The Dipole Moments of Molecules Containing Two Movable Dipoles

J. Y. Beach and D. P. Stevenson

A. Bethe to the writer, that there ought to be more than one way in which all superlattice lines could be eliminated for a lattice as large as 33A, leads me to admit the possibility, but not the probability, of this unless the local order is in a nucleus as small as 4.14A, when the long range disorder is 100 percent. It should be borne in mind that if one turns the 33A lattice inside out, as it were, that means nothing but an interchange throughout the lattice of iron and lithium atoms, thus giving the same, not a different, solution.

Granted that this 33A, ordered lithium ferrite, according to present notions concerning alloys, could not be produced in the laboratory because of the inordinate amount of time required to set it up, it nevertheless remains as the low temperature form of the disordered 4.14A lattice of lithium ferrite. Further studies on rates of cooling of alloys with specific heat measurements and with the possible use of "stabilizing agents" may help to clarify the knotty problems involved in *order versus disorder* studies. Bragg and Williams[2] in their first study in this field remark as their concluding sentence, "Maxima and minima in physical properties at certain relative proportions (e.g. Fe_3Al and Cu_3Au) are statistical effects, and do not imply the existence of corresponding compounds." It seems conceivable to the writer that an ordered solution of such binary alloys could be found, in which case it would be a fair question to ask whether a single ordered-lattice alloy is not a definite compound. It has been shown that proper ordering causes super-lattice lines to disappear, that a large (33A) lattice of lithium ferrite is the exact equivalent of the small (4.14A) disordered lattice, that a simple cubic lattice of edge 8 times the disordered face-centered cubic lattice gives only face-centered lines on the powder photograph in the case of lithium ferrite.

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The average dipole moment of a molecule containing two movable dipoles has been calculated as a function of temperature and restriction to internal rotation for three different potential functions. The potential functions used are: $(V_0/2)(\cos \phi + 1)$, $(V_0/\pi)(\pi - \phi)$ and $V_0/\pi^2(\pi - \phi)^2$, where V_0 is the difference in potential energy between the *cis* and *trans* forms of the molecule and ϕ is the angle between the planes containing the dipoles and the axis of rotation. Values of the integral $\int_0^\pi \cos x \exp (-bx^2)dx$ are tabulated for values of b ranging from 0 to 2 at intervals of 0.1. The dipole moments of *s*-dichloro-ethane, 1,2-bromo-chloro-ethane and *s*-dibromo-ethane as a function of temperature are used with the three potential functions to determine values of V_0. The values thus obtained are compared with the values obtained by other methods.

INTRODUCTION

THERE have recently been several attempts to determine the magnitude of the potential barrier restricting internal rotation around single carbon-carbon bonds. Most of these attempts have been made on ethane.[1] In attacking the problem from the standpoint of dipole moments it is necessary to substitute for symmetrically located hydrogen atoms, polar groups whose relative orientations will have a large effect on the resultant dipole moment of the molecule. In order to treat successfully the dipole moment data of such molecules as the 1,2,di-substituted ethanes it is necessary to derive expressions relating the observed dipole moment to the height and shape of the potential barrier and the individual bond moments. We have de-

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[1] Kemp and Pitzer, J. Chem. Phys. **4**, 749 (1936); J. Am. Chem. Soc. **59**, 276 (1937). Howard, Phys. Rev. **51**, 53 (1937). Kistiakowsky and Nazmi, J. Chem. Phys. **6**, 18 (1935). Bartholomé and Karweil, Zeits. f. physik. Chemie **39**, 1 (1938). Hunsman, Zeits. f. physik. Chemie **39**, 23 (1938).

rived such expressions for the cases of cosine, linear and parabolic potential functions. To find the average dipole moment it is necessary to calculate the average value of the square of the dipole moment, averaging over all possible configurations of the molecule and weighting each configuration with a Boltzmann factor taken from the assumed potential function. The square of the moment rather than the moment itself, is averaged because the Debye[2] equation applied to each molecular species gives the square of the moment, rather than the first power of the moment, as a function of the dielectric constant and the refractivity.

