

properties between such π -electron systems as discussed by Koutecký²³ and from the theorem¹¹ about mirror-image relation between MCD spectra of paired systems. On the other hand, effects of purely inductive substituents on benzene MCD are predicted to be much smaller.

Because of the generality of the pairing theorems^{11,23} one can predict the existence of similar mirror-image relationships for other alternant hydrocarbons with substituents of the donor and acceptor types. Theoretical and experimental work on such compounds is presently under way.

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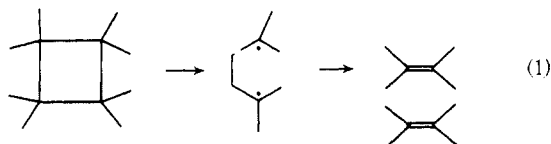
Organic Transition States. III.¹ An *ab Initio* Study of the Pyrolysis of Cyclobutane *via* the Tetramethylene Diradical

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Abstract: An *ab initio* calculation has been carried out for the potential energy surface of the pyrolysis of cyclobutane to form two ethylene molecules *via* a nonconcerted pathway. The computations involve SCF calculations at the STO-3G level followed by a 15-dimensional configuration interaction treatment. It is found that the tetramethylene diradical is a thermodynamically stable species represented by two energy wells corresponding to two conformations of the molecule. The first of these, a *gauche* geometry, presents a barrier to dissociation of 3.6 kcal/mol and a barrier to reclosure of ~ 2 kcal/mol. The energetics of dissociation *via* the other favored conformation, *trans*, are similar.

The thermal dissociation of cyclobutane to form two ethylene molecules has widely been held to be a nonconcerted process which proceeds by way of a transitory intermediate species, the tetramethylene diradical.



This reaction is one of the most elementary considered by Woodward and Hoffmann,⁴ who conclude that the $\sigma_{2s} + \sigma_{2s}$ concerted addition of two ethylenes to form cyclobutane is symmetry forbidden while the $\sigma_{2s} + \sigma_{2a}$ non-least-motion path is symmetry allowed. Examination of this latter path, however, reveals strong steric interactions which lead to a large energy of activation along such a reaction coordinate. Attempts to show that the reaction proceeds in a concerted but symmetry allowed fashion have proven negative⁵ and an *ab initio* calculation for the least-motion path reveals a large activation energy.⁶

If one then concludes that the dissociation takes place in a nonconcerted manner, a diradical intermediate is probably the simplest valence form that one can imagine for the result of breaking but one of the two bonds of cyclobutane.

It should be noted that the diradical structure in (1) implies nothing about whether the ground state of such a species is a singlet or triplet or about the nature of the orbitals that the unpaired electrons occupy, except that the concept is only useful if the orbitals are more or less nonbonding.⁷ As pointed out by Hoffmann, *et al.*,⁸ the oxygen molecule should not be considered to be a diradical in this sense.

There exists a persuasive body of indirect evidence⁹ for the participation of such diradical states in many nonconcerted reactions of which reaction 1 may be considered a prototype. Nevertheless, such a species has never been observed in a thermal reaction, although recent CIDNP experiments provide evidence for a nonconcerted diradical path in the *photolysis* of cyclic ketones.¹⁰

The tetramethylene diradical has, however, been predicted to be thermodynamically stable. The pyrolysis of cyclobutane is known to be a first-order reaction with an activation energy of 62.5 kcal/mol.¹¹ Benson¹² has carried out a thermodynamic estimation of the enthalpy of $\cdot\text{CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\cdot$ which he finds to lie at least 4 kcal/mol below the activation energy for the reaction. He thus argues that the tetramethylene diradical is thermodynamically stable and represents an energy well on the potential energy surface of reaction 1.

A key feature of this analysis is the assumption that the removal of two hydrogens from C_4H_{10} to give the tetra-

methylene diradical is a noncooperative process, *i.e.*, that the energy to remove the second hydrogen three C–C bonds away from the first is unaffected by the removal of the first. With this assumption, the total energy of abstraction is just twice ΔH for the scission of one CH bond. If the removal of the second hydrogen cost 4 kcal/mol less energy than the first, the estimated minimum on the potential energy surface would vanish.

Benson's analysis,¹² with the same assumption of noncooperativity, leads to a similar prediction of stability for the trimethylene diradical, the presumed intermediate in the geometrical isomerization of cyclopropane. An *ab initio* potential energy surface for this reaction has been calculated¹ and shows no secondary minimum corresponding to a thermodynamically stable trimethylene diradical. Benson's assumption would then appear to have broken down for the case of CH bonds separated by only two C–C bonds.

Hoffmann and coworkers⁸ have carried out a theoretical investigation of the potential energy surface for the pyrolysis of cyclobutane using extended Hückel theory. A salient feature of this semiempirical study is the lack of any energy well on the surface corresponding to the tetramethylene diradical. Once the first bond is broken, various minima appear on their surface corresponding to angular motions of the molecule, but all of these are dissociative with respect to the breaking of the second bond. According to this study then, the tetramethylene diradical is not a thermodynamically stable species.

