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Infrared Study of the Conformational Equilibria of *meso*- and *racemic*-2,3-Dichlorobutanes

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The conformational equilibria of rotational isomers of *meso*- and *racemic*-2,3-dichlorobutanes were investigated in various solvents by an infrared method. The coexistence of three rotational isomers was found for each of the *meso* and *racemic*-2,3-dichlorobutanes. However, the equilibrium concentrations changed depending on the solvent dielectric constant. The equilibrium concentration of the less polar form of a rotational isomer, in which the conformation is extended *trans* with respect to the Cl–C–C–Cl linkage, decreased as the solvent dielectric constant increased. The energy differences between the rotational isomers in the gaseous state and in acetonitrile solvent were also discussed.

One of the present authors has examined the solvent effect on the unperturbed molecular dimensions of chlorinated *trans*- and *cis*-1,4-polybutadienes, and has found that those of chlorinated *trans*-1,4-polybutadiene changed depending on the solvent dielectric constant.[1] For chlorinated *cis*-1,4-polybutadiene the situation was obscure. These experimental findings, however, can be correlated with the solvent effect on the conformational changes of the polymer chain.

The chemical structure of chlorinated 1,4-polybutadiene manifests a head-to-head linkage of polyvinyl chloride and has adjacent CHCl groups in the polymer chain. If the *trans* chlorination takes place to the unsaturated double bond of 1,4-polybutadiene, the chemical structures of the chlorinated parts of *trans*- and *cis*-1,4-polybutadienes become the *meso* and *racemic* structures respectively. In solution, the conformation of the chlorinated part having adjacent polar C–Cl bonds would vary under the influence of an electrostatic interaction by the surrounding solvent molecules. However, the conformation of the ethylenic linkage of chlorinated 1,4-polybutadiene may not strongly depend on the solvents. The conformational structure of chlorinated 1,4-polybutadiene in solution may, therefore, be mainly subjected to the local conformations of the chlorinated parts.

An infrared study of the conformations of *meso*- and *racemic*-2,3-dichlorobutanes (hereafter abbreviated as *meso*-DCB and *racemic*-DCB respectively) should give basic information on the stable local conformations of chlorinated *trans*- and *cis*-1,4-polybutadienes respectively. Although quantitative investigations of the equilibrium concentrations of rotational isomers of *meso*- and *racemic*-DCB have been reported by Bothner-By and Naar-Colin[2] and by Anet[3] using NMR method, no detailed studies of the equilibrium concentrations in solvents with different dielectric constants have been reported. Taufen *et al.*[4] have reported on the Raman spectra of *meso*- and *racemic*-DCB and discussed the qualitative equilibrium concentrations of the rotational isomers in pure liquids only.

In the present study the infrared spectra of *meso*- and *racemic*-DCB are examined in different solvents and are discussed in terms of the solvent effect on the equilibrium concentrations of rotational isomers. In addition, the energy difference between the rotational isomers is also discussed.

Experimental

Preparations of *meso*- and *racemic*-DCB. Dried chlorine gas was reacted with *trans*- and *cis*-2-butenes (Matheson Co.; purity, 99.8%) at −20°C for 3 hr in order to prepare *meso*- and *racemic*-DCB respectively. The products were washed with water and then with a 10% sodium carbonate solution, and were dried over anhydrous calcium chloride. The *meso*- and *racemic*-DCB were distilled under atmospheric pressure, whereupon fractions with boiling points of 113—114°C and 116—118°C respectively were collected.[5] A gas-chromatographic analysis (stationary phase, Carbowax 20 M; column temperature, 117.5°C; column length, 1 m; carrier gas, helium with a speed of 40 m*l*/min) indicated that the amount of impurity due to

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[1] M. Takeda, R. Endo and K. Ishizaki, Preprints for the 20th Annual Meeting of The Chemical Society of Japan, (April, 1967), 4N-205.

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

[3] A. L. Anet, *ibid.*, **84**, 747 (1962).

[4] H. J. Taufen, M. J. Murray and F. F. Cleaveland, *ibid.*, **65**, 1130 (1943).

