

Dipole Moments and Conformational Energies of the Chloroethanes¹

J. E. Mark* and C. Sutton

Contribution from the Department of Chemistry and the Macromolecular Research Center, University of Michigan, Ann Arbor, Michigan 48104. Received July 10, 1971

Abstract: Dipole moments have been calculated for all members of the chloroethane series, using charge distributions based on the semiempirical method of Smith, Eyring, and coworkers. In the case of chloroethane, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1,1,2-tetrachloroethane, pentachloroethane, and hexachloroethane, the dipole moments are independent of internal rotation and the charge distributions lead directly to predicted values of the dipole moments. For 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane, however, the dipole moments must be averaged over all conformations of the molecules. This averaging was carried out by weighting each conformation of the structurally fixed charges by a Boltzmann factor in the conformational energy, which was calculated from an inherent torsional potential derived from ethane, Coulomb's law for electrostatic interactions, and the potential functions of Scheraga and coworkers for van der Waals interactions. The integrals arising in the averaging procedure were evaluated by both a direct numerical method, which corresponds to permitting a continuum of conformations, and by the widely-used rotational isomeric state approximation. When rotational states are located so as to correspond to conformations of minimum *total* conformational energy, the rotational isomeric state scheme yields root-mean-square dipole moments essentially the same as those calculated taking account of the entire continuum of conformations. For both types of chloroethanes, calculated dipole moments were found to be in good agreement with experimental results reported in the literature. This model for the chloroethanes was further tested by calculation of the magnitudes of the rotational barriers in all of these molecules and, where appropriate, the differences in energy between rotational minima and their location. Although experimental studies of these quantities are rather limited, they provide strong support for the general validity of the present model for this series of molecules.

During the last several decades there have been a large number of experimental studies²⁻⁶ of the dipole moments of the chloroethane series, the nine members of which range from ethyl chloride or chloroethane to hexachloroethane. A general theoretical interpretation of these experimental results has not been given, however, presumably for a number of reasons. Most importantly, in the case of such relatively complicated molecules rigorous quantum mechanical methods are not yet at the stage where they can provide charge distributions, obviously a fundamental requirement in the calculation of dipole moments. In addition, calculations are somewhat complicated by the fact that the dipole moments of several members of this series are dependent on internal rotation about carbon-carbon bonds;^{7,8} in these cases the methods of statistical mechanics must be employed to obtain an appropriately averaged dipole moment.

It should be possible to obtain sufficiently good charge distributions for the purpose at hand by use of a semiempirical method, developed by Smith, Eyring, and coworkers,^{9,10} which explicitly takes into account in-

ductive effects. These workers have in fact demonstrated the general validity of their theory⁹⁻¹³ and, in particular, its utility in the calculation of dipole moments for a variety of nonconjugated molecules which, if internal rotation is present, have elements of symmetry such that their dipole moments are independent of such rotations.^{9,10} Although several chloroethanes were included in these studies,^{9,10} recent evidence suggests a minor modification in the parameters used in these cases.

It is the purpose of the present study to utilize this semiempirical theory to calculate charge distributions for all of the chloroethanes. In the case of those molecules which contain a threefold symmetric group, either CH₃ or CCl₃, the dipole moments are independent of internal rotation and may be calculated directly from the charge distributions. For the remaining members of the series, average dipole moments may be calculated by weighting each conformation with a Boltzmann factor in the conformational energy, the required energies being calculated from bond torsional potentials, simple electrostatic theory, and widely used semiempirical functions for van der Waals interactions. Since in these conformationally simple molecules there is only one bond giving rise to internal rotation, the averaging of the dipole moment can be carried out in two ways: (i) permitting the molecules a continuum of conformations by evaluating the integrals arising in the averaging procedure by direct numerical analysis and (ii) by constraining the molecules to any one of three discrete "states" associated with minima in the conformational energy, thereby replacing these integrals

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(2) Measurements of dipole moments of these molecules which had been reported prior to 1962 are summarized in ref 3; several more recent studies are described in refs 4-6.

(3) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

(4) J. Crossley and S. Walker, *J. Chem. Phys.*, **45**, 4733 (1966).

(5) J. Crossley and S. Walker, *ibid.*, **48**, 4742 (1968).

(6) J. Crossley and C. P. Smyth, *J. Amer. Chem. Soc.*, **91**, 2482 (1969).

(7) Extensive general discussions of the properties of molecules of this type are given in ref 8.

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

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

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

(11) R. P. Smith and H. Eyring, *ibid.*, **74**, 229 (1952).

(12) R. P. Smith and H. Eyring, *ibid.*, **75**, 5183 (1953).

(13) R. P. Smith and J. J. Rasmussen, *ibid.*, **83**, 3785 (1961).

by simple sums over three terms. The latter method is of course the rotational isomeric state approximation, a representation widely used in the conformational analysis of small molecules^{8,14,15} because it is convenient, and in the interpretation of the statistical properties of polymer chains¹⁶⁻¹⁸ because the large number of rotatable skeletal bonds and the interdependence of rotational states in these molecules make direct evaluation of the corresponding integrals virtually impossible. Comparison of dipole moments calculated by these two computational techniques should therefore provide extremely useful information on the degree of approximation involved in the use of rotational isomeric state theory. The validity of the charge distributions in all the chloroethanes may be gauged by comparison of theoretical and experimental values of both the dipole moments and the heights of the barriers separating minima in the conformational energy. In the case of those chloroethanes lacking a threefold symmetric group, calculation of differences in energy at these minima, and their location, provides additional possible tests of the present model.

