\nu} + F'_{\mu\nu} \quad (2)$$

$$F'_{\mu\nu} = \{J_1\}_{\mu\nu} + \{TP\}_{\mu\nu} \quad (3)$$

where $F^{\circ}_{\mu\nu}$ and $F'_{\mu\nu}$ is the matrix elements for the molecule in vacuo and for the perturbation term, respectively, and P is the density matrix. The operators J_1 and T mediate the interaction between the solute and its surrounding dielectric.[1] The electrostatic potential ϕ, generated from the charge distribution of the solute, must be calculated in order to obtain T and J_1. The following approximation was used for this purpose. A point dipole was placed at each atomic center of first row atoms in order to take into account the contribution of the differential overlap between 2s and 2p orbitals. Then, the total electrostatic potential ϕ was evaluated as the sum of the contributions ϕ_{charge} from point charges placed at each atomic center and those ϕ_{dipole} from the point dipoles. The value of each point charge is equal to that of the net charge on the corresponding atom. The electrostatic potential ϕ_{dipole} from the kth component of the dipole is given at the point s as follows:

$$\phi_{\text{dipole}} = -\frac{5}{2(3)^{\frac{1}{2}}\zeta}(P_{\text{A2s,2p}_k} + P_{\text{A2p}_k\text{,2s}}) \times \frac{(\boldsymbol{s} - \boldsymbol{N}_{\text{A}})_k}{|\boldsymbol{s} - \boldsymbol{N}_{\text{A}}|} \times f \quad (4)$$

where $\boldsymbol{N}_{\text{A}}$ and ζ are the position vector of atom A and the orbital exponent, respectively. $P_{\text{A2s,2p}_k}$ ($=P_{\text{A2p}_k\text{,2s}}$) is the density matrix element between 2s and 2p$_k$(k=x, y, or z) orbitals centered on atom A. The adjustable parameter f in Eq. 4 was taken to be 0.5. These computational procedures correspond to 'Approximation IV' described in Ref. 2.

^{13}C shielding constants were estimated using the finite perturbation method with gauge invariant atomic orbitals(GIAO)[6] and the London approximation[15] at the INDO level of approximation. The average shielding tensor, σ^{M}, of atom M is expressed as follows:

$$\sigma^{\text{M}} = \sigma^{\text{d}}(\text{M}) + \sigma^{\text{d}}(\text{KK}) + \sigma^{\text{p}}(\text{M}) + \sigma^{\text{p}}(\text{KK}) + \sigma^{\text{d}}(\text{MK}) + \sigma^{\text{d}}_{0}(\text{MK}) + \sigma^{\text{p}}(\text{MK}) \quad (5)$$

where the superscripts p and d indicate paramagnetic and diamagnetic shieldings, respectively, and the terms other than $\sigma^{\text{d}}(\text{M})$ and $\sigma^{\text{p}}(\text{M})$ indicate contributions of nonlocal atomic currents related to atom K. The term $\sigma(\text{MK})$ arises from the use of GIAO. The detailed expressions of Eq. 1 are given in Ref. 12. In this study, three center terms such as $\sigma^{\text{p}}(\text{MKK}')$ are omitted due to relatively minor contribution to the ^{13}C shielding constants.[12] The derivatives of density matrices were obtained by solving the Roothaan equation perturbed by a small magnetic field (1.0×10^{-3} a.u.).

The calculations were carried out for all the molecules except β-ionone, which was beyond the present computational facilities due to the larger number of atoms.

The QCPE 441 program[16] was used after some modifications including the incorporation of the solvation theory.

Results and Discussion

In the dielectric medium as shown in Fig 1, the intensity of a reaction field, resulting from polarization of the dielectric, should be approximately proportional to the factor of $(\varepsilon-1)/(\varepsilon+1)$.[1] The observed ^{13}C chemical shifts, δ, are thus plotted against $(\varepsilon-1)/(\varepsilon+1)$ as illustrated in Figs. 2 and 3 for crotonaldehyde and 2,4-hexadienal, respectively. The chemical shift of each carbon nonlinearly depends on the value of $(\varepsilon-1)/(\varepsilon+1)$. This trend most clearly appears in the case of the odd-numbered carbons: namely, the steep downfield shifts are induced in the range of higher dielectric constants. The points deviating from the experimental curves correspond to the data for the hydrogen bonding solvents. Similar trends were also observed for the other solutes studied here.