[5] H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

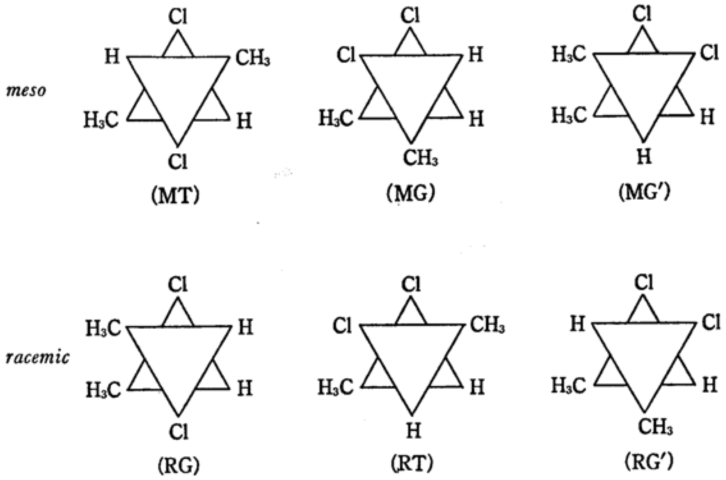

Fig. 1. The possible conformations for *meso*- and *racemic*-2,3-dichlorobutanes.

trichlorobutane is less than 1% for both isomers. The NMR spectra of the samples were completely identical with those observed by Bothner-By and Naar-Colin.[2]

Measurements of Infrared Spectra. The infrared spectra were recorded mainly for the region of 400—800 cm^{-1} using a Hitachi EPI-2 double-beam spectrophotometer with a KBr prism. Spectral observation was also made in the region of the NaCl prism for reference. In measuring the solution spectra, the absorption due to the solvent was compensated for by a variable-thickness cell filled with the solvent.

Results and Discussion

Spectra of Liquid State and the Existence of Rotational Isomers. The possible rotational isomers of *meso*- and *racemic*-DCB are shown in Fig. 1, and are designated by T, G or G′; in them the two terminal C–CH_3 bonds are located *trans* and *gauche* to each other. The *meso* and *racemic* isomers are identified by prefixing M and R respectively. In the case of the *meso* isomers, MG is a mirror image of MG′. Hence, both MG and MG′ should give the same spectrum.

In general, the frequencies of C–Cl stretching vibrations, which will hereafter be abbreviated as ν(C–Cl), appearing in the region of 760—550 cm^{-1} are characteristic of the geometrical arrangments near the C-Cl bond of chlorohydrocarbons.[6-8] The number of absorption bands and their relative intensities in this region should, therefore, give information on the existence of rotational isomers of DCB. Actually, as Fig. 2 shows, two bands, at 695 and 650 cm^{-1} for *meso*-DCB, and four bands, at 703, 692, 652, and 596 cm^{-1}, for *recemic*-DCB are observed in the ν(C–Cl) region. No absorption band attributable to the ν(C–Cl) is observed in the range from *ca.* 700 cm^{-1} up to 850 cm^{-1} for either *meso*- or *racemic*-DCB. All the absorption bands appearing at frequencies higher than 850 cm^{-1} can be assigned to the C–H stretching and deformation, and C–C stretching, vibrations. The bands at 535 and 420 cm^{-1} of *meso*-DCB, like those at 559 and 522 cm^{-1} of *racemic*-DCB, can be assigned to the skeletal bending vibrations, because the frequencies of these bands are too low to be assigned to the ν(C–Cl) vibrations.

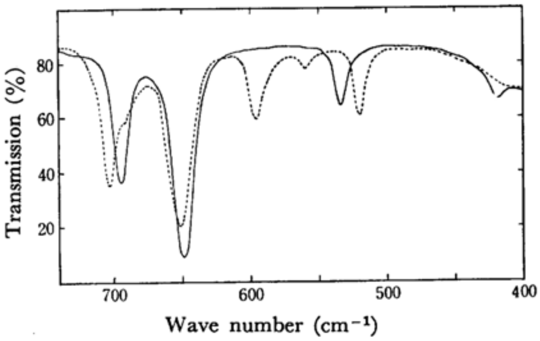

Fig. 2. The infrared spectra of liquid state.
Full line: *meso*, broken line: *racemic*

In the case of *meso*-DCB, MT should give only one infrared active ν(C–Cl) because of its C_i symmetry. The relative intensities of the two absorption bands observed in the ν(C–Cl) region would not depend on the solvents if these bands arose merely from MG and MG′. The relative intensities of these two bands, however, strongly depend on the solvents, as will be described below. This experimental finding suggests that these two bands are caused by two different components, namely, MT and MG or MG′.

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6) T. Shimanouchi, S. Tsuchiya and S. Mizushima, *Kobunshi (High Polymers, Japan)*, **8**, 202 (1959).

7) K. Nakamura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **78**, 1164 (1957).

8) J. J. Shimpman, J. L. Folt and S. Krimm, *Spectrochim. Acta*, **18**, 1603 (1962).

As for the liquid *racemic*-DCB, two absorption bands due to the ν(C–Cl) may be expected for each of the rotational isomers. The four absorption bands observed in the ν(C–Cl) region indicate the existence of more than one rotational isomer.

