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On the Determination of Interaction Energy Surfaces
I. Formic and Acetic Acid Dimers

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ABSTRACT

A strategy is developed for obtaining molecular interaction energy functions by shaping energy surfaces to fit equilibrium energy and geometry data for strongly coupled systems in the gas phase such as the carboxylic acid dimers. The surface is shaped such that its lowest point corresponds to the known energy and equilibrium geometry. The procedures and simulation techniques used to accomplish this are described. The formic acid dimer was successfully used as a model system to derive a set of 1 – 4 – 6 – 12 atom–atom interaction energy functions. The atom–atom terms were transferred to acetic acid and used to calculate the mechanically stable conformations of acetic acid dimers. The calculated acetic acid dimer conformation of lowest energy is in excellent agreement with that experimentally determined. The experimental energy of acetic acid dimerization was not available for comparison.

INTRODUCTION

In this paper we develop a set of atom–atom interaction energy functions by use of a computer simulation of molecular interactions. These functions are for use in calculating molecular interaction energy surfaces. Ideally, interaction energy surfaces should be calculated from the wave equation as has been done for simple systems such as He ... He [1], etc. Since this is usually not feasible for molecular systems, many investigators [2], [7] have considered molecular interaction energy functions as expansions in inverse powers of atom–atom distances and have attached physical significance to each of the terms contributing to the total inter-

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action energy. What the approach presented in this paper directs attention to and emphasizes is not the individual terms such as linear hydrogen bonds, London forces, overlap repulsion and the like, but rather the detailed shape of the entire complex energy surface created by the integrated mutual interactions of the molecules involved. The experimental information pertaining to interaction energies relates to the energy surface and not directly to the individual contributions.

In the usual way, we consider molecular interaction energy as a pairwise sum of atom–atom interactions, which are expressed as an expansion in inverse powers of intermolecular atom–atom distances. Four inverse powers were chosen. The ones chosen have been used to describe the generally recognized contributions to molecular interaction energies [8]:

(1) a very short range (R^{-12}) orbital-overlap repulsion,

(2) a short range (R^{-6}) dispersive attraction,

(3) a medium range (R^{-4}) electrostatic-induced dipole attraction, and

(4) a long range (R^{-1}) coulombic electrostatic interaction.

As an initial set of values for the coefficients of these terms we used published values and values calculated from approximate quantum mechanical formulae.

The simulation of molecular interactions between two molecules was done with an IBM 360/50 computer. This was accomplished by placing one molecule in a three-dimensional conformation relative to a second, which was held fixed. The first molecule was then allowed to slide down the path of the steepest gradient on the energy surface, which is created by the molecular interaction. The first molecule slides down the energy surface until it reaches a point where further changes in the independent variables, which determine the geometry of one molecule relative to a second, produce a rise in the energy. The geometry corresponding to this point is taken to be a mechanically stable configuration.

We selected the formic acid dimer as a test system since it is unusual in having a known interaction energy and a known stable geometry in the gas phase. When the initial set of values for the coefficients of the inverse power terms were used, we found that a single deep well was formed with its bottom having a value approximately equal to the known energy but corresponding to a completely incorrect dimer geometry. Since there are no published procedures for making desired changes in energy surfaces, it became necessary to develop one. The procedure involves a systematic variation of the values of the coefficients so that the energy surface would be reshaped to a desired result. The desired result, of course, would be that for which the lowest point of the energy surface would have a value equal to the known energy and correspond to the known stable dimer geometry. This was accomplished. Much of this paper is concerned with a description of the procedure and the results obtained by use of it.

The set of molecular atom–atom interaction energy functions derived from the formic acid dimer data was used to predict the energy and geometry of mechanically stable acetic acid dimers.

TRIAL FUNCTION

The formulation of the molecular interaction energy function, $\phi_{\alpha\beta}$, chosen to describe the interaction energy between molecule α and molecule β is represented as the pairwise sum of the molecular atom–atom interaction energies existing between the atoms of molecule α and those of molecule β. If we represent the molecular atom–atom interaction energy function describing the interaction energy between atom i of molecule α and atom j of molecule β as ϕ_{ij}, then

$$\phi_{\alpha\beta} = \sum_{i=1}^{m} \sum_{j=1}^{n} \phi_{ij}$$

where m is the total number of atoms in molecule α and n that in β. ϕ_{ij} in turn is expressed as an expansion in intermolecular atom–atom distances R_{ij}.

$$\phi_{ij} = \sum_{k=0}^{\infty} c_k R_{ij}^{-k}$$

We picked four terms in inverse powers of R as a minimum number of terms to describe the interaction energies between the highly polar formic acid molecules ($\mu = 1.35D$) [9]. The four terms in inverse powers of R selected are those that have been used to parallel the distance dependencies of the four generally recognized contributions to molecular interaction energies: a very short range (R^{-12}) orbital overlap repulsion, short range (R^{-6}) dispersive attraction, medium range (R^{-4}) electrostatic induced dipole attraction, and a long range (R^{-1}) electrostatic charge interaction, i.e.,

$$\phi_{ij} = A_{ij}R_{ij}^{-1} + B_{ij}R_{ij}^{-4} + C_{ij}R_{ij}^{-6} + D_{ij}R_{ij}^{-12}$$

We designate this as our trial function and will attempt to account for the known properties of the carboxylic acid dimers in terms of this functional form with the coefficients as adjustable parameters.