Theory

Molecular Structure and Charge Distributions. There is some structural information¹⁹ on all the chloroethanes except the two tetrachlorides and the pentachloride. Critical evaluation of these results led to the adoption of the following values for bond lengths (Å) in all the members of this series: $l(\text{C}-\text{C}) = 1.54$, $l(\text{C}-\text{Cl}) = 1.76$, and $l(\text{C}-\text{H}) = 1.09$. Published information¹⁹ regarding bond angles in these molecules is not very conclusive. We assume all bond angles to be tetrahedral, *i.e.*, 109.5° , for two reasons: (i) preliminary calculations of coulombic and van der Waals interactions (see below) indicated that intramolecular interactions between atoms in the chloroethanes do not in general seem to be sufficiently large to cause extensive bond angle distortion, and (ii) most importantly, there is simply insufficient structural evidence¹⁹ to permit modification of this assumption without considerable arbitrariness. (In recent studies of barrier heights in a number of molecules, including several chloroethanes, Scott and Scheraga²⁰ and Liquori and coworkers²¹ have likewise assumed tetrahedral bonding, although Abraham and Parry²² have adopted a value 111° for C-C-Cl bond angles and for Cl-C-Cl bond angles in groups other than CCl_3 .) In all of these treatments, including the present, values of the bond lengths and bond angles are held to be constants and

(14) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965.

(15) M. Hanach, "Conformation Theory," Academic Press, New York, N. Y., 1965.

(16) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience, New York, N. Y., 1963.

(17) T. M. Birshtein and O. B. Ptitsyn, "Conformations of Macromolecules," Interscience, New York, N. Y., 1966.

(18) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

(19) H. J. M. Bowen and L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958; L. E. Sutton, "Interatomic Distances, Supplement," Special Publication No. 18, The Chemical Society, London, 1965.

(20) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).

(21) J. L. De Coen, G. Elefante, A. M. Liquori, and A. Damiani, *Nature (London)*, **216**, 910 (1967).

(22) R. J. Abraham and K. Parry, *J. Chem. Soc. B*, 539 (1970).

thus, the structures are considered rigid except for rotations about carbon-carbon bonds.

We adopt for the calculation of charge distributions in these molecules the theory of Smith, Eyring, and coworkers.^{9,10} This semiempirical theory is qualitatively based on the molecular orbital method, in the approximation of the linear combination of atomic orbitals. It has given satisfactory results, for example, in (i) the calculation of dipole moments of halogenated methanes,⁹ several halogenated ethanes,^{9,10} α,ω -dichloroalkanes and α,ω -dibromoalkanes,¹³ and a variety of aliphatic nitro compounds,²³ oximes,²³ acids,²⁴ and halogenated alcohols,²⁵ (ii) the interpretation of dissociation energies and ionization potentials for a number of molecules and free radicals,¹² and (iii) the interpretation of activation energies for free-radical substitution reactions.¹² The experimental data required for the application of this theory to the chloroethanes are the dipole moment of methyl chloride, bond longitudinal polarizabilities, electron screening constants, and covalent radii; the values of these quantities employed in the present study are those recommended by Smith and Mortensen.¹⁰ It is also necessary to assume values for the magnitude and direction of the CH bond dipole in CH_4 . Smith, Eyring, and coworkers originally chose values for this bond moment, $m_{\text{CH}}(\text{CH}_4)$, of 0.0 and 0.3 D, with both dipole directions, C^+H^- and $\text{C}-\text{H}^+$, being considered for the latter value.⁹ Since in these initial calculations any of these three assignments gave results in satisfactory agreement with experiment, the simplest choice, $m_{\text{CH}}(\text{CH}_4) = 0.0$ D, was used for subsequent calculations.¹⁰⁻¹³ Critical evaluations^{26,27} of pertinent experimental evidence and recent theoretical results²⁸⁻³⁰ support a small but nonzero dipole moment, with the dipole direction corresponding to $\text{C}-\text{H}^+$. Of particular interest in this regard are three theoretical studies of charge distributions in methane and a number of related molecules.²⁸⁻³⁰ Using both semiempirical and *ab initio* molecular orbital methods, Pople and coworkers^{28,29} obtain results in strong support of the dipole direction $\text{C}-\text{H}^+$; their result for the magnitude of this moment in methane, however, is only ~ 0.1 D. It is possibly relevant that of the seven hydrocarbons thus studied,^{28,29} the charge distributions in all but one case led to calculated dipole moments smaller than those experimentally observed. The charge distributions reported by Allen and coworkers,³⁰ on the other hand, yield unrealistically large bond dipoles, *e.g.*, 1.45 D for $m_{\text{CH}}(\text{CH}_4)$. For subsequent analysis, these *ab initio* results³⁰ were then calibrated by use of the proportionality factor between calculated and "standard" values of $m_{\text{CH}}(\text{CH}_4)$; of interest here is the choice by these workers³⁰ of $m_{\text{CH}}(\text{CH}_4) = 0.4$ D, direction $\text{C}-\text{H}^+$, as the best value for this purpose.

(23) S. Soundararajan, *Tetrahedron*, **19**, 2171 (1963).

(24) S. S. Krishnamurthy and S. Soundararajan, *ibid.*, **24**, 167 (1968).

(25) S. S. Krishnamurthy and S. Soundararajan, *J. Phys. Chem.*, **73**, 4036 (1969).

(26) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955.

(27) N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Behaviour," Van Nostrand-Reinhold, London, 1969.

(28) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(29) W. J. Hehre and J. A. Pople, *ibid.*, **92**, 2191 (1970).

(30) M. E. Schwartz, C. A. Coulson, and L. C. Allen, *ibid.*, **92**, 447 (1970).

On the basis of the above information, we employ the general inductive theory of Smith, Eyring, and co-workers to calculate charge distributions in the chloroethanes, the only modification being the adoption of 0.3 D for $m_{\text{CH}}(\text{CH}_4)$, with the dipole in the direction C-H⁺. In consistency with the inclusion of a separate contribution to the conformational energy for an "inherent" torsional potential (see below), the charges thus obtained are assumed to be invariant to internal rotation.

