Steric Effects. II. General Equations. Application to Cis and Trans−2Butene

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Steric Effects. II. General Equations. Application to *Cis*- and *Trans*-2-Butene

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Steric energy and the semi-empirical method of calculating steric energy are discussed in the language of potential surfaces. Equations are given relating $\Delta H_0{}^0$ for several types of reactions commonly used to exhibit steric effects experimentally to the steric energy of the molecules involved in the reactions. The equations of Westheimer and Mayer for the calculation of the steric energy of a molecule are generalized in several respects. The difference in $\Delta H_0{}^0$ (formation) between *cis* and *trans*-2-butene is calculated as a steric effect. Because of various complications the application of the method in its present form to molecules such as H_2O, NH_3, PF_3, etc., is rather unsatisfactory.

I. INTRODUCTION

WESTHEIMER and Mayer[1] and the present author[2] suggested independently a semi-empirical method (method 1, below) for the theoretical investigation of steric effects. The method can be applied without modification to both equilibrium and rate studies, and also to problems in molecular structure without reference to any particular reaction. Westheimer[3] has applied the method in calculating the activation energy for the racemization of 2,2′-dibromo-4,4′-dicarboxydiphenyl.

The purpose of the present series of papers is to investigate this approach to steric effects from as general a point of view as seems profitable at the present time. In paper I of the series[4] a necessary prerequisite study of van der Waals potential energy curves was carried out, and an approximate method of extrapolating our limited knowledge of these curves to new cases was suggested. In this paper (II) we shall discuss the general method and give some applications to molecules. In a proposed third paper, applications to a few chemical reactions will be presented, including some of the cases investigated experimentally by H. C. Brown.[5] The relation between the present point of view and Brown's concepts of B and F strain will be discussed.

The word "steric" is used generally to refer to van der Waals effects (especially repulsions). In most of the applications we have in mind, van der Waals repulsions indeed play a dominant role, but in some cases electrostatic effects are also involved. For convenience we shall often use the words "steric" or "interaction" to include electrostatic effects. As a matter of fact pure electrostatic effects can also be treated by the present method, with appropriate alteration in the equations. However, structural deformations will be small if not negligible here (they have always been ignored hitherto), because V (see below) varies so slowly with distance.

The Method

Consider a certain molecule A with n atoms and in which, in the equilibrium configuration, there are appreciable steric interactions between two or more non-bonded atoms (or groups). In principle it is possible to calculate from quantum mechanics the shape of the potential surface (potential energy U plotted against $3n-6$ or $3n-5$ vibrational coordinates) in the neighborhood (as extensive as necessary) of the configuration of minimum energy (equilibrium configuration) and also the value of the minimum energy referred to infinite separation of atoms as the zero of energy.[6a] Now suppose the calculation is repeated, omitting the contribution V to the

[1] F. H. Westheimer and J. E. Mayer, J. Chem. Phys. **14**, 733 (1946).

[2] T. L. Hill, J. Chem. Phys. **14**, 465 (1946).

[3] F. H. Westheimer, J. Chem. Phys. **15**, 252 (1947). See also I. Dostrovsky, E. D. Hughes, and C. K. Ingold, J. Chem. Soc. 173 (1946).

[4] T. L. Hill, J. Chem. Phys. **16**, 399 (1948).

[5] See, for example, H. C. Brown, J. Am. Chem. Soc. **69**, 1137 (1947); *ibid.* **67**, 378 (1945).

[6a] If the molecule under discussion happens to be an activated complex it is to be understood that the words "equilibrium" and "minimum" are to be replaced by "saddle-point," and that the reaction coordinate is to be omitted in calculating zero-point vibrational energy and thermodynamic functions.

STERIC EFFECTS

potential energy caused by the interactions between the atoms (or groups) mentioned above. This will lead to a new potential surface ^0U corresponding to a hypothetical molecule ^0A. If the normal coordinates of A and ^0A are now obtained using the shapes of the potential surfaces near their respective minima, the minimum (equilibrium) energies may be corrected for zero-point vibrational energy. The steric energy E associated with the particular interactions omitted in the ^0A calculation is then defined as the difference between the two equilibrium energies corrected for zero-point vibrational energy (Fig. 1). Let E' be the uncorrected steric energy. It is clear from the definition of steric energy that this energy is, to some extent, (a) arbitrary (it depends on which interactions are chosen) and (b) artificial (in a complete quantum-mechanical calculation for the molecule A the energy E does not enter in a natural way).

The surface V in Fig. 1 represents the potential energy of interaction between the atoms (or groups) being considered, as a function of nuclear configuration. A procedure for obtaining the surface ^0U may be represented by $U - V \rightarrow {}^0U$. It is also possible to find U from ^0U and V: $^0U + V \rightarrow U$. In fact, these procedures are the basis of the method used here for computing steric energies: although the quantum-mechanical calculations are, with rare exceptions,[6b] not possible in practice, such calculations may be replaced by a semi-empirical calculation based on the procedure (1) $^0U + V \rightarrow U$ or on (2) $U - V \rightarrow {}^0U$.

Method 1

In many cases the equilibrium configuration of ^0A and the shape (but, in general, not the absolute energy) of the potential surface in the immediate neighborhood of the equilibrium configuration of ^0A can be obtained from experimental data in related compounds. Thus the equilibrium configuration can be deduced from known structures of similar molecules unperturbed by the steric interaction or interactions being studied, and the shape of the potential

surface can be calculated using force constants[7a] found for other appropriate molecules. If now for each interaction the interaction energy is available as a function of distance, one can carry out the procedure $^0U + V \rightarrow U$, and hence find the steric energy E, provided that the equilibrium configurations of A and ^0A are not too far apart. For in having to use force constants we obtain information concerning the shape of the potential surface for ^0A to quadratic terms only.

Physically, the point of view is the following. If the steric interactions are introduced into the hypothetical unperturbed molecule ^0A, the interacting atoms or groups will tend to move apart (for repulsions). But this will generally require the stretching or bending of bonds with a related increase in energy. The final configuration will thus be the result of a compromise between the two types of force, and will be the configuration of minimum energy (the equilibrium configuration of A). An analogous discussion of method 2 can be given.

Method 2

In other cases it may be desirable, assuming the quantum-mechanical calculation is impossible, to use V and the experimental force constants for A itself in order to calculate E by the process $U - V \rightarrow {}^0U$. Again we have to restrict ourselves to cases in which the equilibrium configurations of A and ^0A are not too different.

