

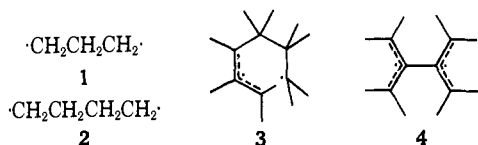
## A Potential Surface for a Nonconcerted Reaction. Tetramethylene

Roald Hoffmann,\* S. Swaminathan, Brian G. Odell, and Rolf Gleiter

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received April 9, 1970

**Abstract:** We study a potential surface for the tetramethylene diradical,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ , a likely intermediate in the nonconcerted fragmentation of cyclobutane to two ethylenes. Outside a clearly defined region of a distorted cyclobutane we find two apparent minima, in geometry close to trans and gauche conformations of a model *n*-butane. These minima appear to be unstable with respect to fragmentation to two ethylenes. In fact, a motion in any degree of freedom away from the distorted cyclobutane region leads to a level crossing and a tetramethylene species whose orbitals resemble those of two interacting ethylenes. If by the term "intermediate" is meant a true minimum in the many dimensional potential surface then our calculations imply there is no such species intervening between cyclobutane and two ethylenes. We suggest that a large energetically flat region of a potential surface will in the context of modern collision theory have the same operational consequences as a true intermediate, and that such a region, termed a "twixtyl," may be a common feature of nonconcerted reactions.

What is the molecular structure of hydrocarbon diradicals? Species such as trimethylene (1), tetramethylene (2), as well as more complex molecules such as 3 or 4 have certainly been the subject of much

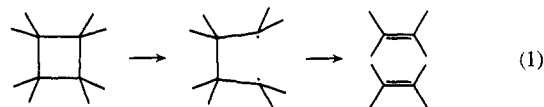


discussion in recent years. Postulated as thermodynamically stable but kinetically unstable molecules, they have been invoked as transient intermediates in many thermal and photochemical reactions. Their thermodynamic properties may be accurately estimated,<sup>1</sup> yet their fleeting existence has generally not allowed the application of any of the standard methods of structure determination. In this contribution we begin a study of one of these species, tetramethylene.

It is important to make clear at the outset our use of the work diradical. Our definition carries no implication of the spin state of the molecule. We term a diradical any molecule which possesses two more or less nonbonding energy levels into which must be placed two electrons. In the majority of such cases the only valence bond structure which can be reasonably written down is one with two unpaired electrons (1-4); this is not a necessary condition, as evidenced by species such as cyclobutadiene, benzynes, and the oxygen molecule. Whether the ground state of a diradical is a singlet or a triplet is a delicate balance of several factors: the energy splitting between the

nonbonding levels, the magnitude of the singlet-triplet splitting in the excited configuration, and the extent of configuration interaction. These considerations have been discussed by us elsewhere.<sup>2,3</sup>

The tetramethylene diradical is most often invoked as an intermediate in the pyrolysis of cyclobutanes to ethylenes.<sup>4</sup> The parent reaction has an activation



energy of 62.5 kcal/mol,<sup>5</sup> consistent with estimates of thermodynamic properties of the diradical.<sup>1</sup> Though the diradical has never been directly observed the indirect evidence for its existence is impressive.<sup>1,4,5</sup>

Until recently it was assumed that were there a concerted pathway for reaction 1 it would be a least-motion process in which the stereochemical integrity of cyclobutane labeling would be retained in the product ethylenes. The absence of stereospecificity<sup>6</sup> was in

(2) (a) R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, **89**, 5215 (1967); (b) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *ibid.*, **90**, 1485 (1968); (c) R. Hoffmann, *ibid.*, **90**, 1475 (1968); (d) R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968).

(3) An interesting comment on the biradical problem may be found in G. R. Freeman, *Can. J. Chem.*, **44**, 245 (1966).

(4) The role of tetramethylene in the cycloaddition of two ethylenes has been studied in a classic series of contributions by P. D. Bartlett and collaborators: P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Amer. Chem. Soc.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964); P. D. Bartlett, G. E. H. Wallbilich, and L. K. Montgomery, *J. Org. Chem.*, **32**, 1290 (1967); P. D. Bartlett, G. E. H. Wallbilich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *J. Amer. Chem. Soc.*, **90**, 2049 (1968); J. S. Swenton and P. D. Bartlett, *ibid.*, **90**, 2056 (1968); P. D. Bartlett, A. S. Wingrove, and R. Owyang, *ibid.*, **90**, 6067 (1968); P. D. Bartlett and K. E. Schueller, *ibid.*, **90**, 6071, 6077 (1968); P. D. Bartlett, *Science*, **159**, 833 (1968).

