Dipole Moments of 2,3-Dihalogeno-2,3-dimethylbutanes

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Introduction

It has been shown by the measurements of the Raman effect, infrared spectra, dipole moment, etc., that 1,2-dihalogenoethanes[1,2] and simple hydrocarbons[2] are the equilibrium mixtures of the rotational isomers. However, 2,3-dibromo-2,3-dimethylbutane has been concluded by the spectoscopic investigation by Cleveland and Lamport[3] to have only one isomer (the *trans* isomer with center of symmetry in benzene and in carbon tetrachloride solutions). On the other hand van Arkel and Snoeck[4] reported a fairly large value 1.35 D of the dipole moment of 2,3-dichloro-2,3-dimethylbutane in benzene solution in spite of the vanishing moment in carbon tetrachloride solution. According to this result we have to assume the existence of both the *trans* and gauche forms in benzene solution, whereas we assume only the *trans* form with no moment in carbon tetrachloride solution. This does not seem to be compatible with our conclusions on rotational isomerism. At least, such a large solvent effect as that found by van Arkel and Snoeck will not be expected. In view of this situation it is desirable to measure the dipole moments of these substances more accurately in various solvents and at different temperatures.

Experimental

$Cl(CH_3)_2C$-$C(CH_3)_2Cl$.—Pinacon was treated with aqueous solution of hydrochloric acid saturated at -20°C, and the reaction product was allowed to stand for several days. The precipitate was recrystalized with ethyl ether and purified by sublimation: m.p. 155–156°C.

$Br(CH_3)_2C$-$C(CH_3)_2$.—The sample was supplied by Professor Cleveland, Illinois Institute of Technology. It is the same sample as that used by him and Lamport for the measurement of the Raman and infrared spectra. It was recrystalized from the solution and purified by sublimation: m.p. 157.4–158.5°C.

Benzene.—The commercial product was boiled with aluminium chloride for one hour, treated with concentrated sulphuric acid several times, dried over sodium, and then fractionally distilled: b.p. 80.0–80.5°C.

Carbon Tetrachloride.—The commercial product was dried over calcium chloride and then fractionally distilled: b.p. 75.6–75.9°C.

The apparatus and the method of the measurement of dielectric constant were already described in a previous paper[5]. The density of the solution at 25°C was measured with a pycnometer, and those at other temperatures were obtained by measuring the volume change of the solutions by use of a dilatometer.

Results

The observed values of dielectric constant ϵ and the density d of these substances in carbon tetrachloride and benzene solutions are shown in Tables I and II, where w is the

TABLE I

DIELECTRIC CONSTANT, DENSITY, AND MOLECULAR POLARISATION OF 2,3-DICHLORO-2,3-DIMETHYLBUTANE

($P_E+P_A=MR_D=39.66$ cc.).

Benzene Solution (25°C).

w	ε	d
0.00000	2.2720	0.8721
0.01439	2.3023	0.8755
0.02365	2.3198	0.8767
0.04225	2.3561	0.8797
0.06983	2.4089	0.8835
0.09048	2.4512	0.8865

$\varepsilon_\infty=2.2740$, $d_\infty=0.8734$,

$a=1.945$, $b=0.145$, $P_{2\infty}=101.0\pm0.4$ cc.

Carbon Tetrachloride Solution (-20°C).

w	ε	d
0.00000	2.3109	1.6770
0.01053	2.3344	1.6677
0.01428	2.3426	1.6644
0.02134	2.3584	1.6582
0.02650	2.3700	1.6537

$\varepsilon_\infty=2.3111$, $d_\infty=1.6771$,

$a=2.23$, $b=0.880$, $P_{2\infty}=76.4$ cc.

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[1] S. Mizushima, Y. Morino, I. Watanabe, T. Shimanouchi, and S. Yamaguchi, *J. Chem. Phys.*, 17, 591 (1949).

[2] S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press Inc., New York (1954).

[3] F. F. Cleveland and J. E. Lamport, *J. Chem. Phys.*, 18, 1320 (1950).