Method 1 above is the most useful in connection with steric effects on chemical equilibrium
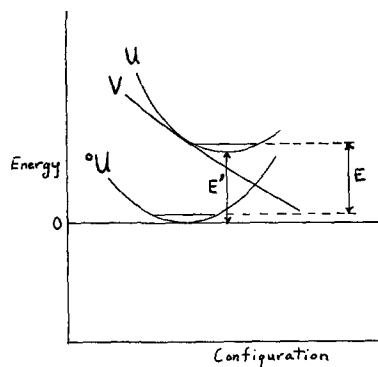

FIG. 1. Plot of energy against configuration.

[6b] An approximate calculation of essentially this type has been carried out for H_2O. See J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1934).

[7a] Force constants obtained on the assumption of valence forces (with or without cross products) will be most convenient.

because such effects are usually exhibited experimentally in complicated molecules for which force constants (for the molecule A with the steric interaction) are not yet available. Force constants for the unperturbed molecule ^0A can usually be taken from simpler molecules. In rate studies method 1 is most convenient to use on the activated complex since force constants will, of course, not be available for this structure.[7b] On the other hand, method 2 is probably the most natural to use for investigations on steric energy and molecular structure in simple molecules for which force constants are available. In the present paper method 1 is emphasized.

In Section II we give a rather formal but necessary discussion of the application of the method to chemical reactions. The problem reduces essentially to the determination of the steric energy of individual molecules. In Section III we consider the calculation of the steric energy of a molecule, and give an application to *cis-* and *trans-*2-butene. Molecules such as H_2O, NH_3, F_2O, etc., are discussed from the present point of view in the appendix.

II. APPLICATION TO REACTIONS

We shall use the language of chemical equilibrium here, but the discussion applies without alteration to reaction rates by considering, in the usual way, the activated complex as a product in a chemical equilibrium.

It involves much less labor to find merely the energy difference between the minima in the potential surfaces for A and ^0A than to obtain, in addition, the shapes of the potential surfaces and the normal coordinates and vibrational frequencies. We shall confine our interest here to obtaining this energy difference. This restricts our investigation of chemical reactions to steric effects on ΔH_0^0 for the reactions, and even here making the approximation of neglecting zero-point vibrational energies[8] (that is, we use E'

[7b] The introduction of the saddle-point property into ^0U may sometimes be awkward. Because of the special nature of the reaction coordinate in Westheimer's case,[3] this complication did not arise.

[8] In most cases the zero-point vibrational energies should largely cancel. One exception is a reaction involving an activated complex, since one vibrational frequency is missing here. The cancellation is especially effective where one takes first and second differences in ΔH_0^0 values in comparing related reactions (see below).

as an approximation to E; see Fig. 1). It should be emphasized, however, that the calculation of the vibrational frequencies of ^0A and A is straightforward in principle and hence it is not only possible to correct for zero-point vibrational energy but also to obtain the entropy difference between ^0A and A at any temperature. This is the way in which steric entropy effects would have to be investigated using the present method.[1]

Experimental studies on steric effects are usually carried out as a comparison method. A related standard molecule A_0 undergoes the same reaction as A. If possible A_0 is chosen so that the steric interaction of interest in A is negligible in A_0. Differences in rate constant, equilibrium constant or ΔH are then attributed to the steric interaction. We shall formulate our equations making use of this procedure. To simplify notation we now let Q stand for H_0^0. Our object is to relate ΔQ for a given reaction to the steric energies of the substances entering the reaction. Or, where necessary, we take differences in ΔQ values in order to relate the ΔQ's to steric energies.

In the following outline we do not attempt to achieve complete generality; the purpose is simply to include the important cases. Further extensions are rather self-evident.

A. Equilibrium between Rotational or Structural Isomers

This is the simplest type of equilibrium of interest here. By rotational isomers we mean two compounds which can go over into one another by rotation about bonds (e.g., two geometrical isomers, or a substituted diphenyl and the activated complex in the racemization reaction). By structural isomers we mean here (a restricted definition) two compounds which differ only in the location of some substituent (e.g., 2-picoline and 4-picoline).

Let A be the isomer in which the steric interaction (or interactions) is most important. Consider the other isomer as the standard, A_0. Then for the equilibrium $A_0 \rightleftharpoons A$ we have

$$\Delta Q = Q_A - Q_{A_0}. \qquad (1)$$

We now remove the *same* interactions in A and

A_0, obtaining ^0A and $^0A_0$ with energies ^0Q_A and $^0Q_{A0}$. The steric energies (associated with the particular interactions removed) E_A and E_{A0} are

$$E_A = Q_A - {}^0Q_A, \quad E_{A0} = Q_{A0} - {}^0Q_{A0}. \tag{2}$$

Then

$$\Delta Q = (E_A - E_{A0}) + ({}^0Q_A - {}^0Q_{A0}). \tag{3}$$

In general, in deciding which interactions are to be removed in A and A_0, we choose those and only those whose removal are necessary in order to lead to ^0A and $^0A_0$ having all remaining interaction energies the same (to the accuracy desired). In the case of rotational isomers corresponding force constants in ^0A and $^0A_0$ should then be nearly equal and also $^0Q_A = {}^0Q_{A0}$ to a very good approximation (since all bonds are of the same type and all distinguishing interactions have been removed). The normal coordinates and vibrational frequencies of ^0A and $^0A_0$ will, however, be different owing to different geometry. These approximations should also be valid, though somewhat less so, for structural isomers (e.g., resonance and inductive effects may complicate matters, especially in aromatic compounds). Hence, for these cases,

$$\Delta Q = E_A - E_{A0}. \tag{4}$$

An important special case of the above is the following: the interactions of importance in A cause no appreciable effect on A_0 on their removal from this latter molecule. That is, $^0A_0 = A_0$ (structure) and $^0Q_{A0} = Q_{A0}$. Hence, $E_{A0} = 0$, and Eq. (4) becomes

$$\Delta Q = E_A. \tag{5}$$

The case studied by Westheimer[3] is of this type.

Another special case: on the removal of the important interactions in A, corresponding force constants in ^0A and A_0 are taken as being approximately equal, but we do *not* assume $^0Q_A = Q_{A0}$ (this is an approximate method; strictly speaking the two assumptions just mentioned are probably inconsistent in most cases). We use the exact equation

$$\Delta Q = E_A + ({}^0Q_A - Q_{A0}), \tag{6}$$

but the evaluation of E_A and $^0Q_A - Q_{A0}$ involves approximations. This method is used in Section III in calculating ΔQ for the equilibrium between

cis- and trans-2-butene and will be further discussed there.

