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Infrared Study of Rotational Isomers of *meso*- and *racemic*-2,3-Dibromobutane

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The infrared spectra of *meso*- and *racemic*-2,3-dibromobutanes in solution and in gaseous states were obtained in the study of the rotational isomers. The occurrence of three rotational isomers was confirmed for both *meso*- and *racemic*-isomers. The quantitative estimation of the equilibrium concentrations of the rotational isomers was also made in various solvents. The energy difference between the rotational isomers was determined by measuring the temperature-dependence of the absorption intensities of ν(C–Br) vibrations.

In our infrared investigation of *meso*- and *racemic*-2,3-dichlorobutanes,[1] it has been shown that three rotational isomers exist for both *meso*- and *racemic*-isomers, and that the equilibrium concentrations change depending upon the solvent dielectric constants.

In the present study the infrared spectra of *meso*- and *racemic*-2,3-dibromobutanes, the molecular structures of which are analogous to those of *meso*- and *racemic*-2,3-dichlorobutanes, will be observed, and the conformational equilibria of the rotational isomers in solvents of different dielectric constants and the energy difference between the rotational isomers in the gaseous state will be investigated.

The existence of three rotational isomers for both *meso*- and *racemic*-isomers has been established by studies of the Raman spectra[2] and of the nuclear magnetic resonance (NMR).[3,4] However, in these investigations, no quantitative spectroscopic estimation of the conformational equilibria in various solvents, or of the difference in energy between the rotational isomers were made. In the recent NMR investigation of *meso*-2,3-dibromobutane reported by Deb,[5] the energy difference between the rotational isomers was determined to be 1.0 kcal/mol. However, this value seems too small compared with that of 1,2-dibromoethane.

Experimental

The *meso*- and *racemic*-2,3-dibromobutanes (hereafter abbreviated as *meso*- and *racemic*-DBB respectively) were prepared by the addition of bromine to *trans*- and *cis*-butene-2 (Matheson Co.; purity, 99.8%) at −15—−18°C. The materials were distilled, and the fractions with boiling points of 73.0—75.0°C/55 mmHg for the *meso* isomer and of 77.0—79.0°C/60 mmHg for the *racemic* isomer were collected (reported boiling points: *meso*, 74—74.2°C/50 mmHg; *racemic*, 75.6°C/50 mmHg[6]). The NMR spectra of the materials were completely identical with those observed by Bothner-By and Naar-Colin[3] and by Anet.[4] A gas-chromatographic analysis indicated also that the purity is more than 99% for both isomers. The infrared spectra were recorded mainly for the region of 800—400 cm^{-1} using a Hitachi EPI-2 double-beam spectrophotomer 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-thickenss cell filled with the solvent. The gas-phase spectra were obtained using a gas cell with an optical path-length of 7 cm and with a heating device.

Results and Discussion

ν(C–Br) Bands and Rotational Isomers. As Fig. 1 shows, it is possible for three rotational isomers to exist in both *meso*- and *racemic*-DBB. The conformations of the rotational isomers are designated by T, G, or G′, indicating whether the carbon chains are located *trans* or *gauche*. As for the *meso*-isomer, MG and MG′ are mirror images of each other and are not different in their infrared spectra.[*1]

The ν(C–Br) vibrations for bromine attached to the secondary carbon atom are usually observed in the region of 620—520 cm^{-1}; they appear at different frequencies depending upon the conformational

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1) K. Iimura, M. Kawakami and M. Takeda, This Bulletin **42**, 2091 (1969).

2) N. J. Taufen, M. J. Murray and F. F. Cleaveland, *J. Am. Chem. Soc.*, **65**, 1130 (1943).

3) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **84**, 743 (1962).

4) A. L. Anet, *ibid.*, **84**, 747 (1962).

5) K. K. Deb, *J. Phys. Chem.*, **71**, 3095 (1967).

6) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 1577 (1939).

[*1] Hereafter the term MG will be used to represent two *gauche* forms, MG and MG′.