[4] A. E. van Arkel and J. L. Snoeck, *Z. Physik. Chem.*, B18, 159 (1932).

[5] Y. Morino, I. Miyagawa, and T. Oiwa, *Botyu-Kagaku*, 15, 181 (1950).

(0°C).

0.00000	2.2722	1.6346
0.01053	2.2954	1.6257
0.01428	2.3037	1.6226
0.02134	2.3192	1.6167
0.02650	2.3301	1.6123

$\varepsilon_\infty=2.2720$, $d_\infty=1.6346$,
$a=2.20$, $b=0.840$, $P_{2\infty}=77.2$ cc.

(25°C).

0.00000	2.2254	1.5840
0.01053	2.2480	1.5757
0.01428	2.2557	1.5727
0.02134	2.2710	1.5671
0.02650	2.2821	1.5630

$\varepsilon_\infty=2.2252$, $d_\infty=1.5840$,
$a=2.14$, $b=0.791$, $P_{2\infty}=77.8$ cc.

(55°C).

0.00000	2.1651	1.5270
0.01053	2.1872	1.5189
0.01428	2.1954	1.5160
0.02134	2.2098	1.5105
0.02650	2.2206	1.5066

$\varepsilon_\infty=2.1653$, $d_\infty=1.5270$,
$a=2.10$, $b=0.771$, $P_{2\infty}=79.8$ cc.

TABLE II

DIELECTRIC CONSTANT, DENSITY, AND MOLECULAR POLARISATION OF 2,3-DIBROMO-2,3-DIMETHYLBUTANE

($P_E+P_A=MR_D=45.46$ cc.).

Benzene Solution (25°C).

0.00000	2.2720	0.8721
0.01529	2.2830	0.8785
0.01929	2.2858	0.8801
0.02903	2.2926	0.8841
0.03837	2.2987	0.8876

$\varepsilon_\infty=2.2729$, $d_\infty=0.8725$,
$a=0.679$, $b=0.454$, $P_{2\infty}=76.6\pm0.4$ cc.

Carbon Tetrachloride Solution (−15°C).

0.00000	2.3032	1.6662
0.00828	2.3102	1.6659
0.01100	2.3124	1.6664
0.01591	2.3170	1.6658
0.02046	2.3202	1.6665

$\varepsilon_\infty=2.3032$, $d_\infty=1.6662$,
$a=0.84$, $b=0$, $P_{2\infty}=63.7$ cc.

(+6°C).

0.00000	2.2622	1.6224
0.00828	2.2692	1.6221
0.01100	2.2716	1.6225
0.01591	2.2762	1.6220
0.02046	2.2800	1.6224

$\varepsilon_\infty=2.2620$, $d_\infty=1.6223$,
$a=0.86$, $b=0$, $P_{2\infty}=65.9$ cc.

(25°C).

0.00000	2.2259	1.5849
0.00828	2.2332	1.5847
0.01100	2.2354	1.5851
0.01591	2.2398	1.5845
0.02046	2.2450	1.5851

$\varepsilon_\infty=2.2261$, $d_\infty=1.5849$,
$a=0.86$, $b=0$, $P_{2\infty}=67.1$ cc.

(55°C).

0.00000	2.1640	1.5259
0.00828	2.1714	1.5255
0.01100	2.1740	1.5259
0.01591	2.1788	1.5257
0.02046	2.1831	1.5261

$\varepsilon_\infty=2.1640$, $d_\infty=1,5258$,
$a=0.91$, $b=0$, $P_{2\infty}=69.8$ cc.