Solvent Effect on the Spectra and Assignment of the ν(C–Cl) Bands. Using the method proposed by Miyagawa,[9] we have calculated the dipole moments of the rotational isomers of *meso*- and *racemic*-DCB. The calculated values are listed in Table 1. In accounting for the difference in dipole moments, it can be said that the equilibrium concentrations of rotational isomers in solution vary because they are affected by a reaction field induced from the solvent molecules;[10] the polar forms of rotational isomers are stabilized in the solvent with a larger dielectric constant.

It follows that the ν(C–Cl) bands can be assigned to a definite rotational isomer by observing the intensity change in the ν(C–Cl) bands in solvents with different dielectric constants. Indeed, the changes in the spectra of *meso*- and *racemic*-DCB with the solvents are remarkable as is shown in Fig. 3.

TABLE 1. CALCULATED DIPOLE MOMENTS (in D.U.) FOR *meso*- AND *racemic*-2,3-DICHLOROBUTANES

Isomer	Chain conformation	Dipole moment
meso-DCB	MT	0
	MG	3.08
	MG′	3.08
racemic-DCB	RG	0.66
	RT	2.64
	RG′	3.33

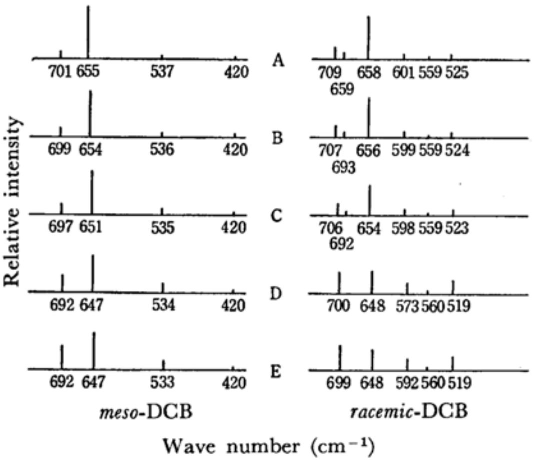

Fig. 3. The relative intensities of absorption bands in the various solvents (concentration: 0.8—0.5 mol/*l*, cell thickness: 0.047—0.055 mm).
A: *n*-Hexane, B: Cyclohexane,
C: Carbon disulfide, D: Cyclohexanone,
E: Acetonitrile

In the spectra of *meso*-DCB, the intensities of the bands at 695, 535, and 420 cm^{-1} increase, and that of the bands at 650 cm^{-1} decreases, as the dielectric constant of the solvent increases from 1.89 (*n*-hexane) to 37.5 (acetonitrile). At the same time, a downward shift of the absorption frequency is noted in the polar solvents.[*1] In the light of the notations proposed by Shimanouchi *et al.*,[6] the types of ν(C–Cl) bands for DCB may be classified as S_C, S_{CI} and S_H, where the subscripts represent the *trans* substituents on the C–C bond adjacent to a C–Cl bond. According to this classification, the types of ν(C–Cl) bands arising from the individual rotational isomers are denoted as S_{CI} for MT and RG, as S_C for RG′, as S_H for RT, and as S_C and S_H for both MG and MG′.

In the spectrum of *meso*-DCB, the intense bands at 650 cm^{-1}, the intensity of which decreases in the solvent with the larger dielectric constant, is ascribed mainly to the antisymmetric S_{CI}-type vibration of the nonpolar MT. The 695 cm^{-1} band is assigned to the S_C-type vibration of the polar MG and MG′ by taking account of the increase in its intensity in the solvent with the larger dielectric constant. A remaining band, due to the S_H-type vibration of MG and MG′, may be expected in the range around 640—600 cm^{-1}. In the Raman spectrum[4] of liquid *meso*-DCB, an intense band at 703 cm^{-1} and a somewhat weak band at 652 cm^{-1} are found in the ν(C–Cl) region. The antisymmetric S_{CI}-type vibration of MT is a Raman inactive vibration and, hence, should not be observable in the Raman spectrum. The weak Raman band at 652 cm^{-1} must, therfore, be assigned to the infrared and Raman-active S_H-type vibrations of MG and MG′. The intense Raman band at 703 cm^{-1} probably involves the symmetric S_{CI}-type vibration of MT and the infrared and Raman-active S_C-type vibrations of MG and MG′. The Raman-active symmetric S_{CI}-type vibration should not give any infrared absorption because of the C_i symmetry of MT. Consequently, the infrared band at 695 cm^{-1} may be attributed to the S_C-type vibration of MG and MG′, while that at 650 cm^{-1} may be said to consist of two components of ν(C–Cl) bands; one arises from the S_{CI}-type vibration of MT, and the other, from the S_H-type vibrations of MG and MG′.