B. Other Reactions Involving Rotational and Structural Isomers

Here the same reaction is studied on both isomers for comparison purposes. For example, the addition of $B(CH_3)_3$ to 2-picoline and to 4-picoline, or the rate of esterification of ortho and paramethyl benzoic acid. Let the reactions be (this is sufficiently general for our purposes)

$$A + B \rightleftharpoons C + D; \Delta Q,$$
$$A_0 + B \rightleftharpoons C_0 + D; \Delta Q_0. \tag{7}$$
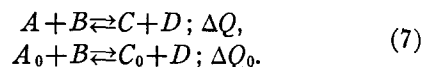
Then

$$\Delta Q - \Delta Q_0 = (Q_C - Q_{C0}) - (Q_A - Q_{A0}). \tag{8}$$

In analogy with Eq. (3) we have

$$\Delta Q - \Delta Q_0 = (E_C - E_{C0}) - (E_A - E_{A0})$$
$$+ ({}^0Q_C - {}^0Q_{C0}) - ({}^0Q_A - {}^0Q_{A0}), \tag{9}$$

where the interactions used in obtaining E_C and E_{C0} may be different than those used in obtaining E_A and E_{A0}. As before, we put $^0Q_C - {}^0Q_{C0} = 0$ and $^0Q_A - {}^0Q_{A0} = 0$[9] so that
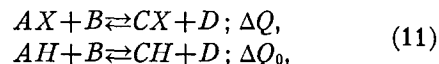
$$\Delta Q - \Delta Q_0 = (E_C - E_{C0}) - (E_A - E_{A0}). \tag{10}$$

Thus first differences in ΔQ values are necessary in reactions of this type to exhibit a steric effect. An important special case is $E_A = E_{A0} = 0$.

C. Reactions Involving Different Substituents

Consider reactions of the type

$$AX + B \rightleftharpoons CX + D; \Delta Q,$$
$$AH + B \rightleftharpoons CH + D; \Delta Q_0, \tag{11}$$

where H is a substituent with a small or negligible steric interaction (e.g., hydrogen) for comparison, and X is a substituent with considerable steric interaction. X and H are substituted into identical positions in AX and AH, and in CX and CH. Examples are (a) the rate of esterification of benzoic acid compared to o-methyl benzoic acid, (b) the dissociation equilibrium of benzoic acid as an acid compared to o-methyl benzoic acid, and (c) the addition of $B(CH_3)_3$ to NH_3 as compared to CH_3NH_2.

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[9] The two separate assumptions are not necessary. It is obviously sufficient to make the single assumption $^0Q_C - {}^0Q_{C0} = {}^0Q_A - {}^0Q_{A0}$, which should be even more exact.

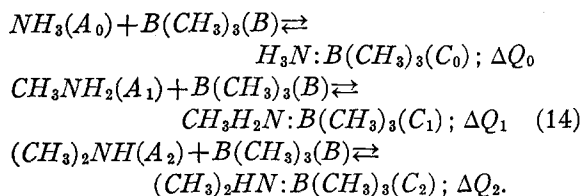Let $A_0 = AH$, $A_1 = AX$, $C_0 = CH$, and $C_1 = CX$. Then, as for Eq. (9), we find

$$\Delta Q - \Delta Q_0 = (Ec_1 - Ec_0) - (E_{A_1} - E_{A_0}) + (^0Qc_1 - {}^0Qc_0) - (^0Q_{A_1} - {}^0Q_{A_0}). \quad (12)$$

Here we cannot assume $^0Qc_1 = {}^0Qc_0$ and $^0Q_{A_1} = {}^0Q_{A_0}$ because there are different bonds and therefore bond energies involved (the force constants will also be different). However, in many cases it will still be a very good assumption to set $^0Qc_1 - {}^0Qc_0 = {}^0Q_{A_1} - {}^0Q_{A_0}$ since the *differences* in bond energies will often be effectively the same in the two pairs of compounds (e.g., in the benzoic acid examples above, except for small resonance and inductive effects). In these cases

$$\Delta Q - \Delta Q_0 = (Ec_1 - Ec_0) - (E_{A_1} - E_{A_0}). \quad (13)$$

First differences in ΔQ values are thus sufficient here.

In other reactions, as, for example, the addition of $B(CH_3)_3$ to NH_3 and to CH_3NH_2, it would not be safe to assume that Eq. (12) reduces approximately to Eq. (13). In this case the *type* of bond is different in A_0 and A_1 as compared to C_0 and C_1, and hence the energy differences $^0Qc_1 - {}^0Qc_0$ and $^0Q_{A_1} - {}^0Q_{A_0}$ may be appreciably different. It is necessary in this case and related cases to use *second* differences in ΔQ values. Thus, Brown[5] has studied

$$NH_3(A_0) + B(CH_3)_3(B) \rightleftarrows$$
$$H_3N:B(CH_3)_3(C_0); \Delta Q_0$$
$$CH_3NH_2(A_1) + B(CH_3)_3(B) \rightleftarrows$$
$$CH_3H_2N:B(CH_3)_3(C_1); \Delta Q_1 \quad (14)$$
$$(CH_3)_2NH(A_2) + B(CH_3)_3(B) \rightleftarrows$$
$$(CH_3)_2HN:B(CH_3)_3(C_2); \Delta Q_2.$$

We have

$$(\Delta Q_2 - \Delta Q_1) - (\Delta Q_1 - \Delta Q_0)$$
$$= [(Ec_2 - Ec_1) - (Ec_1 - Ec_0)]$$
$$\quad - [(E_{A_2} - E_{A_1}) - (E_{A_1} - E_{A_0})]$$
$$\quad + \{[(^0Qc_2 - {}^0Qc_1) - (^0Qc_1 - {}^0Qc_0)]$$
$$\quad - [(^0Q_{A_2} - {}^0Q_{A_1}) - (^0Q_{A_1} - {}^0Q_{A_0})]\}. \quad (15)$$

It is now a good approximation to set $\{\ \} = 0$ in Eq. (15), for even the separate expressions in square brackets in $\{\ \}$ should be approximately equal to zero.

In all of the above reactions the problem has thus been reduced to the calculation of the steric energy in individual molecules. This calculation has been discussed in Section I and will be discussed further in Section III. It will be noted that the question of *method 1-vs.-method 2* examined in Section I has not arisen in the present section since we have been interested in formal relations between ΔQ values and steric energies without considering methods of calculating these steric energies.

We have ignored solvent effects above, and we do so throughout the paper. The equations derived are therefore most appropriate for gaseous reactions, but they should also apply, to varying degrees of approximation, to reactions in solution. Van der Waals interactions are presumably relatively insensitive to solvent effects compared to electrostatic interactions. Also, in most cases, the solvent should have only a small perturbing effect on internal molecular vibrations. In any case, practically nothing fundamental is known about solvent effects, so there is little choice here but to ignore them.

