Bull. Chem. Soc. Jpn., **53**, 1257—1262 (1980)

Effect of a Polar Solvent on the $^1J_{CH}$ Spin-coupling Constants in Chlorine-substituted Ethanes

Shosuke Watanabe* and Isao Ando†

Minato High School of Technology, 18-13, Nishi-shinbashi 3-chome, Minato-ku, Tokyo 105

† *Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*

(Received October 11, 1979)

The directly-bonded ^{13}C–H spin-coupling constants ($^1J_{CH}$) for two chlorine-substituted ethanes, $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$, have been measured in various solvents with a wide range of dielectric constants and/or as a function of the temperature. Also, these two effects were estimated by the finite perturbation theory based on the CNDO/2 approximation with the solvaton theory. Both experimentally and theoretically, the dielectric constant of a solvent affects the $^1J_{CH}$ more than the temperature. It is shown that the solvent effect on the $^1J_{CH}$ spin couplings in $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$ arises mainly from electronic changes in the solute molecules caused by intermolecular solute-solvent interaction, more than from the change in the population of the rotational isomers.

The effects of solvents on spin-coupling constants have been widely studied by many authors. Some excellent reviews[1)] have been presented on these effects.

In a previous paper,[2)] we have ourselves treated numerically the effect of a polar solvent on directly-bonded ^{13}C–H spin-coupling constants for molecules in which unsaturated bonds fix the relative spatial positions of the atoms with each other (*e.g.*, CH_2=CHCN), and for halomethanes, with the aid of the finite perturbation theory[3)] (hereafter, an acronym FPT will be used) with the solvaton model.[4)] This approach successfully provided a quantitative description of the solvent effects on $^1J_{CH}$, following the Johnston-Barfield approaches, the reaction field model,[5)] the cluster model[6)] and the rotating-point dipole model.[7)]

There is another category of solvent effects of coupling constants, namely, the solvent effects of the coupling constants of molecules which can take into account two or more conformations. In this case, we must consider two effects on the coupling constants; one is due to solvent-induced electronic changes in the solute molecules, and the other, to the change in the relative populations between the isomers because of intermolecular solute-solvent interaction. Barfield and Johnston[1a)] calculated the vicinal H-F coupling constants in 1,1,1-trifluoroethane using the reaction-field model and concluded that the contribution from the solvent-induced electronic changes on the observed solvent effect is by no means negligible. The purpose of the present work is to separate the above two effects both experimentally and theoretically, and to discuss the mechanism of the solvent effect on the $^1J_{CH}$'s of molecules with rotational isomerism. We will analyze this problem with the term of FPT considering the effect of the aprotic polar solvent on the $^1J_{CH}$ coupling constants in chlorine-substituted ethanes, $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$.

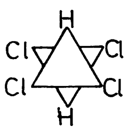
Experimental

The ^{13}C NMR spectra were measured by means of a JEOL PS-100 spectrometer with the PFT-100 Fourier transform system operating at 25.15 MHz. The Fourier-transformed spectra contain 4096 data points within spectra width of 1000 Hz. This indicates a limit of 0.25 Hz on the resolution. The temperatures are considered to be controlled within ±1 °C. The NMR tube used was 8 mm in diameter. The concentration of the sample in solution is 10% v/v.

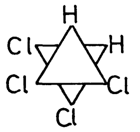
The chlorine-substituted ethanes and solvents were obtained from the Tokyo Kasei Co. and were used without further purification.

Theoretical

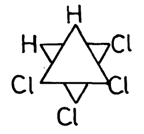
Rotational Isomerism. Both $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$ take the three energetically-preferred isomeric states as follows;[8] $CHCl_2CHCl_2$:



1-I

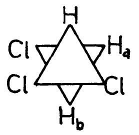


1-II

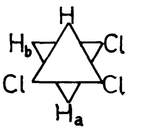


1-III

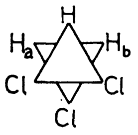
$CHCl_2CH_2Cl$:



2-I



2-II



2-III

The observed coupling constant is given by[9)]

$$\langle J_{CH}\rangle = X_{I}J^{I}_{CH} + X_{II}J^{II}_{CH} + X_{III}J^{III}_{CH}, \tag{1}$$

when the exchange rate is sufficiently larger than the difference between J_{CH}'s, where X_I, X_{II}, and X_{III} are the molar fractions of the three isomers, I—III, respectively. Each of the molar fractions can be expressed in terms of the relative energy, ΔE, of the isomer with respect to that of the reference conformer, III. Equation 1 can be reduced into the following forms if the coupling constants are assumed to be temperature-independent;[10)]