Conformational Energies. The now widely used classical approach³¹ was employed in the calculation of the energy of these molecules as a function of the rotation angle ϕ about their carbon-carbon bonds. This conformational energy E was expressed as

$$E = (E_0/2)(1 - \cos 3\phi) + \sum_{i < j} [a_{ij} \exp(-b_{ij}r_{ij}) - c_{ij}r_{ij}^{-6} + q_i q_j / \epsilon r_{ij}] \quad (1)$$

where the sum extends over all pairs i, j of atoms whose distance of separation r_{ij} depends on ϕ . The first term on the right-hand side of eq 1 represents an "inherent" torsional potential,^{20,32,33} assumed to be constant for the series of chloroethanes, with E_0 representing the barrier height in the absence of nonbonded interactions (both van der Waals and coulombic). We adopt for E_0 the barrier height observed for ethane, 2.9 kcal/mol;³⁴ contributions from nonbonded interactions are removed by expression of the nonbonded interactions in the chloroethanes *relative* to the corresponding nonbonded interactions calculated for ethane. These interactions are given by the three terms in the sum in eq 1, the first two representing the van der Waals interactions and the last the coulombic interactions. The values adopted for the parameters a_{ij} , b_{ij} , and c_{ij} are those recommended by Scott and Scheraga;²⁰ for distances in ångströms and energies in kilocalories per mole, these are: H...H 9.17×10^3 , 4.54, and 45.2, respectively; H...Cl 3.90×10^4 , 4.15, and 321, respectively; and Cl...Cl 3.14×10^5 , 3.75, and 2520, respectively. Our final term in eq 1, where q_i and q_j are the charges on atoms i and j , respectively, and ϵ is the dielectric constant of the medium separating them, replaces their corresponding term for the coulombic energy. We feel that their method²⁰ for calculating these interactions in the chloroethanes is unrealistic in that it assumes (i) in the case of H...H and H...Cl interactions the charges on these atoms are negligibly small and (ii) in the case of the Cl...Cl interactions, the charges are independent of the presence of other Cl atoms in the molecule, *i.e.*, inductive effects are totally neglected. The interatomic distances required for the application of eq 1 were calculated using orthogonal transformation matrices in the usual manner.³⁵

Conformationally Averaged Dipole Moments. According to the methods of statistical mechanics, the mean-square dipole moment $\langle \mu^2 \rangle$ of substituted

ethanes having dipole moments dependent on internal rotation is given by⁸

$$\langle \mu^2 \rangle = \int_0^{2\pi} \mu^2(\phi) \exp[-E(\phi)/RT] d\phi / \int_0^{2\pi} \exp[-E(\phi)/RT] d\phi \quad (2)$$

with the root-mean-square dipole moment being defined by $\mu = \langle \mu^2 \rangle^{1/2}$. Direct numerical integration may be used to evaluate such dipole moments by replacing the integrals in this averaging process by the corresponding sums³⁶

$$\langle \mu^2 \rangle \cong \sum_i \mu_i^2 \exp[-E_i/RT] \Delta\phi / \sum_i \exp[-E_i/RT] \Delta\phi \quad (3)$$

where the dipole moments μ_i and conformational energies E_i are evaluated at a number of equally spaced values of ϕ over the same interval, 0 to 2π . Use of sufficiently small intervals $\Delta\phi$, of course, brings eq 2 and 3 into coincidence. Alternatively, values of μ may be calculated using the rotational isomeric state approximation in which rotational angles are restricted to any one of a small number of discrete values,¹⁶⁻¹⁸ these values generally being chosen so as to correspond to minima in the conformational energy. In the case of the chloroethanes, the discrete "states" thus defined are designated *trans* (t), *gauche positive* (g⁺), and *gauche negative* (g⁻) and would be located at values of ϕ of approximately 0, 120, and -120°, respectively.⁸ According to this scheme, the mean-square dipole moment is simply

$$\langle \mu^2 \rangle \cong \sum_{i=t, g^+, g^-} \mu_i^2 \exp(-E_i/RT) / \sum_{i=t, g^+, g^-} \exp(-E_i/RT) \quad (4)$$

Location of the rotational states at minima in the conformational energy is expected to make this a good approximation on physical grounds;¹⁶⁻¹⁸ at ordinary temperatures the great majority of molecules at any instant would be found within a relatively small interval about one of these minima.¹⁸ Furthermore, except in the case of extremely asymmetric potential wells, positive and negative departures from the rotational states would be expected, to a large extent, to be mutually compensatory.¹⁸

Results and Discussion

The nine members of the chloroethane series are shown in Figure 1. The first six molecules are those for which $\mu \neq f(\phi)$; they are (a) chloroethane, (b) 1,1-dichloroethane, (c) 1,1,1-trichloroethane, (d) 1,1,1,2-tetrachloroethane, (e) pentachloroethane, and (f) hexachloroethane, and are all shown in their staggered conformations. The remaining members, which have $\mu = f(\phi)$, are (g) 1,2-dichloroethane, (h) 1,1,2-trichloroethane, and (i) 1,1,2,2-tetrachloroethane; they are shown in their arbitrarily designated *trans* forms, for which ϕ is taken to be zero. The direction of internal rotation is relevant only in the case of the dependence of conformational energy on rotational angle in 1,1,2-trichloroethane and thus the direction arbitrarily chosen for positive ϕ is indicated in this portion of the figure. Shown for each molecule in the series is the charge distribution, in units of 10^{-2} electron, calculated as

(31) For a recent review of this approach, see J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).

(32) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(33) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966).

(34) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

(35) D. A. Brant and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 2791 (1965).

(36) See, for example, W. Kaplan, "Advanced Calculus," Addison-Wesley, Reading, Mass., 1952.