concentration of the solute in weight fraction. The molecular polarisation $p_{2\infty}$ of the solute extrapolated to infinite dilution was calculated by use of the Halverstadt and Kumler equation[6]:

$$p_{2\infty}=(\varepsilon_0-1)/(\varepsilon_0+2)\cdot M_2/d_0\cdot\{1+3a/(\varepsilon_0-1)(\varepsilon_0+2)-b/d_0\}, \qquad (1)$$

where M_2 denotes the molecular weight of the solute, ε_0 and d_0 the dielectric constant and the density extrapolated to zero concentration, and a and b the inclination of the lines of ε vs. w and d vs. w respectively. The dipole moment was calculated by the Debye equation:

$$\mu=0.0128\{p_{2\infty}-(p_E+p_A)\}^{1/2}T^{1/2} \qquad (2)$$

where p_E and p_A are the electronic and atomic polarisations. p_E+p_A was assumed to be equal to MR_D, which was calculated from the atomic refractions of the constituent atoms. It is easily seen that this approximation does not affect our conclusion on the temperature dependence of dipole moment.

Discussion of Results

1. Rotational Isomers.—In the present experiment finite moments were observed for 2,3-dichloro-2,3-dimethylbutane in carbon tetrachloride solution as well as in benzene solution, in contrast to the result obtained by van Arkel and Snoek. This was also shown to be the case for 2,3-dibromo-2,3-dimethylbutane. Our results are shown in Table III, in which the experimental data in heptane solution obtained previously by one of us[7] are also included.

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[6] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem Soc.*, 64, 2988 (1942).

[7] I. Miyagawa, *J. Chem, Soc. Japan*, 75, 1162 (1954).

TABLE III

DIPOLE MOMENTS OF 2,3-DICHLORO- AND 2, 3-DIBROMO-2, 3-DIMETHYLBUTANE IN VARIOUS SOLUTIONS (D)

°C	Chloro-compound			Bromo-compound		
	B a)	CT b)	Hp c)	B a)	CT b)	Hp c)
−20		1.24	1.14			0.77
−15					0.88	
0		1.30				
1			1.23			0.84
6					0.97	
25	1.74	1.37	1.31	1.24*	1.03*	0.96
50			1.41			1.02
55		1.47			1.15	

a) Benzene solution,

b) Carbon tetrachloride solution,

c) Heptane solution7).

* The values referred to by Cleveland and Lamport3), 1.20 and 1.01 D, in B and CT solution respectively, should be corrected as shown in the Table. The difference between the values of Cleveland and Lamport and of us comes from whether P_E+P_A is taken as MR_D or as 1.05 MR_D (the former).

The result obtained by Cleveland and Lamport on the Raman and infrared spectra of dibromodimethylbutane was explained by the existence of the *trans* form only, and therefore, was in apparent agreement with van Arkel's result of vanishing moment of dichlorodimethylbutane in carbon tetrachloride solution. Actually, however, there is a difficulty in this explanation, since the finite moment was observed in benzene solution and no difference in Raman spectra have been detected between benzene and carbon tetrachloride solutions. Thus van Arkel's result is not consistent with that obtaind by Cleveland and Lamport.

The dipole moment of the rigid *trans* form is evidently zero, and even if the rotational vibration about the trans position is taken into account, the moment value will not exceed 0.3 *D* (see Appendix). Therefore, we have to conclude the existence of a rotational isomer with a finite moment. This should be the less stable isomer, since the apparent moments of these compounds increase with temperature. From the analogy to 1,2-dihalogenoethanes this isomer can reasonably be assumed to be the gauche form, which is obtained from the *trans* form by an internal rotation by about 120°C.

The values of the dipole moment observed at a fixed temperature depend considerably upon the solvent as shown in Table III. In particular, the values observed in benzene solutions are much higher than those in other solutions. This result is quite analogous to that obtained for 1,2-dihalogenoethanes and many other compounds showing rotational isomerism2) and is a further evidence of the existence of rotational isomers for dichloro- and dibromo-dimethylbutanes.