In most actual cases the experimental data are at best in the form of ΔH^0 values and not ΔQ.[10] The usually difficult calculation of ΔH^0 from ΔQ can in principle be carried out using the potential surfaces. The alternative is to assume that differences between ΔH^0 and ΔQ values cancel. We illustrate this for only one case: Referring to Eq. (10) we have [11]

$$\Delta H^0 - (\Delta H^0)_0 = (\Delta Q - \Delta Q_0) + \{(\Delta H^0 - \Delta Q) - [(\Delta H^0)_0 - \Delta Q_0]\}. \quad (16)$$

Although $\Delta H^0 \neq \Delta Q$ and $(\Delta H^0)_0 \neq \Delta Q_0$, in most cases it is probably a good approximation to write

$$\Delta H^0 - \Delta Q = (\Delta H^0)_0 - \Delta Q_0.$$

Then

$$\Delta H^0 - (\Delta H^0)_0 = \Delta Q - \Delta Q_0$$
$$= (E_C - Ec_0) - (E_A - E_{A_0}). \quad (17)$$

Thus, when first, or especially when second,

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[10] In rate studies there is ordinarily available the experimental activation energy E_{exp} defined by $d \ln k/dT = E_{exp}/RT^2$. See Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 197–199. See also footnote 12 of paper I.

[11] In these equations the symbol $(\Delta H^0)_0$ represents the value of ΔH^0 for the reference reaction, in conformity with our notation. It is *not* to be confused with ΔH_0^0.

differences in ΔQ values are used the above approximation may be a good one (see also footnote 8).

III. APPLICATION TO MOLECULES

The principal point of this section is to generalize somewhat the equations of Westheimer and Mayer[1] and to apply the results to *cis*- and *trans*-2-butene as an example. We follow the notation of Westheimer and Mayer as closely as possible.

Let a set of $3n-6$ or $3n-5$ coordinates q_i represent displacements from the equilibrium configuration of ^0A. If we choose the zero of energy as the bottom of the ^0A potential surface (Fig. 1), we have

$$U(q) = \tfrac{1}{2}\sum a_{ij}q_iq_j + V(q) \quad (a_{ij}=a_{ji}) \quad (18)$$

as the expression giving the shape of the potential surface for A, provided the equilibrium configurations of A and ^0A are not too different, where $V(q)$ is the steric interaction energy and the a_{ij} are unperturbed force constants. V depends on one or more interatomic or intergroup distances, and these in turn depend on the q_i. The minimum in U is determined by setting $\partial U/\partial q_i=0$ $(i=1, 2, \cdots)$. Suppose the minimum occurs at $q_i=q_i^0$ $(i=1, 2, \cdots)$. Then

$$E' = U(q^0) = \tfrac{1}{2}\sum a_{ij}q_i^0q_j^0 + V(q^0). \quad (19)$$

Let another set of coordinates η_i represent displacements from the equilibrium configuration of A. Let ^0U be the potential energy of ^0A. Then

$$^0U(\eta) = E' + \tfrac{1}{2}\sum \alpha_{ij}\eta_i\eta_j - V(\eta) \quad (\alpha_{ij}=\alpha_{ji}), \quad (20)$$

where the α_{ij} are perturbed force constants. The minimum in ^0U is determined by $\partial^0U/\partial\eta_i=0$ $(i=1, 2, \cdots)$. Suppose the minimum occurs at $\eta_i=\eta_i^0$ $(i=1, 2, \cdots)$. Then $^0U(\eta^0)=0$ (our choice of the zero of energy) and

$$-E' = \tfrac{1}{2}\sum \alpha_{ij}\eta_i^0\eta_j^0 - V(\eta)^0. \quad (21)$$

Equations (19) and (21) show how to calculate E' by methods (1) and (2), respectively. On adding these two equations one gets

$$V(\eta^0) - V(q^0) = \tfrac{1}{2}(\sum\alpha_{ij}\eta_i^0\eta_j^0 + \sum a_{ij}q_i^0q_j^0), \quad (22)$$

a relation which might be used to obtain some information about V if both equilibrium configurations and both sets of force constants are known.

The general relationship of U to ^0U is summarized by:

$$U(q) = \tfrac{1}{2}\sum a_{ij}q_iq_j + V(q) = E' + \tfrac{1}{2}\sum\alpha_{ij}\eta_i\eta_j,$$
$$^0U(q) = E' + \tfrac{1}{2}\sum\alpha_{ij}\eta_i\eta_j - V(\eta) = \tfrac{1}{2}\sum a_{ij}q_iq_j. \quad (23)$$

We now give explicit equations for calculating E' based on Eq. (19) (method 1). In the treatment of Westheimer and Mayer[1] cross products were not allowed in the potential function. They pointed out that although the coordinates chosen were to be such that cross products did not appear, for the calculation of E' these coordinates need not be normal coordinates (i.e., the kinetic energy need not be diagonalized). We shall derive the slightly more complicated equations here for the case where cross products in the potential energy are permitted. The use of these more complicated equations entails much less labor in many cases (e.g., the application treated at the end of this section) than would be involved in the diagonalization of the potential energy.

Westheimer and Mayer[1] included only a repulsive term of the form $P \exp(-d/\rho)$ in $V(q)$, where d is an interatomic or intergroup distance. In paper I an attractive term was introduced. Let us consider first the case where there is just one steric interaction and

$$V = P \exp(-d/\rho) - (\mu/d^6), \quad (24)$$

so that

$$U(q) = \tfrac{1}{2}\sum a_{ij}q_iq_j + P \exp(-d/\rho) - (\mu/d^6). \quad (25)$$

Here P, ρ, and μ are parameters discussed in detail in paper I. Let d_0 be the distance between the interacting atoms or groups in the equilibrium configuration of ^0A. We are already restricted to cases where there is a small change in configuration on the introduction of the steric interaction into ^0A (because of the inclusion of only quadratic terms in Eq. (19)), so we include only linear terms in the expansion of d about d_0:

$$d = d_0 + \sum b_iq_i. \quad (26)$$

Let $P \exp(-d_0/\rho) = E_{d_0}$. Then

$$\frac{\partial U}{\partial q_k} = -\frac{b_k}{\rho}E_{d_0}\exp\left(-\frac{1}{\rho}\sum b_iq_i^0\right) + \frac{6\mu b_k}{(d_0+\sum b_iq_i^0)^7}$$
$$+ \sum_j a_{jk}q_j^0 = 0 \quad (k=1, 2, \cdots). \quad (27)$$

Define

$$Z = E_{d_0} \exp\left(-\frac{1}{\rho}\sum b_i q_i{}^0\right) - \frac{6\mu\rho}{(d_0 + \sum b_i q_i{}^0)^7}. \quad (28)$$

Eq. (27) becomes

$$\sum_i a_{jk} q_j{}^0 = \frac{b_k}{\rho} Z \quad (k = 1, 2, \cdots). \quad (29)$$