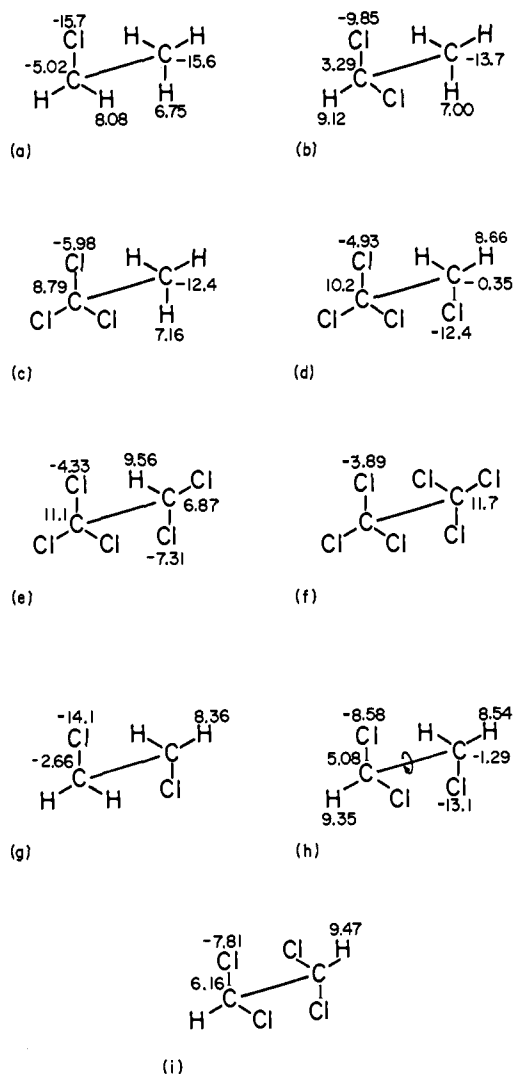


Figure 1. The chloroethane series. Members a through f, which contain threefold symmetric groups and thus have dipole moments independent of rotation angle ϕ , are shown in their staggered conformations. The remaining members, which lack this symmetry, are shown in their arbitrarily designated trans forms, for which $\phi = 0$. The arrow in part h shows the direction of rotation of the atoms about the second carbon atom which is associated with positive values of ϕ . Charge distributions, calculated as described in the text, are given in units of 10^{-2} electron.

already described. A similar calculation gave the charge distribution in ethane itself; it is characterized by a charge of 6.33×10^{-2} electron unit on each H atom. The most striking feature of these distributions is the marked decrease, by a factor of approximately 0.25, of the magnitude of the charge ascribed to a Cl atom as the series chloroethane through hexachloroethane is traversed. Although such charge distributions are admittedly approximate, these results already seem to indicate that considerable error is committed in those studies of chloroethanes which assume constant²⁰⁻²² charges on Cl atoms, irrespective of the number of such atoms in the molecule.

In the case of those chloroethanes having $\mu \neq f(\phi)$, these charge distributions are sufficient for immediate calculation of predicted values of the dipole moments;¹⁰ these results are given in the third column of Table I. The second column of this table shows the results obtained from the model²² adopted by Abraham and Parry

Table I. Dipole Moments^a of Chloroethanes Having $\mu \neq f(\phi)$

Molecule	Calcd		Obsd	
	Abraham model ^b	Present model	Vapor phase ^c	Solution
CH ₂ Cl-CH ₃	1.70	1.86	1.75-2.09	
CHCl ₂ -CH ₃	1.93	1.79	2.07-3.33	1.95 ^d
CCl ₃ -CH ₃	1.70	1.55	1.79, 2.03	1.84 ^d
CCl ₃ -CH ₂ Cl	1.93	1.58		1.44 ^d
CCl ₃ -CHCl ₂	1.67	1.09	0.92	1.07 ^d
CCl ₃ -CCl ₃	0.00	0.00		0.00 ^e

^a Debyes. ^b Reference 22. ^c Reference 3. ^d Reference 6.

for the calculation of rotational barriers in these six molecules. This model assigns a constant charge of approximately -15.3×10^{-2} electron to all chlorine atoms, in all molecules of this group. Difficulties inherent in this model are already apparent from these results. The predicted equivalence of the dipole moments of chloroethane and 1,1,1-trichloroethane, for example, parallels, of course, the prediction of the constant bond dipole model that methyl chloride and chloroform should have nearly the same dipole moment.³⁷ As pointed out many years ago by Smith and Eyring,¹¹ however, the observed dipole moment of chloroform (1.0 D³) is only approximately half that of methyl chloride (1.9 D³). In this case, the inductive effect causing this difference could be described in particularly simple, qualitative terms: "chloroform has a much lower moment because three chlorine atoms cannot remove from the central carbon atom three times as much charge as can one chlorine atom, since as the carbon effective nuclear charge is increased by the removal of negative charge from the atom, it becomes increasingly difficult to remove electronic charge from the carbon."¹¹ We nonetheless include values calculated from this model in the comparison with experimental results in order to determine the magnitude of the error committed by total neglect of inductive effects.

Experimental values have been reported for the dipole moments of all of the chloroethanes listed in Table I. We consider first the results obtained for these molecules in the vapor phase, since measurements carried out in solution require consideration of the possible effect of solute-solvent interactions on the dipole moment.^{5,6,26,38-41} Since in these molecules the only possible effect of temperatures on the dipole moment would arise from the presumably small changes in bond lengths and bond angles with temperature, we accept values of the dipole moment at any temperature for the comparison of experiment with theory. The experimental results,³ which substantiate the expected independence of dipole moment on temperature, are summarized in the fourth column of this table. As is immediately obvious, the disagreement between reported values of the dipole moment in the vapor phase prevents the use of these experimental results alone as a definitive test of the calculated values. We therefore consider as well dipole moments obtained from measurements on these molecules in solution. By far the most complete set of such results is given in the re-

(37) See, for example, ref 27, p 248.

(38) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(39) K. Chitoku and K. Higasi, *Bull. Chem. Soc. Jap.*, **40**, 773 (1967).

(40) H. Müller, *Phys. Z.*, **34**, 689 (1933).

