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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH]

The Inductive Effect and Chemical Reactivity. V. Theoretical Dipole Moments of α,ω -Dichloroalkanes and α,ω -Dibromoalkanes¹

By RICHARD P. SMITH² AND JEWELL J. RASMUSSEN

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The theory of earlier papers in this series^{3,4} has been applied to the calculation of dipole moments of α,ω -dichloroalkanes and α,ω -dibromoalkanes of up to ten carbon atoms. The molecules are assumed to be distributed over the possible staggered conformations; the excluded volume problem is handled by omitting the conformations for which there is appreciable atom interference. The few available experimental data are compared with the theory.

Introduction

The first paper of this series³ (I) presented a method for estimating charges on atoms in saturated organic molecules. In these molecules, the so-called inductive effect is predominant in determining the net charges on the atoms. After a readjustment of one of the parameters for the C-C bond in part IV of this series⁴ (IV), (this readjustment being in line with a reconsideration of the C-C bond longitudinal polarizability⁵), the theory successfully explained the charges in many halogenated hydrocarbons, as evidenced by the good agreement of calculated and observed dipole moments shown in I and IV. The success of the theory is exemplified by the close verifications of the predicted dipole moment of CH_2F_2 ⁶ and of the separate components, and hence angle with C-C axis, of the dipole moment of CH_3CHF_2 .⁷

So far, this series has been concerned only with halogenated alkanes for which there are no configurational problems, *i.e.*, molecules for which internal rotation, if present, does not affect the dipole moment. We now turn our attention to a class of molecules where the effect of internal rotation on dipole moment is very pronounced. The α,ω -dihaloalkanes have long been the subject of theoretical interpretation in this connection. Their dipole moments are strongly temperature dependent, and the moments of members of an homologous series vary in a way that appears irregular, although there are not enough reliable data to settle the problem of just how they do vary. Now, the theory and parameters of I and IV lead to a predicted dipole moment for any given α,ω -dihaloalkane configuration. Also, simple methods for tabulating and weighting *n*-alkane configurations have been reported from this

Laboratory⁸; as shown below, minor extensions allow the α,ω -disubstituted molecules to be tabulated and weighted. Therefore, we have performed the following calculations to determine how the experimental moments might be expected to vary with both temperature and chain length. We have confined ourselves to chlorine and bromine substituents, as there are practically no experimental data for the other halogens.

Recently, Hayman and Eliezer⁹ have considered the dibromoalkanes, using the theory of I and IV. However, the configurational problem is approached in the present paper in a way that permits the "excluded volume effect" to be taken into account; *i.e.*, geometrically impossible configurations are omitted. This was the case with neither the work of Hayman and Eliezer nor with earlier explorations of this problem.¹⁰ Also, both temperature and chain length are treated as variables in the present work.

Configurations.—Normal alkane chains may assume various configurations in which all bonds are staggered, which is equivalent to saying that the carbon atoms fit on a diamond lattice.^{3,10} The configurations which depart from complete staggering of all sets of bonds joined to all C-C bonds are not so stable and may be ignored. The staggered configurations may be described by codes in which the digit 2 represents a *trans* arrangement of three successive C-C bonds, and the digits 1 and 3 represent the two mirror-image gauche arrangements (*G'* and *G*, respectively, of Mizushima¹⁰). With this notation *n*-pentane, for example, has nine configurations which may be grouped into four sets as

22
11, 33
13, 31
12, 21, 32, 23

Here all configurations in each group are identical or mirror images. The smallest number in each group may be called the "standard configuration

(1) (a) This work was partially supported by a National Science Foundation undergraduate research participation grant to J. J. R. (b) Presented at the Fall Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) Esso Research and Engineering Co., Linden, N. J.

(3) R. P. Smith, T. Ree, J. L. Magee and H. Eyring, *J. Am. Chem. Soc.*, **73**, 2263 (1951).

(4) R. P. Smith and E. M. Mortensen, *ibid.*, **78**, 3932 (1956).