$CHCl_2CHCl_2$:

$$\langle J_{CH}\rangle = [2J^{II}_{CH}+J^{I}_{CH}\exp(-\Delta E/RT)]/[2+\exp(-\Delta E/RT)] \tag{2}$$

$CHCl_2CH_2Cl$:

$$\langle J_{CH}\rangle = \frac{1}{2}[(J^{III}_{CH_a}+J^{III}_{CH_b})+2(J^{I}_{CH_a}+J^{I}_{CH_b})\exp(-\Delta E/RT)]/[1+2\exp(-\Delta E/RT)] \tag{3}$$

We can evaluate, in principle, the relative energies,

ΔE's of the isomers and the coupling constants, J^{i}_{CH}'s, from the temperature dependence of $\langle J_{CH}\rangle$'s. It is, however, hard to determine them because of the small change in $\langle J_{CH}\rangle$'s. Gutowsky *et al.*[9] have estimated the relative energies of the isomers through the temperature dependence of the vicinal proton-proton spin couplings in halogen-substituted ethanes by means of a least squares method with a computer. In our previous work, the values of the relative energies of the isomers were estimated by Gutowsky's treatment[9] from the temperature dependence of the vicinal proton-proton spin coupling[11] in calculating Eqs. 2 and 3.

$^1J_{CH}$ *Spin-coupling Constant.* In previous papers,[2,12] we have applied the solvaton model to interaction with a solvent with the aid of semi-empirical SCF calculations. The "solvaton" is convenient for the description of the distribution of the oriented solvent around each atom in a molecule. Only a few important basic assumptions are introduced there: i) A counter charge (the solvaton) is induced on the surface of the solute molecules upon the addition of the solute to an aprotic polar solvent: (ii) each solvaton is associated individually with each atom of the solute, and the charge is equal in magnitude, but opposite in sign, to that of the associated atom: (iii) there are no interactions between the solvatons themselves, and (iv) the solvent-solute interaction is approximated by the Born equation,[13] which describes the energy of the solvaton of an ion in a dielectric continuum.

We will calculate $^1J_{CH}$ coupling constants as a function of the dielectric constant(ε) with the aid of the CNDO/2 approximation[14] in consideration of the above-mentioned solvent-solute interaction using the FPT theory. In this calculation, we will consider only the Fermi contact interaction, which seems to be predominant in $^1J_{CH}$ coupling constants.

The spin-unrestricted SCF equations on the Fock matrices, $F^{\alpha}_{\mu\nu}$ and $F^{\beta}_{\mu\nu}$, for α and β electrons are given by

$$\begin{aligned} F^{\alpha}_{\mu\nu} = H^{\text{core}}_{\mu\nu} &+ \sum_{\lambda\sigma}[P_{\lambda\sigma}(\mu\nu|\lambda\sigma)-P^{\alpha}_{\lambda\sigma}(\mu\sigma|\lambda\nu)] \\ &+ \frac{\varepsilon-1}{\varepsilon}\int\phi_{\mu}\left(\sum_{s}^{N}\frac{Q_s}{r_{s1}}\right)\mathrm{d}\tau \\ &+ \frac{8}{3}\pi\beta\mu\int\phi_{\mu}\delta(r_B)\phi_{\nu}\mathrm{d}r \end{aligned} \tag{4-1}$$

$$\begin{aligned} F^{\beta}_{\mu\nu} = H^{\text{core}}_{\mu\nu} &+ \sum_{\lambda\sigma}[P_{\lambda\sigma}(\mu\nu|\lambda\sigma)-P^{\beta}_{\lambda\sigma}(\mu\sigma|\lambda\nu)] \\ &+ \frac{\varepsilon-1}{\varepsilon}\int\phi_{\mu}\left(\sum_{s}^{N}\frac{Q_s}{r_{s1}}\right)\mathrm{d}\tau \\ &- \frac{8}{3}\pi\beta\mu\int\phi_{\mu}\delta(r_B)\phi_{\nu}\mathrm{d}r \end{aligned} \tag{4-2}$$