Let the number of the *trans* molecules be N_t and that of the gauche molecules be N_g. Then we have:

$$N_g/N_t=2(\Omega_V{}^g\Omega_R{}^g\Omega_{int}{}^g)/(\Omega_V{}^t\Omega_R{}^t\Omega_{int}{}^t)\cdot \exp(-\Delta E/kT), \qquad (3)$$

where Ω_{int} is the partition function for the internal rotation about the C−C axis, Ω_V and Ω_R the vibrational and rotational partition functions (excluding the internal rotation), and ΔE the energy difference of the two isomers. For the vibrational and rotational partition functions Gwinn and Pitzer8) have shown the approximate relation:

$$\Omega_V{}^g\Omega_R{}^g/\Omega_V{}^t\Omega_R{}^t=1. \qquad (4)$$

Therefore, we may assume the same relation for dichloro- and dibromo-dimethylbutane and can avoid the difficulty arising from the ambiguity of the assignment of the normal frequencies. If we assume further that $\Omega_{int}{}^g/\Omega_{int}{}^t=1$, eq. (3) is reduced to:

$$N_g/N_t=2\exp(-\Delta E/kT), \qquad (5)$$

and the mean dipole moment is calculated as:

$$\begin{aligned}\bar{\mu}^2&=(N_t\mu_t{}^2+N_g\mu_g{}^2)/(N_t+N_g)\\&=\{\mu_t{}^2+2\mu_g{}^2\exp(-\Delta E/kT)\}/\\&\quad\{1+2\exp(-\Delta E/kT)\},\end{aligned} \qquad (6)$$

or

$$\bar{\mu}^2-\mu_t{}^2=(\mu_g{}^2-\mu_t{}^2)G(x), \qquad (7)$$

where

$$G(x)=2\exp(-x)/\{1+2\exp(-x)\}, \qquad (8)$$

and

$$x=\Delta E/kT. \qquad (9)$$

The calculation of the energy difference ΔE and the moment μ_g of the gauche form from the mean moments observed at different temperatures is made according to the method proposed by Lennard-Jones and Pike9).

First $G(x)$ is calculated for various values of $x=0\sim\infty$, and a curve is drawn for log $G(x)$ against log x. The experimental curve representing log $(\mu_{\text{obs}}{}^2-\mu_t{}^2)$plotted against log $1/T$ should be superposable on some part of the theoretical curve log $G(x)$ *vs.* log x. Hence, by shifting the experimental curve along x- and y-axes so as to superpose it on the $G(x)\sim\log(x)$ curve as much as possible, ΔE and $(\mu_g{}^2-\mu_t{}^2)$ are obtained from the displacements in x- and y-directions. In this treatment the value of μ_t should be known

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8) W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.*, 16, 303 (1948).

9) J. E. Lennard-Jones and H. H. M. Pike, *Trans. Faraday Soc.*, 30, 830 (1934).

in advance. We have used two extreme values of μ_t, 0.0D and 0.3D, since as referred to above μ_t should be less than 0.3D.*

The results thus obtained are shown in Table IV, the estimated error in the value of the energy difference being ±0.15 kcal/mol. It makes almost no difference, whether the value of μ_t be taken as 0.0D or as 0.3D. We see that there is dependence upon the solvent of the energy difference of dichlorodimethylbutane, although this is less pronounced than that observed for 1,2-dihalogenoethanes[10]. An explanation of the change of ΔE with solvent has been given in the case of 1,2-dihalogenoethanes[11,12]. In a medium of dielectric constant ε the gauche isomer is stabilized by an amount of energy $(\epsilon-1)/(2\varepsilon+1)\cdot\mu^2/a^3$ as compared with the trans isomer, where a is the radius of the solute molecule. In other words the energy difference between the rotational isomers of dichloroethane decreases with the increasing polarity of the solvent. The same consideration would apply for dichlorodimethylbutane.