(41) M. Kubo, *Bull. Inst. Phys. Chem. Res., Tokyo*, **13**, 1221 (1934).

cent study by Crossley and Smyth⁶ of seven of the chloroethanes, including 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1,1,2-tetrachloroethane, and pentachloroethane, in a variety of nonpolar solvents, at a number of temperatures. The solvents employed were cyclohexane, benzene, *p*-xylene, mesitylene, and *p*-dioxane; we adopt for the present purposes the results obtained in cyclohexane, since this solvent is regarded^{6,38} as the most nearly "inert," *i.e.*, having the least tendency to interact strongly with the solute, through dipole-induced dipole interactions,^{6,38} weak hydrogen bonds,^{5,6,39} or possibly even complexation.^{40,41} In any case, solvent effects on the dipole moment through changes in conformational energy are of course absent in the group of chloroethanes presently under consideration. Because of the lack of a value of the dipole moment of chloroethane in this solvent, we accept the value 2.04 D recommended³ for this molecule in the vapor state. These results are given in the last column of the table; also included, for completeness, is the dipole moment reported for hexachloroethane in *n*-hexane.³

The general trend shown by these experimental results is a continuous decrease in dipole moment from approximately 2 to 1 D as the degree of substitution is increased in the manner shown. Because of symmetry, the dipole moment of hexachloroethane obviously does not constitute a test of charge distributions and will not be included in the present discussion. Dipole moments calculated from the model of Abraham and Parry do not reproduce the observed trend in dipole moments, obviously because of the neglect of inductive effects. In the model of Scott and Scheraga,²⁰ the magnitude of the charge assigned to a Cl atom, apparently calculated from atomic electronegativities, is only -5.91×10^{-2} electron unit, approximately one-third the value chosen by Abraham and Parry. Correspondingly, values of the dipole moment calculated from this model are approximately one-third those obtained using the charge distributions of Abraham and Parry. For obvious reasons, we exclude from further discussion of both dipole moments and energy barriers the model²¹ of Liquori and coworkers, in which charge distributions and coulombic interactions are apparently entirely neglected.

The dipole moments calculated from the present model are given in the third column of the table; they are approximately 0.2 D lower than those calculated by Smith and Mortensen, in the approximation that $m_{\text{CH}}(\text{CH}_4) = 0.0$ D. This relative insensitivity of the dipole moment to the value adopted for $m_{\text{CH}}(\text{CH}_4)$ was previously noted for a variety of halogenated methanes and ethanes.⁹ Both sets of calculated results satisfactorily reproduce the experimental values of the dipole moments and their decrease with increasing degree of substitution; in both cases, the average difference between calculated and experimental values is only ± 0.15 D.

As has been shown, calculation of the dipole moments of this group of chloroethanes does not require information regarding conformational energies. Calculation of such energies, however, provides estimates of additional quantities suitable for comparison of theory and experiment. They are therefore reported here for this series of chloroethanes as well as the remaining group, where their determination is required for the

statistical mechanical averaging of the dipole moment. In the present series of molecules, the threefold symmetry of either a CH_3 or CCl_3 group imposes threefold symmetry on the dependence of conformational energy on rotational angle. Specifically, the three rotational minima correspond to the same energy, and the heights of the three barriers separating these minima are all of the same magnitude.

Since measurements of barrier heights are almost invariably carried out in the vapor phase,³⁴ we adopt a value of $\epsilon = 1.0$ ⁴² for the dielectric constant required in the calculation of conformational energies, as given in eq 1. Because of symmetry, the barrier heights in these molecules, and also in ethane itself, are simply the difference in energy between the conformations $\phi = 0^\circ$ and $\phi = 60^\circ$. The torsional potential of ethane, $(2.9/2)(1 - \cos 3\phi)$ kcal/mol, was corrected to account for nonbonded interactions as already described; the correction was found to be small, amounting to a decrease in the energy barrier, for example, of only approximately 0.2 kcal/mol. Barrier heights thus calculated, as well as values calculated by Abraham and Parry²² and by Scott and Scheraga,²⁰ are listed in columns two through four in Table II. The experimental

Table II. Barrier Heights,^a in the Vapor Phase, for Chloroethanes Having $\mu \neq f(\phi)$

Molecule	Calcd			Obsd ^d
	Abraham model ^b	Scheraga model ^c	Present model	
$\text{CH}_2\text{Cl}-\text{CH}_3$	3.8	3.4	3.0	3.7
$\text{CHCl}_2-\text{CH}_3$	4.6	3.6	3.1	3.5
CCl_3-CH_3	5.9	3.7	3.3	2.8
$\text{CCl}_3-\text{CH}_2\text{Cl}$	17.7		8.7	10.0
$\text{CCl}_3-\text{CHCl}_2$	29.4		14.1	14.2
$\text{CCl}_3-\text{CCl}_3$	49.5	20.9	19.6	17.5

^a Kilocalories per mole. ^b Reference 22. ^c Reference 20. ^d Reference 43.

values for these barrier heights were taken from a recent study of all the chloroethanes by Allen and coworkers.⁴³ This study presents new results using vibrational spectroscopy, as well as reanalysis and critical evaluation of some previously reported values of the barrier heights in these molecules. The values recommended by these authors are given in the last column of Table II. These results seem to indicate that the barrier heights are essentially independent of chlorine substitution which is restricted to one carbon atom; the value 3.3 kcal/mol represents the three such barrier heights to within a few tenths of a kilocalorie per mole. Additional substitution, involving both carbon atoms, however, markedly increases the barrier height, to a maximum value of approximately 18 kcal/mol for hexachloroethane.

The results calculated by Abraham and Parry²² give a very poor representation of the experimental results; the average discrepancy between theory and experiment amounts to almost 10 kcal/mol, with the largest disagreement occurring for the most heavily substituted molecules. These workers ascribe the poor agreement

(42) This choice of ϵ constitutes an approximation, since, for some interactions, the electrostatic lines of force pass through the molecule itself. There is at the present time no reliable, objective way of modifying the dielectric constant of the medium to take this into account.