This paper reports the calculation of an *ab initio* potential energy surface for reaction 1. It is known that extended Hückel theory, while qualitatively accurate for the variation of energy with respect to angular motions of a molecule, is rather untrustworthy with respect to bond stretching coordinates. *Ab initio* calculations of the type described here, although far from quantitative, do not suffer from this imbalance and should therefore be considered to be a more realistic theoretical test of the existence of the tetramethylene diradical as a thermodynamically stable, if short lived, intermediate along the nonconcerted pathway for the pyrolysis of cyclobutane.

The reactant and products of this reaction are singlet species. Although it is entirely possible that the most probable reaction pathway involves crossing, *via* spin-orbit coupling, from the initial singlet to a triplet state, followed by a second multiplicity change to yield singlet products, there exists no evidence to say that this is so and the weight of evidence in such reactions seems to indicate that they remain of singlet character throughout their course. Theoretical considerations also suggest that this should be so.⁷ The surface calculated for this thermal reaction is therefore the lowest singlet state, although, as will be described below, there is a low-lying triplet state nearby in important regions of the surface.

The study of the potential energy surface over all chemically important motions for a system of 12 atoms represents a formidable computational task. The most significant angular coordinates varied in the study and the numbering system chosen is given in Figure 1. The only parameters which were held fixed were the CH bond distances which were taken to be 1.095 Å everywhere. The breaking of the first bond, C₁–C₄, is described by α , the C₁C₂C₃ and C₄C₃C₂ angles. The twisting of the carbon frame is expressed by θ , the dihedral angle between the C₁C₂ and C₄C₃ lines, which was defined as 0 for the planar *cis* orientation. The flap angle of the hydrogens at C₂ and C₃ is ϕ , defined as the angle between the bisectors of the HCH planes and the C₂C₃ line. Possible hydrogen wagging motions are ignored in that this bisector was always taken to lie in the appropriate CCC plane so that, for instance, the hydrogens at

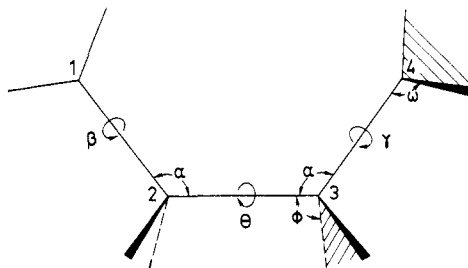


Figure 1. The coordinate system.

C₃ rotate along with C₃C₄ as θ is varied. The pyramidalization of the CH₂ groups at C₁ and C₄ is described by ω , the angle between the bisectors of the HC₁H and HC₄H planes and the C₁C₂ and C₄C₃ lines, respectively. Wagging motions are again ignored. Finally, the rotation of the HC₁H and HC₄H groups relative to the C₁C₂C₃ and C₄C₃C₂ planes is described by β and γ . The origins of β and γ are taken to be the configuration where the planes of the appropriate CH₂ and CCC groups are perpendicular when ω is 180°. The parameters α , ϕ , and ω , which are labeled symmetrically in the figure, were occasionally treated in an unsymmetric fashion as described below.

Additional variable parameters of the calculation were the various HCH angles and, of course, the three remaining carbon-carbon bond lengths: r_{12} , r_{23} , and r_{43} .

The GAUSSIAN 70¹³ Gaussian orbital SCF system of programs was used to carry out the necessary Hartree-Fock calculations. The STO-3G basis set contained in this program was used everywhere, the choice of this fairly low-level basis set being dictated by the complexity and size of the molecule being treated. The implications of this choice of basis will be discussed below. As is well known, Hartree-Fock theory breaks down for the breaking of a single bond as in (1), since it leads to improper ionic character at the dissociation limits. A correct representation of the surface therefore requires that the SCF calculation be followed by a configuration interaction calculation. This was done using a configuration interaction package for GAUSS 70 which has been written in the author's laboratory.

The nature of the SCF and configuration interaction chosen for this calculation can best be understood by regarding Figure 2 which shows the behavior of the eigenvalue of the two highest occupied and two lowest unoccupied orbitals upon variation of α , *i.e.*, breaking of the first bond. While the geometries of the points plotted are somewhat arbitrary with respect to hydrogen placement due to the fact that ϕ is 180° everywhere, the crossing between the HOMO and LUMO is a feature which persists at various values of α for a large number of geometries. The geometry chosen for Figure 2 is such that a symmetry plane exists which is perpendicular to and bisects the C₂–C₃ bond. The HOMO and LUMO have odd and even symmetries with respect to this plane, a fact which is indicated by the letters S and A.

As one departs from cyclobutane, the HOMO (S) and LUMO (A) rapidly become heavily concentrated on carbons 1 and 4 and principally represent the bonding and antibonding orbitals with respect to the 1–4 bond which is being broken as a result of the increase in α . This crossing was also observed in the EHT calculations of Hoffmann, *et al.*⁸ The fact that at some geometries the antibonding orbital lies below the bonding is lucidly explained by them as an example of through bond coupling. We shall not reproduce their argument here but refer the reader to the original paper.