On solving this set of linear equations for $q_k{}^0$ we get

$$q_k{}^0 = \frac{Z}{\rho} \frac{D_k}{D}, \quad (30)$$

where

$$D = |a_{ij}| = \begin{vmatrix} a_{11} & a_{21} & \cdots \\ a_{12} & a_{22} & \cdots \\ \cdot & & \\ \cdot & & \\ \cdot & \cdot & \cdots \end{vmatrix}, \quad (31)$$

and D_k is the determinant obtained by replacing the k-th column $a_{k1}, a_{k2}, \cdots$ in D by $b_1, b_2, \cdots$. On substituting Eq. (30) into Eq. (28) we have

$$Z = E_{d_0} \exp\left(-\frac{Z}{\rho^2 D}\sum b_i D_i\right) - \frac{6\mu\rho}{\left(d_0 + \dfrac{Z}{\rho D}\sum b_i D_i\right)^7}. \quad (32)$$

This equation can be solved numerically for Z. Finally, from Eqs. (25) and (30),

$$E' = E_{d_0} \exp\left(-\frac{Z}{\rho^2 D}\sum b_i D_i\right) - \frac{\mu}{\left(d_0 + \dfrac{Z}{\rho D}\sum b_i D_i\right)^6} + \tfrac{1}{2}\frac{Z^2}{\rho^2 D^2}\sum a_{ij} D_i D_j. \quad (33)$$

Two or more interactions. If there are two interactions of the above type in the molecule,

we have

$$U(q) = \tfrac{1}{2}\sum a_{ij} q_i q_j + P \exp(-d/\rho) - \frac{\mu}{d^6} + P' \exp(-d'/\rho') - \frac{\mu'}{d'^6}, \quad (34)$$

where $d' = d_0' + \sum b_i' q_i$. On setting $\partial U/\partial q_k = 0$ $(k = 1, 2, \cdots)$, one finds

$$q_k{}^0 = \frac{Z}{\rho} \frac{D_k}{D} + \frac{Z'}{\rho'} \frac{D_k'}{D}, \quad (35)$$

where

$$Z' = E_{d_0'} \exp\left(-\frac{1}{\rho'}\sum b_i' q_i{}^0\right) - \frac{6\mu'\rho'}{(d_0' + \sum b_i' q_i{}^0)^7}, \quad (36)$$

and D_k' is obtained from D by using the b_i' instead of the b_i. Putting Eq. (35) into Eqs. (28) and (36) one obtains

$$Z = E_{d_0} \exp\left(-\frac{Z}{\rho^2 D}\sum b_i D_i\right) \times \exp\left(-\frac{Z'}{\rho\rho' D}\sum b_i D_i'\right) - \frac{6\mu\rho}{\left(d_0 + \dfrac{Z}{\rho D}\sum b_i D_i + \dfrac{Z'}{\rho' D}\sum b_i D_i'\right)^7}, \quad (37)$$

$$Z' = E_{d_0'} \exp\left(-\frac{Z'}{\rho'^2 D}\sum b_i' D_i'\right) \times \exp\left(-\frac{Z}{\rho\rho' D}\sum b_i' D_i\right) - \frac{6\mu'\rho'}{\left(d_0' + \dfrac{Z'}{\rho' D}\sum b_i' D_i' + \dfrac{Z}{\rho D}\sum b_i' D_i\right)^7}. \quad (38)$$

These two equations must be solved numerically and simultaneously for Z and Z'. Finally, one

finds

$$E' = E_{d_0} \exp\left(-\frac{Z}{\rho^2 D}\sum b_i D_i\right)$$

$$\times \exp\left(-\frac{Z'}{\rho\rho' D}\sum b_i D_i'\right)$$

$$-\frac{\mu}{\left(d_0 + \frac{Z}{\rho D}\sum b_i D_i + \frac{Z'}{\rho' D}\sum b_i D_i'\right)^6}$$

$$+E_{d_0}' \exp\left(-\frac{Z'}{\rho'^2 D}\sum b_i' D_i'\right)$$

$$\times \exp\left(-\frac{Z}{\rho\rho' D}\sum b_i' D_i\right)$$

$$-\frac{\mu'}{\left(d_0' + \frac{Z'}{\rho' D}\sum b_i' D_i' + \frac{Z}{\rho D}\sum b_i' D_i\right)^6}$$

$$+\tfrac{1}{2}\sum a_{ij}\left(\frac{Z}{\rho}\frac{D_i}{D} + \frac{Z'}{\rho'}\frac{D_i'}{D}\right)$$

$$\times\left(\frac{Z}{\rho}\frac{D_j}{D} + \frac{Z'}{\rho'}\frac{D_j'}{D}\right). \quad (39)$$

It is obvious that any number of interactions can be taken into account in this way, but the numerical solution for Z, Z', Z'', $\cdots$ would become quite difficult. It is also obvious that there would be no difficulty in including any term or terms of the form $1/d^n$ $(n \geqslant 1)$ in Eq. (24) (see, for example, Eq. (44)).

The above equations apply to method 1. They also apply to method 2 if we make the appropriate change in the meaning (replace ^0A by A) of d_0, the q_i, the a_{ij}, and the b_i, and substitute everywhere $-P$ for P, $-\mu$ for μ, and $-E'$ for E' (Eq. (21)).

In summary, the generalizations included here and in paper I over the treatment of Westheimer and Mayer are: (a) the inclusion of terms of the form $1/d^n$ $(n \geqslant 1)$ in V; (b) the inclusion of two or more different steric interactions; (c) the introduction of cross products; and (d) the introduction of method 2.

Cis- and Trans-2-Butene

Consider the equilibrium
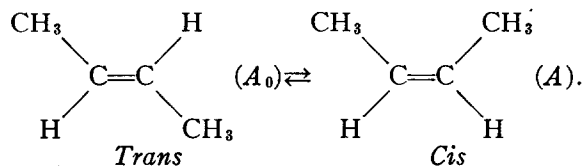
ΔQ for this reaction is available from the heats of formation:[12] $\Delta Q = 1.288$ kcal./mole. A is less stable energetically than A_0, presumably primarily as a result of the van der Waals repulsion between the methyl groups in A.

In addition to the $CH_3 - CH_3$ van der Waals interactions, there are also to be considered the $H - CH_3$ van der Waals interactions, the $H - H$ van der Waals interactions, and the interactions between the CH dipoles (we assume no CCH_3 dipole). The force constants for A and A_0 are not available, but a set of force constants has been determined for propylene.[13] Hence the way to proceed in order to use Eq. (4) in this case would be to: (a) take into account in propylene all interactions of the type mentioned above and obtain for this molecule the unperturbed potential surface by method 2; (b) the valence force constants (with cross products) associated with this surface should be very nearly the same as the corresponding force constants for $^0A_0$ and ^0A above, again omitting, in obtaining $^0A_0$ and ^0A, interactions of the sort mentioned; (c) then using method 1 and these unperturbed force constants, E_A and E_{A_0} could be calculated. In view of various uncertainties mentioned below this tedious program hardly seems worth while for the present.