if the Fermi contact interaction[3] and the solvent-solute interaction are taken into account. The third terms including ε correspond to the solvent-solute interaction given by the solvaton theory, while the final terms in both equations correspond to the Fermi contact interaction. μ denotes the magnetic moment of the nucleus B, and $\delta(r_B)$, the Dirac delta function for the contact term between the electron and the nucleus B. The other symblos are used in the usual manner. The charge, Q_s, is defined by the (i) assumption. In a previous paper,[2] we assumed an inequality between Q^{α} and Q^{β} in the solvaton, but this assumption tends to overestimate the values of the $^1J_{CH}$ coupling constant. Thus, in this work, we modified this assumption by terms including ε in Eq. (4): that is, Q_s is handled without being separated into Q^{α}_s and Q^{β}_s. Further, r_{s1} is the solvaton-electron distance and is estimated as follows: (i) if the AO's and solvatons are associated with the same atomic center, the van der Waals' radius, r_v, of the corresponding atom can be used for the solvaton-electron distance, and (ii) if the AO's and solvatons are associated with different atomic centers with a separation of r_R, r_{s1} is approximated by:

$$\sqrt{r_v^2 + r_R^2}.$$

The expression for the coupling constant between A and B becomes:

$$J_{AB} = \frac{16}{9}h\gamma_A\gamma_B\beta^2 s_A^2(0)s_B^2(0)\left[\frac{\partial}{\partial h_B}\rho^{\text{spin}}_{s_A s_A}(h_B)\right]_{h_B=0} \tag{5}$$

using the FPT theory, where:

$$h_B = \frac{8}{3}\pi\beta\mu_B s_B^2(0)$$

Here, γ is the gyromagnetic ratio, $s_B{}^2(0)$ is the density at the nucleus of the valence s orbital of the B atom, and $\rho^{\text{spin}}_{s_A s_A}(h_B)$ is the spin-density matrix corresponding to the valence s orbital of the A atom.

In calculation, the bond lengths and bond angles used are the standard values proposed by Pople and Gordon[15] except for the C–Cl bond length, the value of the C–Cl is not given there. Instead, 1.71 Å, which appears elsewhere, is adopted.[16] The values used for the effective van der Waals' radii are 1.20, 1.59, and 1.8 Å in hydrogen, carbon, and chlorine atoms respectively.[17] All the calculations were carried out with the HITAC-M180 computer at the Tokyo Institute of Technology.

Results and Discussion

In Table 1 are shown the observed $^1J_{CH}$ values of $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$ in solvents with various dielectric constants. From these data, it is found that the $^1J_{CH}$ values increase with an increase in ε. The ε dependence of $^1J_{CH}$ in $CHCl_2CHCl_2$ is nearly equal to that in $CHCl_2CH_2Cl$. Also in $CHCl_2CH_2Cl$ the ε dependence of $^1J_{CH}$ for CH is larger than that for CH_2. In a previous paper[2] we have reported that the observed and calculated $^1J_{CH}$ values can be approximated by:

$$^1J_{CH} = a\left(\frac{\varepsilon-1}{\varepsilon}\right) + b\left(\frac{\varepsilon-1}{\varepsilon}\right)^2 + c \tag{7}$$

From the plot of $^1J_{CH}$ against $(\varepsilon-1)/\varepsilon$, the values of the a, b, and c parameters were obtained, they are tabulated in Table 2. The c parameter means the $^1J_{CH}$ value at $\varepsilon=1$, that is, for an isolated molecule. The a and b parameters provide measures of the magnitude of the solvent effect of $^1J_{CH}$ coupling. In the case of chlorine-substituted methanes,[2] the b parameter is nearly equal to zero. However, in $CHCl_2CHCl_2$

Table 1. The $^1J_{CH}$ spin coupling constants of $CHCl_2CHCl_2$ observed in various solvents with a wide range of dielectric constants (ε) at 25 °C