(5) R. P. Smith and E. M. Mortensen, *J. Chem. Phys.*, **32**, 508 (1960).

(6) D. R. Lide, Jr., *J. Am. Chem. Soc.*, **74**, 3548 (1952).

(7) G. H. Kwei and D. R. Herschbach, *J. Chem. Phys.*, **32**, 1270 (1960).

(8) R. P. Smith and E. M. Mortensen, *ibid.*, **35**, Aug. (1961).

(9) H. J. G. Hayman and I. Eliezer, *ibid.*, **28**, 890 (1958).

(10) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954.

code." For most purposes, then, it may be considered that there are four *n*-pentane configurations, *i.e.*, 22, 11, 13 and 12, with weights 1, 2, 2 and 4, respectively, and symmetry numbers 2, 2, 1 and 1, respectively. From previous work,⁸ we had available an IBM card for every standard configuration code up to and including the *n*-decane configurations. For these chains of ten or fewer carbons, the geometrically impossible chains are those for which a 13 or 31 sequence occurs in the standard configuration code. The excluded volume problem may be handled by simply culling out these disallowed configurations.⁸ If a certain configuration code for a hydrocarbon corresponds to a disallowed configuration, there will still be interference of atoms when end hydrogens are replaced by halogens. Hence only the allowed alkane configurations are used in forming dihalogen derivatives. Each such alkane configuration was prefixed and suffixed by all combinations of the digits 1, 2, 3 to indicate the relations of the carbon-halogen bonds to the carbon skeleton. The large sizes of the chlorine and bromine atoms now require that a number of the dihalogen molecules be disallowed and omitted from further calculations. Thompson and Sweeney¹¹ have discussed this problem. In the first place, if we temporarily take the C-C and C-Hal. distances equal, we must exclude isomers for which the two halogen atoms would occupy adjacent lattice sites on a diamond lattice. This situation is impossible for ethane and propane derivatives; the 313 dihalobutane configuration must be omitted; and a very few of the configurations for long chains should be omitted, although this correction is so small that we have not made it for longer chains, where isomers which might be excluded on this basis are such a small fraction of the total. The case of next-nearest halogen neighbors on a diamond lattice must also be considered. The halogens in CH₂Cl₂ are almost this close without evidence of appreciable strain,¹² but the van der Waals radii seem to demand the elimination of isomers in which these halogen distances occur.¹¹ The situation is impossible for ethane derivatives. The 13 dihalopropane configuration was omitted on this basis; and the situation arises again only for longer chains, where the effect was ignored. The next largest possible interhalogen separation is that found in gauche dichloroethane. This is clearly allowed.

Dipole Moments of Configurations. Averaging.—The theory of I, with parameters of I except for the revised C-C bond parameter given in IV, was used for the calculation of charges on the atoms in the molecules under consideration. For the longer molecules the theory requires the tedious solution of a large number of simultaneous equations. To facilitate these, and future calculations, a program for the application of the theory of I to any molecule was written for the Burroughs 205 electronic computer. The computational scheme used could be adapted easily to any com-

puter with several hundred or more words of storage. A relaxation method¹³ was used, as this conveniently allows the number of bonds, and hence the number of simultaneous equations, to be variable, without the complications this variability would involve if a determinantal method were employed. As a first approximation, charges on all atoms are taken to be zero. The residuals

$$F_{ab} = Q_a^b - \alpha_{ab} - \beta_b^a \epsilon_b + \beta_a^b \epsilon_a$$

[*cf.* eq. 11 of I] are computed for all bonds a-b, and the largest one is set to zero by appropriately correcting the corresponding Q_a^b . The Q_b^a is changed by an equal but opposite amount, so that the total charge on the molecule remains zero. These changes require alteration of certain other residuals and of certain total net charges ϵ_i . Then the largest residual is again found and set to zero, and so on, until the largest residual is sufficiently small. Cards are initially read into the computer with the desired values of the bond parameters. Then cards having codes describing the connections of the bonds in the molecules under consideration are called for. Thus one may change parameters, without the necessity of changing the permanent "molecule" file of cards specifying bond connections for various molecules. The larger molecules involved in this study required two or three minutes of computer time each.