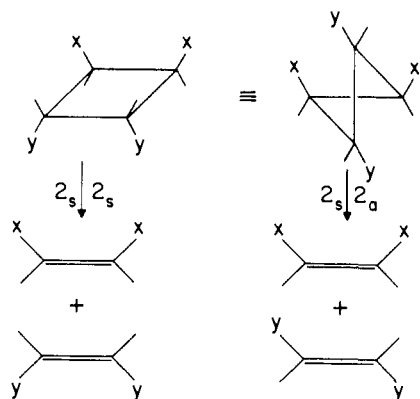
(5) C. T. Genaux and W. D. Walters, *J. Amer. Chem. Soc.*, **73**, 4497 (1951); R. W. Carr and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963).

(6) H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 4884 (1961).

\* To whom correspondence should be addressed.

(1) (a) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961); *ibid.*, **46**, 4920 (1967); S. W. Benson and P. S. Nangia, *ibid.*, **38**, 18 (1963); H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969); in press; S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 148 (1966), and references therein.

fact often cited as part of the evidence for the nonconcerted mechanism. Orbital symmetry considerations however provided a novel insight in that they dictated a non-least-motion path for the concerted reaction—a  $\sigma_s + \sigma_a$  cycloaddition.<sup>7</sup> The transition state for this



process is highly constrained—it requires high energy steric interactions and torsions. The concerted reaction comes to the fore only when these constraints are removed or circumvented in some manner.<sup>7</sup> There is little reason to believe that in the parent reaction of cyclobutane to two ethylenes there exists any preference for the symmetry-allowed process; moreover several recent experiments designed to probe this possibility have proved negative.<sup>8</sup>

This returns us to our primary concern: the molecular structure of tetramethylene, the way it is formed from cyclobutane, and the manner in which it decomposes to two ethylenes.

Our efforts are perforce limited to calculation of a potential energy surface. We cannot estimate the corresponding configurational entropy, and would prefer in fact a direct evaluation of the rate equation from a study of molecular dynamics on our calculated surface.

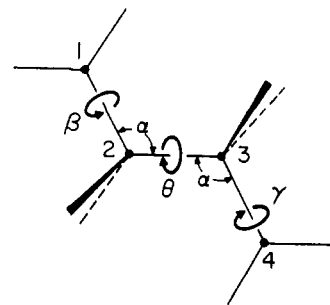
The initial calculations are of the extended Hückel type.<sup>9</sup> These are quantitatively unreliable but have consistently yielded the qualitative features of any molecular problem. Electron interaction is not explicitly included and thus the calculation of spin states is not possible. Only average energies of excited configurations are available.<sup>2</sup>

We began with the model tetramethylene geometry shown below. All CC distances were fixed at 1.54 Å, all CH distances at 1.10 Å. The terminal methylene groups were trigonal, *i.e.*, locally planar, with all angles 120°. Four internal angles were varied:  $\alpha = C_1C_2C_3$  angle, always kept equal to the  $C_2C_3C_4$  angle;  $\theta =$  angle of rotation around the  $C_2C_3$  bond,  $\theta = 0$  corresponding to the trans conformation shown;  $\beta$  and  $\gamma$ , angles of rotation of the terminal methylene groups. The reference zeroes for  $\beta$  and  $\gamma$  were for conformations eclipsing the  $C_2-C_3$  bond, independent

(7) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

(8) (a) G. L. Closs, private communication; (b) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969); L. A. Paquette, private communication; W. R. Roth, private communication.

(9) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964); *Tetrahedron*, **22**, 521, 539 (1966), and subsequent papers. The parameters used here are those quoted in the above references, except for a H-1s exponent of 1.3.

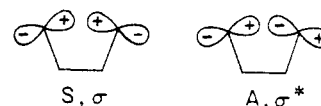


of the value of  $\theta$ . The hydrogens at  $C_2$  and  $C_3$  were maintained at a tetrahedral HCH angle but were moved with  $\alpha$  so that the HCH plane was along the bisector of  $\alpha$ .

