April, 1981] © *1981 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **54**, *1241—1242 (1981)* 1241

The Effect of Polar Solvent on the $^1J_{CH}$ Spin-Spin Coupling Constants in Halomethanes and Haloethylenes

Shosuke WATANABE*,† and Isao ANDO

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

(Received March 31, 1980)

Synopsis. The solvent effect on the ^{13}C–^1H nuclear spin-spin coupling constants ($^1J_{CH}$) of halomethanes and haloethylenes is calculated by means of the finite perturbation theory based on the CNDO/2 approximations incorporating the 'solvaton' theory. The results of the calculation explained the tendency of the observed solvent effect data in the literature.

Nuclear spin-spin coupling constants are known to be solvent-dependent,[1] and Johnston and Barfield[2–4] have handled the observed solvent effect on spin-spin coupling constants by means of the so-called reaction field model,[2] the cluster model[3] and the rotating-point dipole model.[4] So far as $^1J_{CH}$ is concerned, that is, they have numerically estimated the solvent effect on the $^1J_{CH}$ values of fluoromethanes only.

Most recently,[5,6] we have quantitatively calculated the solvent effect of the one-bond ^{13}C–^1H coupling constant($^1J_{CH}$) by applying the finite perturbation theory (FPT)[7] with the INDO and CNDO/2 MO methods incorporating Klopman's solvaton theory.[8] This approach successfully offers a quantitative description of the solvent effects on the $^1J_{CH}$ values of some small organic compounds (*e.g.*, methane derivatives,[5] acrylonitrile,[5] $CHCl_2CHCl_2$,[6] and $CHCl_2CH_2Cl$[6]).

In the present work we applied the FPT method which we have developed ourselves[5,6] to estimate the substitution effects on the solvent effect of $^1J_{CH}$ coupling constants in such rigid molecules as halomethanes (fluoro- and chloro-) and haloethylenes (fluoro- and chloro-). The results of the calculation are compared with the tendency of the observed solvent effects in the literature.

Results and Discussion

In all the calculations of this work, $S_C^2(0)S_H^2(0)=2.2240$ a.u. was used as the value of the integral product.

Table 1 shows the results of the calculation of fluoromethanes using the experimental values reported by Cox and Smith[9] and of that on chloromethanes using the experimental values obtained by Watts and Goldstein.[10]

It is evident from the results in Table 1 that the calculated results agree qualitatively well with such observed results as that the solvent-induced change in the $^1J_{CH}$ value increases as the number of substituted fluorine or chlorine atoms increases, or that the $^1J_{CH}$ value increases as the dielectric constant (ε) of the solvent increases.

It is also evident from Table 1 that the respective $^1J_{CH}$ values increase in the order of mono-, di- and trihalogen-substituted compounds, and also that, when the number of substituting halogen atoms is equal in the molecules under consideration, the fluorine deriva-

TABLE 1. DEPENDENCE OF $^1J_{CH}$ SPIN-COUPLING CONSTANTS OF FLUOROMETHANES AND CHLOROMETHANES UPON THE DIELECTRIC CONSTANT(ε)

Solute	Solvent	ε	Observed		Calculated	
			$^1J_{CH}$/Hz	Δ^1J_{CH}/Hz	$^1J_{CH}$/Hz	Δ^1J_{CH}/Hz
CH_3F		2.02	—	—	161.62	0.0
		20.5	—	—	163.01	1.39
		46.0	—	—	163.16	1.54
CH_2F_2	Cyclohexane	2.02	182.10[a]	0.0	197.58	0.0
	Acetone	20.5	184.80[a]	2.70	201.61	4.03
	DMSO	46.0	186.50[a]	4.40	201.87	4.29
CHF_3	Cyclohexane	2.02	238.10[a]	0.0	257.72	0.0
	Acetone	20.5	245.35[a]	7.25	263.54	5.82
	DMSO	46.0	247.30[a]	9.20	264.15	6.43
CH_3Cl	Cyclohexane	2.02	148.58[b]	0.0	148.05	0.0
	CCl_4	2.23	149.64[b]	1.06	148.26	0.21
	DMF	35.0	150.40[b]	1.82	150.20	2.15
CH_2Cl_2	Cyclohexane	2.02	176.48[b]	0.0	160.91	0.0
	CCl_4	2.23	178.75[b]	2.27	160.97	0.06
	DMF	35.0	180.55[b]	4.07	164.69	3.78
$CHCl_3$	Cyclohexane	2.02	208.11[b]	0.0	178.49	0.0
	CCl_4	2.23	208.26[b]	0.15	178.96	0.47
	CMF	35.0	216.46[b]	8.35	183.57	5.08

a) R. H. Cox and S. L. Smith, *J. Magn. Reson.*, **1**, 432 (1969). b) V. S. Watts and J. H. Goldstein, *J. Phys. Chem.*, **70**, 3887 (1966). c) The calculated values represent the differences between the values in the indicated solvent and in cyclohexane.