The crossing of the symmetric and antisymmetric levels

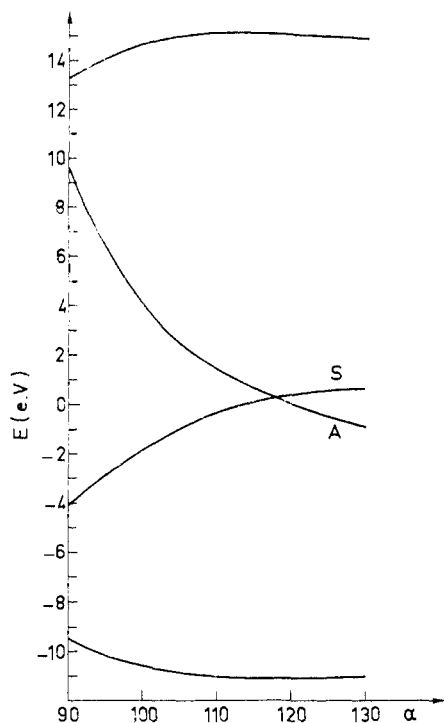


Figure 2. Behavior of the eigenvalues of two highest occupied and two lowest unoccupied molecular orbitals upon variation of α : $r_{12} = r_{23} = r_{34} = 1.54 \text{ \AA}$, $\phi = \omega = 180^\circ$, $\beta = -\gamma = 0^\circ$, $\theta = 0^\circ$.

implies that there will actually be an avoided crossing between the configurations $\dots(S^2)$ and $\dots(A^2)$, *i.e.*, between the SCF ground state and the lowest doubly excited state. This can only be produced by a configuration interaction calculation between these two states.

At $\alpha = 90^\circ$ with proper hydrogen placement for planar cyclobutane, however, the two highest occupied orbitals will be degenerate, as will be the two lowest unoccupied orbitals, corresponding to the two possible ways of splitting cyclobutane into two ethylenes. At this latter limit, the two HOMO's and two LUMO's will also form two degenerate pairs, since these will be the π and π^* orbitals of two ethylene molecules at infinite separation. It is then clear that in order to span the symmetry of the problem and keep the effect of CI on the correlation energy balanced over the entire surface, it is necessary to carry out a configuration interaction calculation which includes all possible double excitations between the two highest occupied and two lowest unoccupied orbitals. Completeness then demands that one include all possible single excitations as well. This amounts to a configuration interaction calculation involving 15 states, and this has been done everywhere.

It is to be expected of course that the $(S)^2$ and $(A)^2$ configuration will remain of primary importance over the surface except as one approaches the cyclobutane or, possibly, the separated ethylene limit and will mix into the lowest energy configuration interaction vector with roughly equal weighting in the region of the avoided crossing as would be the case if one limited the calculation to a simple two-state CI. This is completely in accord with the idea of the occurrence of a diradical in the region of the crossing, as shown in (1), involving two unpaired electrons in an essentially nonbonding situation. The simplest analog for this is the textbook example of the dissociation of H_2 to form two hydrogen atoms. Molecular orbital theory leads to a ground state $(\sigma)^2$ which is an equal mixture of ionic and covalent terms. Proper dissociation is only obtained by configuration interaction between this and the configuration $(\sigma^*)^2$, thus allowing the elimination of ionic terms from the trial func-

tion and leading to two weakly interacting hydrogen atoms at long separation distances. This is precisely the form of calculation forced upon us by the nature of the molecular orbitals of cyclobutane, which lead to a calculation which would be expected to be of the diradical form in the region of the crossing. The question remains as to whether it is thermodynamically stable when all the geometrical variables are considered, the most important of these being, of course, the C_2-C_3 bond.

The final result of such a calculation is the CI eigenvalue and eigenfunction. The SCF calculation that precedes this provides basis functions (molecular orbitals) for building the Slater determinants which form the basis for the CI, and these MO's should be chosen such that the CI provides, within the few determinants chosen, the best possible representation of the results of a full CI calculation. In a situation like that shown in Figure 2, it is unclear as to whether these best molecular orbitals are those calculated as eigenfunctions of the electronic potential of the closed shell ground state of the system, *e.g.*, $(S)^2$ or $(A)^2$, or those calculated for the lowest singly excited state of the molecule $\dots(SA)$, since both orbitals are strongly involved in the final result. We have chosen to try both and accept the calculation which yields the lower final energy after completion of the CI. The closed shell calculations were carried out in the usual way,¹⁴ while the open shell state calculation was carried out in the Nesbet approximation¹⁵ which has the virtue of simplicity. This latter does not distinguish between singlet and triplet states for the same orbital occupancy, the potential being the average of the two, so no question of choice of multiplicity arises.

It is found that the molecular orbitals produced by the Nesbet calculation, *i.e.*, by single occupation of the orbitals S and A, are preferable everywhere on the surface except very close to the limits cyclobutane and two ethylenes, and the results reported below utilize this approximation except where otherwise noted.