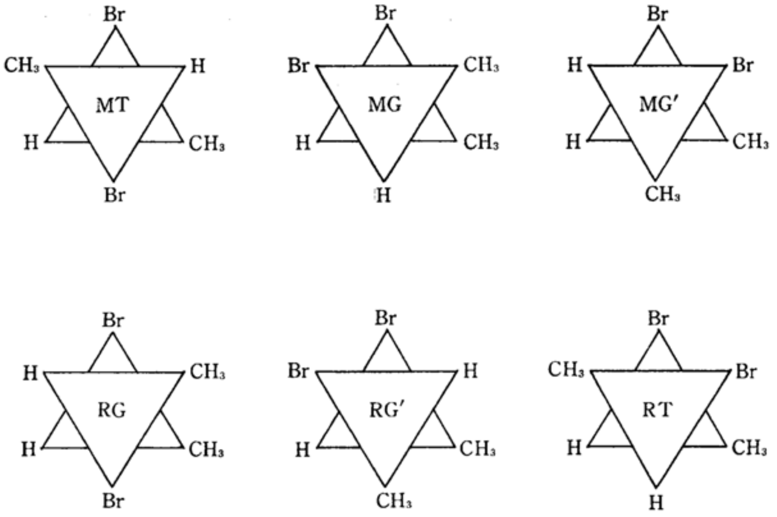

Fig. 1. The posible conformations of rotational isomers.

structures of the rotational isomers.[7,8] Figure 2 shows the infrared spectra of *meso*- and *racemic*-DBB in the pure liquid state. The strong band at 552 cm^{-1} and the weaker band at 600 cm^{-1} of *meso*-DBB, and the two strong bands at 561 and 543 cm^{-1} of *racemic*-DBB, can be assigned to the ν(C–Br) vibrations. The absorption band at 635 cm^{-1} of *meso*-DBB and those at 648 and 632 cm^{-1} of *racemic*-DBB are found somewhat apart from the ν(C–Br) region. However, these absorption bands can safely be assigned to the ν(C–Br) vibrations, because the infrared spectra in the NaCl region of *meso*- and *racemic*-DBB correspond fully to those of *meso*- and *racemic*-2,3-dichlorobutanes respectively[9] and because the frequencies of these absorption bands are too low to be assigned to the CH_3 rocking vibrations. The frequencies associated with the skeletal bending modes occur, in general, below 500 cm^{-1}. The bands at 466 cm^{-1} of *meso*-DBB and at 444 cm^{-1} of *racemic*-DBB are assigned to these modes. The weak band at 502 cm^{-1} of *racemic*-DBB is perhaps due to the skeletal bending mode.

We have calculated the dipole moment of the rotational isomers by means of the method proposed by Miyagawa.[10] The values thus calculated are listed in Table 1. In accounting for the difference in dipole moment, it can be said that the population of the rotational isomers in solution changes because it is affected by a reaction field induced by the solvent molecules.[11] The assignment of ν(C–Br) bands to each of the rotational isomers, therefore, becomes possible if we measure the intensity change of these bands in a different solvent, because a

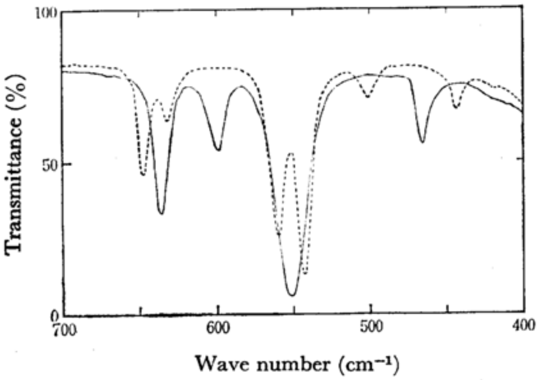

Fig. 2. Infrared spectra in liquid state.
Full line;*meso*-DBB, broken line; *racemic*-DBB.