INITIAL SET OF COEFFICIENTS

The initial set of coefficients was obtained as follows: For A_{ij} we used the relationship

$$A_{ij} = 331.9833 q_i \cdot q_j$$

where q_i and q_j are the fractional electronic charges located at the atom centers. The charges were calculated by summing the σ and π charges which were determined by the Del Re and Huckel Molecular-Orbital Methods respectively [10].

B_{ij} was calculated by use of the formula

$$B_{ij} = -\tfrac{1}{2} \times 331.9833(\alpha_i q_j^2 + \alpha_j q_i^2)$$

where α_i is the polarizability of atom i and α_j that of atom j [11].

For C_{ij} we used the Slater–Kirkwood formula [12].

$$C_{ij} = -\frac{3}{2}\,\frac{e\hbar\alpha_i\alpha_j}{m^{1/2}\left[\left(\frac{\alpha_i}{N_i}\right)^{1/2} + \left(\frac{\alpha_j}{N_j}\right)^{1/2}\right]}$$

where e is the charge of one electron; m is the electron mass; $\hbar$ has its usual meaning; N_i is the effective number of valence electrons for atom i and N_j that for atom j.

For D_{ij} we used the values employed by T. Ooi, *et al.*; [13] in subsequent calculations we employed the rule that

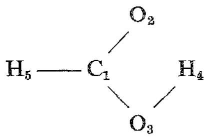
$$D_{ij} = D_i \cdot D_j$$

which reduces the number of independent variable parameters.

Table I contains the values of the parameters used.

TABLE I

PARAMETERS FOR THE MOLECULE



	$\alpha_i X\, 10^{24}$ cm^3				D_i		Monomer Coordinates in A°		
	Initial	Final	N_i	q_i	Initial[a]	Final	X	Y	Z
C_1	1.51	1.00	5.25	+0.4663	534.79	1000.	0.00	0.00	0.00
O_2	0.84	0.79	7.00	−0.4267	380.789	496.	0.00	0.59	1.08
O_3	0.59	0.10	7.00	−0.3958	380.789	534.	0.00	0.66	−1.19
H_4	0.42	0.32	0.80	+0.3020	67.08	5.4772	0.00	1.60	−0.96
H_5	0.42	0.42	0.80	+0.0542	67.08	141.42	0.00	−1.09	0.00

[a] For the initial coefficients we used $D_{CO} = 205 \times 10^3$, $D_{CH} = 38 \times 10^3$ and $D_{OH} = 25 \times 10^3$ following the reference cited above.

ENERGIES OF DIMERIZATION

The vapor phase dimerization of formic acid has been studied by a number of investigators [14]. Halford [15] evaluated the standard heat of dimerization at 25° C. as -14.40 ± 0.12 kcal. mole^{-1}. Muller and Spangenberg [16] evaluated the standard energy of dimerization at 0° K. as -14.169 kcal. mole^{-1} using the usual quantum statistical equations and Halford's value of the $\Delta H^{\circ}_{298^{\circ}}$.

The computer was programmed to calculate an interaction energy between two rigid monomers as a function of their relative positions. This corresponds to the electronic kinetic and potential energy of two interacting monomers exclusive of their translational, rotational and vibrational energies. The experimental quantity with which we are to compare the lowest calculated interaction energy is obtained from the standard energy of dimerization at 0° K by subtracting out the contributions of the zero point vibrational energies. Using the vibrational frequencies as presented by Muller and Spangenberg one obtains a spectroscopic energy of dimerization (ϕ_{KN}),

$$\phi_{KN} = -14.169\ (\pm 0.12) - 2.079 = -16.248 \pm 0.12 \text{ kcal. mole}^{-1}.$$

For our computations ϕ_{KN} was rounded off to -16.2 kcal. mole^{-1}.

MONOMER AND DIMER GEOMETRIES

The computer simulation as applied to formic acid dimers requires knowledge of the monomer and dimer equilibrium geometries. The structure used for the formic acid monomer was that determined by Karle and Karle [17] by microwave spectroscopy (Table I). The properties of the formic acid dimer were derived from the electron diffraction results of L. Su [18]. Thee is some deformation of the monomer structure when it forms the dimer, e.g., $<$ C–O–H increases from 107.6° to 114.0°. However, in the present calculations such deformations were not taken into account. We take the dimer geometry to be coplanar, with a center of symmetry, and with $O_2 \cdots O_3$ contact distances (in the future to be referred to as $O \cdots O$ contact distances) of 2.76 A° as found by Su, but the bond angles and distances within each monomer are the same as in the isolated monomers. In other words we simulated the formation of the dimer with the observed $O \cdots O$ contacts and symmetries from completely rigid monomers.

In all cases bond lengths were rounded off to 0.01 A°.