(43) G. Allen, P. N. Brier, and G. Lane, *Trans. Faraday Soc.*, **63**, 824 (1967).

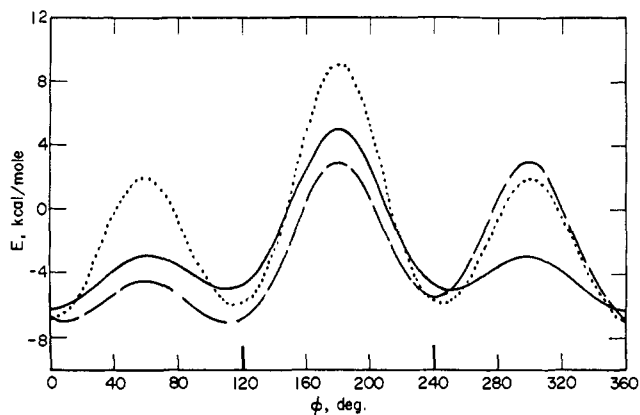


Figure 2. The conformational energy shown as a function of rotation angle for 1,2-dichloroethane (—), 1,1,2-trichloroethane (---), and 1,1,2,2-tetrachloroethane (····) in the vapor phase ($\epsilon = 1.0$).

to their failure to permit even larger bond angle distortions in eclipsed conformations, and also to their use of van der Waals potential functions which are slightly too "hard."⁴⁴ The present calculations indicate, however, that some of the discrepancy is simply due to neglect of the fact that inductive effects cause decreasing coulombic repulsions for Cl···Cl interactions as the degree of substitution increases.²¹ The energy barriers calculated by Scott and Scheraga²¹ are in reasonable agreement with the experimental values, the average difference between theoretical and experimental values being 1.2 kcal/mol. Possibly relevant here, however, is the fact that only one of the chloroethanes considered, hexachloroethane, has interactions between Cl atoms which are dependent on rotational angle. Furthermore, the value 3.23 kcal/mol adopted in these calculations²⁰ for the inherent torsional potential about carbon-carbon bonds seems to be unrealistically high.

The present calculations give the best account of the observed barrier heights, with the average difference between experimental and theoretical values amounting to approximately only 0.8 kcal/mol. The relative importance of van der Waals and coulombic interactions in the present model can be seen by comparison of results calculated for the two extreme cases, 1,2-dichloroethane and hexachloroethane, in which there are Cl···Cl interactions dependent on rotational angle. In 1,2-dichloroethane, the van der Waals interactions between the two Cl atoms in conformations corresponding to $\phi = 0, 120,$ and 180° are $-0.37, -0.36,$ and 5.60 kcal/mol, respectively; the corresponding coulombic interactions, for $\epsilon = 1.0$, are 1.53, 2.06, and 2.42 kcal/mol, respectively. (The small difference between the first two values of the energy of van der Waals interaction is coincidental; the two values of the distance of separation of the Cl atoms is such as to give energies on opposite sides of the potential minimum.) For a pair of Cl atoms in the same conformations in hexachloroethane, in the same assumption of tetrahedral bonding, the energies of the van der Waals interactions

(44) Abraham and Parry adjust the potential functions for van der Waals interactions so as to give an interaction energy of zero for two atoms at a distance of separation equal to the sum of their van der Waals radii; the normal procedure²⁰ is to require that this energy merely be a minimum.

would be the same, but the coulombic energies would be substantially decreased, to 0.12, 0.16, and 0.19 kcal/mol, respectively.

Conformational energies were also calculated, in 1° intervals of ϕ , for the remaining molecules, 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane, which have $\mu = f(\phi)$; the results for these molecules in the vapor phase ($\epsilon = 1.0$) are shown in Figure 2. The relationship between conformational energy and rotational angle is expected to be rather complex in these molecules, and there are sufficient experimental data to evaluate the validity of only a few features of the calculated curves. In addition, many of the relevant experimental data on both energy barriers and dipole moments pertain to the molecules in solution and thus, calculated values of these quantities must be corrected to take into account the change in medium. There are a number of rather elaborate methods⁴⁵⁻⁴⁸ which can be used to correct conformational energies which pertain to the vapor state, to values appropriate to the pure liquid state, or to solutions. (These changes in conformational energy would presumably also effectively correct the dipole moments of the molecules.) Such methods, however, generally involve a great deal of arbitrariness in that values must be assumed for a number of quantities required in such calculations, e.g., the effective size and shape of the solute domain or cavity and the locations of the bond dipoles within the cavity. In this context, recent claims⁴⁸⁻⁵³ that even quadrupole interactions must be taken into account in these corrections are not very convincing; the calculations on which this contention is based are probably unreliable because they inadequately account for charge induction effects. For simplicity, we therefore assume that such changes in conformational energy result primarily from changes in coulombic interaction, which can be accounted for by simple modification of the dielectric constant in the Coulomb's law term in eq 1. Whenever possible, we exclude from consideration measurements carried out in solvents known to interact strongly with polar solutes; aromatic solvents are apparently particularly suspect in this regard.^{5,6,38-41} It should be noted, however, that recent measurements of the influence of solvents on C-Cl stretching absorption bands in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane suggest that even in the case of aromatic solvents, the primary effect of solvent on conformational energy is simply through modification of electrostatic interactions.⁵⁴

In the case of these molecules, the barrier heights quoted by Allen and coworkers are unsuitable, since they are calculated assuming symmetric threefold barriers for each rotational isomer.⁴³ The most reliable estimates of such barrier heights are probably those

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obtained from ultrasonic relaxation measurements.^{55,56} Such measurements on 1,2-dichloroethane in diethyl ether solution, from -90 to 40° , yield the value $3.2 (\pm 0.5)$ kcal/mol for the height of the barrier for the conversion of a gauche to a trans isomer. The calculated value for $\epsilon = 1.0$ is 2.0 kcal/mol (Figure 2); modification of ϵ to 4.3 , the dielectric constant of diethyl ether^{42,37} in the vicinity of room temperature, increases this value to 2.6 kcal/mol, in reasonable agreement with experiment. Ultrasonic measurements on 1,1,2-trichloroethane in the pure liquid state, from -5 to 90° , yield 7.9 and 5.8 kcal/mol for the heights of the barriers to the transition trans to gauche negative (Figure 1) and its reverse, respectively. Calculated values for these two barriers in the vapor state are 9.8 and 8.5 , respectively. Barrier heights obtained by revision of ϵ to the value 7.1 determined for 1,1,2-trichloroethane at 25° ⁵⁸ are 9.1 and 8.6 , respectively, in fair agreement with the experimental results. There seems to be a total lack of reliable experimental data on the barrier heights in 1,1,2,2-tetrachloroethane.