TABLE IV

THE ENERGY DIFFERENCE BETWEEN THE ROTATIONAL ISOMERS OF DIHALOGENO-DIMETHYLBUTANE

Compound	Solvent	ΔE (kcal./mol.)	μ_t (D)	μ_g^{obs} (D)	μ_g^{calc} (D)
DCl	CT	1.10	0	2.8	3.33
		1.10	0.3	2.8	
	Hp	1.30	0	3.1	
		1.30	0.3	3.2	
DBr	CT	1.45	0	2.6	3.30
		1.60	0.3	2.6	
	Hp	1.50	0	2.6	
		1.50	0.3	2.6	

In contrast to the case of dichlorodimethylbutane, ΔE of the corresponding dibromo-compound was found to be almost independent of the solvent and, accordingly, ΔE in vacuum will also be 1.5 kcal./mol. In connection with this it may be noted that the change of ΔE of 1,2-dibromoethane with solvent was found by the earlier measurements[13,14,15] to be small as compared with dichloroethane. The accuracy of these measurements is not so high as in the case of those made recently, but they can be considered as experimental evidence in support of our conclusion on dichloro- and dibromo-dimethylbutanes.

In the earlier investigations on the internal rotation[2,13], the temperature dependence of dipole moment was explained on the assumption that the molecules exert rotatory vibration about the *trans* position which corresponds to the single minimum of the potential curve. The mean dipole moment was calculated by Lennard-Jones and Pike[9] as:

$$\bar{\mu}^2 = 2\mu_{2\perp}{}^2 F(x), \tag{11}$$

where

$$F(x) = \int_0^{2\pi} (1-\cos\theta)\exp\{-x(1-\cos\theta)\}d\theta \Big/ \int_0^{2\pi} \exp\{-x(1-\cos\theta)\}d\theta, \tag{12}$$

and

$$x = V_0/2kT, \tag{13}$$

and

$$V = 1/2\cdot V_0(1-\cos\theta). \tag{14}$$

Here $\mu_\perp$ is the component of the dipole moment of the rotating group perpendicular to the rotation axis. As shown by curve **a** of Fig. 1, the observed values of 1,2-dichloro

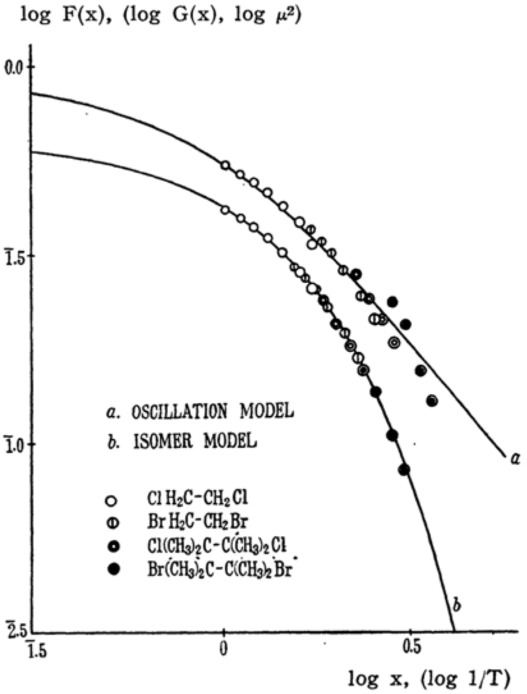

Fig. 1. The observed values of dipole moments and the computed values obtained on the assumption of the rotatory vibration about the *trans* position and on the assumption of the coexistence of two rotational isomers.

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* Strictly speaking, the value of μ_t depends on temperature. However, as the temperature dependence can be shown to be small, we can safely use a constant value for μ_t.

[10] Y. Morino, S. Mizushima, K. Kuratani, and M. Katayama, *J. Chem. Phys.*, 18, 754 (1959).

[11] I. Watanabe, S. Mizushima, and Y. Masiko, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), 40, 425 (1943): cf. P. J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, 73, 1815 (1951).

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

[13] S. Mizushima, Y. Morino, and K. Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), 25, 159 (1934).

[14] C. P. Smyth, R. W. Dornte, and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, 53, 4242 (1931).

[15] G. I. M. Bloom and L. E. Sutton, *J. Chem. Soc.*, 727 (1941).

and 1,2-dibromo-ethane are in agreement with the computed values. Yet the observed values can also be brought into agreement with the theoretical curve computed from eq. (7) which was derived on the assumption of the coexistance of two rotational isomers (curve **b** in Fig. 1). Therefore, so far as the dipole moments of 1,2-dihalogenoethanes are concerned, we can not tell which of the two explanations is preferable, the vibration of two halves of molecules against each other in one potential trough or the coexistence of two rotational isomers.