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

Isomer	Chain conformation	Dipole moment
meso-DBB	MT	0
	MG	2.78
	MG′	2.78
racemic-DBB	RG	1.08
	RT	2.24
	RG′	3.30

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

[8] F. F. Bentley and N. T. McDevitt, *Spectrochim. Acta*, **20**, 105 (1964).

[9] K. Iimura, M. Kawakami and M. Takeda, unpublished data.

[10] I. Miyagawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 1165 (1954).

[11] I. Watanabe, S. Mizushima and Y. Mashiko, *ibid.*, **64**, 962 (1943).

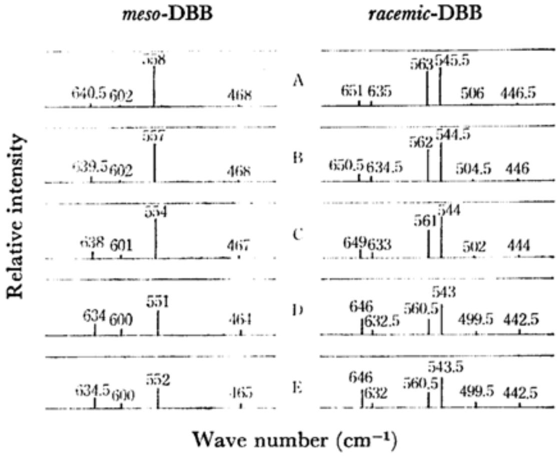

Fig. 3. Infrared spectra in various solvents.
A, *n*-hexane; B, cyclohexane; C, carbon disulfide, D, cyclohexanone; E, acetonitrile.
Temperature, 29°C, Concentration, 0.50—0.85 mol/*l*; Cell-thickness, 0.047—0.054 cm

change in the intensity will result from a change in the population. Figure 3 gives the solvent-effect for the intensity of the ν(C–Br) bands.

In the solution spectra of *meso*-DBB, the intensities of the bands at 635 and 600 cm^{-1} increase, and that of the band at 552 cm^{-1} decreases, as the dielectric constant of the solvent increases from 1.89 (*n*-hexane) to 37.5 (acetonitrile). At the same time it is noted that the positions of the ν(C–Br) bands shift downward in their frequencies by *ca.* 2—6 cm^{-1}.*[2] According to Watanabe *et al.*,[11] when a molecule of the dipole moment, μ, in the gaseous state is transferred from the vacuum into the solvent medium of a dielectric constant, ε, the potential energy is lowered by:

$$Er = (\varepsilon-1)\mu^2/(2\varepsilon+1)a^3 \tag{1}$$

where a is the radius of the solute molecule. In view of the above findings, the population of the polar rotational isomer may be expected to become dominant in the solvent of the larger dielectric constant, since the values of a can be considered to be not very different for each rotational isomer. The two bands at 635 and 600 cm^{-1} can, therefore, be assigned to the ν(C–Br) vibrations arising from the polar MG, and the band at 552 cm^{-1}, to that arising from the nonpolar MT, the population of which would be expected to decrease in the polar solvent. As MT has a center of symmetry, only one ν(C–Br) vibration is possible in an infrared absorption; this is related to the antisymmetric stretching vibration of the C–Br bonds. The band at 552 cm^{-1} must be due to the antisymmetric ν(C–Br) vibration. On the other hand, two ν(C–Br) vibrations may be expected from MG, since this conformation has no center of symmetry. The two bands at 635 and 600 cm^{-1} correspond exactly to these vibrations. In the Raman spectrum of liquid *meso*-DBB,[2] an intense band at 632 cm^{-1} and a weaker band at 600 cm^{-1} are found in the ν(C–Br) region. Since the ν(C–Br) vibrations of MG are active for both Raman and infrared spectra, these two bands, the frequencies of which coincide exactly with those of the infrared bands, are considered to have arisen from MG. However, the intense Raman band at 632 cm^{-1} possibly involves the Raman active symmetric ν(C–Br) vibration of MT. It is very probable that no Raman band is found near 550 cm^{-1} because the infrared band at 552 cm^{-1} is a Raman-inactive antisymmetric ν(C–Br) vibration.