We content ourselves with the approximate treatment discussed in connection with Eq. (6). Also, we treat the methyl group as an atom. The most important interaction is the $CH_3 - CH_3$ interaction in A. We therefore remove only this interaction from A in forming ^0A. We then assume as an approximation that corresponding bond angles, bond distances, and valence force constants are the same in ^0A, A_0, and propylene.

[12] A. P. I. Research Project 44, National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Table 8w (Part 1), 1944–1946.
[13] E. B. Wilson, Jr. and A. J. Wells, J. Chem. Phys. 9, 319 (1941).
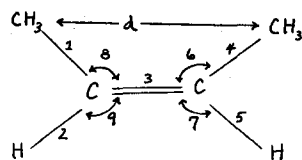
FIG. 2. Coordinates of *cis*-2-butene.

When the CH_3-CH_3 interaction is introduced into ^0A, the observed deformations will result from a compromise between this interaction and the force constants. The effect of other interactions on the deformations is automatically included, approximately, in the force constants (i.e., these are not the completely unperturbed force constants mentioned in the preceding paragraph).

We do not assume that $^0Q_A = Q_{A0}$. We can estimate $^0Q_A - Q_{A0}$ by calculating (a) the interaction energy in the equilibrium configuration of ^0A due to all interactions other than CH_3-CH_3 and (b) the interaction energy in the equilibrium configuration of A_0 due to *all* interactions, and assuming that $^0Q_A - Q_{A0}$ is equal to the difference in these interaction energies. Here again we are neglecting zero-point vibrational energies, and this could be serious here.

The $3n - 6 = 12$ internal coordinates for ^0A suggested by the force constants given for propylene by Wilson and Wells[13] are shown in Fig. 2. The q_i are valence displacement coordinates. Let q_{10} be the angle between one

$$CH_3$$
$$\diagdown$$
$$C$$
$$\diagup$$
$$H$$

plane and the $C=C$ axis and q_{11} be the other similar angle. Let q_{12} be the angle of torsion between these two planes. The deformation potential function suggested by the propylene force constants is[14]

$$\tfrac{1}{2}\sum a_{ij}q_iq_j = \tfrac{1}{2}a_{11}(q_1^2+q_4^2)+\tfrac{1}{2}a_{22}(q_2^2+q_5^2)$$
$$+\tfrac{1}{2}a_{33}q_3^2+\tfrac{1}{2}a_{66}(q_6^2+q_8^2)$$
$$+\tfrac{1}{2}a_{77}(q_7^2+q_9^2)+\tfrac{1}{2}a_{10,10}(q_{10}^2+q_{11}^2)$$
$$+\tfrac{1}{2}a_{12,12}q_{12}^2+a_{37}(q_3q_7+q_3q_9)$$
$$+a_{36}(q_3q_6+q_3q_8)+a_{67}(q_6q_7+q_8q_9)$$
$$+a_{10,11}q_{10}q_{11}. \quad (40)$$

[14] For an excellent discussion of valence force constants and generalizations, see G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), pp. 168–191.

We have $d = d_0 + \sum b_i q_i$. Let $^0\alpha_i$ and ^0r_j be the equilibrium bond angle and bond distance in ^0A associated with $q_i = 0$ and $q_j = 0$, respectively. Then it is easy to see that

$$b_1 = b_4 = \sin\left(^0\alpha_6 - \frac{\pi}{2}\right),$$
$$b_2 = b_5 = b_7 = b_9 = 0,$$
$$b_3 = 1, \quad (41)$$
$$b_6 = b_8 = {}^0r_4 \cos\left(^0\alpha_6 - \frac{\pi}{2}\right),$$
$$b_{10} = b_{11} = b_{12} = 0.$$

Clearly d is affected by changes in q_{10}, q_{11}, and q_{12}, but *not* to linear terms. So $b_{10} = b_{11} = b_{12} = 0$.

It follows from Eq. (30) (or on physical grounds) that if $b_i = 0$ and q_i appears in Eq. (40) only in a squared term (i.e., no cross products involve q_i), then $q_i^0 = 0$. Hence we can ignore q_i from the outset without loss of generality. This applies to q_2, q_5, and q_{12}. Also, if $b_j = b_k = 0$ and the only cross product which involves either q_j or q_k is $a_{jk}q_jq_k$, then $q_j^0 = q_k^0 = 0$. Hence we also ignore q_{10} and q_{11}. Equation (40) reduces to

$$\tfrac{1}{2}\sum a_{ij}q_iq_j = \tfrac{1}{2}a_{11}(q_1^2+q_4^2)+\tfrac{1}{2}a_{33}q_3^2$$
$$+\tfrac{1}{2}a_{66}(q_6^2+q_8^2)+\tfrac{1}{2}a_{77}(q_7^2+q_9^2)$$
$$+a_{37}(q_3q_7+q_3q_9)+a_{36}(q_3q_6+q_3q_8)$$
$$+a_{67}(q_6q_7+q_8q_9). \quad (42)$$

The determinants D and D_i to be evaluated are thus of order seven. However they can be reduced readily to order 2×3. Let

$$J = \begin{vmatrix} a_{77} & a_{67} \\ a_{67} & a_{66} \end{vmatrix}, \qquad K = \begin{vmatrix} a_{37} & a_{67} & a_{77} \\ a_{36} & a_{66} & a_{67} \\ a_{33} & 2a_{36} & 2a_{37} \end{vmatrix},$$

$$K_1 = \begin{vmatrix} 0 & a_{67} & a_{77} \\ b_6 & a_{66} & a_{67} \\ b_3 & 2a_{36} & 2a_{37} \end{vmatrix}, \qquad K_2 = \begin{vmatrix} a_{37} & 0 & a_{77} \\ a_{36} & b_6 & a_{67} \\ a_{33} & b_3 & 2a_{37} \end{vmatrix},$$

and

$$K_3 = \begin{vmatrix} a_{37} & a_{67} & 0 \\ a_{36} & a_{66} & b_6 \\ a_{33} & 2a_{36} & b_3 \end{vmatrix}.$$

Then one finds

$$D = -a_{11}{}^2 JK, \qquad D_6 = D_8 = -a_{11}{}^2 JK_2,$$

$$D_1 = D_4 = -a_{11}b_1 JK, \quad D_7 = D_9 = -a_{11}{}^2 JK_3. \quad (43)$$

$$D_3 = -a_{11}{}^2 JK_1,$$

The structure of propylene, which we need for ^0A and A_0, has apparently not been determined by electron diffraction. The structures of cis- and trans-2-butene are not known accurately.[15] So we take the following reasonable structure parameters for ^0A and A_0: from ethylene,[16a]

$$^0\alpha_6 = {}^0\alpha_7 = {}^0\alpha_8 = {}^0\alpha_9 = 122°; \quad {}^0r_1 = {}^0r_4 = 1.54\text{A};$$
$$^0r_2 = {}^0r_5 = 1.09\text{A}; \quad \text{and} \quad {}^0r_3 = 1.34\text{A}.$$

In Table I we give the force constants[13] used and the values of b_i and D_i calculated from Eqs. (41) and (43).

