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Solvent Effects on the Proton Magnetic Resonance Spectra of 2,3-Dichlorobutane and the Problem of Rotational Isomers

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Effect of solvent on the coupling and magnetic shielding constants of *meso* and *racemic* 2,3-dichlorobutanes has been examined using proton magnetic resonance (PMR). The iterative method of spectrum analysis is applied to the simple sub-state in order to improve the computation speed and the computer capacity. The variations in the coupling constants for the *meso* configuration are to some extent correlated with the population as a function of dielectric constant ε of solvent using an Onsager model. The coupling constants of the *racemic* configuration were almost independent of the solvent dielectric constant. The estimated chemical shift dependence on ε of the reaction field does not adequately describe the experimental data.

The PMR spectra of 2,3-dichlorobutane have been studied by Bothner-By *et al.*,1) but further investigation seems worthwhile concerning the change in spectra with solvent polarity. A molecule having rotational isomers is known to have various populations in solution, since the relative energies of these isomers are considerably affected by the medium. This is due to the fact that the polar isomer, which corresponds to a higher energy in the gaseous state than the nonpolar isomer, is stabilized in solution by the action of a reaction field induced by the surrounding polar medium. In this paper, the effect of solvent on the population, obtained from the vicinal coupling constant, and on the chemical shift will be discussed in terms of reaction field theory.

Experimental

The preparation and characterization of the *meso* and *racemic* 2,3-dichlorobutanes will be described elsewhere. PMR spectra were taken on a Varian A-60 as 5 and 10% wt/vol solutions in solvents with different dielectric constants and recorded over a temperature range of −60 to 40°C.

The spectrum was calculated as a $X_3AA'X_3'$ system. The Hamiltonian matrix is factorized to reduce it to minimal dimensions by taking advantage of magnetic equivalence.2) The spectrum of a $X_3AA'X_3'$ system is made up of a superposition of four sub-spectra $Q_XD_AD_{A'}Q_{X'}$, $Q_XD_AD_{A'}D_{X'}$, $D_XD_AD_{A'}Q_{X'}$ and $D_XD_AD_{A'}D_{X'}$. A nomenclature has been developed for the sub-states corresponding to the possible values

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1) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962).

2) R. C. Ferguson and D. W. Marquart, *J. Chem. Phys.*, **41**, 2087 (1964).

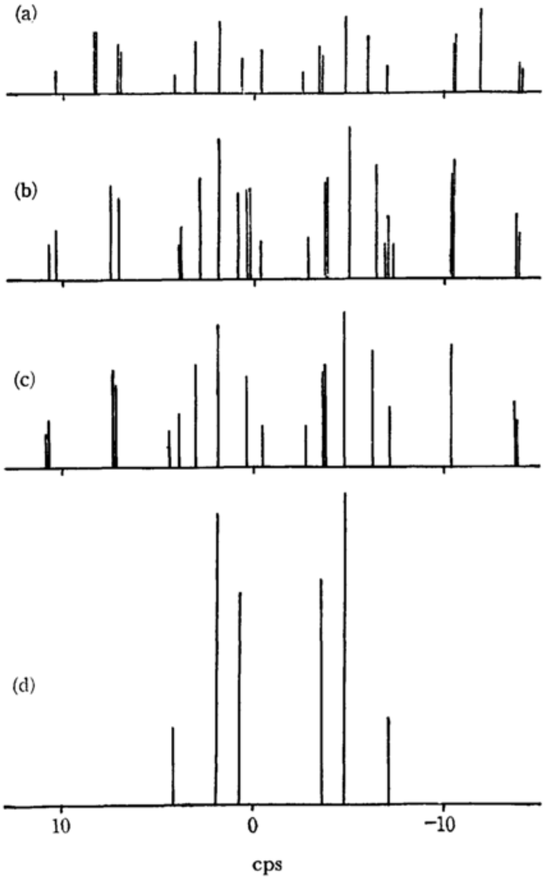


Fig. 1. "Stick spectra" of each substate.
(a) $Q_XD_AD_{A'}Q_{X'}$ (b) $Q_XD_AD_{A'}D_{X'}$
(c) $D_XD_AD_{A'}Q_{X'}$ (d) $D_XD_AD_{A'}D_{X'}$