As is evident from Fig. 3, the intensity change in the ν(C–Br) band of *racemic*-DBB depending with the solvent is also remarkable. Two ν(C–Br) vibrations are possible in the infrared absorption for each of the three rotational isomers of *racemic*-DBB, which have no center of symmetry. The bands at 632 and 561 cm^{-1}, the intensities of which decrease with an increase in the solvent dielectric constant, can be assigned to the ν(C–Br) vibrations of the less polar RG. On the other hand, the 648 and 543 cm^{-1} bands may be ascribed to the ν(C–Br) vibrations of polar RG′ or RT, since their intensities increase as the dielectric constant of solvent increases. It is noted, however, that the solvent-effect on the intensity change of the 648 cm^{-1} band is different from that on that of 543 cm^{-1} band; that is, the increase in the relative intensity of the 648 cm^{-1} band in the polar solvent is remarkable in comparison with that of the 543 cm^{-1} band. By taking account of the facts that the potential energies of RG′ and RT in the gaseous state are almost the same order in magnitude, and that both are higher than that of RG by approximately 1.5 kcal/mol, as will be described below, the population of the most polar RG′ may be expected to become dominant in the acetonitrile solvent over that of RT. Therefore, the bands at 648 and 543 cm^{-1} may be considered to arise from RG′ and RT respectively. This assignment is also in accord with the experimental finding that the position of the ν(C–Br) vibration *trans* to a C–C bond appears usually at a frequency higher than that *trans* to a C–H bond.[7,8] Although a residual ν(C–Br) vibration must be expected for both RG′ and RT, no bands except the 648 and 543 cm^{-1} bands are found in the ν(C–Br) region. The absence of bands cannot be explained at present.

Taufene *et al.*[2] have found three Raman bands, at 633, 563, and 540 cm^{-1}, for *racemic*-DBB in the liquid state; they have ascribed them to RG, RG′, and RT respectively. The assignment of the former two bands is the reverse of our interpretation. It

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*[2] A downward shift of absorption frequencies is also noted for *racemic*-DBB; hence, hereafter for convenience the frequencies of the absorption bands will be given by those observed in the pure liquid spectra.

can be seen, however, that the most intense band is found at 567 cm^{-1} in the infrared spectrum of *racemic*-DBB in the gaseous state (see Fig. 4). Judging from the electron diffraction investigation by Stevenson and Schomaker,[12] where they have shown that the *trans* conformation for the bromine atoms predominates in the gaseous state, the very intense 567 cm^{-1} band, which corresponds to the 563 cm^{-1} band in the Raman spectrum, must be assigned to the ν(C–Br) vibration arising from RG. The weaker bands at 651 and 547 cm^{-1} appearing in the infrared spectrum of the gaseous state may be ascribed to RG′ and RT respectively, both of which are relatively small in population.

Energy Difference between the Rotational Isomers in the Gaseous State. As Fig. 4 shows, the bands appearing at 646, 607, and 559 cm^{-1} of *meso*-DBB correspond to those at 635, 600, and 552 cm^{-1} respectively in the liquid state. For the gaseous *racemic*-DBB, the bands corresponding to those at 648, 561 and 543 cm^{-1} of the liquid state are observed at 651, 567, and 547 cm^{-1} respectively.

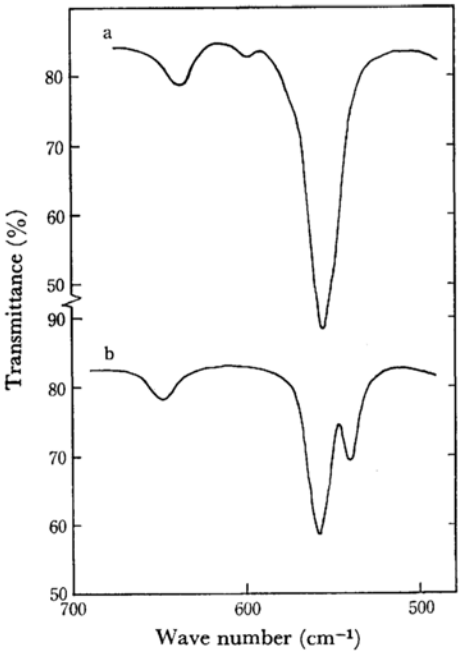

Fig. 4. Infrared spectra in gaseous state.
a, *meso*-DBB (at 96°C); b, *racemic*-DBB (at 98°C)