PROCEDURE AND RESULTS

1. *Procedure and Results Using the Initial Set of Coefficients*

A computer program (WPM 810) was written to simulate molecular interactions between any given pair of molecules and for any given set of atom–atom interaction energy functions. Essentially the program minimizes molecular interaction energy with respect to dimer geometry. In particular, starting from a specified dimer geometry one molecule is held fixed while the other slides down the path of steepest gradient on the energy surface to a point where further changes in the position of the movable molecule in relation to the fixed, would produce a rise in the molecular interaction energy. The geometry and energy corresponding to this point are recorded. We will refer to the process carried out in this program (WPM 810) as dimer simulation. The initial specified dimer geometry from which the process of steepest descent begins will be referred to as a starting geometry. Appendix AIII contains a description of the steepest descent method as adapted to dimer simulation.

In order to find different energy wells that may exist on an energy surface in conformation space, dimer simulations must be carried out from many different starting geometries. In the case of formic acid dimers twenty-four starting geometries were employed. One of the twenty-four starting geometries corresponded to the known dimer geometry. The other twenty-three were chosen as regularly-spaced representatives of all the geometries generated as follows:

(1) Place the two formic acid molecules in the same plane with their C–H bonds pointing in opposite directions and their carbon atoms separated by 4.0 A°, then

(2) precess one molecule around the other in such a way that the two molecules are always in parallel planes with their C–H bonds pointing in opposite directions. The path of the precessing molecule is made to form a hemisphere whose flat surface contains the other molecule. Only one of the two possible "hemispheres of starting geometries" generated by the precessing molecule need be considered since the two are identical. The 23 regularly spaced geometries chosen from the "hemisphere of starting geometries" were obtained by taking 23 of the 56 possible combinations of the polar angles θ and φ, where θ goes from 0° to 315° inclusive in increments of 45° and φ goes from 90° to 270° inclusive in increments of 30°. The 56 geometries are comprised of only 23 unique ones (see Appendix AII: Exchange Symmetry). Appendix AI contains a description of the coordinate systems and the vector transformations used in this paper.

When the energy surface is defined by the initial set of coefficients, the same crater is reached from all 24 starting geometries. The energy corresponding to the

TABLE II

ENERGIES AND CONFORMATION FOR THE EXPERIMENTALLY DETERMINED FORMIC ACID DIMER AND THE CALCULATED STABLE ONE OBTAINED BY USE OF THE INITIAL SET OF COEFFICIENTS.[a]

	R in A°	θ	φ	X	Y	Z	Energy in kcal. mole^{-1}
Experimental	3.97	82°	90°	180°	0°	0°	−16.2
Calculated	2.77	103°	166°	91°	18°	−5°	−16.8

[a] Dimer conformations are given in terms of Eulerian angles relating one monomer to the other; refer to Appendix AI for details.

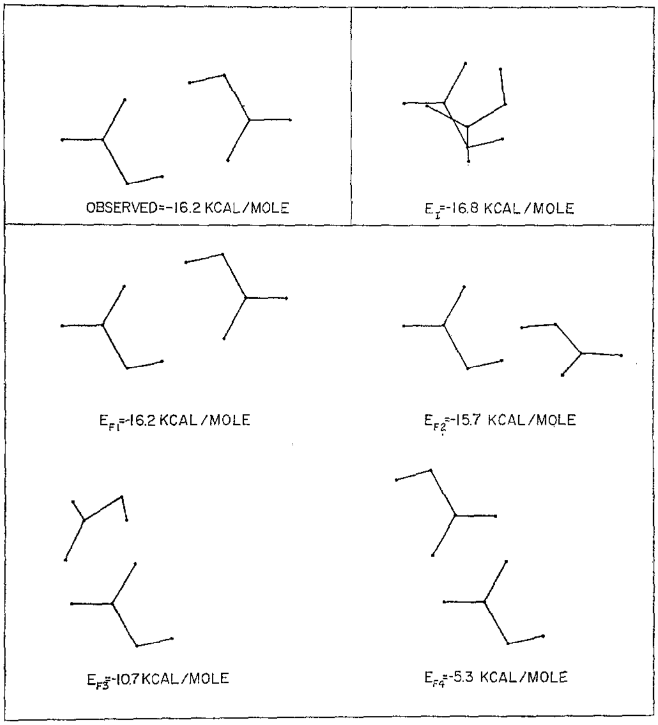


FIG. I. Y–Z planar projections of the experimentally observed formic acid dimer conformation and those calculated as mechanically stable. The calculated conformations are identified by subscripted energies. E_I represents the energy of the mechanically stable conformation found when using the initial set of coefficients for the molecular atom–atom interaction energy functions; E_{F1} to E_{F4} represent those found when using the final set of coefficients.

lowest point of the crater (-16.8 kcal. mole^{-1}) is approximately equal to that of the known value, ϕ_{KN}, (-16.2 kcal. mole^{-1}) but the geometry is not (see Table II and Figure I). Furthermore, when the energy is computed with the dimer held in the observed conformation a value of $+16.2$ kcal. mole^{-1} is obtained.