The above assignments agree almost entirely with an empirical rule established by Shimanouchi

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9) I. Miyagawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 1061 (1954).

10) I. Watanabe, S. Mizushima and Y. Mashiko, *Nippon Kwagaku Kwaishi (J. Chem. Soc. Japan)*, **64**, 962 (1943).

[*1] Hereafter, for convenience, the frequencies of absorption bands given are those observed in the liquid spectra.

et al.[6] and by Shipman *et al.*[8] According to this rule, the ν(C–Cl) *trans* to a C–Cl or C–C bond and that *trans* to a C–H bond usually appear in the frequency regions of 700—655 cm^{-1} and 640—600 cm^{-1} respectively. With respect to *racemic*-DCB, therefore, two ν(C–Cl) bands arising from each of RG and RG′ may be observed nearly in the former frequency region, and those arising from RT, in the latter one. The 692 and 652 cm^{-1} bands, the intensities of which decrease with an increase in the solvent dielectric constant, can be assigned to the S_{Cl}-type vibrations of the less polar RG. The 703 and 596 cm^{-1} bands can be assigned to the S_{C} and S_{H}-type vibrations of polar RG′ and RT respectively, since their intensities increase with an increase in the solvent dielectric constant. Although two S_{C} bands and two S_{H} bands must be expected for RG′ and RT respectively, in this case no bands except the 703 and 596 cm^{-1} bands are found in the ν(C–Cl) region. This absence of bands cannot be explained at present.

For liquid *racemic*-DCB, Taufen *et al.*[4] have observed the three Raman bands at 695, 653, and 599 cm^{-1} and have assigned them to RG, RG′, and RT respectively. The assignment for the former two bands is the reverse of our interpretation. However, the Raman band at 695 cm^{-1} is believed to be related not only to RG but also to RG′, for the more intense band at 703 cm^{-1} of RG′ and the weaker band at 692 cm^{-1} of RG in the infrared spectrum of the liquid state are so close in their frequencies (see Fig. 2) that the Raman bands corresponding to them could not be separately observed in the Raman spectrum. As is evident from the behavior of the infrared band at 652 cm^{-1} for the solvents, the Raman band at 653 cm^{-1} can be assigned to the S_{Cl}-type vibration of RG.

The empirically-established correlations between the infrared absorption bands and the structures of rotational isomers are summarized in Table 2.

TABLE 2. ASSIGNMENTS OF ABSORPTION FREQUENCY

Isomer	Frequency	Assignment[a)]	Rotational isomer
meso-DCB	695	S_{C}	MG, MG′
	650	S_{Cl} S_{H}	MT MG, MG′
	535	δ	
	420	δ	
racemic-DCB	703	S_{C}	RG′
	692	S_{Cl}	RG
	652	S_{Cl}	RG
	596	S_{H}	RT
	559	δ	
	522	δ	

a) S and δ denote C–Cl stretching and skeletal bending vibrations respectively.

Equilibrium Concentrations of Rotational Isomers in Various Solvents. We can determine the change in the equilibrium concentrations of rotational isomers in solution from the change in the intensity ratio of the ν(C–Cl) bands belonging to each of the rotational isomers.

In the case of *meso*-DCB, the optical densities of the 695 cm^{-1} and 650 cm^{-1} bands, D_{695} and D_{650}, can be represented with reference to the concentrations of rotational isomers as follows:

$$D_{695} = K_{\mathrm{G}} C_{\mathrm{G}} l \tag{1}$$

$$D_{650} = K_{\mathrm{G}}' C_{\mathrm{G}} l + K_{\mathrm{MT}} C_{\mathrm{MT}} l \tag{2}$$

where C_{MT} is the concentration of MT; C_{G}, the sum of the concentrations of MG and MG′, which are equal in population, and l, the optical path-length of the cell. K_{G} is the absorption coefficient of the 695 cm^{-1} band, which arises from MG and MG′. Equation (2) is introduced by considering the 650 cm^{-1} band to be composed of two types of ν(C–Cl) bands belonging to MT and to MG and MG′; hence, K_{MT} and K_{G}' are the absorption coefficients arising from the component of MT and from that of MG and MG′ respectively. Dividing Eq. (2) by Eq. (1), we obtain:

$$C_{\mathrm{MT}}/C_{\mathrm{G}} = (K_{\mathrm{G}}/K_{\mathrm{MT}})(D_{650}/D_{695}) - (K_{\mathrm{G}}'/K_{\mathrm{MT}}) \tag{3}$$