A simple entry to the visualization of the potential energy surface for pyrolysis is provided by Figure 3 which yields a rough picture of the variation of energy as a function of the two variables α and θ . This figure is calculated for all carbon-carbon bond lengths 1.54 \AA , $\phi = 109.47^\circ$, HC_1H and HC_4H angles of 120° , HC_2H and HC_3H angles of 109.47° , and $\omega = 180^\circ$. It corresponds to the breaking of the C_1C_4 bond with concomitant twisting of the molecule. Given the constraints on these geometric parameters, the energies which are plotted relative to the lowest point actually calculated in obtaining the figure ($\theta = 0^\circ$, $\alpha = 100^\circ$) are fairly far from those of the true minimum energy surface but suffice to give a rough picture of it. An important additional pair of variables which must be varied in order to obtain some semblance of reality for this two dimensional surface are the twist angles of the terminal methylenes, β and γ , which should be optimized for each θ, α pair. This would be an expensive *ab initio* calculation, given the number of points necessary to produce the figure, but Hoffmann, *et al.*, have calculated the same figure using EHT and varying β and γ for each point. They have published their optimum values for $\alpha = 100^\circ$ as a function of θ , the motion being essentially such as to maximize the residual C_1-C_4 bonding. Since EHT is expected to give reasonable results for angular variations and since our aim in producing this figure is only to get a rough idea of the surface in these two dimensions, we have utilized their published¹⁶ values of β, γ as a function of θ in producing this figure. The values they calculated at $\alpha = 100^\circ$ are used at all α , the justification for this being that the principal variation of β and γ will be with θ since the methylene groups twist to optimize the direction for C_1C_4 bonding. Calculations to check that this

Table I. Important Geometries and Energies on the Surface

Variable	Planar cyclobutane ^a	Gauche	Trans	Two ethylenes ^a
r_{12} and r_{34} , Å	1.556	1.529	1.524	1.306
r_{23} , Å	1.556	1.557	1.555	∞
α , deg	90	111.3	113.6	
ϕ , deg	135.0	125.1	123.1	180.0
θ , deg	0.0	63.4	180.0	
ω , deg	135.0	152.3	202.0	180.0
β and γ , deg	0.0	65.4, -65.4	0.0	0.0
Energy, au	-154.2812	-154.1631	-154.1648	-154.2250
Relative energy, kcal/mol	0.0	74.10	73.04	35.26

^a Closed shell SCF.

procedure does not badly distort the surface have been carried out and this was found to be the case.

Figure 3 is qualitatively similar to that produced by EHT, as is to be expected since EHT is a reasonable tool for studying variations of energy as a function of angular motions in hydrocarbons. It exhibits three minima. The first of these, in the upper left-hand corner of the figure, represents a puckered cyclobutane, given that the hydrogens are incorrectly placed, and represents the lowest energy region on the surface. The orbital crossing between the S and A molecular orbitals occurs in the general region of the 0.4-eV ridge which must be crossed to reach the second minimum.

This second minimum, in the center of the figure, represents cyclobutane with the first bond essentially broken and the molecule in a gauche conformation with θ in the 60° region and α between 110 and 120°.

The third minimum, which also has a broken C₁-C₄ bond, occurs for a trans conformation of the four-carbon skeleton.

Horizontal motion along the line $\theta = 0$, α increasing, represents the breaking of the first bond with concurrent release of the ring-strain energy since the C₁C₂C₃ and C₄C₂C₁ angles are increasing. Vertical motion along the left-hand coordinate with $\alpha = 90^\circ$, θ increasing, on the other hand, represents the breaking of the C₁C₄ bond through a twisting motion with retention of the ring-strain energy at C₂ and C₃. This difference accounts for the high-energy region in the figure where the bond is broken but ring strain is retained. The figure then provides an extremely rough, due to lack of geometry optimization, estimate of the ring strain energy, which is of the order of 32 kcal/mol, a not unreasonable number. Benson¹² has estimated the ring-strain energy in a carbon-carbon bond in cyclobutane as 26 kcal/mol.

The next step in this study was to fully optimize the energy with respect to all salient coordinates for the gauche and trans minima. The final values are marked by the letters G and T on Figure 3 and all coordinates are given in Table I, as are the final energies. The trans form is found to be more stable than the gauche by 1.06 kcal/mol as might be expected from steric considerations. In both cases, the pyramidalization angle on the terminal methylenes, ω , is such as to maximize residual C₁-C₄ bonding, although the motion is energetically much more important in the gauche conformation than in the trans. At the gauche minimum the C₁-C₄ distance is 3.07 Å so that the bond is well and truly broken. The analogous trans distance is 3.94 Å.