2. *Procedure for Reshaping Energy Surfaces*

Having obtained an energy surface which does not correctly account for formic acid dimerization, a procedure for reshaping energy surfaces was developed. It consists of the following steps:

Step 1. In this step the shape of the incorrect energy surface is altered with a bias to forming only one deep well on its surface, with the deep well located in the vicinity of the point corresponding to the correct dimer geometry. The depth of the well is regulated to be approximately equal to the known energy.

Step 2. The one deep well created in step 1 is altered so as to make its lowest point correspond to the known energy and correct dimer geometry. In the process of altering the one deep well, however, the entire energy surface is altered. We will refer to this new energy surface as the crater-shaped energy surface.

Step 3. The crater-shaped energy surface is now searched to determine if the point corresponding to the energy of the dimer in its correct geometry is, in fact, the lowest point on the surface. If it is not, the procedure is repeated starting with step 1 in which the crater-shaped energy surface is used as the incorrect surface to be altered. The procedure may have to be repeated several times before the best solution, if not an absolutely exact solution, is found.

Details of Step 1. To alter the incorrect energy surface with a bias to forming only one deep well located near the correct dimer geometry, a function F was formed.

$$F = (k - 1)\,\phi_1 - \phi_2 - \phi_3 \cdots \phi_k$$

where ϕ_1 represents the energy of the dimer in its correct geometry for any given set of interaction energy functions. ϕ_2 up to and including ϕ_k represent the energies of the dimer in representative conformations that span the entire energy surface save for the immediate area surrounding the correct conformation.

The incorrect energy surface is altered by minimizing the function F with respect to any or all of the parameters common to the ϕ_i. The minimization tends to decrease the value of ϕ_1 and increase the values of the other ϕ_i's and in so doing provides information concerning the direction of change for the values of the variable parameters necessary to obtain a desired solution. In traversing parameter space during minimization of F, local minima may be encountered before a desired solution is reached. In which case the local well is escaped by changing the values of the parameters in the direction that led into it. The amount by which to change the values of the parameters is roughly estimated by comparing the computed energies before and after the last minimization. The minimization of the function F is continued until a satisfactory solution is obtained.

In the formic acid dimer case the representative geometries (ϕ_2 to ϕ_k), which were employed in the function F, were chosen on the basis of being representatives of areas on the incorrect energy surface where the slopes were almost flat (i.e. where a change of 1° in each of the Eulerian angles and 0.005 A° in R would produce a $\Delta\phi$ of < 0.1 kcal.). We felt that these areas would be more likely to develop into craters when the parameters were varied. To obtain these representative conformations, dimer simulations were performed using the 24 starting geometries described previously. The dimer simulations were performed exactly as before except that the movable molecule was made to stop when it reached a position where the gradient was as small or smaller than that indicated above.

Details of Step 2. In this step an attempt is made to find values for the parameters varied in step 1 which will produce an energy well whose lowest point corresponds to the known energy and correct dimer geometry. The computer was programmed to try many different sets of values for the parameters. The sets tried were obtained by computing all possible combinations of selected parameter values. The selected values for any particular parameter ranged from 0.95 P to 1.05 P in increments of 0.025 P where P represents the value obtained for that parameter after completing step 1. Each set of parameters tried was tested to

(1) determine if the computed energy, ϕ_0, for the dimer in the observed geometry was within an arbitrary range ($\phi_{KN} \pm 0.049$ kcal. mole^{-1}) and if so, to

(2) determine if ϕ_0 was less than each of the computed energies for the dimer in nine geometries slightly different than the observed. Each of the nine different geometries was obtained by increasing or decreasing one of the Eulerian angles independently by a small amount (0.01 A° or 3 degrees). If ϕ_0 was less than each of the other nine computed energies, the set of parameters was further tested to

(3) determine whether the observed geometry for the dimer was located at the very bottom of the energy well by evaluating the gradients of ϕ with respect to each of the six Eulerian angles.

Details of Step 3. To search the energy surface for the bottom of other energy wells that may exist on it, dimer simulations are performed using representative starting geometries that span the surface. In the formic acid dimer case the 23 starting geometries described previously were used.

3. *Variation of the Trial Function Coefficients*

The choice of parameters to vary in altering the formic acid dimer energy surface defined by the initial set of coefficients is somewhat arbitrary in the sense that the [redacted] and dimerization energy of formic acid. In applying the reshaping procedure the R^{-12} coefficients were allowed to vary such that two constraints were not violated:

(1) $D_{ij} = D_i \cdot D_j$

(2) Every $D_i > 0$

We found that it was possible to successfully complete step 1 and then step 2, but not step 3 of the procedure despite many iterations. In other words, it was possible to create an energy surface with a minimun at the correct energy and geometry but this minimum could not be made to be the lowest on the surface. The deeper minima found always had shorter O ··· O contact distances than those of the correct dimer conformation. Because of this we decided to repeat the reshaping procedure using longer O ··· O contact distances for the observed equilibrium geometry. The O ··· O contact distances were lengthened in small increments (0.02 A°) until we found a set of R^{-12} coefficients which produced an energy surface with the following characteristics:

(a) The depth of the lowest well being -16.2 kcal. and at least 5 kcal. lower than any other well on the surface.