Additional discussion of features of the dependence of conformational energy on rotational angle will pertain to the molecules in the vapor state. According to the results shown in Figure 2, rotational minima in 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane in the vapor state should occur at $0, \pm 10, \text{ and } -110^\circ$; $9, 111, \text{ and } -120^\circ$; and $0, 116, \text{ and } -116^\circ$, respectively. The calculated displacement of gauche states in 1,2-dichloroethane is in the same direction and of approximately the same magnitude as that calculated³³ and observed⁵⁹ in *n*-butane, the 1,2-dimethyl analog of 1,2-dichloroethane. In the present case, the values predicted for the location of gauche states is also subject to experimental test; it is found to be in excellent agreement with the values, $\pm 109 (\pm 5^\circ)$, obtained from electron diffraction data on 1,2-dichloroethane by Ainsworth and Karle.⁶⁰ For this molecule, the energy of a gauche state relative to trans is calculated to be 1.3 kcal/mol, in excellent agreement with the value $1.2 (\pm 0.1)$ ³⁴ kcal/mol based on a variety of experimental measurements. Similarly, the value of 1.6 kcal/mol calculated for the energy of a gauche negative state relative to trans in 1,1,2-trichloroethane is in satisfactory agreement with the range^{34,61} $2.0\text{--}3.0$ kcal/mol obtained from experimental data. The calculated value of the energy of a gauche state relative to trans in 1,1,2,2-tetrachloroethane is 1.0 kcal/mol; this result is significantly larger than the experimental value, 0.0 ± 0.2 kcal/mol.³⁴ It has been suggested^{62,63} that the surprisingly small value of the observed energy difference is due to distortion of Cl-C-Cl bond angles. We have chosen not to investigate this possibility at the present time, since the complete absence¹⁹ of structural

information on 1,1,2,2-tetrachloroethane prevents this from being done in an objective manner.

The dipole moments of these three molecules in the vapor phase were calculated using the rotational isomeric state model. For purposes of illustration, the rotational states were located at 0 and $\pm 120^\circ$, as well as the more realistic values which correspond to minima in the calculated conformational energy. The results are shown in the third column of Table III. Dipole

Table III. Dipole Moments,^a in the Vapor Phase, for Chloroethanes Having $\mu = f(\phi)$

Molecule	Temp, °C	Calcd		Obsd ^c
		Rotational isomeric state model	Continuum model	
CH ₂ Cl-CH ₂ Cl	25	0.89, 1.05 ^b	1.03	1.13-1.84
CHCl ₂ -CH ₂ Cl	25	1.49, 1.32	1.28	
	90	1.53, 1.35	1.30	1.25-1.42
CHCl ₂ -CHCl ₂	25	0.92, 0.97	0.94	
	130	1.09, 1.12	1.09	1.29, 1.37

^a Debyes. ^b For the first of each pair of entries, the rotational states are assumed to be located at $0, \pm 120^\circ$; for the second, they are located at the minima in the conformational energy. ^c Reference 3.

moments were also calculated by means of eq 3 which, in the limit of infinitesimal intervals in ϕ , corresponds to the most realistic model, that permitting a continuum of conformations. Although the dipole moments for these molecules were found essentially to converge to these limiting values for intervals as large as 20° , intervals of 1° were adopted for all calculations based on this continuum model. Such limiting values for the dipole moments are given in column four of Table III. In the case of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, results of both schemes are given at 90 and 130° , respectively, as well as 25° . This has been done to facilitate comparison with results of experiments which, in the case of these two molecules, are carried out at elevated temperatures because of their relatively low volatility. As can be seen from this table, the rotational isomeric state model gives a much better approximation to the more rigorous continuum model when the rotational states are located at minima in the total conformational energy, rather than simply at the minima ($0, \pm 120^\circ$) in the torsional contribution to this energy. As expected, the difference between the two rotational isomeric state results is largest for 1,2-dichloroethane and 1,1,2-trichloroethane since, as shown above, displacements of the minima from $0, \pm 120^\circ$ in these cases are significantly larger than they are in the case of 1,1,2,2-tetrachloroethane. Dipole moments calculated from the continuum model seem to be in reasonable agreement with experiment, but the large degree of scatter in the experimental results again requires consideration of calculated and experimental dipole moments which pertain to these molecules in nonpolar solvents.