of I in which the state with $I=1/2$, $3/2$ is known as a doublet, quartet (abbreviated to D and Q). Each spectrum is weighted by the factor 1, 2, 2 and 4, respectively. In Fig. 1, dividing the methine proton spectrum into contributions from sub-spectra, it is seen that a $X_3AA'X_3'$ system contains lines at the same position as in $D_XD_AD_{A'}D_{X'}$. An iterative method is used for the $D_XD_AD_{A'}D_{X'}$ system only to obtain improvements in computation speed, computer program capacity and convenience of use. Calculations of PMR spectra were carried out on an IBM 1620 computer using Fortran II_D.

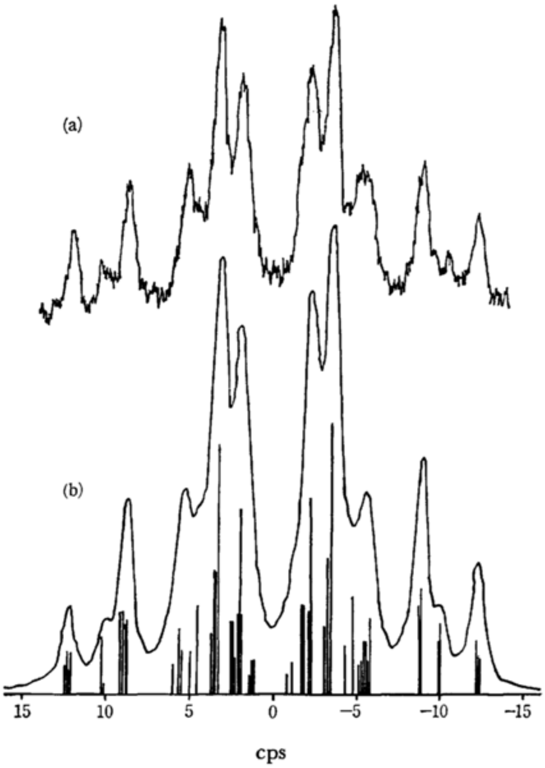


Fig. 2. *Racemic* 2,3-dichlorobutane in carbon tetrachloride.
(a) Observed methine proton spectrum
(b) Calculated spectrum (line width = 0.4 cps) and "Stick spectrum"

The final calculated spectra obtained by this method agreed very closely with the observed spectra. As an example of the fit achieved, a methine proton spectrum of *racemic* 2,3-dichlorobutane in carbon tetrachloride is compared with the calculated spectra in Fig. 2.

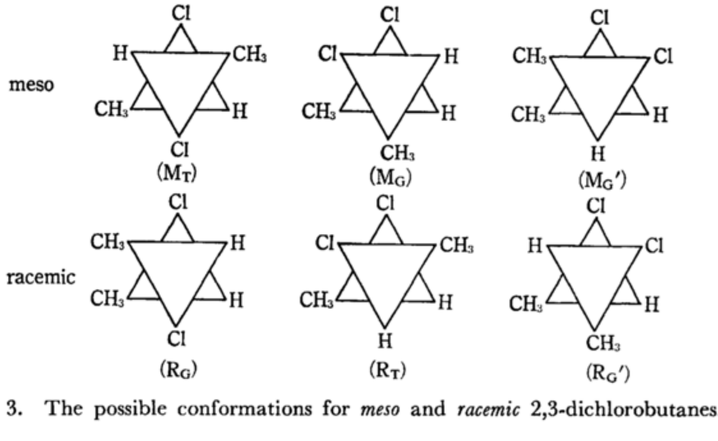


Fig. 3. The possible conformations for *meso* and *racemic* 2,3-dichlorobutanes.