		$CHCl_2CHCl_2$		$CHCl_2CH_2Cl$			
Solvents	ε	CH		CH_2		CH	
		$^1J_{CH}$/Hz	ΔJ/Hz d)	$^1J_{CH}$/Hz	ΔJ/Hz d)	$^1J_{CH}$/Hz	ΔJ/Hz d)
Hexane	2.02a)	179.69	0	155.15	0	181.40	0
$CDCl_3$	4.806a)	181.15	1.46	155.27	0.12	181.89	0.49
$CHCl_2CH_2Cl$	7.12b)	—	—	155.64	0.49	181.98	0.58
$CHCl_2CHCl_2$	8.20c)	181.15	1.46	—	—	—	—
Acetone	20.0a)	184.08	4.39	155.88	0.73	183.59	2.19
Acetonitrile	35.8a)	184.09	4.40	156.25	1.10	183.35	1.95
Dimethylsulfoxide	46.0a)	185.54	5.85	156.66	1.51	184.04	2.64

a) National Bureau of Standards, Circular No. 514, 1951. b) Beil. E III, 1-154. c) J. A. Ridick and W. B. Bunger, "Organic Solvents", Wiley-Interscience, New York (1970). d) ΔJ is the difference between the coupling constants in the indicated solvent and in hexane.

Table 2. The values of the *a*, *b*, and *c* parameters in Eq. 7 for $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$

	$CHCl_2CHCl_2$	$CHCl_2CH_2Cl$	
Parameter	CH (Hz)	CH_2 (Hz)	CH (Hz)
a	3.5	0.5	2.0
b	4.0	1.3	3.0
c	178.3	154.9	180.3

Table 3. Temperature dependence of the $^1J_{CH}$ spin coupling constants of $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$ in neat liquid

	$^1J_{CH}$/Hz		
Temp / °C	$CHCl_2CHCl_2$	$CHCl_2CH_2Cl$	
	CH	CH_2	CH
25	181.15	155.64	181.98
40	181.15	155.81	181.88
60	181.15	155.52	181.84
70	181.16	155.55	181.81
80	181.15	155.64	181.75
90	181.15	155.54	181.70
100	181.15	155.52	181.69

and $CHCl_2CH_2Cl$ the *b* parameter is finite, but larger than the value of the *a* parameter. The values of these parameters for CH are larger than those for CH_2. This fact coincides with the results for chlorine-substituted methanes,2) in which an increase in the number of chlorine atoms induces an increase in the solvent effect.

Table 3 shows the temperature dependences of the $^1J_{CH}$ values of neat $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$. The $^1J_{CH}$ coupling is hardly dependent at all on the temperature. Thus, the temperature dependence for $^1J_{CH}$ is much smaller than the dependence on the polarity of the solvents. The difference in the $^1J_{CH}$ values in various solvents may not be the result of the difference in the populations of rotational isomers, but of the difference in electronic states in the molecules induced by the difference in solvent species. We will consider which difference is predominant through the calculation of the $^1J_{CH}$ couplings for a wide variety of dielectric constants and examples of rotational isomerism.

Before the numerical calculation, however, it is important to specify at the amounts of integral products, $s_C^2(0)s_H^2(0)$, chosen according to the FPT theory. The values will not only reflect the difference between the atomic or molecular environments of the nuclei, but will also be affected by the order of approximation in the molecular orbital theory. Thus, these values have often been proposed to coincide satisfactorily with the experimental results. Different values for the integral products seem to be different approximations inherent in the finite, self-consistent, and sum-over-states perturbation approximations. Two kinds of values will be used in this work: (i) Pople's value ($s_C^2(0)s_H^2(0)=1.5014$ a.u.),3) and (ii) the ($s_C^2(0)s_H^2(0)=1.644$ a.u.) value, which gives the best agreement between the experimental results and our calculations. Table IV shows the calculated ε dependence of the $^1J_{CH}$ coupling constants of $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$ in *trans* and *gauche* conformations, using both values of the integral products. It is clear that the choice of the larger value (1.644 a.u.) for $s_C^2(0)s_H^2(0)$ decreases the difference between the calculated and experimental values. The dependence of the $^1J_{CH}$ coupling upon the dihedral angle, ϕ, is calculated at intervals of 10° as a function of ε, they are plotted in Fig. 1. The $^1J_{CH}$ value shows the dihedral-angle dependence as well as that of the coupling through three bonds. However, its dependence is very small compared with the latter case. Each of the dihedral-angle dependences for CH in $CHCl_2CHCl_2$ and $CHCl_2CH_2Cl$ have three minima and three maxima, while that for CH_2 in $CHCl_2CH_2Cl$ has two minima and two maxima. These positions are different in each case. The $^1J_{CH}$ values are not very much affected by $\phi(|^1J_{CH}(trans)-{}^1J_{CH}(gauche)|<0.5\text{ Hz})$. The $^1J_{CH}$ values in the *trans* and *gauche* positions are close to each other. From this, the temperature independence of the $^1J_{CH}$ couplings can be expected. On the other hand, the ε dependence can be expected to be large.