We have at present no available information for determining the ratios of the absorption coefficients in Eq. (3). However, in the case of liquid *meso*-2,3-dibromobutane the values of $K_{\mathrm{G}}/K_{\mathrm{MT}}$ and $K_{\mathrm{G}}'/K_{\mathrm{MT}}$ are determined to be 0.534 and 0.223 respectively.*2 Taking into account the similarity in the molecular structures, the ratios of absorption coefficient which are experimentally determined for *meso*-2,3-dibromobutane can be transferred to those for *meso*-DCB; we thus obtain:

$$C_{\mathrm{MT}}/C_{\mathrm{G}} = 0.534(D_{650}/D_{695}) - 0.223 \tag{4}$$

Putting 2.27, the observed value of D_{650}/D_{695} for the liquid state, into Eq. (4), we obtain the equilibrium concentrations of the rotational isomers of liquid *meso*-DCB at 28°C as $C_{\mathrm{MT}}=0.50$ and $C_{\mathrm{G}}=0.50$. Further, it is also possible to determine the value of the equilibrium concentration by an independent method; *e. g.*, the mean dipole moment of the liquid state, which can be calculated from the dielectric constant of the liquid through

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*2 Unlike the results obtained for *meso*-DCB, in the spectrum of liquid *meso*-2,3-dibromobutane the three ν(C–Br) bands are separately observed at 552 cm^{-1} for MT, and at 636 and 600 cm^{-1} for MG and MG′. Therefore, the determination of the values of $K_{\mathrm{G}}/K_{\mathrm{MT}}$ and $K_{\mathrm{G}}'/K_{\mathrm{MT}}$ becomes possible on the basis of the ratios of the observed optical densities, D_{636}/D_{552} and D_{600}/D_{552}, and the equilibrium concentrations of each rotational isomer, which are calculated from the dielectric constant (6.245) of the liquid.[11]

11) K. Iimura, to be published.

TABLE 3. EQUILIBRIUM CONCENTRATIONS OF THE ROTATIONAL ISOMERS IN THE VARIOUS SOLVENTS

Solvent	MT	MG	MG′	RT	RG	RG′	Method
n-Hexane (1.89)	0.74	0.13	0.13	0.24	0.58	0.18	IR study (at 28°C) present investigation
Cyclohexane (2.02)	0.71	0.14_5	0.14_5	0.24	0.58	0.18	
Carbon disulfide (2.64)	0.70	0.15	0.15	0.26	0.52	0.22	
Liquid sample*	0.50	0.25	0.25	0.34	0.39	0.27	
Cyclohexanone (18.3)	0.49	0.25_5	0.25_5	0.42	0.27	0.31	
Acetonitrile (37.5)	0.30	0.35	0.35	0.43	0.25	0.32	
Carbon disulfide	0.58	0.21	0.21			0.14	NMR study (at 29°C) by Kondo *et al.*[17]
Acetonitrile	0.33	0.33	0.33				
Carbon disulfide	0.64	0.18	0.18				NMR study by Bothner-By and Naar-Colin[2]
Liquid sample	0.52	0.24	0.24	0.33	0.33	0.33	

The numerals in parentheses indicate the dielectric constant of solvent.

* Dielectric constants of pure liquids are 8.823 and 9.761 for *meso*- and *racemic*-DCB, respectively.[5]

Onsager equation.[*3] The equilibrium concentration at 25°C thus determined is $C_{MT}=0.49$ and $C_G=0.51$. It will be seen that the agreement with the equilibrium concentration observed by the infrared method is very satisfactory.

In estimating the equilibrium concentration in solution, it is necessary to examine the applicability of Eq. (4) since, in general, the value of the absorption coefficient of an infrared band changes depending upon the nature of the solvent.[13] According to the study by Hirota, however, the ratio of the absorption coefficients of an infrared band in two solutions is kept constant, is determined by the solvents, and is common to the absorption bands of any molecules.[14] The ratio of the absorption coefficient of the ν(C–Cl) bands of DCB in a solvent may, therefore, change little; hence, no serious error will be introduced into the values of the equilibrium concentrations in the various solvents obtained through Eq. (4). The equilibrium concentrations thus obtained for *meso*-DCB are listed in Table 3.