In Table 2 are summarized the chemical shift differences, $\Delta\delta$, evaluated by subtracting δ in pentane from that in DMSO-d_6. The following characteristic trends are deducible: i) with increasing dielectric constant the resonances of the odd-numbered carbons shift towards downfield, while those of the even-numbered carbons show very small down- or upfiled-shifts, ii) the $\Delta\delta$ values of the π-conjugated carbonyl carbons are smaller than those of nonconjugated ones(acetone and acetaldehyde), iii) in the cases of acrolein and crotonaldehyde the $\Delta\delta$ values of the C3 carbons are about 1 ppm larger than that of the C1 carbonyl carbons, and iv) the resonances of all the methyl carbons tend to downfield-shift with increasing dielectric constant. The slope of the experimental line

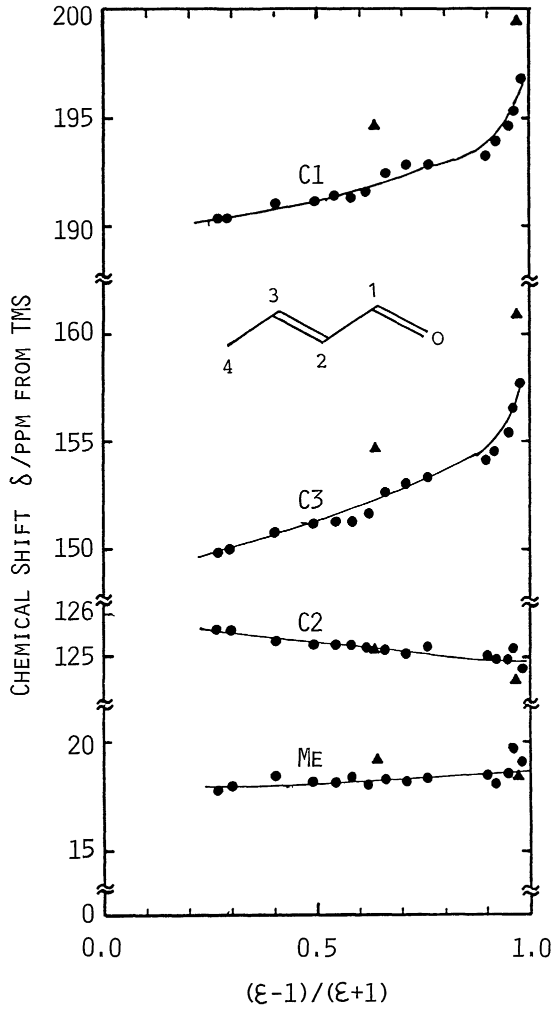

Fig. 2. Dielectric constant dependence of observed ^{13}C chemical shifts for crotonaldehyde. ▲: Data for hydrogen bonding solvents.

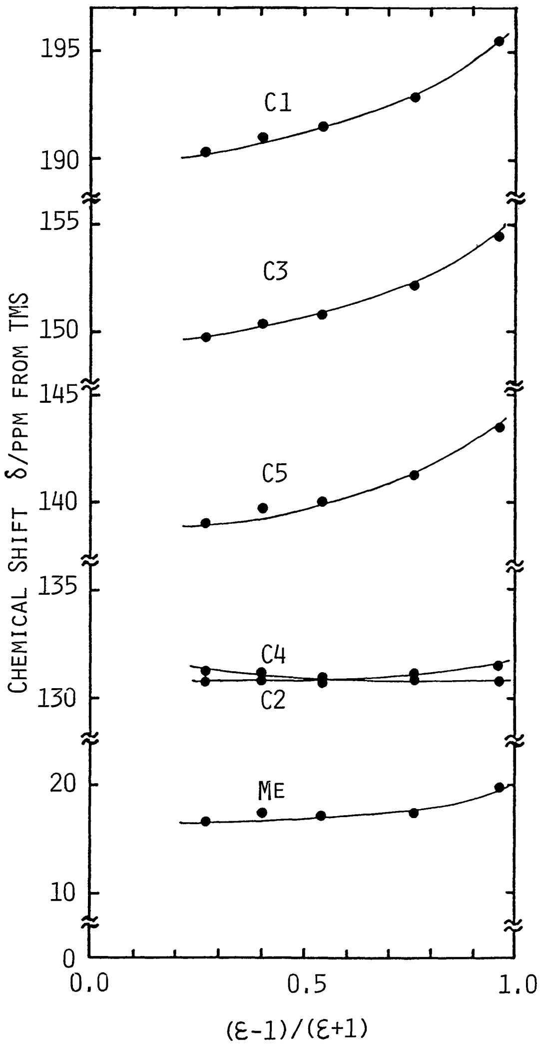

Fig. 3. Dielectric constant dependence of observed ^{13}C chemical shifts for 2,4-hexadienal.