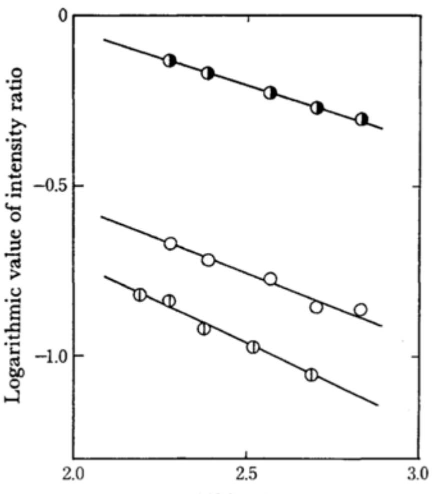

Fig. 5. Relations of the intensity ratio of ν(C–Br) bands against $1/T$ in the gaseous state.

◐: log (D_{547}/D_{567}) of *racemic*-DBB
○: log (D_{651}/D_{567}) of *racemic*-DBB
⦶: log (D_{646}/D_{559}) of *meso*-DBB

As Fig. 5 shows the relations of the logarithmic values of the intensity ratios for the ν(C–Br) bands in the gaseous state against 1/T were found to be linear. From the slope of the straight lines, the energy differences in the gaseous state are found to be:

$$\Delta E^{\text{gas}}_{\text{MG-MT}} = 2.2 \text{ kcal/mol}$$
$$\Delta E^{\text{gas}}_{\text{RG}'\text{-RG}} = 1.7 \text{ kcal/mol}$$

and;

$$\Delta E^{\text{gas}}_{\text{RT-RG}} = 1.5 \text{ kcal/mol}$$

by means of a previously-reported method.[1] It may be noted that the observed values of ΔE^{gas} are higher by approximately 0.5 kcal/mol than those corresponding ΔE^{gas} values for *meso*- and *racemic*-2,3-dichlorobutanes.[1] The relative behavior of chlorine and bromine substituents for ΔE^{gas}, in these cases, is in harmony with the findings for 1,2-dihalogenoethanes; *i. e.*, the values of ΔE^{gas} between the *gauche* and *trans* forms have been determined to be 1.45—1.70 kcal/mol for 1,2-dibromoethane and 1.0—1.1 kcal/mol for 1,2-dichloroethane respectively.[13,14]

The energy difference for *meso*-DBB, however, can be determined by an independent method, *e. g.*, by studing the solvent effect upon the intensity of the ν(C–Br) band. Since the MT-form has no dipole moment, its potential energy may be not subjected to any influence from the solvent dielectric constant (see Eq. (1)). The lowering in the potential energy of MG, Er, in the solvent of the dielectric constant, ε, can, therefore, be represented with reference to the energy differences between MG and MT in the gaseous state, ΔE^{gas}, and that in solution, ΔE^{soln}, as follows:

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[12] D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 3173 (1939).

[13] T. Shimanouchi, H. Tsuruta and S. Mizushima, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **42**, 51 (1944).

[14] K. Kuratani, T. Miyazawa and S. Mizushima, *J. Chem. Phys.*, **21**, 1411 (1953).

$$Er = \Delta E^{\text{gas}} - \Delta E^{\text{soln}} = (\mu^2/a^3)[(\varepsilon-1)/(2\varepsilon+1)] \quad (2)$$