CALCULATIONS

The square of the dipole moment of a molecule containing two dipoles capable of relative motion to the extent of rotating about an axis in the molecule is:

$$\mu(\phi) = A + B \cos \phi, \qquad (1)$$

where $A = m_1^2 + m_2^2 - 2m_1 m_2 \cos \alpha_1 \cos \alpha_2$, and $B = 2m_1 m_2 \sin \alpha_1 \sin \alpha_2$. m_1 and m_2 are the magnitudes of the two movable dipoles. α_1 and α_2 are the angles made by the dipoles with the axis of rotation. ϕ is the angle between the plane containing one dipole and the axis of rotation and the plane containing the other dipole and the axis of rotation. For α_1 and α_2 tetrahedral and $m_1 = m_2 = m$, A and B each become 16/9 m^2.

The observed, or average dipole moment for the molecule is

$$\mu^2 = \overline{\mu^2(\phi)} = \frac{\int_0^\pi \mu^2(\phi) \exp(-V(\phi)/RT)d\phi}{\int_0^\pi \exp(-V(\phi)/RT)d\phi}. \qquad (2)$$

TABLE I. ρ for linear and cosine potential functions.

a	$-\rho$ (LINEAR)	$-\rho$ (COSINE)	a	$-\rho$ (LINEAR)	$-\rho$ (COSINE)
0.0	0.000	0.000	4.0	0.868	0.863
0.5	0.199	0.242	4.5	0.892	0.880
1.0	0.378	0.446	5.0	0.910	0.892
1.5	0.527	0.596	6.0	0.935	0.912
2.0	0.640	0.698	7.0	0.952	0.927
2.5	0.727	0.765	8.0	0.963	0.935
3.0	0.788	0.808	9.0	0.970	0.944
3.5	0.835	0.841	10.0	0.977	0.954

[2] Debye, *Polar Molecules*.

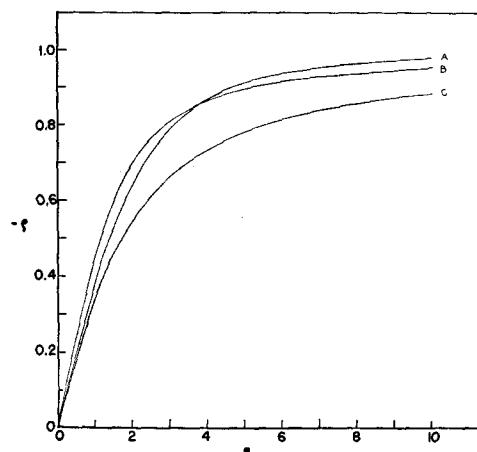FIG. 1.

The effect of the angle ϕ on the moments of inertia and thus the entropy of the various configurations is negligible except for small ϕ,[3] and will be neglected. Integrating ϕ from 0 to π is equivalent to integrating from 0 to 2π. $V(\phi)$ is only required to represent the potential function when ϕ is between 0 and π. Substituting Eq. (1) into Eq. (2) we obtain

$$\mu^2 = A + B\rho \qquad (3)$$

where $\rho = \dfrac{\int_0^\pi \cos \phi \exp(-V(\phi)/RT)d\phi}{\int_0^\pi \exp(-V(\phi)/RT)d\phi}$.

We shall first evaluate ρ for the linear potential function

$$V(\phi) = (V_0/\pi)(\pi - \phi).$$

V_0 is the difference in potential energy between the *cis* and *trans* configurations of the molecule. In this case

$$\rho = \frac{\int_0^\pi \cos \phi \exp(-V_0(\pi-\phi)/\pi RT)d\phi}{\int_0^\pi \exp(-V_0(\pi-\phi)/\pi RT)d\phi}$$

$$= -(a^2/(a^2 + \pi^2/4)) \coth a,$$

where $a = V_0/2RT$. $\rho = 0$ when $a = 0$ and ap-

[3] Altar, J. Chem. Phys. **3**, 460 (1935).

proaches -1 as a becomes large. When a is large and $\rho = -1$, the dipole moment $\mu = (A-B)^{\frac{1}{2}}$, which is the moment of the *trans* molecule. When a is small, the moment approaches $A^{\frac{1}{2}}$ the value for free rotation. ρ is tabulated in Table I and plotted in Fig. 1, curve A, as a function of a.