For the dipole moments of these molecules in an inert, nonpolar solvent, we again adopt the values measured by Crossley and Smyth⁶ in cyclohexane, at 25° . Calculations carried out using the continuum model, a temperature of 25° , and the dielectric constant 2.015 ^{42,57} of cyclohexane at this temperature gave the

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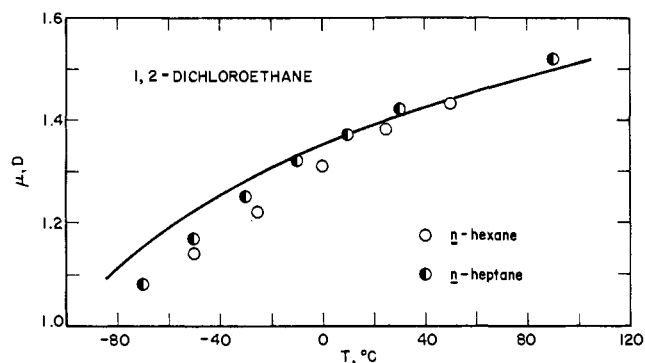


Figure 3. The dipole moment of 1,2-dichloroethane shown as a function of temperature. The experimental points refer to results in *n*-hexane⁶⁵ and *n*-heptane;⁶⁶ the theoretical curve was calculated using dielectric constants⁵⁷ for these hydrocarbons which have been reported for the indicated range of temperature.

results shown in column two of Table IV. These values are significantly larger than those calculated for the vapor phase, since increase in dielectric constant mitigates the suppression of high-energy conformations which, in these molecules, correspond to high dipole moments. Calculated values of $d \ln \mu / d\epsilon$ in the vicinity

Table IV. Dipole Moments and Their Temperature Coefficient, in Solution, for Chloroethanes Having $\mu = f(\phi)$

Molecule	μ^a		$10^3 d \ln \mu / dT^b$	
	Calcd ^c	Obsd ^d	Calcd ^e	Obsd
CH ₂ Cl-CH ₂ Cl	1.43	1.46	1.18, 1.20	1.6 (± 0.5) ^f
CHCl ₂ -CH ₂ Cl	1.38	1.42	0.56, 0.40	
CHCl ₂ -CHCl ₂	1.15	1.59	0.92, 1.03	0.68 ^g

^a Debyes, 25°. ^b Degrees⁻¹, 25°. ^c Continuum model. ^d Reference 6. ^e The first of each pair of entries is the result using a rotational isomeric state model with states located at minima in the conformational energy; the second is the result obtained from the continuum model. ^f Reference 3. ^g S. Mizushima, Y. Morino, and K. Kojima, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **29**, 111 (1936).

of $\epsilon = 2.0$ for 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane are 0.185, 0.057, and 0.123 deg⁻¹, respectively. Unfortunately, there are insufficient experimental data to evaluate the validity of the calculated values of this coefficient. In the case of 1,2-dichloroethane and 1,1,2-trichloroethane, the calculated and experimental results are in excellent agreement,⁶⁴ the difference between calculated and experimental values of the dipole moment amounting to only 0.04 D. The relatively large difference, 0.4 D, observed for 1,1,2,2-tetrachloroethane, could be due to the possible overestimation, already discussed, of the

(64) Preliminary calculations were also carried out using the present charge distributions and the continuum model but potential functions recommended by Hill [T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948)] and by Liquori and coworkers [P. De Santis, E. Giglio, A. M. Liquori, and A. Ripamonti, *J. Polym. Sci., Part A*, **1**, 1383 (1963)]. In the case of 1,2-dichloroethane, which was chosen as the most definitive test case, the potential functions of Hill gave a value of the dipole moment significantly lower than that found experimentally. This is due to the fact that the Hill potential function for the very important Cl...Cl interactions is relatively "hard," i.e., it assigns relatively large van der Waals repulsions to Cl atoms at small distances of separation; this of course tends to excessively suppress high-energy conformations, of high dipole moment. The Cl...Cl potential functions used by Liquori and coworkers specify even larger repulsions and, as a result, the dipole moment predicted in this case is only approximately one-third the experimental value.

energy of gauche states in this molecule; such states correspond of course to relatively high dipole moments.

Temperature coefficients of the dipole moment, $10^3 d \ln \mu / dT$, in the vicinity of 25° were calculated for these molecules in cyclohexane, taking into account the small contribution due to the temperature dependence of the dielectric constant of this solvent.⁵⁷ Both the rotational isomeric state model with states located at minima in the conformational energy and the continuum model were used. These calculated results, which are in close agreement, are given in the fourth column of Table IV. The fact that the values of this coefficient are positive is due to the already mentioned correspondence between high conformational energy and large dipole moment. An average, approximate value for this coefficient for 1,2-dichloroethane was calculated from reported experimental values³ of its dipole moment as a function of temperature in a variety of nonpolar, nonaromatic solvents having dielectric constants close to that of cyclohexane. As shown in the table, the experimental and calculated values of this quantity are in good agreement. It is useful to consider in detail two studies of the temperature dependence of the dipole moment of 1,2-dichloroethane, since they represent the most extensive set of such measurements available on any of the chloroethanes. Consequently, the dipole moments obtained for this molecule in *n*-hexane ($\epsilon = 1.882^{57}$ at 25°) by Higasi⁶⁵ and in *n*-heptane ($\epsilon = 1.917^{57}$ at 25°) by Smyth and coworkers⁶⁶ are shown as a function of temperature in Figure 3. Results calculated from the continuum model, taking into account the temperature dependence⁵⁷ of ϵ , are essentially identical for these two alkane solvents; they are therefore shown by the single curve in the figure. Theoretical and experimental results are seen to be in excellent agreement. Although there are no experimental data from which to evaluate $d \ln \mu / dT$ for 1,1,2-trichloroethane, the value of this quantity for 1,1,2,2-tetrachloroethane may be estimated from values reported for its dipole moment in *n*-hexane over the temperature range -20 to 50°. This approximate experimental result, given in the last column of Table IV, is also in good agreement with the result calculated from theory.

Conclusions

The model described in this study gives a remarkably consistent account of a variety of the known properties of the chloroethanes. Perhaps most importantly, these results clearly demonstrate that proper recognition of charge induction effects in these molecules is absolutely essential to any meaningful interpretation of their properties.

The success of the present calculations would seem to encourage application of these methods to other substituted ethanes. Such work is in progress.

Acknowledgments. It is a pleasure to acknowledge financial support from the National Science Foundation under Grant No. GP-16028. C. S. also wishes to thank the Gulf Oil Company for a predoctoral fellowship during the academic year 1969-1970.

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