In the solution, on the other hand, the ratio of the optical density of the ν(C–Br) bands can be written with reference to ΔE^{soln} as follows:

$$D_{\text{MG}}/D_{\text{MT}} = (2k_{\text{MG}}f_{\text{MG}}/k_{\text{MT}}f_{\text{MT}})\exp(-\Delta E^{\text{soln}}/\boldsymbol{R}T) \quad (3)$$

where k is the absorption coefficient and f, the partition function. Combining Eqs. (2) and (3), we thus obtain:

$$\begin{aligned}\log(D_{\text{MG}}/D_{\text{MT}}) &= \log(2k_{\text{MG}}f_{\text{MG}}/k_{\text{MT}}f_{\text{MT}}) \\ &\quad - \Delta E^{\text{gas}}/2.303\boldsymbol{R}T \\ &\quad + (\mu^2/2.303\boldsymbol{R}Ta^3)[(\varepsilon-1)/(2\varepsilon+1)] \quad (4)\end{aligned}$$

At a constant temperature, the log $(D_{\text{MG}}/D_{\text{MT}})$ should be a linear function with $(\varepsilon-1)/(2\varepsilon+1)$. Taking the 635 cm^{-1} band to MG, and the 552 cm^{-1} band to MT, as in Fig. 6, the relation of $\log(D_{635}/D_{552})$ to $(\varepsilon-1)/(2\varepsilon+1)$ at the constant temperature of 29°C is found to be linear. This result agrees satisfactorily Eq. (4). The value of the first two terms of the right-hand equation gives -1.34 as the value of $\log(D_{635}/D_{552})$ at $(\varepsilon-1)/(2\varepsilon+1)=0$, where ε is extraporated to 1. We then have:

$$\log(2k_{\text{MG}}f_{\text{MG}}/k_{\text{MT}}f_{\text{MT}}) - \Delta E^{\text{gas}}/2.303\boldsymbol{R}T = -1.34 \quad (5)$$

Assuming $f_{\text{MG}}/f_{\text{MT}}=1$,[1] and into Eq. (5) putting the value of $k_{\text{MG}}/k_{\text{MT}}$, which has been determined to be 0.534, as will be described below, we have found the value of ΔE^{gas} to be 1.9 kcal/mol. The value of ΔE^{gas} thus obtained is approximately the same as that obtained by measuring the temperature-change in the absorption intensity in the gaseous state.

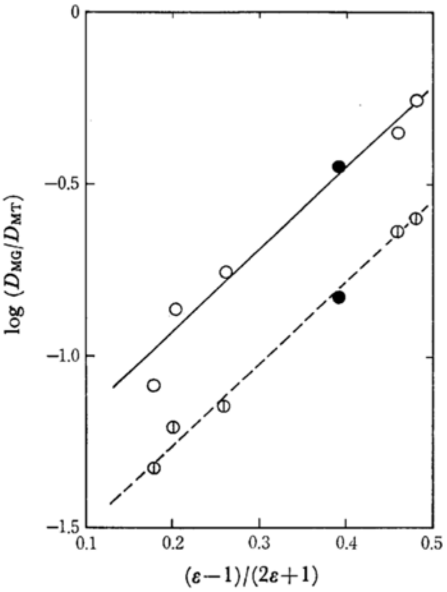

Fig. 6. Relations of log $(D_{\text{MG}}/D_{\text{MT}})$ against $(\varepsilon-1)/(2\varepsilon+1)$ at 29°C.
○: $D_{\text{MG}}/D_{\text{MT}}=D_{635}/D_{552}$
⦶: $D_{\text{MG}}/D_{\text{MT}}=D_{600}/D_{552}$
Black circles: data for the pure liquid.

As is presented in Fig. 6, it should also be noted that the origin of the 600 cm^{-1} band seems to be same as that of the 635 cm^{-1} band, since the two lines are parallel in direction. This result gives a basis for the assignment of the 635 and 600 cm^{-1} bands to MG.