Table 2. Observed ^{13}C Chemical Shifts, δ,[a] in Several Solvents and Chemical Shift Differences, $\Delta\delta$[b]

Compound	Carbon	Solvent No. 1	3	5	10	14	$\Delta\delta$
Acetaldehyde	C1	195.23	196.31	196.59	198.63	202.27	7.04
	Me[c]	30.34	30.68	30.48	30.69	31.85	1.51
Acetone	C1	200.94	201.65	202.17	204.08	207.61	6.75
	Me	29.73	30.20	30.42	30.10	31.97	2.24
Acrolein	C1	191.05	191.94	192.16	193.83	196.63	5.57
	C2	139.55	139.52	139.32	139.54	193.36	−0.19
	C3	134.14	135.52	135.74	137.23	140.88	6.73
Crotonaldehyde	C1	190.38	191.09	191.54	192.93	195.54	5.16
	C2	135.66	135.70	135.50	135.41	135.35	−0.31
	C3	149.80	150.80	151.34	153.30	156.52	6.73
	Me	17.80	18.43	18.16	18.38	19.72	1.91
2,4-Hexadienal	C1	190.39	191.09	191.44	192.86	195.48	5.09
	C2	130.81	130.85	130.77	130.98	130.86	0.06
	C3	149.74	150.39	150.72	152.15	154.40	4.67
	C4	131.23	131.15	130.95	131.10	131.41	0.18
	C5	139.06	139.91	140.15	141.24	143.55	4.37
	Me	18.32	18.73	18.53	18.74	19.96	1.63
β-Ionone[d]	C9	193.68	194.89	196.37	196.57	199.06	5.38
	C8	132.81	132.65	132.67	132.86	132.56	−0.25
	C7	141.00	141.50	141.95	142.14	143.12	2.12
	C6	136.69	136.53	136.61	136.81	136.75	0.06
	C5	133.30	134.10	133.76	135.11	136.87	3.57

a) ppm from external tetramethylsilane. Positive values indicate downfield shifts. b) Obtained by subtracting chemical shifts in solvent 1 (pentane) from those in solvent 14 (DMSO-d_6). c) Methyl carbon. d) The numbering of carbon atoms is given in the following fashion:

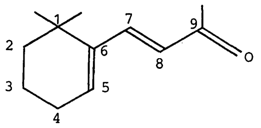

Table 3. Dielectric Constant Dependence of Calculated Shelding Constants, σ,[a] and Shielding Differences, $\Delta\sigma$[b]

Compound	Carbon	ε[c] 1	2	80	$\Delta\sigma$
Formaldehyde	C1	−144.34	−145.91	−147.73	−3.39
Acetaldehyde	C1	−146.71	−148.25	−149.92	−3.21
	Me[d]	20.48	20.26	19.84	−0.64
Acetone	C1	−148.14	−149.45	−150.97	−2.83
	Me	19.64	19.45	19.21	−0.43
Acrolein	C1	−144.50	−145.79	−146.94	−2.44
	C2	−90.43	−90.30	−90.18	0.25
	C3	−92.97	−94.11	−95.41	−2.44
Crotonaldehyde	C1	−144.61	−145.54	−147.00	−2.39
	C2	−90.38	−90.20	−89.78	0.60
	C3	−102.45	−103.68	−105.43	−2.98
	Me	20.92	21.13	20.06	−0.86
2,4-Hexadienal	C1	−145.85	−147.15	−148.35	−2.50
	C2	−84.85	−84.54	−84.34	0.51
	C3	−97.56	−98.66	−100.18	−2.62
	C4	−97.41	−96.39	−96.73	0.68
	C5	−103.21	−104.45	−104.66	−1.45
	Me	19.86	19.62	17.39	−2.47

a) Given in ppm. Minus sign indicates deshielding. b) Obtained by subtracting shielding constants in the medium of $\varepsilon=1$ from those in the medium of $\varepsilon=80$. c) Dielectric constant. d) Methyl carbon.

is a measure of the susceptibility of each carbon shielding against the reaction field. The trends i)—iv) can be used as criteria to examine the reproducibility of calculated results.