TABLE 1. SOLVENT EFFECTS ON COUPLING CONSTANTS AND CHEMICAL SHIFTS OF 2,3-DICHLOROBUTANE

Compound	Solvent	$J_{AA'}$	ν_{CH_3}	ν_{CH}	P_{MT} or $P_{RG'}$
meso	1. CCl_4	7.7	99	237	0.63
	2. C_6H_6	6.3	95	216	0.48
	3. C_2Cl_4	7.8	99	238	0.64
	4. CS_2	7.2	97	234	0.58
	5. $CHCl_3$	6.5	98	243	0.50
	6. CH_2Cl_2	5.9	96	247	0.43
	7. $(CH_3)_2CO$	5.2	95	256	0.35
	8. $C_6H_5NO_2$	5.4	94	250	0.38
	9. CH_3CN	4.9	93	255	0.33
racemic	1. CCl_4	3.4	92	251	0.16
	3. C_2Cl_4	3.3	91	250	0.14
	4. CS_2	3.3	92	244	0.14
	5. $CHCl_3$		95	254	
	7. $(CH_3)_2CO$		94	263	
	8. $C_6H_5NO_2$	3.2	92	252	0.13
	9. CH_3CN		93	259	
		in cps			

Note: P_{MT} and $P_{RG'}$ indicates the populations of M_T in *meso* and of $R_{G'}$ in *racemic* configurations, respectively.

Results and Discussion

Estimation of Population of Rotational Isomers from the Vicinal Coupling Constants. The values of chemical shifts and coupling constants $J_{AA'}$ for various solvents are shown in Table 1. Three different rotational isomers are possible for both *meso* and *racemic* 2,3-dichlorobutane as shown in Fig. 3.

1) Experimental Results of meso 2,3-Dichlorobutane. The *meso* configuration has two effective conformations, the trans (M_T) and gauche (M_G), ($M_{G'}$) existing in two mirror-image forms. First, we shall attempt to obtain some information concerning the molecular conformation of the isomers in solution from the values of the vicinal coupling constants, $J_{AA'}$, of *meso*-DCB which is solvent dependent. $J_{AA'}$ may be regarded as an average value, given by

$$J_{AA'} = P_T J_T + P_G J_G, \qquad P_T + P_G = 1 \qquad (1)$$

where P_T and P_G are the populations of M_T and $(M_G + M_{G'})$, respectively, and J_T and J_G are the coupling constants for 60° and 180° dihedral angles between the methine protons. In Table 1 the populations obtained at 29°C, are summarized, assuming $J_T = 11$ c/s and $J_G = 2$ c/s.[*3] As can be seen in Fig. 4, there is a fair correlation between the population and the dielectric constant of the solvent, except for benzene solution. Thus, the populations are shown to be given by the following experimental equation, as shown in Fig. 4.

$$\log(P_G/P_T) = -0.66 + 2.0(\varepsilon - 1)/(2\varepsilon + 1)$$

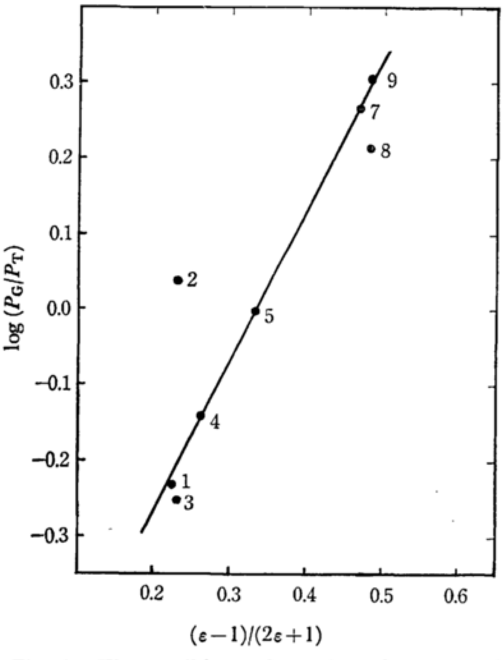


Fig. 4. The possible conformations for *meso* and *racemic* 2,3-dichlorobutanes.