The atom charges were used to compute bond moments, using the assumed distances $R_{CC} = 1.541$ Å., $R_{CH} = 1.091$ Å., $R_{CCl} = 1.767$ Å. and $R_{CBr} = 1.937$ Å. These distances have been obtained¹⁴ by averaging observed distances in a number of alkanes and their halogen derivatives. Some variability of distances might be expected, but this should affect the results only slightly.

As discussed above, the carbon skeleton for every configuration was constrained to a diamond lattice. In addition, all bond angles involving hydrogen and halogens were assumed strictly tetrahedral. Thus every bond is parallel to one of the four bond directions of a diamond lattice, so that the dipole moment components for the *i*th configuration μ_{ij} ($j = x, y, z$) were very easy to calculate; the coordinate axes were chosen to coincide with the edges of the diamond lattice unit cell. These computations were facilitated by the methods discussed by Smith and Mortensen⁸ for assigning direction numbers to bonds. The mean square moments, $\bar{\mu}^2$, were computed as

$$\bar{\mu}^2 = \frac{\sum_i \sum_j (w_i/\sigma_i) \mu_{ij}^2 x_i^{t_i} y_i^{T_i}}{\sum_i (w_i/\sigma_i) x_i^{t_i} y_i^{T_i}}$$

Here w_i and σ_i are the weight and symmetry number of the *i*th configuration; t_i and T_i are the numbers of *trans* C-C-C-C and C-C-C-Hal.

(13) D. N. de G. Allen, "Relaxation Methods in Engineering and Science," McGraw-Hill Book Co., Inc., New York, N. Y., 1954.

(14) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, pp. S 12-S 15.

(11) H. B. Thompson and C. C. Sweeney, *J. Phys. Chem.*, **64**, 221 (1960).

(12) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 193.

arrangements, respectively; and x and y are stabilization factors given by

$$x = \exp(\Delta E_1/RT)$$

$$y = \exp(\Delta E_2/RT)$$

where ΔE is the energy stabilization per *trans* C-C-C-C arrangement and $\Delta E'$ is the energy stabilization per C-C-C-Hal. arrangement. The quantities w_i , σ_i , h_i , and T_i were found readily by the methods of Smith and Mortensen,⁸ with some small and obvious extensions.

For the two-carbon compounds, T_1 is the number of Hal.-C-C-Hal. arrangements (0 or 1) and y is assumed the same for *trans* stabilization here as for *trans* C-C-C-Hal. stabilization.

Computing procedures were developed to take full advantage of the equivalences of bonds in a molecule (as the four C-H bonds in 1,2-C₂H₄Cl₂) and of the equivalence of x , y and z coordinates in the numerator sum. Also, it was possible to carry out part of the process of evaluating the summations before inserting specific numbers for bond dipole vectors. Thus various parameters, including bond vectors, could be changed and revised results obtained with minimum expenditure of computer time.

Results

We present a selection of our results in the accompanying tables and graphs. The reasonable value^{8,10} $\Delta E_1 = 0.8$ kcal./mole is used throughout; we have varied this parameter, without obtaining better results. Most of the theoretical values for both dichloro and dibromo compounds are presented for $\Delta E_2 = 1.4$ kcal./mole. As satisfactory results as can be obtained for any value of this parameter are thus found. The *trans-gauche* Br-C-C-Br and Cl-C-C-Cl energy differences have been found to be of about this magnitude.¹⁰