(b) The dimer conformation corresponding to the lowest well being planar, with a center of symmetry and linear O–H ··· O contacts. To obtain an energy surface with these characteristics it was necessary to use O ··· O contact distances 0.14 A° larger than those determined by electron diffraction. Although this is a considerable improvement over the initial set of coefficients in that it adequately satisfies the thermal data and partially satisfies the electron diffraction data for the formic acid dimer, we continued to search for a better set of coefficients.

Having satisfied ourselves that we could not further improve our energy surface by varying only the R^{-12} coefficients, we decided to also adjust the invariably attractive R^{-4} and R^{-6} terms by considering α as a variable parameter. As before, we began the reshaping procedure by using as the incorrect energy surface to be altered that defined by the initial set of coefficients. This time, however, two sets of parameters, the α_i and D_i, were allowed to vary. The best set of parameter values found which we refer to as our final set (see Table I), produced an energy well with its lowest point having a value of -16.2 kcal. and its corresponding geometry almost identical with the observed (see Table III and Figure I). It will

TABLE III

ENERGIES AND CONFORMATION FOR THE CALCULATED STABLE FORMIC ACID DIMERS USING THE FINAL SET OF COEFFICIENTS[a]

Conformation	R in A°	θ	φ	X	Y	Z	Energy in kcal. mole^{-1}
1	3.94	79°	90°	180°	0°	0°	−16.2
2	3.84	101°	89°	174°	−52°	13°	−15.7
3	3.68	−52°	14°	210°	30°	126°	−10.7
4	3.47	−48°	162°	180°	0°	0°	−5.3

[a] Dimer conformations are given in terms of Eulerian angles relating one monomer to the other; refer to Appendix AI for details.

be noted that four energy wells were found. The desired well is of lower energy than any of the three false ones, although it is only 0.5 kcal. lower than the lowest of the false wells. If there were such a well (0.5 kcal. higher than the true well) in the actual energy surface and it had roughly the same shape as the true well, then it would be nearly as densely populated as the true well at ordinary temperatures. As a result it would make a significant contribution to the electron diffraction pattern. Since the recent electron diffraction pattern for formic acid dimers seems to be well accounted for in terms of a single dimer structure, it is probable that a further minor reshaping of the energy surface would be in order.

4. *Results for Acetic Acid Dimers*

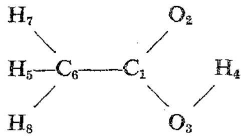
The practical value of any set of interaction energy functions is of course, their transferability to different molecular systems, i.e. in predicting results rather than in explaining results from which they may have been derived. To test the transferability of the set of atom–atom interaction energy terms derived from formic acid dimers to at least one other system, we performed the dimer-simulation using two acetic acid molecules without coefficient adjustment. We again used rigid monomer geometries [20] (Table IV) with the methyl group in a staggered conformation. The dimer-simulation was carried out in the same way as for formic acid and from the same 24 starting geometries.

The dimer-simulation with acetic acid was performed first with an initial set of energy functions obtained in the same way as was the original initial set for formic acid (Table IV) and then repeated using the final set of energy functions (Table IV).

(a) *Results with the Initial Set.* Five energy wells were found when the initial set of energy functions was used (Table V). The energies range from −22.7 kcal. mole^{-1}

TABLE IV

PARAMETERS FOR THE MOLECULE



	$\alpha_i X\ 10^{24}$ cm³				D_i		Monomer Coordinates in A°		
	Initial	Final	N_i	q_i	Initial[a]	Final	X	Y	Z
C_1	1.51	1.00	5.25	+0.5101	534.79	1000.	0.00	0.00	0.00
O_2	0.84	0.79	7.00	−0.4714	380.789	496.	0.00	0.61	1.08
O_3	0.59	0.10	7.00	−0.4016	380.789	534.	0.00	0.64	−1.14
H_4	0.42	0.32	0.80	+0.3014	67.08	5.4772	0.00	1.57	−0.95
H_5	0.42	0.42	0.80	+0.0409	67.08	141.42	−1.00	−1.91	0.00
C_6	0.93	1.00	5.25	−0.0612	534.79	1000.	0.00	−1.50	0.00
H_7	0.42	0.42	0.80	+0.0409	67.08	141.42	0.50	−1.91	0.87
H_8	0.42	0.42	0.80	+0.0409	67.08	141.42	0.50	−1.91	−0.87

[a] For the initial coefficients we used $D_{CO} = 205 \times 10^3$, $D_{CH} = 38 \times 10^3$ and $D_{OH} = 25 \times 10^3$ as before with formic acid.