We must now make some assumptions about interactions. The van der Waals parameters are uncertain. We refer to paper I for a detailed discussion. Using the method described there we take for the $CH_3 - CH_3$ interaction $r^* = 4.0\text{A}$ and $\epsilon = 16.0 \times 10^{-15}$ erg, and for the $H - H$ interaction[16b] $r^* = 2.4\text{A}$ and $\epsilon = 2.92 \times 10^{-15}$ erg. These automatically determine r^* and ϵ for the $CH_3 - H$ interaction and then P, ρ, and μ for all three interactions. We assume that the CH dipole is located in the middle of the CH bond and that the bond moment is $\mu = 0.4 \times 10^{-18}$ e.s.u.[17a] The dipole-dipole interaction energy is then given by $2\mu^2 \cos^2\theta/r^3$, where $\theta = 58°$ in ^0A and $\theta = 32° \ 16'$ in A_0. r is the dipole-dipole distance.

Using the unperturbed structure parameters and the above energy parameters, interatomic distances and interaction energies can be calculated and $^0Q_A - Q_{A0}$ estimated as discussed above. One finds, with these parameters, $^0Q_A - Q_{A0} = -0.365$ kcal./mole. Equations (32) and (33) may now be used to calculate $E_A \cong E_A'$. The result is $E_A' = 2.217$ kcal./mole. Hence, from Eq. (6), $\Delta Q \cong E_A' + (^0Q_A - Q_{A0}) = 1.852$ kcal./mole, compared to the known value 1.288 kcal./mole. This is certainly satisfactory agreement considering all the uncertainties involved in the calculation (e.g., structure, force constants, van der Waals parameters, bond dipole moment, and especially zero-point vibrational energy).

It is hoped that the zero-point vibrational energy correction can be made in a future calculation. G. W. Wheland has suggested[17b] a perturbation procedure which may be useful for this purpose. Of course the fact that a quite satisfactory result is obtained, ignoring zero-point vibrational energy, implies that the large zero-point energies in ^0A and A must almost cancel.

If we take $\epsilon = 10.0 \times 10^{-15}$ erg for the $CH_3 - CH_3$ interaction, and make the corresponding change in ϵ for $CH_3 - H$, but make no other changes in the fundamental parameters, one gets $^0Q_A - Q_{A0} = -0.373$ kcal./mole, $E_A' = 1.674$ kcal./mole, and $\Delta Q \cong 1.301$ kcal./mole, in virtual agreement with 1.288 kcal./mole. However, the present calculation is certainly not accurate enough to conclude from these results that $\epsilon < 16.0 \times 10^{-5}$ erg. We give a few more

TABLE I.

i	a_{ii}	b_i	D_i(c.g.s., rad.)	$q_i{}^0 (\epsilon = 10)$
1 or 4	4.50×10^5 dyne/cm	0.5299	6.57×10^{-34}	0.0045A
3	9.72×10^5 dyne/cm	1.000	0.763×10^{-34}	0.00052A
6 or 8	1.20×10^{-11} dyne cm/rad.^{2}	1.306×10^{-8} cm/rad.	121.0×10^{-26}	0.0830 rad. = 4.8°
7 or 9	0.939×10^{-11} dyne cm/rad.^{2}	0.000	-97.2×10^{-26}	-0.0667 rad. $= -3.8°$

$a_{37} = 0.66 \times 10^{-3}$ dyne/rad.
$a_{36} = 0.73 \times 10^{-3}$ dyne/rad.
$a_{67} = 0.75 \times 10^{-11}$ dyne cm/rad.^{2}

$D = 55.8 \times 10^{-29}$

[15] L. O. Brockway and P. C. Cross, J. Am. Chem. Soc. 58, 2407 (1936).
[16a] E. H. Eyster, J. Chem. Phys. 6, 580 (1938).
[16b] Strictly speaking, the $H - H$ van der Waals interaction chosen includes already some dipole interaction. However, this van der Waals curve does not give any angular dependence to the dipole interaction as it properly should. Also, since the van der Waals parameters are in any case very uncertain for this interaction, we ignore this complication in the present case.
[17a] L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, 1945).
[17b] Personal communication to F. H. Westheimer.

TABLE II. ($\epsilon = 10$.)

Interaction	^0A	A_0
$2 \times (CH_3 - H)$	-0.155 kcal./mole	0.197 kcal./mole
$H - H$	-0.050	-0.019
dipole-dipole	0.183	0.341
$CH_3 - CH_3$	—	-0.168
Total	-0.022 kcal./mole	0.351 kcal./mole

details below concerning the second calculation ($\epsilon = 10$).

In Table II we list the individual interaction energies found in computing $^0Q_A - Q_{A_0}$ ($\epsilon = 10$). The contributions to E_A' are the following: van der Waals repulsion, 2.312 kcal./mole; van der Waals attraction, -1.250 kcal./mole; and deformations, 0.612 kcal./mole. Also, $d_0 = 2.972$A and d (equilibrium configuration of A) = 3.194A. The net $CH_3 - CH_3$ van der Waals energy corresponding to a distance of 2.972A between methyl groups amounts to 2.993 kcal./mole compared to 1.062 kcal./mole for a distance of 3.194A. The deformations are given in Table I (q_i^0). It is seen that bond stretching is negligible but that there are small but appreciable changes predicted in bond angles: in A, $\alpha_6 = \alpha_8 = 126.8°$ and $\alpha_7 = \alpha_9 = 118.2°$. The $H - C - CH_3$ angle is then 115°. It is interesting that the angles α_7 and α_9 play an important role in the calculation even though $b_7 = b_9 = 0$. This is, of course, a result of the inclusion of cross-products in the potential function.

It is gratifying that reasonable results have now been obtained by this type of calculation in a case[3] where there is a large steric effect (about 20 kcal./mole) and also in a case (the above) where the steric effect is small (about 2 kcal./mole).