For Br(CH₂)_nBr at 25°, Fig. 1 shows the theoretical effect of chain lengthening on average dipole moment for three choices of ΔE_2 . (The Cl(CH₂)_nCl moments yield a very similar graph.) The experimental values tend to lie between the two lower "curves"; in Table I we compare the experimental values with the theoretical values for $\Delta E_2 = 1.4$. The agreement is good, considering the uncertainty of the relation of the measured moment in solution to the gas moment, which of course is the quantity provided by the theory. Table I also indicates theoretical and experimental moments for the dichlorides. The theoretical temperature dependencies for the dichlorides (again, the dibromides yield very similar curves) are shown in Fig. 2. It is remarkable that for $n = 3$ there is practically no temperature variation, while large positive temperature coefficients are found for the other shorter chains. Reliable temperature coefficient data are scarce. Working with the Br(CH₂)₃Br liquid, Ketelaar and van Meurs¹⁵ found a slight negative temperature coefficient. It is unfortunate that the relation-

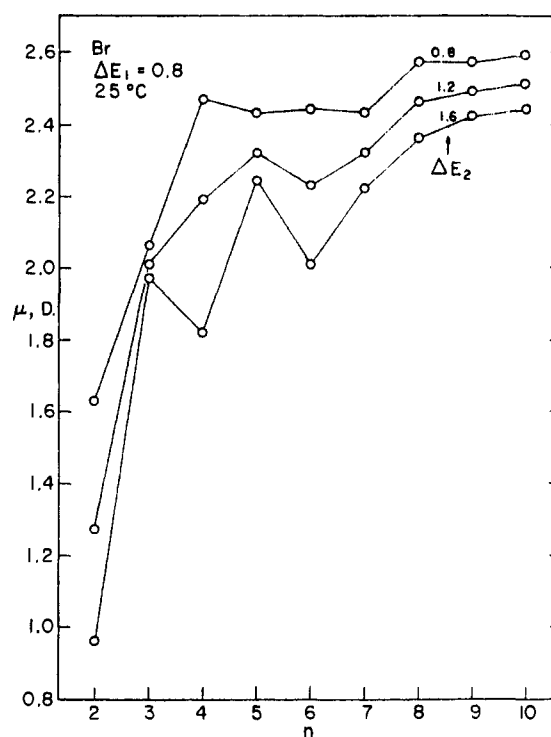


Fig. 1.—Theoretical effect of chain lengthening on Br(CH₂)_nBr dipole moments at 25°, $\Delta E_1 = 0.8$ kcal./mole.

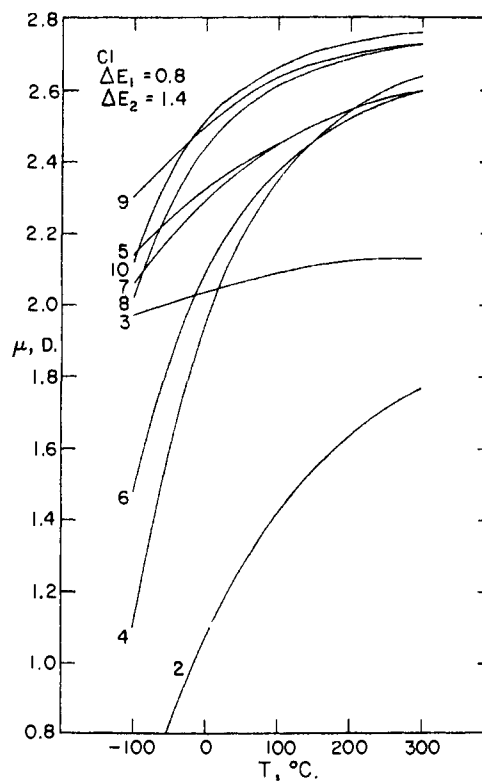


Fig. 2.—Theoretical temperature dependencies of Cl(CH₂)_nCl dipole moments.

ship of gas moment to measurements on a pure dipolar liquid is uncertain. The theoretical increase in dipole moment in going from -100 to

(15) J. A. A. Ketelaar and N. van Meurs, *Rec. trav. chim.*, **76**, 437 (1957).