Table I also gives the equilibrium bond lengths for planar cyclobutane in the STO-3G basis set, 1.556 Å. A remarkable feature of these calculations is that the breaking of the C₁C₄ bond and the twisting motions to the gauche or trans

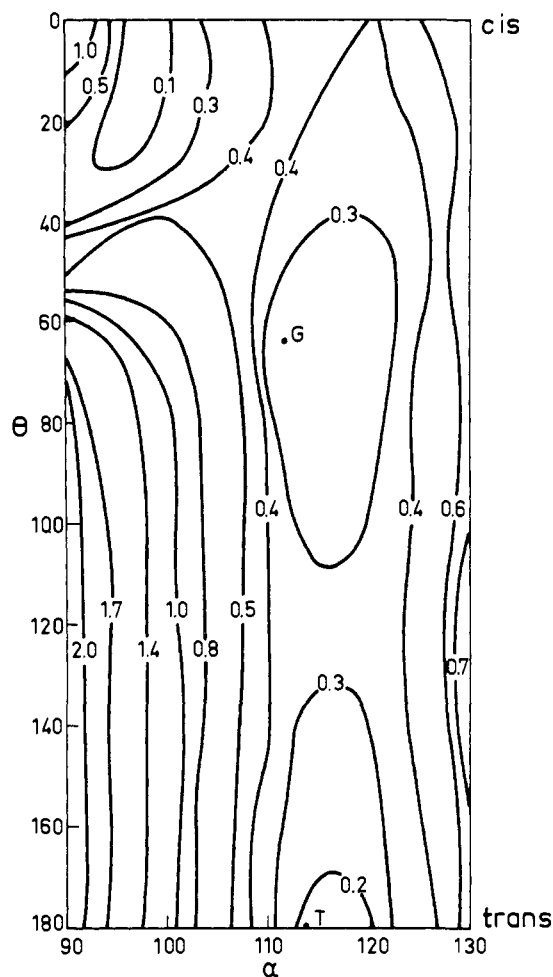


Figure 3. Potential energy surface for simultaneous variation of α and θ for particular β and γ (see text). Energies are plotted in eV relative to the lowest point on the surface actually calculated, $\theta = 0^\circ$, $\alpha = 100^\circ$. The locations of the true minima are the points G (gauche) and T (trans).

minima leave the C₂C₃ bond length essentially unaffected, this being 1.557 Å gauche and 1.555 Å at trans. We thus have an indication that we are truly dealing with a two-step dissociation in full accord with the usual conception of a nonconcerted reaction mechanism.

The gauche and trans conformation represent true minima with respect to all the geometrical variables we have considered. In finding these minima, the various parameters were varied in an asymmetric manner, *i.e.*, the C₁C₂C₃ angle (α) was allowed to differ from the C₄C₃C₂ angle, etc., but it was found that the lowest energy occurred for the symmetric conformation. In both of these geometries, the lowest triplet state, (AS), is almost degenerate with the singlet ground state. The triplet is 0.38 kcal/mol above the singlet at the gauche minimum and 0.06 kcal/mol above it at trans. This implies that there exist other geometries at which the triplet lies below the singlet and that the two are nearby over large regions of the surface. Despite this proximity, as mentioned earlier, there is no evidence for significant triplet participation in the pyrolysis. The triplet is, of course relatively far from the singlet in the initial, cyclobutane, portion of the surface.

In order to examine the behavior of the molecule on dissociation of the second bond, C₂C₃, we have found the minimum energy path from both the gauche and trans minima to two ethylenes. The path from the gauche minimum is shown in Figure 4 and is quite remarkable in that it shows a long flat energy region on elongation of r_{23} which finally

Table II. The Dissociation Path from the Gauche Minimum

r_{23} , Å	1.557, G	1.7	1.8	1.9	2.0
r_{12} , Å	1.529	1.476	1.438	1.418	1.384
α	111.3	108.1	109.8	112.3	113.6
ϕ	125.1	132.2	136.2	141.3	150.0
θ	63.4	70.4	76.8	71.1	69.8
β and γ	± 65.4	± 4.0	0	0	0
Energy, au	-154.1631	-154.1623	-154.1596	-154.1574	-154.1628
Relative energy, kcal/mol	0	0.5	2.2	3.6	0.2

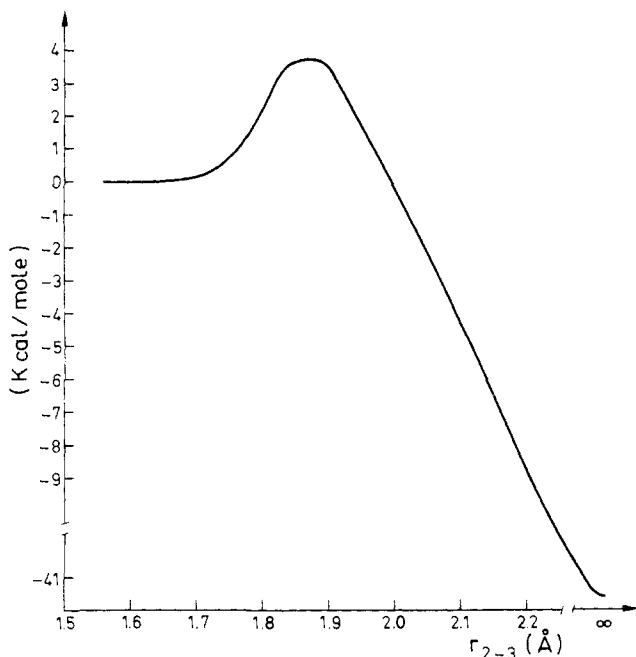


Figure 4. Potential energy profile for dissociation from the gauche minimum.