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† Permanent address: Minato High School of Technology, 18-13, Nishi-shinbashi 3-chome, Minato-ku, Tokyo 105.

Table 2. Dependence of $^1J_{CH}$ spin-coupling constants of chloroethylenes upon the dielectric constant(ε)

Solute	Solvent	ε	Observed[a]		Calculated	
			$^1J_{CH}$/Hz	Δ^1J_{CH}/Hz[b]	$^1J_{CH}$/Hz	Δ^1J_{CH}/Hz[b]
CH_2=CCl_2	Cyclohexane	2.02	166.3	0.0	195.57	0.0
	DMF	35.0	167.0	0.7	199.36	3.79
cis-$C_2H_2Cl_2$	Cyclohexane	2.02	197.1	0.0	203.66	0.0
	DMF	35.0	200.1	3.0	208.57	4.91
trans-$C_2H_2Cl_2$	Cyclohexane	2.02	198.4	0.0	203.21	0.0
	DMF	35.0	200.8	2.4	207.45	4.24
C_2HCl_3	Cyclohexane	2.02	200.5	0.0	205.73	0.0
	DMF	35.0	204.2	3.7	211.48	5.75

a) V. S. Watts, J. Loemker and J. H. and J. H. Goldstein, *J. Mol. Spectrosc.*, **17**, 348(1965). b) The calculated values represent the differences between the values in the indicated solvent and in cyclohexane.

Table 3. Dependence of $^1J_{CH}$ spin-coupling constants of dichlorofluoroethylenes upon the dielectric constant(ε)

Solvent	ε	Observed[a]		Calculated	
		$^1J_{CH}$/Hz	Δ^1J_{CH}/Hz[b]	$^1J_{CH}$/Hz	Δ^1J_{CH}/Hz[b]
			(*Z*)-1,2-Dichlorofluoroethylene		
Cyclohexane	2.02	195.6	0.0	198.8	0.0
Benzene	2.26	198.0	2.4	199.4	0.6
$CHCl_3$	4.63	199.6	4.0	201.7	2.9
Acetone	20.0	199.5	3.9	203.4	4.6
DMF	35.0	202.5	6.9	203.7	4.9
DMSO	46.0	202.0	6.4	203.7	4.9
			(*E*)-1,2-Dichlorofluoroethylene		
Cyclohexane	2.02	201.7	0.0	207.9	0.0
Benzene	2.26	204.0	2.3	208.5	0.6
$CHCl_3$	4.63	203.8	2.1	211.0	3.1
Acetone	20.0	205.9	4.2	212.9	5.0
DMF	35.0	208.6	6.9	213.3	5.4
DMSO	46.0	208.1	5.4	213.3	5.4

a) C. L. Bell and S. S. Danyluk, *J. Mol. Spectrosc.*, **35**, 376 (1970). b) The calculated values represent the differences between the values in the indicated solvent and in cyclohexane.

tives exhibit a larger $^1J_{CH}$ value than the chlorine derivatives. This may be due to the greater electronegativity of the fluorine atom. This tendency agrees with the observed result.

The calculated results of the solvent effect on the $^1J_{CH}$ calculation of dichloroethylenes and trichloroethylene are tabulated in Table 2 in comparison with the corresponding experimental values reported by Watts *et al.*[11]) It is now clear that the $^1J_{CH}$ value of 1,1-dichloroethylene is smaller than those of the 1,2-dichloroethylenes and that those of its *trans*- and *cis*-forms are nearly equal to each other. It is found that the trisubstituted ethylene has a larger $^1J_{CH}$ value than the disubstituted one and that, in both cases, its values depend highly on ε.

Table 3 shows the calculated results of the solvent effect on the $^1J_{CH}$ for 1,2-dichlorofluoroethylenes, together with the corresponding experimental data reported by Bell and Danyluk.[12]) The (*E*) form exhibits a larger $^1J_{CH}$ value than the (*Z*) form, and both values depend on ε. The calculated results agree well with the experimental findings.

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

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