From his NMR study of *meso*-DBB, Deb[5] has found the value of ΔE^{gas} to be 1.0 kcal/mol. This value of ΔE^{gas}, however, seems to be too small as compared with the energy difference between the *gauche* and *trans* forms of 1,2-dibromoethane, for which the value of ΔE^{gas} was found to be 1.45—1.70 kcal/mol.[13,14] Since, on going from MT to MG, the number of *gauche* interactions between bulky groups, Br and CH$_3$, is increased from two to three, the difference in steric potential between the MG of *meso*-DBB and the corresponding *gauche* form of 1,2-dibromoethane may be larger than that between the *trans* forms of these two substances. In this case, a contribution of the electrostatic repulsion between the bromine atoms to ΔE^{gas} is considered to be approximately the same for the corresponding *gauche* and *trans* forms of these two substances. The values of ΔE^{gas} between the MG and MT may, therefore, be expected to exceed that between the *gauche* and *trans* forms of 1,2-dibromoethane.

For the gaseous *racemic*-DBB, it may be noted that the potential energies of RG′ and RT are almost the same in magnitude and that both are higher than that of RG. The same situation has been found for *racemic*-2,3-dichlorobutane, as has been reported in our previous paper.[1]

The Equilibrium Concentrations of Rotational Isomers in Various Solvents. The equilibrium concentrations of rotational isomers in various solvents were determined by measuring the intensity ratio of the ν(C–Br) bands. The ratio of the concentrations of the two rotational isomers, I and II, $C_{\text{I}}/C_{\text{II}}$, can be represented with reference to the optical densities of the ν(C–Br) bands belonging to these rotational isomers as follows:

$$C_{\text{I}}/C_{\text{II}} = (k_{\text{II}}/k_{\text{I}})(D_{\text{I}}/D_{\text{II}}) \quad (7)$$

where D is the optical density and k, the absorption coefficient. In general, the determination of the $k_{\text{II}}/k_{\text{I}}$ value is a little more difficult. Fortunately, in the case of liquid *meso*-DBB, the ratio of the concentration of MG to MT, $C_{\text{MG}}/C_{\text{MT}}$, can be calculated to be 0.667 from the observed dielectric constant and the density of the liquid.*3 Putting into Eq. (7) the $C_{\text{MG}}/C_{\text{MT}}$, and the observed value of $D_{\text{MG}}/D_{\text{MT}}$, 0.356, for the pure liquid *meso*-DBB at room temperature, we have then

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*3 The value of $C_{\text{MT}}/C_{\text{MG}}$ was calculated by a method reported in our previous paper.[1] The observed data of the dielectric constant ($\varepsilon=6.245$), the density ($d=1.7747$), and the refractive index ($n=1.5091$) at 25°C were taken from the paper of Winstein and Wood.[15]

15) S. Winstein and R. E. Wood, *J. Am. Chem. Soc.*, **62**, 548 (1960).

TABLE 2. EQUILIBRIUM CONCENTRATIONS OF THE ROTATIONAL ISOMERS IN *meso*-2,3-DIBROMOBUTANE

Solvent	D_{635}/D_{552}	C_{MT} %a)	$J_{AA'}$ (cps)b)	C_{MT} %a,c)
n-Hexane (1.89)	0.081	87	9.00	80—78
Cyclohexane (2.02)	0.141	79	8.93	80—78
Carbon disulfide (2.64)	0.175	75	8.69	77—74
Pure liquid (6.245)	0.356	60		
Cyclohexanone (18.3)	0.461	54		
Acetonitrile (37.5)	0.566	49	6.55	56—51
Carbon disulfided)			8.81	*ca.* 80
Pure liquidd)			7.81	70—66

a) Composition of MG, C_{MG} %, is given by 100-C_{MT}.
b) Data by Deb.5)
c) Calculated from the values of $J_{AA'}$ by Deb assuming $J_T=11$ cps and $J_G=1$—2 cps.3,4,16)
d) NMR data from the paper of Bothner-By and Naar-Colin.3)