In Table 3 are summarized the calculated ^{13}C shielding constants, σ, and the shielding constant differences. As shown in Fig. 4, there is a good correlation between the calculated ^{13}C shielding

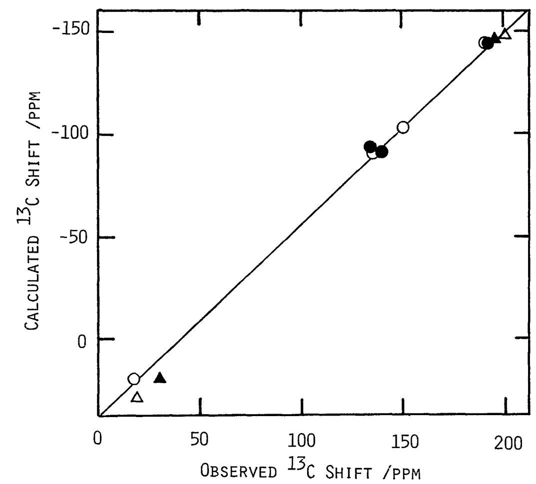

Fig. 4. Correlation between observed and calculated ^{13}C chemical shifts for acetaldehyde (▲), acetone (△), acrolein (●), and crotonaldehyde (○).

constants (ε=1) and the observed (in pentane) chemical shifts for acetaldehyde, acetone, acrolein, and crotonaledehyde, supporting the reliability of the finite perturbation method. However, for 2,4-hexadienal there were serious disagreements between the calculated and the observed data, namely, the relative order of C3 and C5 was not reproduced by the calculations. This order was not reversed by the medium effects considered here. A series of calculations were carried out for longer-chain polyenals in vacuo. Similarly, such calculations did not reproduce the relative order between the C3 and the terminal conjugated carbon. These results indicate the inability of the INDO-finite perturbation method itself for the longer polyenals (in vacuo). Thus we do not later discuss the results for 2,4-hexadienal.

In Fig. 5 is shown the dielectric constant dependence of the calculated ^{13}C shielding constants, σ^M, of crotonaldehyde. The shielding constant is almost proportional to $(\varepsilon-1)/(\varepsilon+1)$. The calculations (Table 3) underestimate the amounts of chemical shift changes compared with the observed data (Table 2). However, the four trends described above are well reproduced as described below.

The values of $\Delta\sigma$ indicate the downfield shift of the odd-numbered carbons, and the relatively small upfield shifts of the even-numbered carbons (C2 carbons), which is consistent with the trend i). By comparing the $\Delta\sigma$ of the carbonyl resonances, their relative sensitivity to dielectric effects can be estimated. Such a comparison produces the following sensitivity values; acetone 1.00, acetaldehyde 1.04, acrolein 0.83, crotonaldehyde 0.76. The corresponding calculated values are 1.13, 0.86, 0.84 for acetaldehyde, acrolein, and crotonaldehyde, respectively. Thus, the calculations well reproduce the π-conjugation effects (trend ii)). The trend iii) mentioned above means the higher sensitivity of the C3 resonance than the C1. The relative sensitivity of the C3 to C1 resonances is determined as follows: 1.21 (1.00) for acrolein and 1.30 (1.25) for crotonaldehyde, where the values in the parentheses show the calculated data. If the chemical shift difference, $\Delta\delta$, are evaluated by subtracting the shift in pentane from that in the higher dielectric solvents other than DMSO, we obtained 1.05 and 1.30 for the average C3/C1 sensitivity of acrolein and crotonaldehyde, respectively. These are in better agreement with the calculated data. Therefore, it can be concluded that the trend iii) is satisfactorily reproduced by the calculations.