It might be remarked that this semi-empirical approach to steric effects provides, in principle, a method of explaining differences in vibrational frequencies, deduced from infra-red and Raman spectra, in a pair of molecules such as cis- and trans-2-butene.

Another conceivable application is that the present method might in the future be useful in estimating the rate of a reaction involving a substrate molecule or molecules in the presence of an enzyme,[18] in accordance with a recent proposal of Pauling in his Silliman lecture.[19] Pauling suggested that an enzyme has a structure closely complementary to the activated complex for the reaction that is catalyzed by the enzyme. The present method would apply in principle as follows: consider the activated complex for the reaction in the absence of the enzyme as the unperturbed molecule ^0A, with coordinates q_i and force constants a_{ij}, as in connection with Eq. (18). It might be necessary to find the a_{ij} by applying method 1 to a molecule $^0(^0A)$ with internal steric interactions removed. Let $V(q)$ be the (perturbing) energy of interaction between the enzyme and the activated complex as a function of the q_i. Then Eq. (18) gives the potential energy U of the perturbed molecule A in the presence of the enzyme surface. Eq. (19) also applies. If the enzyme surface fits the activated complex ^0A "perfectly" (i.e., if $(\partial V/\partial q_i) = 0$ ($i=1, 2, \cdots$) at $q_1 = q_2 = \cdots = 0$), then $q_i^0 = 0$ ($i=1, 2, \cdots$), $A = ^0A$ (structure) and $E' = U(0) = V(0)$. In this case the energy of the activated complex is lowered ($E' = V(0)$ is negative) in the presence of the enzyme by just the energy of interaction $V(0)$ between the enzyme and the unperturbed activated complex ^0A. In general, though, the fit will not be "perfect:" $q_i^0 \neq 0$ ($i=1, 2, \cdots$) and $E' < V(0)$. In any case, to find the free energy of activation and hence the rate of the reaction, the shape of the potential energy surface U must be studied (normal coordinates) in the neighborhood of its saddle point.

APPENDIX

In the absence of any interaction between the hydrogen atoms in a molecule such as H_2O, we would expect a 90° $H - O - H$ angle owing to directed valence considerations.[17a] The observed angle in H_2O is 104° 31', the increase presumably being due to $H - H$ repulsion. It is clearly of interest to try to apply the present method to this problem.

The results obtained are, on the whole, rather unsatisfactory. The principal sources of difficulty which arise in trying to fit these molecules into the semi-empirical method being used here seem to be: (a) the treatment of the large electrostatic effects (see below); (b) the probability

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[18] The same possibility exists and is, of course, more practical in connection with ordinary catalysts and smaller molecules.

[19] L. Pauling, American Scientist 36, 51 (1948).

that van der Waals parameters for a given type of interaction, say $H-H$, are not constant from case to case when both interacting atoms or groups are bonded to the same atom (see reference 17a, pp. 192–193); (c) uncertainty concerning the extent of hybridization which would tend to increase appreciably the unperturbed bond angle over 90° in some cases (see reference 17a, pp. 86–88); and (d) the treatment of a group, such as a methyl group, as an atom will introduce a relatively large error in a small molecule as compared to a large molecule. In connection with (a), the bond dipoles are so close together that one is hardly justified in treating the electrostatic interaction as a dipole-dipole interaction as in Section III. In the calculations carried out we have gone to the opposite extreme by finding the charge on the terminal atom (H in H_2O) from the equation *bond moment = charge × bond length,* and then calculating the electrostatic repulsion between the terminal atoms from (charge)^2/(interatomic distance). The results (ϵ; see below) obtained for a given interaction ($H-H$, $Cl-Cl$ or $F-F$) show an unexplained systematic trend with charge which probably (other parameters vary concomitantly so this is not certain) indicates that this assumption is not good. Actually, of course, one would expect that only a detailed quantum-mechanical treatment could correctly take into account a large, short range electrostatic interaction of this type.

The above difficulties are in addition to uncertainties in the actual numerical values of force constants, van der Waals parameters, and bond dipole moments.

The procedure used is the following:

(a) We ignore bond stretching. Since many of the increases, $\alpha-90°$, in bond angle over 90° are considerable, we do not assume a linear relation between interatomic distance r and $\alpha-90°$ in analogy with $d=d_0+\sum b_i q_i$ in Section III, but use the general expression $r(\alpha)$. However, we must still assume that Hooke's law holds, for very large displacements in some

cases; this will certainly be an important source of error.

(b) We use method 1.[20] For a triatomic symmetrical molecule such as H_2O, let r_0 be the fixed bond distance, e the charge on the terminal atom, α the bond angle, a the force constant in ^0A, f the force constant in A, let $\alpha=\alpha_0$ in ^0A (equilibrium configuration) and let $\alpha=\beta$ in A (equilibrium configuration). Then (Eq. (18))

$$U(\alpha)=P\exp(-r/\rho)-(\mu/r^6)\\+(e^2/r)+(1/2)a(\alpha-\alpha_0)^2, \quad (44)$$

where $r=2r_0\sin(\alpha/2)$. The equation for a tetra-atomic symmetrical molecule such as NH_3 is similar.

(c) We set $(dU/d\alpha)_{\alpha=\beta}=0$, solve for a, and substitute the expression for a into $(d^2U/d\alpha^2)_{\alpha=\beta}$ $=f$. If we now put[4] $\mu=17.1P\rho^6$, the resulting equation can be regarded as giving $P(\rho)$ (or, the equivalent,[4] $\epsilon(r^*)$) in terms of the known quantities f, e, r_0, β, and α_0. We then choose a reasonable value of r^* (the same value for a given interaction in different molecules) and calculate ϵ. It should be remarked that ϵ is very sensitive to the choice of r^*.

The above calculation was carried out on every suitable molecule (taking $\alpha_0=90°$ in each case; see above) for which r_0, f, β, and the bond dipole moment (or the molecular dipole moment) are available. On the basis of the results found in paper I, the values of ϵ obtained for the interactions in H_2O, NH_3, H_2S, Cl_2O, PCl_3, and F_2O are quite reasonable. However, the values found for PH_3, $AsCl_3$, $SbCl_3$, PF_3, AsF_3, $(CH_3)_2O$, $(CH_3)_3N$ and PBr_3 are not reasonable.[21] In view of this inconsistency one must conclude that the semi-empirical method in its present form is not generally well suited to these small molecules with large electrostatic effects. For this reason we have refrained from giving detailed equations, data, and results here.

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[20] Method 2 leads to essentially the same results.
[21] One is tempted to make the following classification: the reasonable result for PCl_3 is probably fortuitous; for some reason P, As, and Sb compounds are anomolous; methyl compounds are not expected to give good results in view of difficulties (b) and (e) listed above.