TABLE 3. EQUILIBRIUM CONCENTRATIONS OF THE ROTATIONAL ISOMERS IN *racemic*-2,3-DIBROMOBUTANE

Solvent	D_{648}/D_{561}	D_{543}/D_{561}	$C_{RG'}$ %	C_{RG} %	C_{RT} %
n-Hexane (1.89)	0.140	1.102	6	75	19
Cyclohexane (2.02)	0.225	1.202	10	71	19
Carbon disulfide (2.64)	0.314	1.574	13	64	23
Pure liquid (5.758)	0.499	1.618	19	59	22
Cyclohexanone (18.3)	0.958	1.922	30	49	21
Acetonitrile (37.5)	1.174	1.944	34	46	20
Pure liquida)			20	60	20

a) NMR data from the paper of Bothner-By and Naar-Colin.3)

found the value of k_{MT}/k_{MG} to be 1.87. Using this value, the equilibrium concentrations at room temperature for *meso*-DBB in various solvents have been determined from Eq. (7), they are listed in Table 2.[*4]

Deb observed the NMR spectra of *meso*-DBB in various solvents and found that the vicinal coupling constant, $J_{AA'}$, between two methine protons changes depending upon the solvents.5) From these observed $J_{AA'}$ values, we have calculated the equilibrium concentration, C_{MT}, assuming *trans* and *gauche* coupling constants of two methine protons, to be $J_T=11$ cps and $J_G=1$—2 cps respectively.3,4,16) The agreement between the equilibrium concentrations obtained by the two different methods is satisfactory.

Table 3 gives the equilibrium concentrations of the rotational isomers of *racemic*-DBB in solution; these concentrations have been obtained by means of the method1) we previously applied to *racemic*-2,3-dichlorobutane.[*5] It may be seen that the data for the pure liquid state are in accord with those reported in the NMR investigation by Bothner-By and Naar-Colins.3) That the increase in the population of RG′ is remarkable in the polar solvents in spite of the small effect of the solvent on the population of RT can be explained by the fact that the loss in the potential energy of RG′ under the influence of an electrostatic interaction of the solvent dipole is approximately twice that of RT.[*6] A certain increase in the populations of RT may be expected in the polar solvent; at present, however, we have no good explanation for the small effect of the solvent on RT shown in Table 3.

The author wishes to express his hearty thanks to Professor M. Takeda of Science University of Tokyo and Professor T. Shimanouchi of The University of Tokyo for their encouragement during the progress of the work, and to M. Kawakami for his assistance.

[*4] In this case we have taken the 635 cm^{-1} band to MG and the 552 cm^{-1} band to MT. When the remaining band at 600 cm^{-1} is taken to MG, the value of k_{552}/k_{600} becomes 4.48. If either band at 635 or at 600 cm^{-1} is taken for MG, the result is the same as those obtained in the determination of the equilibrium concentrations in various solvents.

16) S. Kondo, E. Tagami, K. Iimura and M. Takeda, This Bulletin, **41**, 790 (1968).

[*5] The existing ratios of the rotational isomers at 80°C, $C_{RG'}/C_{RG}$ and C_{RT}/C_{RG}, were calculated from the observed energy differences, $\Delta E^{gas}_{RG'\text{-}RG}=1.7$ kcal/mol and $\Delta E^{gas}_{RT\text{-}RG}=1.5$ kcal/mol; they were found to be 0.089 and 0.118 respectively. Putting these values and the observed ratios of the optical densities at 80°C, $D_{RG'}/D_{RG}=0.139$ and $D_{RT}/D_{RG}=0.510$, into Eq. (7), the values of $k_{RG'}/k_{RG}$ and k_{RT}/k_{RG} were determined to be 1.56 and 4.32 respectively. The equilibrium concentrations were then calculated using these ratios of the absorption coefficients.

[*6] Using Eq. (1), the losses in potential energies in the acetonitrile solvent ($\varepsilon=37.5$), for instance, are calculated to be 1.6 kcal/mol for RG′, 0.7 kcal/mol for RT, and 0.2 kcal/mol for RG; hence, the energy differences between the rotational isomers in the solvent become $\Delta E_{RG'\text{-}RG}=0.3$ kcal/mol and $\Delta E_{RT\text{-}RG}=1.0$ kcal/mol. In this calculation, the value of the density, 1.7836, was taken from the paper of Winstein and Wood.15)