arrives at a very late barrier, 3.59 kcal above the gauche energy in the vicinity of 1.9 Å. The gauche minimum represents, then, a very loosely coupled complex of two ethylene molecules. The important geometric parameters of some points along this path are given in Table II where it can be seen that r_{12} and r_{34} progress smoothly toward the equilibrium bond length of ethylene in this basis set, 1.306 Å (closed shell SCF), while ϕ proceeds toward 180°, and the other parameters move smoothly toward their ethylenic values with the single exception of α .

The minimum energy dissociation path from the trans conformation exhibits quite different behavior. Its barrier to dissociation, 2.3 kcal/mol above the trans minimum energy, occurs fairly normally at 1.65 Å, all else proceeding toward ethylene in much the same manner as the gauche path. The striking difference between the potential energy profiles on dissociation from the gauche and trans minima can be ascribed to the effect of residual C_1-C_4 bonding. At the gauche conformation, as the C_2C_3 bond elongates, the molecule tends to compensate for the concomitant increase in potential energy by reestablishing some C_1-C_4 bonding. This is easily seen from the behavior of α (Table II), which expresses the optimum C_1-C_4 distance. α first decreases on elongation of r_{23} until the two ethylenes are so far apart at $r_{23} = 1.9$ Å that 1,4 bonding is no longer effective. This compensatory effect results in the long flat potential energy region leading to a late barrier. r_{14} is much longer in the trans conformation so that no such compensation can take place, hence the normal position of the barriers to dissociation.

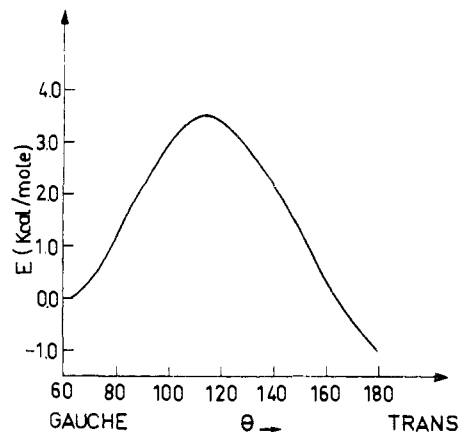


Figure 5. Potential energy profile for the twisting motion leading from the gauche to the trans minimum.

Figure 2 shows a broad flat valley leading from the gauche to the trans minimum. Our best estimate of the barrier between these two wells is 3.55 kcal/mol as measured from the gauche minimum energy; *i.e.*, the activation energy for dissociation by a motion of the molecule from gauche to trans followed by dissociation of the C_2-C_3 bond is slightly less than but almost equivalent to the activation energy for direct dissociation of the second bond from the gauche conformation, 3.59 kcal/mol. The profile of this barrier is shown in Figure 5. The implication, then, is that if a given molecule is vibrationally excited to just the energy of activation, it is free to sample a large number of angular geometries on the road to dissociation. It should, perhaps, be emphasized that in a dynamical sense what a given molecule will actually do will depend not so much upon the minimum energy path but upon the forces upon the nuclei and the requirements of conservation of angular momentum.

If the gauche and trans conformations are to represent true thermodynamically stable intermediates, there must also exist a barrier to reclosure of the molecule to cyclobutane. This obviously exists for the trans form which must reclose *via* a geometry in the vicinity of the gauche conformation. The gauche conformation recloses *via* the ridge delineated by the 0.4-eV contours shown in the upper left of Figure 2. It is an extremely difficult computational task to locate the low point along this long geometrically irregular ridge, particularly since a large number of the geometric variables are strongly coupled in this region so that expensive geometry optimizations are necessary at each point. Our best estimate of the barrier to reclosure from gauche is 2.0 kcal, as measured from the gauche minimum. This is a representative energy for a fairly large number of (θ, α) combinations in the region between $\theta = 50^\circ$, $\alpha = 109^\circ$ and $\theta = 30^\circ$, $\alpha = 105^\circ$. The general features of the surface in this region are that the energy increases with decreasing θ , *i.e.*, that there is a general uphill slope moving directly from gauche to the top of Figure 2, while the energy decreases with decreasing α , *i.e.*, there is a downhill slope from gauche proceeding to the left, provided that one is at small

Table III. Summary of Important Surface Features Calculated

$E(2 \times \text{ethylene}) - E(\text{cyclobutane})$	35.3 kcal/mol
$E(\text{trans}) - E(\text{gauche})$	-1.06 kcal/mol
$E_A(\text{gauche} \rightarrow \text{trans})$	3.6 kcal/mol
$E_A(\text{gauche} \rightarrow \text{cyclobutane})$	2.0 kcal/mol
$E_A(\text{gauche} \rightarrow 2 \times \text{ethylene})$	3.6 kcal/mol
$E_A(\text{trans} \rightarrow 2 \times \text{ethylene})$	2.3 kcal/mol

enough θ to avoid the steep hill on the far left. The overall energetics of the surface, however, indicate that the calculation is more probably in error for this barrier than for the others, the error being in the direction of underestimation.