TABLE V

ENERGIES AND CONFORMATIONS FOR THE CALCULATED STABLE ACETIC ACID DIMERS USING THE INITIAL SET OF COEFFICIENTS. THE EXPERIMENTAL ACETIC ACID DIMER CONFORMATION IS ALSO PRESENTED.[a]

Conformation	R in A°	θ	φ	X	Y	Z	Energy in kcal. mole⁻¹
Experimental	3.96	82°	90°	180°	0°	0°	Not Available
1	2.69	259°	192°	90°	−14°	6°	−22.7
2	2.69	98°	161°	90°	12°	−12°	−22.3
3	2.74	−80°	−20°	281°	8°	−186°	−22.1
4	2.63	94°	167°	121°	−9°	−196°	−21.9
5	2.65	76°	174°	186°	0°	−3°	−21.7

[a] Dimer conformations are given terms of Eulerian angles relating one monomer to the other; refer to Appendix AI for details.

to -21.7 kcal. mole^{-1}. The energy of dimerization with which we are to compare these results is not known because the intermolecular vibrational frequencies of the acetic acid dimer are not available (thus making it impossible to accurately determine the internal energy of dimerization given the enthalpy).

Karle and Brockway [21] have determined the equilibrium geometry of the acetic acid dimer in the gas phase. They reported that the equilibrium geometry for the acetic acid dimer has essentially the same characteristics as that for the formic acid dimer with the exception of a shorter O ··· O contact distance (0.02 A°) for the acetic acid dimer (Table V). None of the geometries corresponding to the bottom of the five energy wells found remotely resemble the observed dimer geometry. The observed dimer geometry and that corresponding to the bottom of the lowest of the five energy wells are shown in Fig. II.

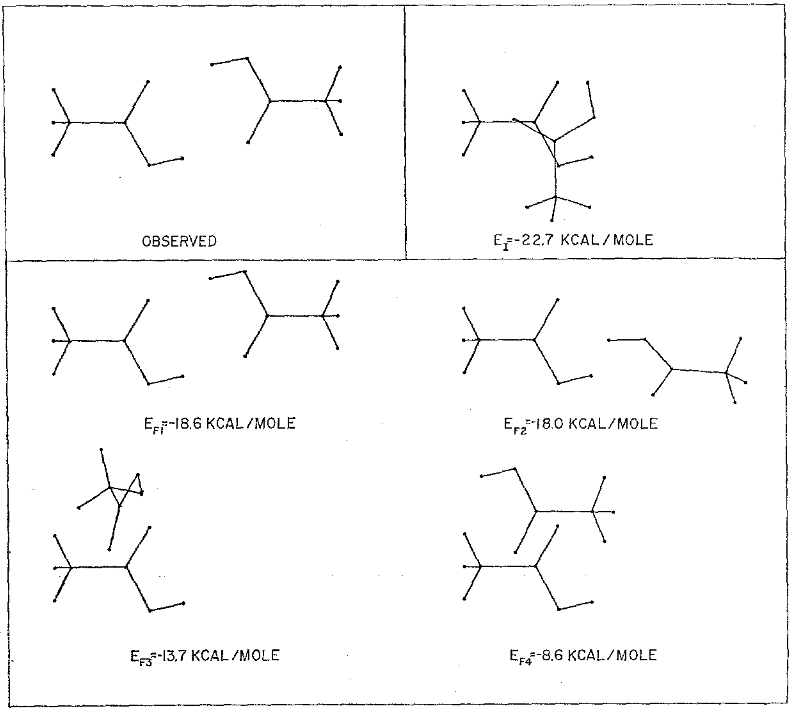


FIG. II. *Y–Z* planar projections of the experimentally observed acetic acid dimer conformation and five of those calculated as mechanically stable. The calculated conformations are identified by subscripted energies. E_I represents the energy of the most mechanically stable conformation found when using the initial set of coefficients for the molecular atom–atom interaction energy functions; E_{F1} to E_{F4} represent four of the six found when using the final set of coefficients.

(b) *Results with the Final Set.* Six energy wells were found when the final set of energy functions was used (Table VI). The energies range from −18.6 kcal. mole^{-1} to −7.8 kcal. mole^{-1}. The second lowest energy well is only 0.6 kcal. higher than the lowest well, a result not unlike that obtained for the formic acid dimer system. The geometry corresponding to the bottom of the lowest energy well is in almost exact agreement with the observed geometry. It differs in that there is a difference of 2 degrees in the O—H ··· O angles and the O ··· O contact distances are 0.01 A° shorter than those of the observed. Four of the six stable geometries are shown in Fig. II; they correspond to the lowest four of the six wells found.

TABLE VI

ENERGIES AND CONFORMATIONS FOR THE CALCULATED STABLE ACETIC ACID DIMERS USING THE FINAL SET OF COEFFICIENTS.[a]

Conformation	R in A°	θ	φ	X	Y	Z	Energy in kcal. mole^{-1}
1	3.94	80°	90°	180°	0°	0°	−18.6
2	3.82	102°	90°	174°	−48°	14°	−18.0
3	3.61	297°	177°	199°	−17°	−106°	−13.7
4	3.32	−64°	182°	180°	−3°	−8°	−8.6
5	3.21	81°	159°	105°	171°	−7°	−8.5
6	3.68	−30°	17°	241°	−45°	−144°	−7.8

[a] Dimer conformations are given in terms of Eulerian angles relating one monomer to the other; refer to Appendix AI for details.