[*3] We have adopted these values instead of $J_T = 11$c/s and $J_G = 1$c/s, which are used by Bothner-By *et al.*,[1] taking account of the theoretically calculated values of $J_T = 9.2$c/s and $J_G = 1.7$c/s for substituted ethanes (see M. Karplus, *J. Chem. Phys.*, **30**, 6 (1958)), and the recent experimental values of $J_T = 13.6$ c/s and $J_G = 2.6$ c/s used for the conformational analysis of amino acid (see H. Ogata, Y. Arata and S. Fujiwara, *J. Mol. Spectroscopy*, **23**, 76 (1967)), and of $J_T = 10$ c/s and $J_G = 2$ c/s used for studying the PMR spectra of 2, 4-dichloropentane (see T. Shimanouchi, M. Tasumi and Y. Abe, *Makromol. Chem.*, **86**, 43 (1965)).

TABLE 2. CONFORMATIONAL ENERGIES (in kcal/mol)

	M_T	M_G	$M_{G'}$	R_T	R_G	$R_{G'}$
Steric interaction (ΔE_1)	1.67	1.96	1.96	1.69	2.10	1.79
Dipole interaction (ΔE_2)	1.56	2.72	2.72	2.72	1.56	2.72
Total energy	3.23	4.68	4.68	4.41	3.66	4.51
$\Delta E(M_G - M_T) = 1.45$			$\Delta E(R_{G'} - R_T) = 0.10$			
			$\Delta E(R_T - R_G) = 0.75$			

2) Estimation of Influence of Solvent upon Population of Rotational Isomers.[3,4] If M_T and M_G are considered to be in simple equilibrium, their relative proportions should be in accordance with the expression

$$P_G/P_T = 2(Z_G/Z_T)\exp(-\Delta E/\boldsymbol{R}T) \quad (2)$$

in which Z_T and Z_G are the partition functions of the two isomers, and the factor 2 is introduced to account for the mirror-image isomerism of the gauche form. It is a well known fact that the energy difference between rotational isomers ΔE changes considerably in the transition from gas to liquid, and is dependent on solvent. The energy of this change, ΔE_{reac}, was calculated by taking Onsager's field[5] as the reaction field,

$$\Delta E_{\mathrm{reac}} = \Delta E_{\mathrm{gas}} - \Delta E_{\mathrm{solu}} = (\varepsilon - 1)\mu^2/(2\varepsilon + 1)a^3$$

$$\Delta E_{\mathrm{solu}} = \Delta E_{\mathrm{gas}} - (\varepsilon - 1)\mu^2/(2\varepsilon + 1)a^3 \quad (3)$$

where ΔE_{gas} and ΔE_{solu} are the energy differences between the gauche and trans forms referred to the gaseous state and to the solution, respectively; μ is the dipole moment of the gauche form, and a the radius of the solute molecule. If the solute molecular radius is estimated from the density and molecular weight of the liquid solute, and by assuming a perfect packing of the spheres, ΔE will be approximately

$$\Delta E = \Delta E_{\mathrm{gas}} - (4\pi \boldsymbol{N}d/3M)\mu^2[(\varepsilon - 1)/(2\varepsilon + 1)] \quad (4)$$

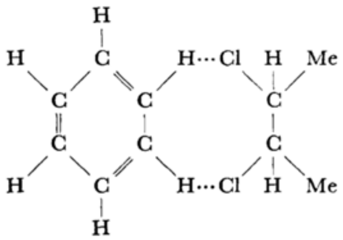
combining with Eq. (2) and substituting numerical values, we obtain at 30°C

$$\log (P_G/P_T) = \log 2(Z_G/Z_T) - (\Delta E_{\mathrm{gas}}/2.303\boldsymbol{R}T) + 2.16[(\varepsilon - 1)/(2\varepsilon + 1)] \quad (5)$$

Here the dipole moment of conformation M_G is approximated by vector addition of bond moment taken from C-Cl (1.86 D). The resultant dipole moment for M_G is 3.08 D.[6]

Furthermore, ΔE_{gas} can be calculated considering two factors; ΔE_1, which results from interactions between non-bonded atoms and groups, and ΔE_2, from the interaction of neighboring dipoles. ΔE_1 has been calculated assuming interactions in accordance with Lennard-Jones type potentials, and ΔE_2 calculated using a point dipole approximation.[7] The calculated results are also given in Table 2.