The temperature dependences of $\langle {}^1J_{CH} \rangle$ were obtained using the calculated ${}^1J_{CH}$ couplings of *trans* and *gauche* conformations tabulated in Table 4, and Eqs. 2 and 3. In these equations the energy differences (ΔE) between the conformers in various solvents were determined with Gutowsky's treatment on vicinal proton-proton spin coupling:[11]

$CHCl_2CHCl_2$: 889 (in CCl_4), 919 (neat liquid), 1165 (in acetone) and 1352 cal/mol (in dimethylsulfoxide), while

$CHCl_2CH_2Cl$: 160 (in CCl_4), 200 (neat liquid), 217 (in acetone) and 504 cal/mol (in dimethylsulfoxide).

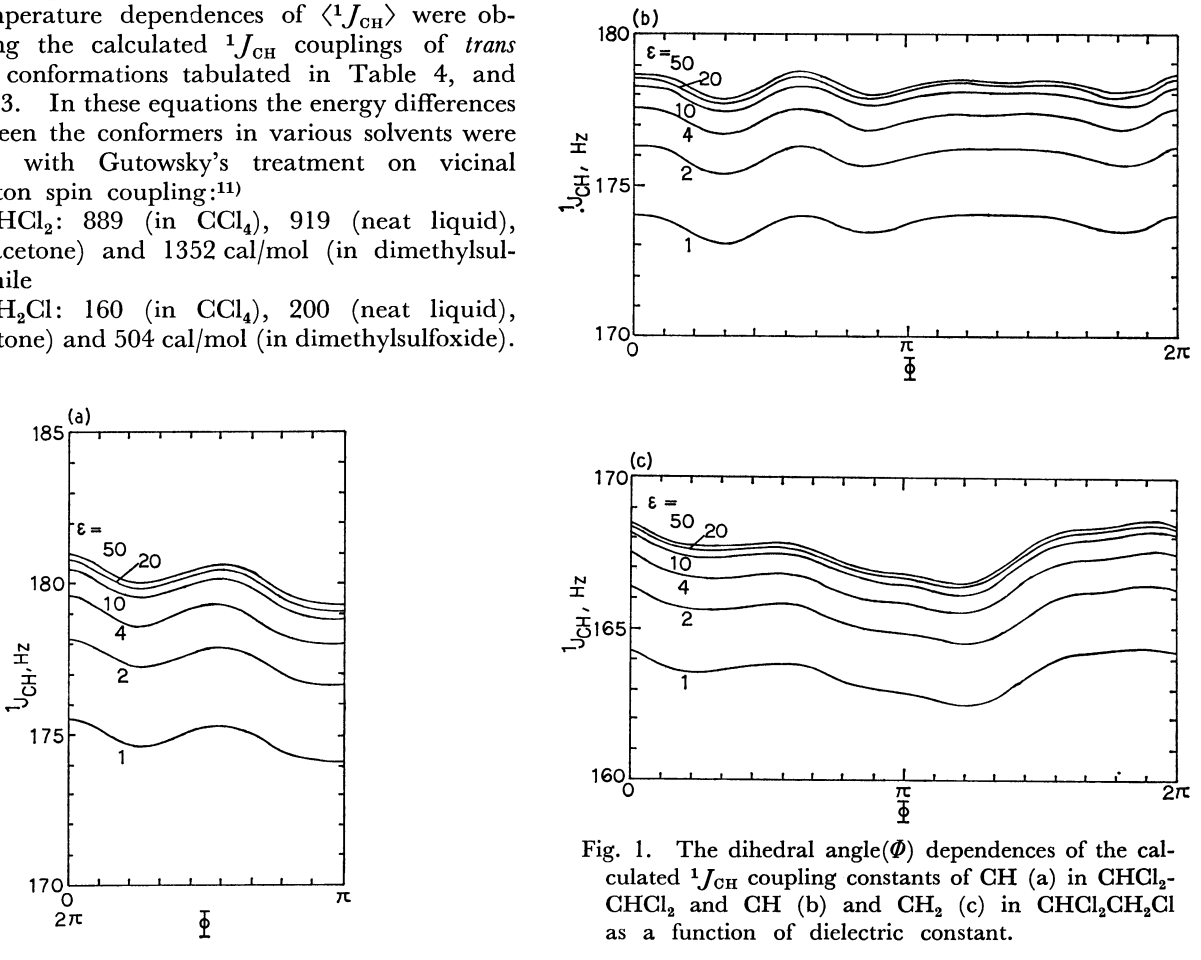
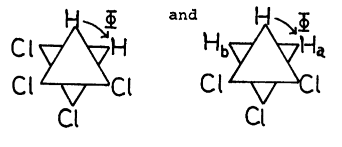