With respect to *racemic*-DCB, the values of the absorption coefficients can not be determined by the above-described method, for all three rotational isomers have different dipole moments. The ratios of absorption coefficients were, therefore, obtained from the equilibrium concentrations, which were themselves estimated by means of the energy difference between the rotational isomers in the gaseous state. Let D be the optical density; k, the absrption coefficient; C, the concentration or the number of molecules of the rotational isomer, and f, the partition function. We then have:

$$D_{\rm I}/D_{\rm II} = (k_{\rm I}/k_{\rm II})(C_{\rm I}/C_{\rm II}) = (k_{\rm I}/k_{\rm II})(f_{\rm I}/f_{\rm II})\exp(-\Delta E/\boldsymbol{R}T) \qquad (5)$$

where ΔE is the energy difference between the two rotational isomers, which are discriminated by the subscripts I and II. The ratio of the partition function can be assumed to be approximately unity.[15] For the case of 1,2-dichloroethane, Watanabe *et al.*[16] have calculated the ratio of the partition function of the *gauche*-form to that of the *trans*-form, and they have determined the value to be 0.95 at 25°C. From the assumption above mentioned, the value of $C_{\rm I}/C_{\rm II}$ can be estimated from ΔE, and then the ratio of the absorption coefficient, $k_{\rm I}/k_{\rm II}$, can be determined by means of the observed ratio of optical densities in Eq. (5).

The energy differences between RG′ and RG and between RT and RG are found to be 1.1 kcal/mol and 1.0 kcal/mol respectively by measuring the temperature change in the absorption intensities, as will be described below. From these data, the values of $C_{RG'}/C_{RG}$ and C_{RT}/C_{RG} at 28°C are calculated as 0.159 and 0.188 respectively. The ratios of the absorption coefficients, $k_{RG'}/k_{RG}$ and k_{RT}/k_{RG}, are then determined to be

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[*3] The equilibrium concentration in the liquid stated is calculated from the following relation:

$$m^2 = (\mu^2_{MT}N_{MT} + \mu^2_G N_G)/(N_{MT} + N_G)$$

where, m is the mean dipole moment of the liquid; μ, the dipole moment, and N, the number of molecules which are discriminated by the subscripts (G shows two *gauche*-forms). The calculated dipole moments listed in Table 1 are used for μ_{MT} and μ_G. The value of m^2 was calculated by the Onsager equation:[12]

$$m^2 = (9\boldsymbol{k}T/4\pi\boldsymbol{N})(M/d)[(\varepsilon-n^2)(2\varepsilon+n^2)/\varepsilon(n^2+2)^2]$$

where $\boldsymbol{k}$ is the Boltzman constant; $\boldsymbol{N}$, the Avogadro number, and M, the molecular weight. The values of the dielectric constant ($\varepsilon=8.823$), the density ($d=1.1023$), and the refractive index ($n=1.4386$) at 25°C were taken from the paper of Lucas and Gould.[5]

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

[13] T. Yoshino, This Bulletin, **27**, 592 (1954).

[14] E. Hirota, *ibid.*, **27**, 295 (1954).

[15] Y. Morino, I. Miyagawa, T. Haga and S. Mizushima, *ibid.*, **28**, 165 (1955).

[16] I. Watanabe, S. Mizushima and Y. Morino, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **63**, 1131 (1942).

[17] S. Kondo, T. Tagami, K. Iimura and M. Takeda, This Bulletin, **41**, 790 (1968).

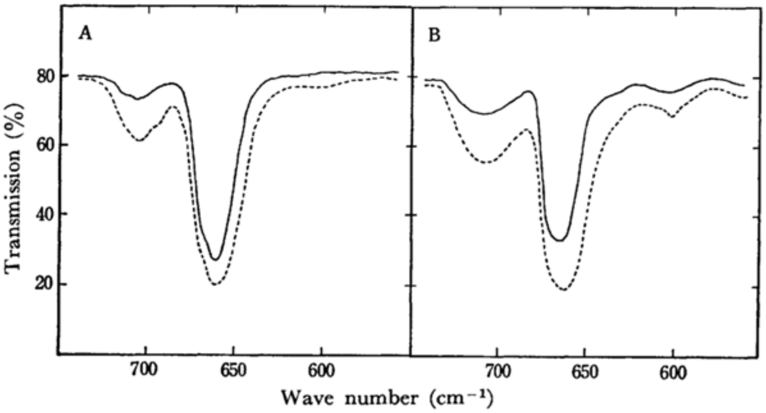

Fig. 4. The infrared spectra of gaseous state at the different temperatures.
A: *meso* (full line: 29°C, broken line: 146°C),
B: *racemic* (full line: 28°C, broken line: 151°C)

0.987 and 0.292 respectively from the observed ratios of the optical densities, $D_{RG'}/D_{RG}=0.157$ and $D_{RT}/D_{RG}=0.055$, at 28°C. The equilibrium concentrations of *racemic*-DCB in various solvents are obtained using these ratios of absorption coefficients; they are listed in Table 3, together with those obtained for *meso*- and *racemic*-DCB by the NMR investigations.[2,17)]