A fundamental test of the validity of the results of this calculation is the calculated overall ΔH for the reaction. If this is badly in error, then the entire surface will be biased toward one or the other of the geometric forms, a situation which will lead to an erroneous picture. The experimental ΔH for the pyrolysis of cyclobutane to two ethylenes is 18.6 kcal/mol while, as mentioned earlier, the energy of activation is 62.5 kcal/mol. Our calculated value of ΔH is 35.3 kcal/mol using a planar cyclobutane and closed shell SCF. This is, in fact, ΔE in the Born Oppenheimer approximation and neglects corrections for zero-point vibrations, etc., but it is clear that 16.7 kcal/mol is a nonnegligible error on the energy scale of the barriers considered here. The calculated fixed nuclei energy of activation is 77.7 kcal/mol. The STO-3G basis set used in this calculation is known, however, to be poor in that it leads to too much stability for small hydrocarbon ring systems. Our situation here is just that: cyclobutane is too stable, on a relative scale, leading to too large a value for ΔH . This may be seen by considering the energy of activation for the inverse reaction, dimerization of two ethylenes to form cyclobutane. The experimental value for this is $62.5 - 18.6 = 43.9$ kcal/mol. Our calculated value is 42.4 kcal/mol. Thus, on our surface, the problem is indeed that cyclobutane is too stable. Upon departure from the small ring structure, *i.e.*, the region from gauche to two ethylenes, the problem would appear to vanish. The implication of this is that the energies calculated in the upper left-hand corner of Figure 2 will tend to be too low relative to the rest of the calculation. While this error would not appear to invalidate the conclusions reached in this study, it is probable that the barrier to reclosure of the gauche conformation to cyclobutane has been underestimated. A summary of the most significant numbers calculated is given in Table III and a schematic profile of the energy along our reaction coordinate is given in Figure 5 where the first maximum is the crossing from cyclobutane to the gauche conformation, the minimum is the gauche conformation, and the second maximum corresponds to dissociation of the C_2-C_3 bond directly from the gauche minimum. Clearly, this second maximum may represent any number of geometries between gauche and trans, all of which would yield roughly the same energy of activation upon elongation of r_{23} .

The calculations reported here clearly indicate that the tetramethylene diradical is a thermodynamically stable intermediate with a well depth which is of the order of 3.6 kcal/mol. The agreement with Benson,¹² who estimated 4 kcal/mol, is remarkably close and probably somewhat fortuitous, given the uncertainties in both estimation procedures. A real distinction would appear to exist between the tetramethylene and trimethylene diradicals, however, since similar level *ab initio* calculations show no minimum corresponding to the latter. From the point of view of Benson's analysis, this would be the additional carbon-carbon bond in tetramethylene, an extra factor which seems to make his assumption of CH bond additivity correct in the four-carbon case.

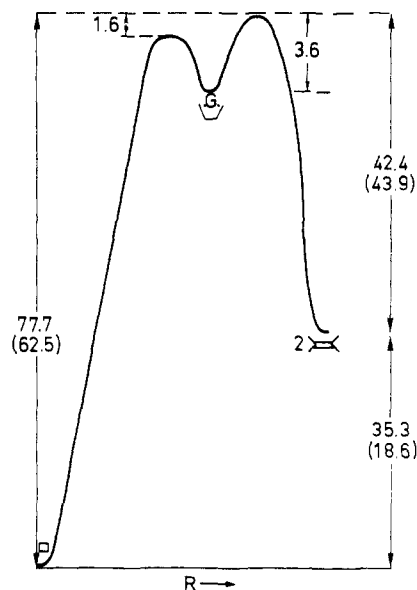


Figure 6. Profile of the potential energy along a typical reaction coordinate (see text). Energies are in kcal/mol and experimental values are in parentheses.

At the gauche minimum, the coefficients of the $\cdots(S)^2$ and $\cdots(A)^2$ configurations are 0.73 and -0.68 , respectively. If one were considering a 2×2 CI involving only the bonding and antibonding orbitals of the 1-4 bond, one would expect 707 and -0.707 by analogy with hydrogen as described above. While some residual bonding does remain, as is shown by both the departure from these numbers and the partial delocalization in the molecular orbitals involved, it is clear that the results of this calculation are in close agreement with the valence concept of (1) which shows a diradical intermediate involving two, essentially nonbonding electrons.