However, in the case of 2,3-dibromo-2,3-dimethylbutane no displacement enables us to superpose the observed values on the theoretical curve **a** obtained on the assumption of the rotatory vibration about the *trans* position. Even in the chloro-compound there is a small but definite discrepancy between the experimental and theoretical curves. The difference in the two cases can be explained as a result of the lower potential barrier for 1,2-dichloro- and -dibromo-ethane and of the higher potential barrier for 2,3-dichloro- and -dibromo-2,3-dimethylbutane. It is quite reasonable to assume that dihalogenodimethylbutanes have barriers higher than dihalogenoethane since the van der Waals radius of methyl group is much larger than that of the hydrogen atom.

2. The Origin of the Energy Difference between the Rotational Isomers. — The nature of the hindering potential to internal rotation has been discussed by several investigators[16–19]. From the comparison of the many experimental data we have come to the conclusion that the stable positions of the internal rotation are determined mainly by the steric repulsion between the atoms of the rotating groups including hydrogen atoms, whereas in the energy difference between rotational isomers there are contributions of other intramolecular forces besides the steric repulsion[19].

As referred to above, the energy difference of 2,3-dibromo-2,3-dimethylbutane was found to be almost the same as that of 1,2-dibromo-ethane. This fact can not be understood, if the hindering potential arises only from the steric repulsion, since the repulsion arising from the CH_3 group may be considered to be almost the same as that from Br-atom. (As referred to above, the van der Waals radius of the bromine atom is of the same magnitude as that of the CH_3-group). In other words, if the energy difference would arise only from the steric repulsion, we should find the vanishing value of ΔE for dibromodimethylbutane, which is inconsistent with the experimental result. Therefore, we have to conclude that electrostatic forces should play an important part in ΔE. This is compatible with the fact that we have found almost the same value of ΔE for 2,3-dibromo-2,3-dimethylbutane and 1,2-dibromo-ethane, both of which are expected to have nearly the same electrostatic potential, since the dipole moments of the rotating groups are almost the same for both cases.

The same conclusion is derived for 2,3-dichloro-2,3-dimethyl-butane by comparing the value of ΔE (1.6kcal)** with that of 1,2-dichloroethane (1.2kcal). There is a small difference between these two values, but all we can say is that ΔE of the former substance is not smaller than that of the latter. We go too far, if we discuss this difference quantitatively.

We should like to refer to a recent paper by one of us (I. M.)[20], in which the configurations of the rotational isomers and the energy difference were discussed on the assumption that the steric repulsion between the rotating groups could approximately be calculated from the interatomic potentials obtainable from the experimental data on the second virial coefficients and the electrostatic energy from the interactions between the point dipoles located at each bond.

3. The Dipole Moment of the Gauche Form.—The dipole moment of the gauche form μ_g was found to be 3.1D for 2,3-dichloro-2,3-dimethylbutane and 2.6D for 2,3-dibromo-2,3-dimethylbutane (in heptane solution). These values are greater than those of 1,2-dichloro- (2.62D)[21] and 1,2-dibromo-ethane (2.23D)[21]. The greater values of the former two substances are considered to arise from the induction effect in the methyl radicals by the C-X dipoles. If the induction effect is calculated according to the empirical rule derived by two of us[22] the resultant moments of the gauche forms of 2,3-dichloro- and 2,3-dibromo-2,3-dimethylbutanes are found to be 3.33D and 3.30D respectively. The corresponding

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[16] E. N. Lassettre and L. B. Dean, *J. Chem. Phys.*, 17, 317 (1949).

[17] H. J. Bernstein, *J. Chem. Phys.*, 17, 262 (1949).

[18] L. J. Oesterhoff, *Discussion of the Faraday Soc.*, 10, 79 (1951).