Although there are only few solvents available to be compared commonly for both infrared and NMR method, a fair agreement between the data obtained by the two independent methods is noted for the liquid state and the acetonitile solution of *meso*-DCB. For the carbon disulfide solution, however, the data for MT obtained by the infrared method are slightly larger than those obtained by the NMR methods. With respect to liquid *racemic*-DCB, the data obtained by the infrared method agree almost entirely with those obtained by the NMR method. In our previous NMR investigation it was noted that the vicinal coupling constants of *racemic*-DCB depends little upon the solvents.[17)] In contrast to the infrared results shown in Table 3, this experimental finding leads to the conclusion that the equilibrium concentrations of *racemic*-DCB does not remarkably change under the influence of solvents. However, as is shown in Fig. 3, the considerable changes in the intensity of the ν(C–Cl) bands in the different solvents suggest that the equilibrium concentrations change depending upon the solvents.

Spectra of the Gaseous State and the Energy Difference of Rotational Isomer. The spectra of gaseous *meso*- and *racemic*-DCB at different temperatures are shown in Fig. 4. The bands appearing at 706 and 661 cm^{-1} of *meso*-DCB correspond to those at 695 and 650 cm^{-1} respectively in the liquid state. For the gaseous *racemic*-DCB the bands corresponding to those at 703, 652, and 596 cm^{-1} of the liquid state are observed at 710, 665, and 603 cm^{-1} respectively. In general, from the temperature-dependence of the band intensities, the energy difference, ΔE, between the rotational isomers can be calculated by Eq. (5). Since, for *racemic*-DCB in the liquid state, the very weak 692 cm^{-1} band appears as a shoulder band on the more intense 703 cm^{-1} band, we have assumed that the broad band at 710 cm^{-1} in the geseous state arises mainly from the RG′.

In the case of *meso*-DCB the ratio of the intensity of the 661 cm^{-1} band to that of the 706 cm^{-1} band does not directly represent the abundance ratio of

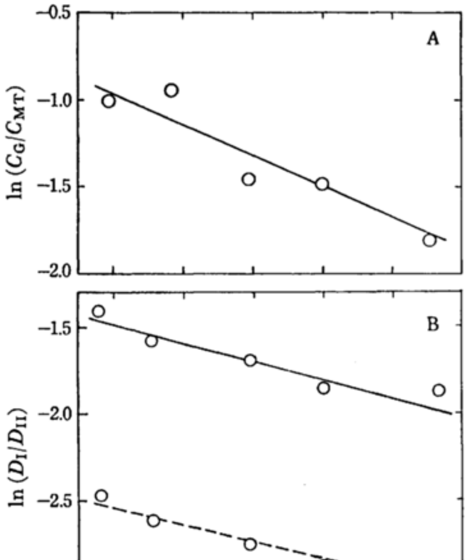

Fig. 5. The temperature dependences of abundance ratio and of intensity ratio in gaseous state.
A: *meso*, B: *racemic* (full line: $D_I/D_{II}=D_{710}/D_{665}$, broken line: $D_I/D_{II}=D_{603}/D_{665}$)

the two isomers. The abundance ratio, C_{MT}/C_G, was, therefore, estimated through Eq. (3), and then ΔE was obtained by means of Eq. (5).

As Fig. 5 shows, relations of the logarithmic values of the intensity ratios or the abundance ratio against $1/T$ were found to be linear. From the slope of the straight lines, the energy differences in the gaseous state are estimated; they are listed in Table 4.

TABLE 4. ENERGY DIFFERENCES BETWEEN THE ROTATIONAL ISOMERS IN GASEOUS STATE (kcal/mol)

Energy difference*	Observed value	Calculated value[17]
$\Delta E^{gas}_{MG\text{-}MT}$	1.7	1.45
$\Delta E^{gas}_{RG'\text{-}RG}$	1.1	0.85
$\Delta E^{gas}_{RT\text{-}RG}$	1.0	0.75

* The energy difference between two rotational isomers of which are shown by the subscripts.

The observed values of ΔE are of the same order as the calculated results of our previous report.[17] The value of $\Delta E^{gas}_{MG\text{-}MT}$ for *meso*-DCB is larger than the ΔE between *gauche* and *trans* forms of 1,2-dichloroethane (1.2 kcal/mol).[18] This is understandable, for the steric repulsion between the two methyl groups is somewhat larger than that between the chlorine atom and the methyl group,[*4] and therefore the difference in steric potential between the MG of *meso*-DCB and the corresponding *gauche* form of 1,2-dichloroethane is to be larger than that between the *trans* forms of these two substances. In the case of *racemic*-DCB, the potential energies of RG′ and RT are almost the same in magnitude, both higher than that of RG by approximately 1.0 kcal/mol. These results suggest that the energy difference between the rotational isomers of 2,3-dichlorobutane is mainly affected, just as in the case of 1,2-dichloroethane, by the skeletal conformations of the Cl-C-C-Cl linkage and an electrostatic interaction induced by the two C-Cl bonds.