3) Comparison with the Experimental Results. To compare this estimate with the experimental results, the energy difference between the two isomers is evaluated to be 1.4 kcal/mol with M_T being the more stable form by extrapolating the line in Fig. 4 to $\varepsilon = 1$, and assuming equal partition functions for M_T and M_G in the liquid state. The agreement between the observed and calculated values of ΔE_{gas} is gratifying, considering the assumptions involved in the calculation of energy difference. The slope predicted by Eq. (5) agrees closely with the observed values, 2.0. An abnormal phenomenon in the benzene solution was observed, and this "benzene effect" is assumed to be due to the fact that the molecule associates with the solvent molecule by affinity between the hydrogen atoms of the benzene ring and halogen atoms in 2,3-dichlorobutane as follows[8]:



4) Interpretation of PMR Spectra of Racemic 2,3-Dichlorobutane. For *racemic* 2,3-dichlorobutane, the coupling constants $J_{AA'}$ are almost independent of the dielectric constant of the solvents within the limits of detection as can be seen in Table 1. This result is in direct contrast to that for the *meso*-2,3-dichlorobutane. The complexity introduced by consideration of three different isomers makes determination of the energy differences between isomers from $J_{AA'}$ of the spectra difficult. The situation is further complicated by the fact that the superposed peaks in the methyl spectrum render accurate measurements very difficult. As shown in Table 2, R_G is assumed to be the lowest in energy in the gaseous state. The energy difference between R_G and the two other conformers was con-

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[3] A. Wada, *J. Chem. Phys.*, **22**, 198 (1954).

[4] E. B. Whipple, *ibid.*, **35**, 1039 (1961).

[5] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

[6] To be published.

[7] I. Miyagawa, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 1169 (1954).

[8] S. Mizushima, Y. Morino and K. Higasi, *Sci. Papers Inst. Phys. Chem. Research*, **25**, 153 (1934).

sidered to be about 0.8 kcal/mol. Since R_T and $R_{G'}$ are polar the energy in solution is stabilized by reaction fields. This energy of stabilization is calculated from Eq. (3) by use of the parameters $\mu=3.0$ D and $(\varepsilon-1)/(2\varepsilon+1)=0.25$ for nonpolar solvents. The value of 0.75 kcal/mol obtained indicates that the energy of each isomer seems to be comparable in nonpolar solvents. As the stabilized energy is 1.38 kcal/mol in acetonitrile which is the most polar solvent used, the energy difference between these and R_G becomes 0.6 kcal/mol which corresponds to a variation of 1 c/s in $J_{AA'}$ It seems to be detectable in the spectra. In contrast to PMR data, the populations of $R_{G'}$ in carbon disulfide and acetonitrile from infrared data are 24% and 43%, respectively.⁶⁾ A change of more than 1 c/s in $J_{AA'}$ is expected because of the difference of 20% in the population obtained from IR. Since accuracy is within ±0.1 c/s, this is considerably different from the result shown in Table 1 that a slight change in $J_{AA'}$ was observed between polar and nonpolar solvents. We have at present no good explanation for this disagreement, but this problem should be worth further investigation.

Solvent Effects on Chemical Shift. The formation of an X–H bond causes an increase in the charge between the two nuclei, and an electric field E applied in the bond direction will draw this excess charge away from the hydrogen nucleus, thus decreasing its shielding coefficient. The magnitude of the decrease is given by the following equation⁹⁾:

$$\sigma = -2\times10^{-12}E\cos\theta-10^{-18}E^2 \qquad (6)$$

where θ is the angle between the X–H axis and E.

This experiment was designed to test qualitatively the validity of Eq. (6) at different protons of *meso*-2,3-dichlorobutane. The chemical shifts of methyl and methine protons are plotted *versus* a function of ε at 29°C in Fig. 5.

If the reaction field is adequately given by Eq. (3) and the population is independent of the ε of the solvent, these curves would be straight lines with the slope for methyl and methine protons of gauche form −0.1 and −0.3 ppm, respectively. Instead of straight lines, however, smooth curves with an opposite slope are obtained. The curvature of the curve for the methine proton may be due to the fact that populations of the gauche form become larger as the ε of the solvent increases. The fact that the curve for σ_{CH_3} bends in the opposite direction indicates that the reaction field along the C–CH_3 bond must have a sign opposite to that along the C–H bond, which is not true considering the molecular structure of the gauche form. Even if the estimated reaction field changes in magnitude and direction at each methyl and methine proton, it does not adequately describe the experimental chemical shift dependence on ε.