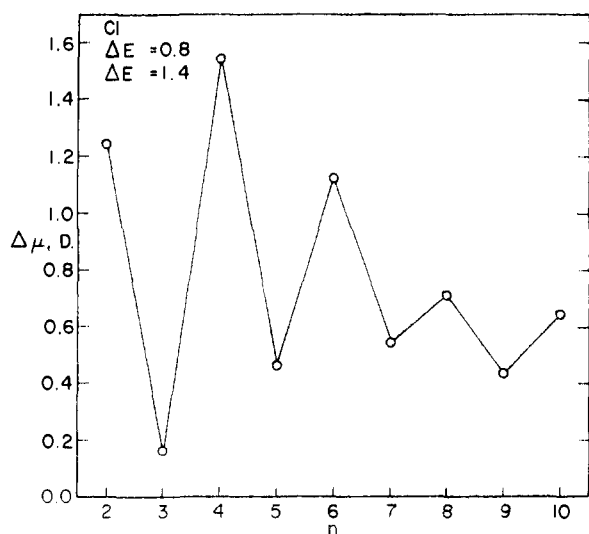


Fig. 3.—Theoretical increase, $\Delta\mu$, of $\text{Cl}(\text{CH}_2)_n\text{Cl}$ dipole moments in going from -100 to 300° .

300° as a function of chain length is shown in Fig. 3.

TABLE I

COMPARISON OF THEORETICAL AND EXPERIMENTAL DIPOLE MOMENTS^a

X	n	Theory		Experiment	
		Moment (D)	Temp. ($^\circ\text{C}$)	Moment (D)	Temp. ($^\circ\text{C}$)
Br	2	1.11	25	0.91, 1.02 ^b	66
		1.34	100	0.97, 1.07 ^b	95
		1.55	200	1.10, 1.19 ^b	164
		1.69	300	1.26 ^b	258
				0.89-0.97 ^c (hex)	20
	3	1.99	25	2.10-2.23 ^c (hex)	20
	4	2.01	25	1.97-2.11 ^c (hex)	20
	5	2.28	25	2.31-2.57 ^c (hex)	20
	6	2.11	25	2.36-2.64 ^c (hex)	20

	7	2.27	25		
	8	2.41	25		
	9	2.45	25	2.43-2.39 ^c (hex)	20
	10	2.47	25	2.56-2.98 ^c (hex)	20
Cl	2	1.16	25	1.19, 1.24 ^b	32-35
		1.41	100	1.39 ^b	99-103
		1.63	200	1.56 ^b	208-212
		1.77	300		
3	2.05	25	2.10 ^d (benz)	25	
	2.09	100	2.07 ^e	101-212	
	2.12	200			
4	2.08	25	2.10 ^d (benz)	25	
	2.35	100	2.22 ^e	160-235	
	2.54	200			
5	2.36	25	2.34 ^d (benz)	25	
6	2.19	25	2.26 ^d (benz)	25	
7	2.34	25			
8	2.50	25			
9	2.54	25			
10	2.57	25	2.60 ^d (benz)	25	

^a Theoretical moments are for $\Delta E_1 = 0.8$, $\Delta E_2 = 1.4$ kcal./mole. Experimental results are for gases, unless indicated hex (*n*-hexane) or benz (benzene) solution. ^b A. A. Maryott and F. Buckley, "Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," National Bureau of Standards Circular 537, U. S. Government Printing Office, Washington, D. C., 1953. ^c Ref. 15. When two values are indicated, the first is calculated from the Böttcher equation (spherical molecules assumed) and the second is for the Scholte equation (stretched molecules). ^d H. B. Thompson, private communication. ^e R. A. Oriani and C. P. Smyth, *J. Chem. Phys.*, 16, 930 (1948); 17, 1174 (1949).

The over-all agreement with experiment is good, considering (a) the uncertainty in our knowledge of the *trans-gauche* energy differences, and (b) experimental uncertainties. Much improvement is needed along both these lines.

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