Temperature Change in Spectra in the Acetonitrile Solution. Figure 6 shows the temperature dependence of the abundance ratio, C_G/C_{MT}, for *meso*-DCB, and the intensity ratio of the infrared band for *racemic*-DCB in the acetonitrile solvent. In contrast with the same relation for the gaseous state (see Fig. 5), in this case positive slopes are obtained against $1/T$. The results can be explained in terms of change in energy difference between the rotational isomers, a change which is caused by an interaction between the molecular dipole and its induced moment in the surrounding solvent medium. By taking Onsager's field[12] as the reaction field,[10] when a molecule of dipole moment, μ, in the gaseous state is transferred from the vacuum into the solvent medium of the dielectric constant, ε, the potential energy is lowered by:

$$E_r = (\varepsilon-1)\mu^2/(2\varepsilon+1)a^3 \qquad (6)$$

where a is the radius of the solute molecule.

Putting the dipole moments listed in Table 1 and the dielectric constant of acetonitrile (37.5) into Eq. (6), the energy differences between the rotational isomers in the solution can be calculated as $\Delta E^{sol}_{MG\text{-}MT} = 0.02$ kcal/mol, $\Delta E^{sol}_{RG'\text{-}RG} = -0.73$ kcal/mol, and $\Delta E^{sol}_{RT\text{-}RG} = -0.24$ kcal/mol.[*5] The observed energy differences in the solution, which are determined from the linear relations shown

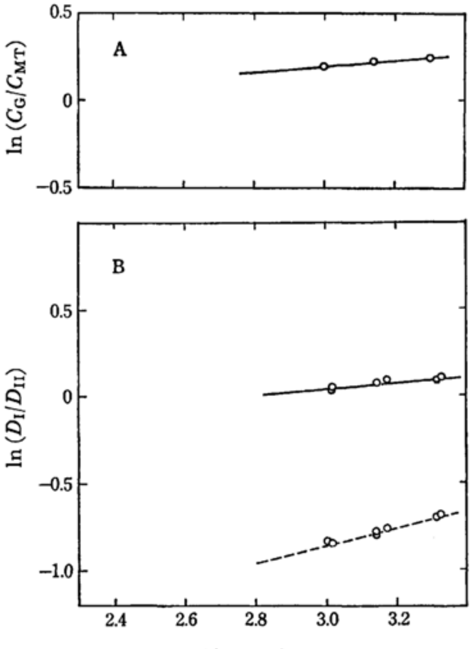

Fig. 6. The temperature dependences of abundance ratio and of intensity ratio in acetonitrile solution.
A: *meso*, B: *racemic* (full line: $D_I/D_{II}=D_{699}/D_{648}$, broken line: $D_I/D_{II}=D_{592}/D_{648}$)

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18) T. Shimanouchi, H. Tsuruta and S. Mizushima, *Sc. Pap. Inst. Phys. Chem. Res. Tokyo*, **42**, 165 (1945).

[*4] The van der Waals radii of the chlorine atom and the methyl group are 1.8 and 2.0 Å respectively (L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York (1940)).

[*5] In calculating E_r, a is roughly estimated by the equation; $M/d=(4\pi a^3/3)\boldsymbol{N}$, where M and d are the molecular weight and the density of the solute molecule, and $\boldsymbol{N}$, the Avogadro number. As the values of the densities, 1.1023 and 1.1063 were used for *meso*- and *racemic*-DCB respectively.[5] To estimate the energy difference in the solution, ΔE^{sol}, the calculated ΔE^{gas} values listed in Table 4 were used.

in Fig. 6, are $\Delta E^{\mathrm{sol}}_{\mathrm{MG\text{-}MT}} = -0.3$ kcal/mol, $\Delta E^{\mathrm{sol}}_{\mathrm{RG'\text{-}RG}} = -0.3$ kcal/mol, and $\Delta E^{\mathrm{sol}}_{\mathrm{RT\text{-}RG}} = -1.0$ kcal/mol.

Although some discrepancies between the calculated and observed energy differences in the solution are noted, the decreases in the potential energy of the polar MG, RG′ and RT conformations in the acetonitrile solvent can be explained qualitativily by appling Onsager's reaction field.

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