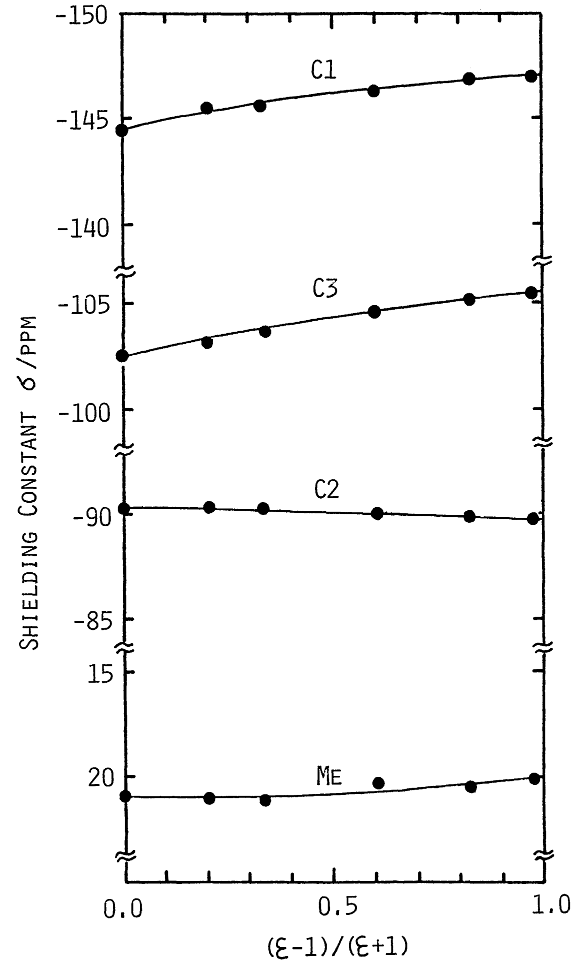

Fig. 5. Dielectric constant dependence of calculated ^{13}C shieldings for crotonaldehyde.

In some points the present results surpasses those of early theoretical studies[4,17] based on the 'solvaton' model. Jallali-Heravi and Webb[17] have obtained the following relative carbonyl sensitivity: acetone 1.00, acetaldehyde 0.70 and formaldehyde −0.14. Clearly, the value for acetaldehyde is too small. Although there is no observed data for formaldehyde, the upfield shift (seen from the minus sign) seems to be unacceptable. Furthermore, in that report, the methyl resonance of acetone shows the considerable amount of up-field shift (7 ppm), which is also inconsistent with the present observed data (trend iv)).

It is well-known that there is a linear relationship between the ^{13}C chemical shifts of π-conjugated carbons and their electron density.[7,18] On the basis of this empirical rule, the trend i) means that with polarization of the terminal carbonyl group positive charges are induced on the odd-numbered carbons, while the charge density on the even-numbered carbons is almost kept constant. This pattern of charge rearrangement is different from that expected from normal inductive effect,[19] which predicts an alternative distribution of positive and negative charges along the polyene chain. Furthermore, on the same assumption, the trend iii) insists that the amount of positive charge induced on the C3 carbon is greater than that on the C1 (carbonyl) carbon, which is clearly in conflict with our intuition. It is thus of interest to clarify the mechanism of the solvent-induced ^{13}C shifts.

Table 4. Dielectric Constant Dependence of Electron Density,a) ρ, on Oxygen and Carbon Atoms of Crotonaldehyde

Atom	ε b)			$\Delta\rho$ c)
	1.0	2.0	80.0	
O	−0.2950	−0.3226	−0.3606	−0.0656
C1	0.3159	0.3324	0.3557	0.0398
C2	−0.0921	−0.0963	−0.1021	−0.010
C3	0.0509	0.0603	0.0753	0.0244
Me d)	0.0040	0.0041	0.0050	0.0010

a) Net charge. b) Dielectric constant. c) Obtained by subtracting net charges at $\varepsilon=1$ from those at $\varepsilon=80$. Minus sign indicates an increase in electron density. d) Methyl carbon.

In Table 4 is shown the dielectric constant dependence of the electron density, ρ, on each atom of crotonaldehyde. With increasing dielectric constant the C=O bond is more polarized, consequently inducing the polarization of the C2=C3 double bond. However, the amount of induced charge on the C2 carbon is considerably smaller than those induced on the neighboring carbons (C1 and C3). This explains the slight change in the chemical shift of the C2 carbon (trend i)). However, the amounts of induced charges on the C3 carbon are smaller than those on the C1 carbonyl carbon. Thus the solvent-induced ^{13}C shifts of these carbons does not follow the empirical rule mentioned above.