[19] S. Mizushima, Y. Morino, and T. Shimanouchi, *J. Phys. Chem.*, 56, 324 (1952).

** ΔE of 2,3-dichloro-2,3-dimethylbutane, 1.6 kcal., has been obtained by extrapolation to $\varepsilon=1$.

[20] I. Miyagawa, *J. Chem. Soc. Japan*, 75, 1169, 1173, 1177 (1954).

[21] I. Miyagawa, *J. Chem. Soc. Japan*, 75, 1057 (1954).

[22] Y. Morino, I. Miyagawa and T. Oiwa, *Botyu-Kagaku*, 15, 181 (1950); I. Miyagawa, *J. Chem. Soc., Japan* 75, 1061 (1954).

experimental values 3.1D and 2.6D are somewhat less than the computed values. However, it should be noted that the experimental values of μ_g are obtained on the assumption that $S=Q_{in}{}^{g}/Q_{in}{}^{t}=1$. If different values are assigned to S, the values of μ_g become quite different from the above ones. If, for instance, S is taken as 1/2, μ_g will be 3.5D for dichloro- and 3.2D for dibromo-dimethylbutanes. It will be shown from the discussion of partition functions that S may be taken to be less than 1[23].

On the other hand the observed value of ΔE does not depend appreciably on the value of S and, therefore, as the experimental molecular constant of rotational isomers the energy difference ΔE is more reliable than μ_g.

4. Molecular Spectra and Dipole Moments.—Let us now discuss the experimental result of Cleveland and Lamport. According to the Raman and infrared spectra observed by them in benzene and carbon tetrachloride solutions the molecules of 2,3-dibromo-2,3-dimethylbutane have been concluded to be in the *trans* form in both solutions. This seems at first sight to be inconsistent with the results of our dipole measurement. However, as the concentration of 2,3-dibromo-2,3-dimethylbutane in their measurement was considered to be less than 0.1 molar fraction and, as ΔE can reasonably be assumed to be 1.5 kcal./mol., the concentration of the gauche form is at most 0.014 in molar fraction. Even if the energy difference is reduced to half ($\Delta E=700$ cal./mol.) the concentration of the gauche form would not exceed 0.02 in molar fraction. Therefore, it is no wonder that the bands arising from the gauche form were not observed.

In connection with this we should like to refer to the Raman spectra of 1,2-dibromoethane. The Raman line at 551 cm^{-1} assigned to the stretching frequency of the gauche form has a fairly strong intensity in the spectra of the pure liquid, but, when it is diluted with *n*-heptane, the intensity decreases more quickly than the line arising from the *trans* form, and finally at the molar fraction of 0.1 the line becomes too weak to be detectable[13]. The most intense line in the spectra of 2,3-dibromo-2,3-dimethylbutane would be the line arising from the corresponding C-Br stretching frequency, which will behave in the same manner as the 551 cm^{-1} line referred to above. Therefore, as the molar fraction of the dibromodimethylbutane solution in the experiment of Cleveland and Lamport was about 0.1 or less, it is quite possible that all the lines of the gauche form of dibromo-dimethylbutane escaped detection.

Appendix

The hindering potential to internal rotation about the central C-C bond as axis is considered to have a form such as shown in Fig. 2. The more stable position corresponds to the *trans* form, and the less stable positions to the gauche forms which are obtained from the *trans* form by an internal rotation by about ±120°. There are two lower barriers A and A' and one higher barrier C in one complete internal rotation. Therefore, in order to obtain the moment of the *trans* isomer, μ_t, or, exactly speaking, the mean moment of all the molecules in the *trans* trough, we must make an integration:

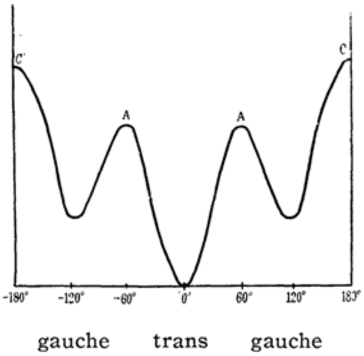

Fig. 2.