The integrals arising when the potential function $V = (V_0/2)(\cos\phi + 1)$ is used have been evaluated by Mizushima and Higasi.[4] In this case

$$\rho = \frac{\displaystyle\int_0^\pi \cos\phi \exp\left(-V_0(\cos\phi+1)/2RT\right)d\phi}{\displaystyle\int_0^\pi \exp\left(-V_0(\cos\phi+1)/2RT\right)d\phi}$$

$$= \frac{\displaystyle\int_0^\pi \cos\phi \exp\left(-a\cos\phi\right)d\phi}{\displaystyle\int_0^\pi \exp\left(-a\cos\phi\right)d\phi}$$

$$= iJ_1(ia)/J_0(ia). \quad a = V_0/2RT.$$

Numerator and denominator are Bessel functions which are tabulated.[5] In this case too $\rho = 0$ for $a = 0$ and -1 for a large. ρ is tabulated in Table I and plotted in Fig. 1, curve B.

In calculating the average moment for the parabolic potential function $V = (V_0/\pi^2)(\pi-\phi)^2$,

$$\rho = \frac{\displaystyle\int_0^\pi \cos\phi \exp\left(-V_0(\pi-\phi)^2/\pi^2RT\right)d\phi}{\displaystyle\int_0^\pi \exp\left(-V_0(\pi-\phi)^2/\pi^2RT\right)d\phi}.$$

Let $b = V_0/\pi^2RT$ and $\pi - \phi = x$, then

$$\rho = -\frac{\displaystyle\int_0^\pi \cos x \exp\left(-bx^2\right)dx}{\displaystyle\int_0^\pi \exp\left(-bx^2\right)dx} = -\frac{S(b)}{B(b)}.$$

The integral $B(b)$ can easily be transformed into an error integral. The result is $B(b) = (\frac{1}{2})$

[4] Mizushima and Higasi, Proc. Imp. Acad. **8**, 482 (1932).
[5] Jahnke and Einde, *Tables.*

$\times (\pi/b)^{\frac{1}{2}}\Phi(b^{\frac{1}{2}}\pi)$. $\Phi(b^{\frac{1}{2}}\pi)$ is the normalized error integral and is tabulated.[5]

The integral $S(b)$ does not become integrable by simple transformations, nor is it tabulated. We found it necessary to expand both $\cos x$ and $\exp(-bx^2)$ in powers of x and integrate term by term. The result is the following double series:

$$S(b) = \sum_{n=0}^\infty c_n b^n, \quad c_n = \frac{1}{n!} \sum_{l=n}^\infty \frac{(-1)^l \pi^{2l+1}}{(2l+1)(2l-2n)!}.$$

This series converges fairly rapidly for small values of b and was used for calculating $S(b)$ when $b = 0.5$ or less. When b is large $S(b)$ can be approximated to by the integral

$$\int_0^\infty \cos x \exp\left(-bx^2\right)dx = \frac{1}{2}(\pi/b)^{\frac{1}{2}} \exp\left(-\frac{1}{4}b\right).$$

We can test the error made by this approximation in the following way. The error is less than the error which would be made by making the same approximation for $B(b)$ because $\cos x$ is always less than 1. The error in $B(b)$ is found, from the error function table, to be 0.1 percent at $b = 0.55$, and to decrease rapidly as b increases. For calculating $S(b)$ when $b = 0.6$ or larger the approximate formula was used. $S(b)$ and ρ are tabulated in Table II. In Fig. 1, curve C ρ is plotted as a function of a. ρ varies from 0 to -1 as b (or a) varies from 0 to ∞.

TABLE II. $S(b)$ and ρ for the parabolic potential function.

b	a	$S(b)$	$-\rho$
0.00	0.000	0.0000	0.0000
0.05	0.247	0.2606	0.0968
0.1	0.495	0.4373	0.1858
0.2	0.988	0.6367	0.3371
0.3	1.48	0.7238	0.4541
0.4	1.97	0.7563	0.5425
0.5	2.47	0.7622	0.6097
0.6	2.96	0.754	0.659
0.7	3.46	0.741	0.700
0.8	3.95	0.724	0.731
0.9	4.45	0.707	0.757
1.0	4.95	0.690	0.779
1.1	5.43	0.673	0.796
1.2	5.92	0.658	0.813
1.3	6.42	0.641	0.825
1.4	6.91	0.626	0.836
1.5	7.40	0.612	0.846
1.6	7.90	0.600	0.855
1.7	8.39	0.587	0.863
1.8	8.88	0.575	0.870
1.9	9.38	0.563	0.876
2.0	9.88	0.552	0.881