5. *Completeness of Results*

The question arises as to whether all the energy wells in conformation space were found in the dimer-simulation step. Thus, for example, when using the final set of coefficients, we found that the movable formic acid descended into a different energy well starting in one position than it did when starting at neighboring positions; it is apparent that the grid of starting geometries determines in a complicated way the crater reached. It is somewhat assuring to note that the number of energy wells found for each system studied was always much less than the number of starting geometries employed in the dimer-simulation step. It will be noted that for the homodimer cases (such as those which we have studied herein) use can be made of the exchange symmetry relations (Appendix AII) to increase the density of points in the grid with no increase in computer time.

Our grid of starting geometries did not span the entire conformation space because this was not feasible in view of the density of the grid that had to be used. However, we did repeat the dimer-simulation for formic acid using the final set of coefficients from 23 new starting geometries, which differed from the former set of starting geometries (not including the observed) in that R was given a value of 2.50 A° instead of 4.00 A°. This new choice of starting geometries was dictated by the observation that all the craters found for formic acid dimers had values of R greater than 2.50 A° (and less than 4.00 A°) so that the new set of starting geometries are all on the "repulsive" side of the gradient. No new craters were found. Since the same craters were found when 23 starting geometries on "repulsive" slopes were used and when 23 starting geometries on "attractive" slopes were used, it is less probable that undiscovered wells exist.

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APPENDIX A

I. *Coordinate Systems and Vector Transformations*

For the purposes of setting up geometrical relationships between two rigid molecules and calculating interatomic distances, we used the standard Eulerian angles. We found it convenient to place one molecule α in a fixed right-handed cartesian coordinate system and relate the other molecule β to it in the following manner:

Molecule β was placed in a movable right-handed cartesian coordinate system whose origin was related to the origin of the fixed right-handed cartesian coordinate system by a polar coordinate system. The axes of the movable cartesian coordinate system were arranged to be parallel to the corresponding axes of the fixed cartesian coordinate system (Figure III).

The origin of the movable cartesian coordinate system is expressable as a point in the fixed cartesian coordinate system by the vector **0** where

$$\mathbf{0} = \begin{pmatrix} R \sin\theta \cos\varphi \\ R \sin\theta \sin\varphi \\ R\cos\theta \end{pmatrix}$$

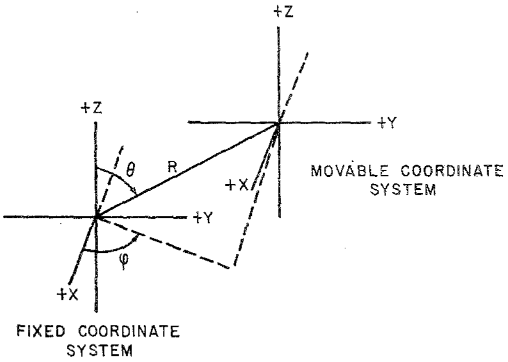

FIG. III. Relationships between Coordinate Systems.

Molecule β was placed in an initial position in the movable cartesian coordinate system. Other positions of molecule β in the movable cartesian coordinate system were obtained by performing the following sequential operations:

(1) *Rotation of molecule β around the X-axis by an angle x.* Angle x is considered positive for counter-clockwise motion when looking from the positive X to the negative X direction. This is represented by the matrix X where

$$X = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos x & -\sin x \\ 0 & \sin x & \cos x \end{pmatrix}$$

(2) *Rotation of molecule β around the Y-axis by an angle y.* Angle y is considered positive for counter-clockwise motion when looking from the positive Y to the negative Y direction. This is represented by the matrix Y where

$$Y = \begin{pmatrix} \cos y & 0 & +\sin y \\ 0 & 1 & 0 \\ -\sin y & 0 & \cos y \end{pmatrix}$$

(3) *Rotation of molecule β around the Z-axis by an angle z.* Angle z is considered positive for the counter-clockwise motion when looking from the positive Z to the negative Z direction. This is represented by the matrix Z where

$$Z = \begin{pmatrix} \cos z & -\sin z & 0 \\ \sin z & \cos z & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

If the vector $\boldsymbol{\beta}_j^{\text{mov init}}$ is used to represent the initial position of the jth atom of molecule β in the movable cartesian coordinate system and vector $\boldsymbol{\beta}_j^{\text{mov fin}}$ its final position in that same system after undergoing the sequence of rotations indicated above, then

$$\boldsymbol{\beta}_j^{\text{mov fin}} = ZYX\boldsymbol{\beta}_j^{\text{mov init}}$$

If the vector $\boldsymbol{\beta}_j^{\text{fix}}$ is used to represent the position of the jth atom of molecule β in the fixed cartesian coordinate system, then

$$\boldsymbol{\beta}_j^{\text{fix}} = \mathbf{0} + \boldsymbol{\beta}_j^{\text{mov fin}}$$

By placing molecule α in a fixed cartesian coordinate system where the position of its ith atom is represented by the vector $\boldsymbol{\alpha}_i^{\text{fix}}$ and varying R, θ, φ, x, y, and z, various dimer conformations can be specified and interatomic distances calculated.

$$\mathbf{R}_{ij} = \boldsymbol{\beta}_j^{\text{fix}} - \boldsymbol{\alpha}_i^{\text{fix}}$$

where $\mathbf{R}_{ij}$ is the vector connecting atom i of molecule α and atom j of molecule β in the fixed cartesian coordinate system.