$$\bar{\mu}_t{}^2=2\mu_{\perp}{}^2\int_{A'}^{A}(1-\cos\theta)\exp(-V(\theta)/kT)d\theta\Big/\int_{A'}^{A}\exp(-V(\theta)/kT)d\theta, \tag{A1}$$

where $\mu_{\perp}$ is the perpendicular component of the moment of the rotating group. The potential function $V(\theta)$ in this expression may reasonably be approximated as:

$$V(\theta)=1/2\cdot V_0(1-\cos 3\theta), \tag{A2}$$

and, furthermore, the limit of integration A and A' in terms of azimuthal angle may be taken as ±60°. Then we have

$$\mu_t{}^2=2\mu_{\perp}{}^2F(x), \tag{A3}$$

where

$$F(x)=3\sqrt{3}/(2\pi I_0(x))\cdot\left[I_0(x)+2\sum_{\Delta=1}^{\infty}(-1)^s/(9\Delta^2-1)\cdot I_s(x)\right], \tag{A4}$$

and

$$x=V_0/2kT. \tag{A5}$$

Here $I_s(x)$ denotes the modified Bessel function of the first kind. If the bond moment of C-Cl is

TABLE V

THE TABLE OF $F(x)$

x	$F(x)$
0	0.1730
0.5	0.1243
1	0.0812
2	0.0413
5	0.0125
10	0.0064

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[23] I. Miyagawa, *J. Chem. Soc. Japan*, 75, 970 (1954).

taken as 1.86D, and the induction effect of C-Cl moment upon the C-CH_3 bonds is calculated according to our empirical rule, the perpendicular component $\mu_\perp$ is obtained as 2.15D. Using this value, μ_t at 300°K is calculated as shown in Table VI. As the value of V_0 for hexachloroethane was found to be about 10 kcal./mol., that of dichlorodimethylbutane must be greater than 10 kcal./mol., since the potential barrier arises mainly from the steric repulsion between the atoms of the rotating groups and is much higher in dichlorodimethylbutane than in hexachloroethane. (As referred to above the van der Waals radius of the methyl group is much larger than that of a Cl atom. In fact, the hindering potential barrier of 1,1,1-trichloroethane was found to be 2.7 kcal./mol.24), while that of neopentane is 4.3 kcal./mol.25), the latter being obtained by the replacement of chlorine atoms of the former by methyl radicals. Therefore, from Table V, we can surely conclude that μ_t is smaller than 0.3D.

TABLE VI

THE CALCULATED MOMENT OF THE TRANS FORM AT 300°K

V_0 (kcal./mol.)	μ(D)
0	1.14
0.5	1.00
1	0.83
2	0.62
3	0.50
5	0.36
10	0.23

The value of μ_t of 2,3-dibromo-2,3-dimethylbutane will be still smaller, since the steric repulsion in dibromo-compound should be much larger than that in dichloro-compound.

Summary

The dipole moments of 2,3-dichloro- and 2,3-dibromo-dimethylbutane were measured in carbon tetrachloride solution in the temperature range from −25° to +55°C, and in benzene solutions at 25°C. The moment was found to increase with temperature in carbon tetrachloride solution. Much higher values of moment were observed in benzene solutions. It was concluded from these experimental results that there exist two rotational isomers, the *trans* isomer with vanishing or a small moment, and the gauche isomer with a finite moment. The experimental result could be explained satisfactorily by the rotational isomer theory, but not on the assumption of only one potential trough at the *trans* position.

By comparing the energy difference between the rotational isomers of these compounds with those of 1,2-dichloro- and 1,2-dibromoethane it was concluded that the electrostatic force plays an important role in the energy difference between the rotational isomers, whereas the potential barrier is mainly determined by steric repulsion.

An explanation was presented to reconcile the result of our dipole measurement with that of Raman and infrared measurement, the two results being in apparent contradiction with each other.

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25) K. S. Pitzer, *Discussion of the Faraday Soc.*, **10**, 66 (1951).