TABLE III. *Potential barrier, V_0.*

$T^\circ K$	$\mu \times 10^{+18}$	POTENTIAL FUNCTION		
		COSINE V_0 KCAL./MOLE	LINEAR V_0 KCAL./MOLE	PARABOLIC V_0 KCAL./MOLE
		$C_2H_4Cl_2$		
305	1.12	4.02	4.17	7.97
341	1.24	3.78	4.15	7.11
376	1.32	3.71	4.46	6.85
419	1.40	3.71	4.26	6.63
457	1.45	3.80	4.41	6.66
480	1.48	3.81	4.52	6.66
485	1.48	3.85	4.57	6.73
544	1.54	4.02	4.80	6.85
		C_2H_4BrCl		
339	1.09	4.65	4.77	9.32
368	1.14	4.67	4.90	9.22
405	1.20	4.74	5.12	9.10
436	1.28	4.54	5.05	8.46
		$C_2H_4Br_2$		
339	0.94	6.00	5.66	12.87
368	0.99	5.92	5.74	12.20
405	1.03	6.12	6.04	12.56
436	1.10	5.85	5.92	11.69

Moment of $CH_2Cl = 2.03^7$
Moment of $CH_2Br = 2.02^7$
The moments of $C_2H_4Cl_2$, C_2H_4BrCl and $C_2H_4Br_2$ from Zahn[6]

DISCUSSION

If one of the potential functions described above is assumed to be the actual one, V_0 can be found from the value of the dipole moment at a single temperature. Substituting in Eq. (3) values for the group moments, bond angles and the observed moment of the molecule, a value of ρ is obtained. From the graph of the relation between ρ and a, a value of a is obtained which, with the temperature at which the dipole moment was measured gives a value of V_0. If values of the dipole moment have been determined for several temperatures several values of V_0 can be obtained. These values should be consistent if the assumed potential function is a good one.

We have taken the dipole moment data for s-dichloro-ethane, 1,2,bromo-chloro-ethane and s-dibromo-ethane[6] and calculated values for V_0 for each of the potential functions. We assumed that $\alpha_1 = \alpha_2 = 109^\circ 28'$ for all three molecules. For the group moments we have used the gas values of the moments of ethyl chloride and bromide.[7] The ethyl rather than the methyl compounds

were used to obtain the group moments in order that the inductive effects should be approximately the same as in the disubstituted ethanes. Gas values of the dipole moments were used for the three disubstituted ethanes. The values of V_0 calculated by the above method are tabulated in Table III. Professor C. P. Smyth has suggested to us that perhaps the group moments should be obtained from the methyl rather than the ethyl compounds. If this is done, the values in Table III are all lowered by about 1 kcal./mole. The arguments in favor of either procedure are not conclusive.

The values of V_0 calculated from the cosine potential function are more consistent than the values obtained from the linear or parabolic potential functions. They are also generally lower. In estimating a probable value for V_0 we shall accordingly give them more weight. From these results the probable values of V_0 for s-dichloro-ethane, 1,2,bromo-chloro-ethane and s-dibromo-ethane are 4, 5, and 6 kcal./mole, respectively. When values of the dipole moments obtained in solution are used somewhat lower values of V_0 are obtained. Lennard-Jones and Pike[8] have treated dichloro-ethane using the cosine potential function. They find that lower values of V_0 are obtained, 2.0 to 3.2 kcal./mole, if a variation of the group moments with ϕ is considered. Altar[3] has treated the dichloroethane dipole moment data using a two-term Fourier series to represent the potential function. This potential curve extended smoothly to small values of ϕ gives a value of V_0 of about 5 kcal./ mole. An extrapolation to $\phi = 0$ is necessary as his potential function does not represent the actual potential function at small values of ϕ. The determination of the potential curve near $\phi = 0$ by any experimental method is doubtful because of the small numbers of molecules in those configurations. The shape of the curve when ϕ is greater than 90° (say) is of much more significance.

The values of V_0 obtained in this paper are in fairly good agreement with electron diffraction results on these compounds.[9]

[6] Zahn, Phys. Rev. **40**, 291 (1932); **38**, 521 (1931).
[7] Smyth and McAlpine, J. Chem. Phys. **2**, 499 (1934).

[8] Lennard-Jones and Pike, Trans. Faraday Soc. **30**, 830 (1934).
[9] Beach and Palmer, in publication; Beach and Turkevich, to be published.