Thus, long range shielding by carbon-carbon single bonds must be considered.¹⁰⁾ The two

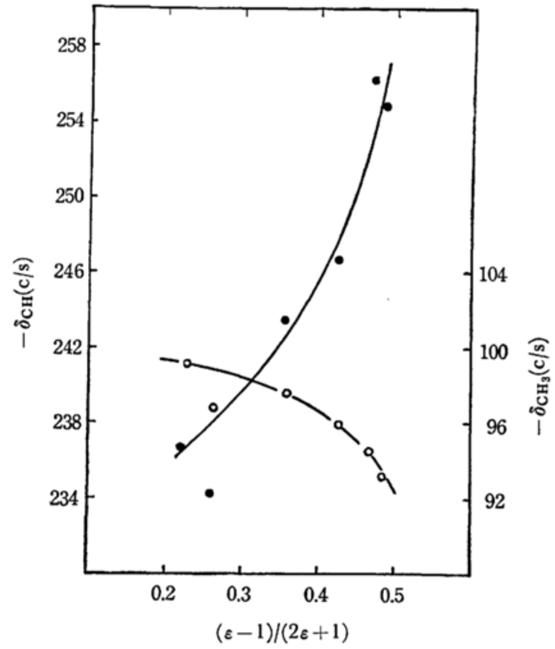

Fig. 5. δ values against the dielectric function. Solid circles indicate methine proton. Open circles indicate methyl proton.

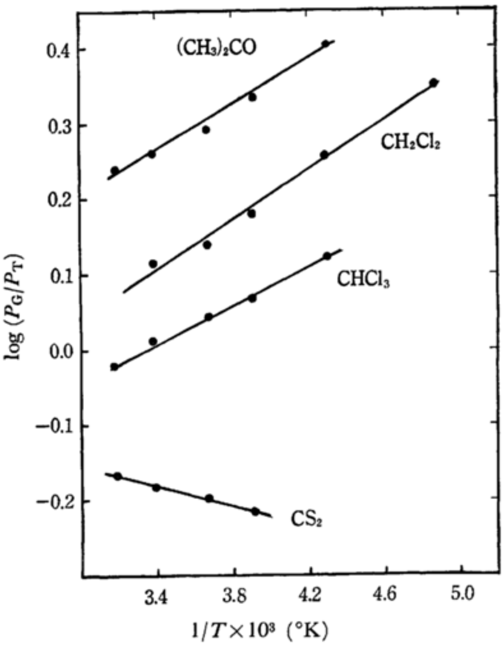

Fig. 6. Variation of population in *meso* 2,3-dichlorobutane as a function of temperature for different solvents.

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9) A. D. Buckingham, *Can. J. Chem. Eng.*, **38**, 300 (1960).

10) A. G. Mority and N. Sheppard, *Mol. Phys.*, **5**, 361 (1962).

forms of the molecule differ in that for M_T, the C-CH_3 bonds are gauche to the methine proton and for M_G, trans and gauche to the methine proton. The chemical shift difference is 0.11 ppm with the methine proton of the M_T to high field. Similarly, for the methyl group, the other C-CH_3 bond is trans to the methyl group in M_T, and gauche in M_G. The predicted shift is 0.15 ppm with the M_T to low field. This is also in fair agreement with the observed shifts for methyl and methine protons. The qualitative agreement is sufficient to support the assumption that the chemical shifts are primarily caused by the anisotropy of the C-C bond due to the difference in population of rotational isomers in each solution, rather than by the reaction field from the polar effect of the solvent. The contributions to the shielding of a nucleus from the two factors appear to be additive.

Temperature Dependence of Isomer Ratio. Figure 6 shows the populations of the trans and gauche forms in solvents as a function of temperature. It will at once be clear that the curves of populations in polar solvents is of opposite slope to that in nonpolar solvents. This result suggests that M_G is preferred in solvents of high dielectric constants. This is coincident with the tendency of solvent effects observed in the preceding section.