In order to investigate the origin of the chemical shift changes in more detail, the total shieldig constant, σ^{M}, for each carbon is decomposed into its components according to Eq. 5. The results for crotonaldehyde are summarized in Table 5. These data indicate that relative order in the chemical shifts of the four carbons is chiefly determined by the monoatomic paramagnetic shieldings, $\sigma^{p}(M)$, which is in agreement with the results of earlier theoretical studies on the ^{13}C shielding.[6–8,12] However, the other components contribute significantly to determining the trend of the solvent-induced shifts. In the case of the C1 resonance, the contribution of $\sigma^{p}(M)$ is decreased considerably owing to the opposite effect of $\sigma^{p}(KK)$, while in the case of the C3 resonance the shielding is little affected by it. As a result of this, the C1 resonance

Table 5. Decompositiona) of Total Shielding Constant, σ^{M}, for Crotonaldehyde

Carbon	ε b)	Component						
		$\sigma^{d}(M)$	$\sigma^{d}(KK)$	$\sigma^{p}(M)$	$\sigma^{p}(KK)$	$\sigma^{d}(MK)$	$\sigma^{d}_{0}(MK)$	$\sigma^{p}(MK)$
C1	1.0	54.88	5.07	−203.35	−0.35	15.45	−0.89	−14.55
	2.0	54.73	5.05	−204.30	−0.06	15.42	−0.92	−14.83
	80.0	54.52	5.14	−205.92	0.35	15.39	−0.96	−15.28
	$\Delta\sigma$ c)	−0.36	0.07	−2.57	0.70	−0.06	−0.07	−0.73
C2	1.0	54.49	3.83	−169.80	−0.09	16.75	−0.08	0.77
	2.0	58.52	3.75	−169.85	0.01	16.75	0.11	0.96
	80.0	58.57	3.76	−169.92	0.145	16.76	−0.14	1.24
	$\Delta\sigma$	0.08	−0.07	−0.12	0.23	0.01	−0.06	0.47
C3	1.0	57.17	4.58	−177.70	1.54	16.01	0.78	−5.47
	2.0	57.11	4.72	−178.36	1.54	15.98	0.75	−5.77
	80.0	56.99	4.60	−179.41	1.55	15.94	0.71	−6.20
	$\Delta\sigma$	−0.19	0.02	−1.71	−0.02	−0.16	−0.07	−0.73
Me d)	1.0	57.73	3.00	−52.72	−1.85	19.16	−4.36	4.26
	2.0	57.73	3.87	−52.82	−1.84	19.17	−4.38	4.28
	80.0	57.73	3.72	−52.94	−1.86	19.17	−4.41	4.28
	$\Delta\sigma$	0.0	0.72	−0.22	−0.01	0.01	−0.05	0.02

a) Total shielding constant was decomposed according to Eq. 5. b) Dielectric constant. c) Obtained by subtracting shielding constants at $\varepsilon=1$ from those at $\varepsilon=80$. Negative values indicate downfield shifts. d) Methyl carbon.

shifts to down-field to less extent compared with the C3 one. σ^{p}(KK) represents the sum of contributions of the paramagnetic currents originated in neighboring atoms, and thereby this term can be further decomposed into each atomic contributions. From such analysis, it was indicated that the paramagnetic current around the carbonyl oxygen is the major contributor to this term. For the induced-shifts of the C2 resonance, the terms σ^{p}(KK) and σ^{p}(MK) are predominant. Thus we can conclude that there is no simple correlation between the solvent-induced ^{13}C shifts and the electron density on the corresponding carbon atom.

Recent theoretical studies on the ^{13}C NMR shielding[20–22] have demonstrated that hydrogen bonding (HB)-induced shifts are mainly originated in the electrostatic interaction between donor and acceptor molecules. This suggests the similarity between the HB- and dielectric shifts. Figure 3 shows that the trend i) holds for the HB-induced shifts. However, the amounts of them are considerably larger than expected from the dielectric constants of the HB solvents. This may be due to the relatively large stabilization of HB complexes. In view of this , solute–solvent aggregations, like dipole–dipole complexes, may be responsible for the nonlinear dependence of the observed ^{13}C shieldings on the reaction field (Figs. 2 and 3).

These results indicate that the present theoretical method well reproduces the observed solvent-induced ^{13}C chemical shift changes. In conclusion, the method provides good perspectives for the behavior of molecules in solution when specific interactions like hydrogen bonding are less important.

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