Fig. 1. The dihedral angle(Φ) dependences of the calculated ${}^1J_{CH}$ coupling constants of CH (a) in $CHCl_2$-$CHCl_2$ and CH (b) and CH_2 (c) in $CHCl_2CH_2Cl$ as a function of dielectric constant.

TABLE 4. THE CALCULATED ${}^1J_{CH}$ VALUES OF $CHCl_2CHCl_2$ AND $CHCl_2CH_2Cl$ IN *trans* AND *gauche* ISOMERS[a] AS A FUNCTION OF DIELECTRIC CONSTANT

	${}^1J_{CH}$/Hz											
	Pople' value $s_C^2(0)s_H^2(0)=1.5014$ a. u.						This work $s_C^2(0)s_H^2(0)=1.644$ a. u.					
	$\varepsilon=1$	2	4	10	20	50	$\varepsilon=1$	2	4	10	20	50
$CHCl_2CHCl_2$:												
trans ($\Phi=\Pi$)	105.95	107.49	108.30	108.81	108.99	109.09	174.18	176.71	178.05	178.88	179.18	179.34
gauche ($\Phi=\pm\Pi/3$)	106.28	107.87	108.72	109.25	109.43	109.54	174.72	177.34	178.74	179.61	179.90	180.04
$CHCl_2CH_2Cl$:												
CH												
trans ($\Phi=\Pi$)	105.65	107.02	107.74	108.20	108.35	108.44	173.69	175.94	177.12	177.88	178.13	178.28
gauche ($\Phi=\Pi/3$)	105.25	106.67	107.43	107.91	108.07	108.17	173.03	175.37	176.61	177.40	177.67	177.83
gauche ($\Phi=5/3\,\Pi$)	105.65	107.02	107.74	108.20	108.35	108.44	173.69	175.94	177.12	177.88	178.13	178.28
CH_2												
H_a												
trans ($\Phi=\Pi$)	99.13	100.29	100.90	101.28	101.41	101.49	162.97	164.88	165.88	166.50	166.72	166.85
gauche ($\Phi=\Pi/3$)	99.52	100.75	101.40	101.81	101.95	102.03	163.61	165.63	166.70	167.38	167.61	167.74
gauche ($\Phi=5/3\,\Pi$)	99.85	101.11	101.77	102.18	102.32	102.03	164.15	166.22	167.31	167.98	168.21	168.36

a) The definition of the dihedral angle, Φ, is as follows:



The results for $^1J_{CH}$ are shown in Table 5. The temperature dependence of the dielectric constants of the solvents is taken into account in Table 5 by the use of:

$$(\varepsilon+1)\cdot T \propto \text{constant} \qquad (8)$$

after Wyman's study[18] of large classes of polar liquids. The calculated $\langle {}^1J_{CH} \rangle$ values are almost independent of the temperatures and can interpret the observed values qualitatively.

In order to obtain the calculated effect of the ε dependences of the $^1J_{CH}$, Eqs. 2 and 3 were used as well as the calculation of the temperature dependence. These results are shown in Table 6.

TABLE 5. TEMPERATURE DEPENDENCES OF THE CALCULATED $^1J_{CH}$ COUPLING CONSTANTS OF $CHCl_2CHCl_2$ AND $CHCl_2CH_2Cl$ IN NEAT LIQUID

Temp °C	$^1J_{CH}$/Hz		
	$CHCl_2CHCl_2$	$CHCl_2CH_2Cl$	
	CH	CH_2	CH
25	177.52	167.17	178.86
40	177.46	167.13	178.84
60	177.39	167.09	178.81
70	177.36	167.07	178.80
80	177.32	167.04	178.78
90	177.29	167.02	178.77
100	177.25	167.00	178.75

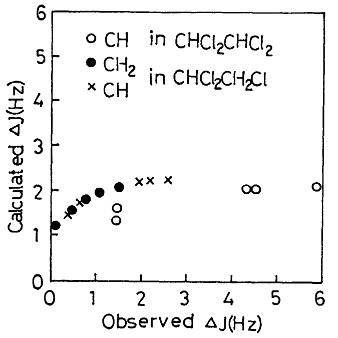


Fig. 2. The plots of calculated ΔJ against observed ΔJ.