The existence of a barrier to reclosure of this diradical would appear to be the result of a geometric minimum at a gauche conformation for the tetramethylene species with respect to the twist angle θ . As mentioned above, the general trend of the two-dimensional θ, α surface, with full optimization of the other parameters, is a decrease in energy with decreasing α (reclosure) and an increase in energy with motion from the optimum value of θ for gauche tetramethylene, 63.4° , toward the cis conformation (0°). The reclosure barrier is fundamentally due to the increase in energy necessary to decrease θ away from the gauche minimum sufficiently as to allow a decrease in α which avoids the high-energy region on the left of Figure 2. The decrease of α at values of θ which are small enough to avoid this area is accompanied by no barrier to reclosure.

θ is a degree of freedom which does not exist for the trimethylene diradical, which recloses without a barrier, and this would appear to explain the difference in the energy surface profile for these two species.

A question remains, of course, as to the lifetime of the tetramethylene diradical on a vibrational time scale under the experimental conditions at which it is actually produced. Elucidation of this point would require dynamics calculations on a potential energy surface of the type outlined here.

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The Weak Attraction between Water and Methane^{1a}Steven R. Ungemach and Henry F. Schaefer III*^{1b}*Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Received June 17, 1974*

Abstract: A series of *ab initio* self-consistent-field calculations have been performed to discern some features of the H₂O-CH₄ potential energy surface. The equilibrium configuration corresponds to a linear O-H-C arrangement, with $r(\text{C-O}) = 3.85 \text{ \AA}$, and a binding energy of 0.5 kcal/mol. Potential curves are presented for a number of other approaches. Using a double ζ basis set, several calculations were also carried out for CH₄-(H₂O)₂. With one water fixed at its equilibrium separation with respect to methane, the approach of a second H₂O in an analogous manner yields a repulsive interaction energy. This result is qualitatively explained by a pairwise additive model of the three-molecule potential surface. Finally, a qualitative discussion is given in terms of Mulliken atomic populations.

The present paper concerns the simplest hydrophobic² interaction, the interaction between a single water molecule and a single methane molecule. One's first inclination might be to assume that biological systems are so much more complex than the H₂O-CH₄ model that such a model is not relevant to an understanding of the hydrophobic effect. However, in his review Tanford² concludes that the hydrocarbon tail of an amphiphile should have thermodynamic properties similar to those of a hydrocarbon molecule in water solution. Since it is clear that the water-methane interaction potential plays a crucial role in determining the latter thermodynamic properties, the relation between the present study and the hydrophobic effect is indirectly established. For physical chemists, of course, the H₂O-CH₄ interaction is of inherent interest, and would probably be estimated to be intermediate between a van der Waals attraction (e.g., Ne-Ne, ~0.09 kcal/mol^{3a}) and a true hydrogen bond (e.g., H₂O-H₂O, ~5 kcal/mol^{3b}).

Despite the large number of hydrogen-bonded systems for which *ab initio* electronic structure studies have been undertaken,⁴ we have been able to find only one such calculation for the H₂O-CH₄ system. This calculation, by Lathan, *et al.*,⁵ was carried out as part of a comprehensive study of the equilibrium geometries of all molecules of the form H_{*m*}ABH_{*n*}, where A and B are first-row atoms C, N, O, and F. They performed self-consistent-field computations with a minimum basis set of Slater functions, each expanded as a linear combination of three Gaussian functions. Lathan, *et al.*, predict the equilibrium structure, seen in Figure 1, to be bound by 0.8 kcal/mol relative to separated CH₄ and H₂O.

The relative dearth of H₂O-CH₄ theoretical studies has

in part been motivated by some skepticism as to the validity of the Hartree-Fock approximation for describing potential surfaces of this type. The qualitative suitability of single configuration wave functions for the descriptions of systems such as H₂O-H₂O and HF-HF seems well established.⁴ However, the failure of Hartree-Fock to predict any attraction at all for He-He, Ne-Ne, and Ar-Ar is equally well established.⁶ It should be noted that for the He-He and Ne-Ne⁸ systems, studies explicitly including correlation effects have yielded qualitatively correct potential energy curves. Thus the inherent inability of the Hartree-Fock model to describe dispersion forces does raise serious questions as to the suitability of this model for describing the CH₄-H₂O interaction. The same questions have been noted by Losonczy, Moskowitz, and Stillinger,⁹ whose H₂O-Ne Hartree-Fock calculations predict a binding energy of only 0.17 kcal/mol. On the other hand, if Pople's prediction⁵ of an 0.8 kcal/mol attraction is qualitatively correct, then the dispersion contribution (which we can guess to be ~0.1 kcal/mol from the Ne-Ne molecular beam results²) will be relatively unimportant.

The purpose of the present study, then, is to carefully study the H₂O-CH₄ interaction at the self-consistent-field level of theory using several different basis sets. A variety of different approaches of H₂O to CH₄ have been considered. Finally, a number of calculations are reported for the H₂O-CH₄-H₂O system.

Comparison of Basis Sets

Four different basis sets of contracted Gaussian functions⁷ have been used in the present work.

A. Minimum Basis. Slater functions 1s, 2s, 2p_x, 2p_y, and