For the calculations performed in this paper molecules α and β were the same and $\boldsymbol{\alpha}_i^{\text{fix}} = \boldsymbol{\beta}_i^{\text{mov init}}$ for all i.

II. *Exchange Symmetry*

Appendix AI described how one monomer, initially occupying the same position as an identical monomer, was translated and rotated to another position in order to establish a three-dimensional relationship between the two monomers. We will refer to a geometrical relationship between two monomers as a dimer conformation. There are, of course, many different sets of values for the Eulerian angles that transform a monomer to the same final position or to different final positions but having the same final dimer conformation. As an example of the latter situation consider the case where one set of values for the Eulerian angles transforms a monomer to produce a dimer conformation → ↑ (the horizontal arrow represents the fixed monomer and the one pointing upwards represents the transformed) and where a different set of Eulerian angles results in the dimer conformation ↓ ← (the arrow pointing downwards represents the transformed monomer). It is obvious that the two dimer conformations are identical. In general, we will refer to dimer conformations as having exchange symmetry when the dimer conformations are produced by different sets of Eulerian angles and are identical.

To determine whether two different sets of Eulerian angles produce dimer conformations with exchange symmetry, a 4 × 4 matrix T was formed for each set. T was formed by combining the 3 × 3 rotational matrix (ZYX) with the

3×1 translational matrix vector **0** in a way similar to Thompson's [23] such that

$$\begin{pmatrix} x_j \\ y_j \\ z_j \\ 1 \end{pmatrix}^{\text{fix}} = T \begin{pmatrix} x_j \\ y_j \\ z_j \\ 1 \end{pmatrix}^{\text{mov init}}$$

where

$$\begin{aligned}
t_{1,1} &= \cos z \cos y \\
t_{1,2} &= \cos z \sin y \sin x - \sin z \cos x \\
t_{1,3} &= \cos z \sin y \cos x + \sin z \sin x \\
t_{1,4} &= R \sin \theta \cos \varphi \\
t_{2,1} &= \sin z \cos y \\
t_{2,2} &= \sin z \sin y \sin x + \cos z \cos x \\
t_{2,3} &= \sin z \sin y \cos x - \cos z \sin x \\
t_{2,4} &= R \sin \theta \sin \varphi \\
t_{3,1} &= -\sin y \\
t_{3,2} &= \cos y \sin x \\
t_{3,3} &= \cos y \cos x \\
t_{3,4} &= R \cos \theta \\
t_{4,1} &= 0.0 \\
t_{4,2} &= 0.0 \\
t_{4,3} &= 0.0 \\
t_{4,4} &= 1.0
\end{aligned}$$

It is trivial to prove that two different sets of Eulerian angles will produce dimer conformations having exchange symmetry if and only if the T matrix of each set is inverse to the other.

For the situation where $R_1 = R_2$, $x_1 = x_2 = 180°$, $y_1 = y_2 = 0°$ and $z_1 = z_2 = 0°$ for two different sets of Eulerian angles, it is easily shown (using the equation $T_1T_2 = T_2T_1 = I$) that the corresponding dimer conformations will have exchange symmetry when either

(1) $\theta_1 = \theta_2$ and $\varphi_1 + \varphi_2 = n\pi$ where n is any odd integer or
(2) $\theta_1 + \theta_2 = 2n\pi$ and $\varphi_1 + \varphi_2 = 2n\pi$ where n is any integer.

It is to be noted that for the special case $\theta_1 = \theta_2 = n\pi$ where n is any integer, no constraints need be imposed on the values of φ_1 and φ_2, i.e. their values become irrelevant.

III. *Method of Steepest Descent*

In order for two dimer conformations having exchange symmetry to follow paths of steepest descent which preserve their exchange symmetry, we found it convenient to define the direction of steepest gradient in the rectangular space of intermolecular atom–atom distances. We therefore defined the distance between points along the path of steepest descent as the root mean square of the changes in the $n \times n$ intermolecular atom–atom distances where n is the number of atoms in one molecule. Call these n^2 distances r_i and the six Eulerian coordinates θ_j. The possible dimer conformations form a six-dimensional curved subspace of the n^2 rectangular space of the r_i's. For a given point, we consider the molecular interaction energy ϕ as a function of the r_i's and find its anti-gradient vector $R = dr_i = -\partial\phi/\partial r_i$. This is the direction of steepest descent in r-space. Now a vector $d\phi_j$ in the θ-subspace will have a steepness of descent (measured in the r-metric) proportional to the cosine of the angle between it and dr_i. Therefore we want to choose $X = d\theta_i$ so as to minimize $1PX - R1$, where P is the $n^2 \times 6$ matrix $\partial r_i/\partial\theta_j$. As is well-known, the formula for this minimization is

$$X = (P^T P)^{-1} P^T R.$$

We use this, rather than $-\partial\phi/\partial\theta_j$, as the direction of steepest descent.

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