For a further comparison of the calculated and experimental results, the differences, ΔJ, between the coupling constants in the indicated solvents and in hexane are shown in the table and also in Fig. 2. The calculated trends reproduce the observed ones in the solvent effect. However, the calculated values in the high-value range in ΔJ are underestimated. This seems to be a result of the exclusion of the one-center exchange integral in our calculation, because the inclusion of its integral leads to an increase in the magnitude of the directly-bonded coupling constant, as has been reported by Pople *et al.*[3]

As these results shows, the ε dependence is very large compared with the temperature dependence. This large dependence on ε is a proof of the larger contribution of the solvent-induced electronic changes of the solute molecules to the solvent effect on the $^1J_{CH}$, resulting from intermolecular solute-solvent interaction.

It can be concluded that there are good gross trends of agreement between the observed and calculated results. This would suggest a potential applicability of the solvaton theory in interpreting solvent effects in dipolar media.

The authors wish to thank Associate Professor R. Chûjô of our department for his many helpful suggestions and discussions.

References

1) a) M. Barfield and M. D. Johnston, Jr., *Chem. Rev.*, **73**, 53 (1973); b) S. L. Smith, *Fortsch. Chem. Forsch.*, **27**, 117 (1972); c) J. Kowalewski, *Prog. NMR Spectrosc.*, **11**, 1 (1977).

2) M. Kondo, S. Watanabe, and I. Ando, *Mol. Phys.*, **37**, 1521 (1979).

3) J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2965 (1967).

4) a) G. Klopman, *Chem. Phys. Lett.*, **1**, 200 (1967); b) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968); c) H. A. Germer, Jr., *Theor. Chim. Acta*, **34**, 145 (1974).

5) M. D. Johnston and M. Barfield, *J. Chem. Phys.*, **54**, 3083 (1971).

6) M. D. Johnston and M. Barfield, *J. Chem. Phys.*, **55**, 3483 (1971).

TABLE 6. THE DIELECTRIC-CONSTANT DEPENDENCES OF THE CALCULATED $^1J_{CH}$ COUPLING CONSTANTS OF $CHCl_2CHCl_2$ AND $CHCl_2CH_2Cl$

Solvents	ε	$CHCl_2CHCl_2$		$CHCl_2CH_2Cl$			
		CH		CH_2		CH	
		$^1J_{CH}$/Hz	ΔJ/Hz[a]	$^1J_{CH}$/Hz	ΔJ/Hz[a]	$^1J_{CH}$/Hz	ΔJ/Hz[a]
Hexane	2.02	175.92	0	165.52	0	177.03	0
$CDCl_3$	4.806	177.21	1.29	166.78	1.26	178.43	1.40
$CHCl_2CH_2Cl$	7.12	177.52	1.60	167.08	1.56	178.76	1.73
$CHCl_2CHCl_2$	8.20	177.60	1.68	167.16	1.64	178.85	1.82
Acetone	20.0	177.93	2.01	167.48	1.96	179.21	2.18
Acetonitrile	35.8	178.03	2.11	167.58	2.06	179.31	2.28
Dimethylsulfoxide	46.0	178.05	2.13	167.61	2.09	179.34	2.31

a) ΔJ is the difference between the coupling constants in the indicated solvent and in hexane.

7) M. D. Johnston and M. Barfield, *Mol. Phys.*, **22**, 831 (1971).

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

9) H. S. Gutowsky, G. C. Beldford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

10) J. C. Shug, P. E. McMahon, and H. S. Gutowsky, *J. Chem. Phys.*, **33**, 843 (1960).

11) I. Ando, unpublished data.

12) I. Ando, M. Kondo, and A. Nishioka, *J. Magn. Reson.*, **21**, 429 (1976).

13) M. Born, *Z. Phys.*, **1**, 45 (1920).

14) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1967).

15) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

16) "Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement," ed by L. E. Sutton, The Chemical Society, London (1965).

17) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca (1960).

18) J. Wyman, *J. Am. Chem. Soc.*, **58**, 1482 (1936).