The lowest energy point on our potential surface is that most closely approaching cyclobutane, given the constraints of the trigonal terminal groups. This minimum, denoted as  $C'$ , occurs at  $\alpha = 99^\circ$ ,  $\beta = 80^\circ$ ,  $\gamma = 100^\circ$ ,  $\theta = 168^\circ$ , at an energy of 0.41 eV above a planar cyclobutane geometry with true hydrogen placement. The deviation of  $C'$  from a square planar ring ( $\alpha = \beta = \gamma = 90^\circ$ ,  $\theta = 180^\circ$ ) is in the angle  $\alpha$  an indication of the constraint of trigonal methylene groups, and in the correlated motions of  $\beta$ ,  $\gamma$ , and  $\theta$  a reflection of the observed preference of cyclobutanes for a puckered ring geometry.<sup>10</sup>

Before we consider the full potential surface for tetramethylene let us examine a particularly simple, and as it turns out representative, way of breaking the 1-4 bond. This is a stretching motion in-plane, in which  $\beta$  and  $\gamma$  remain at  $90^\circ$ ,  $\theta$  at  $180^\circ$ , and only  $\alpha$  is varied. Figure 1 shows the total energy and the important overlap populations along this motion. The expected features of this figure are the fall of  $n(1-4)$  and the relative stability of  $n(1-2)$  and  $n(2-3)$ . The striking and unanticipated observation is the obvious discontinuity in all quantities at  $\alpha \sim 116$ . A level crossing leading to a discontinuity in orbital occupation is indicated. This is confirmed by Figure 2 which shows the variation in energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Both HOMO and LUMO are found to be primarily confined to the 1-4 bond. They may be identified with the localized  $\sigma$  and  $\sigma^*$  combinations sketched in an idealized manner below. The symmetry classifica-



tions S and A stand for symmetric or antisymmetric behavior under the twofold rotation of the  $C_{2v}$  molecular group.

The increase in S energy and decrease in A energy with increasing  $\alpha$  are hardly surprising as they are the anticipated consequence of a diminishing direct through-space interaction of the two orbitals. What is surprising at first sight is the crossing observed, *i.e.*, that at large angles A is more stable than S. This crossing is the result of a through-bond coupling of the

(10) Some leading references are G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Amer. Chem. Soc.*, **75**, 5634 (1953); J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952); W. G. Rothschild and B. P. Dailey, *ibid.*, **36**, 2931 (1962).

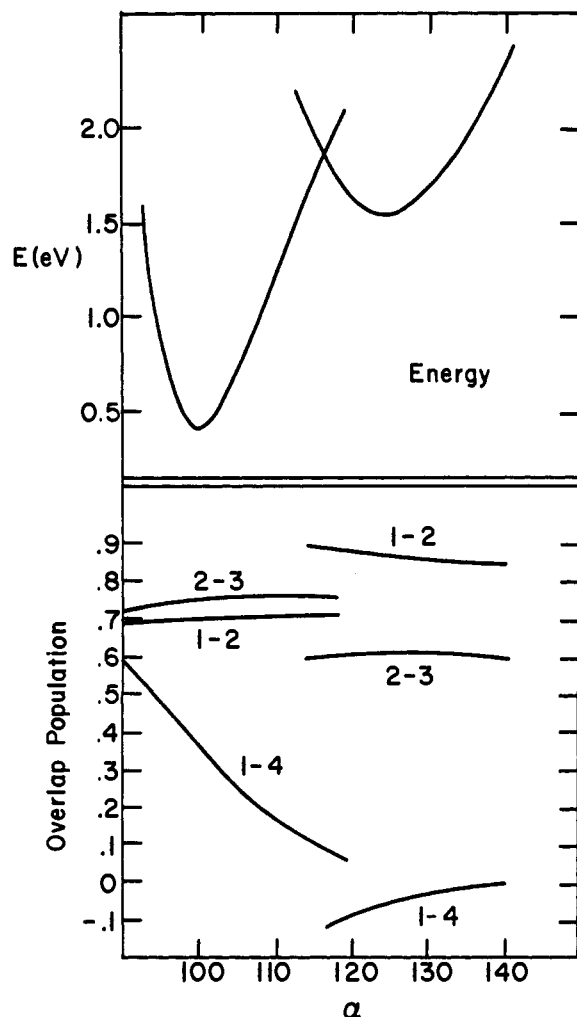


Figure 1. Energy (top) and overlap populations (bottom) for a simple stretching of the 1-4 bond in a model tetramethylene with  $\theta = 180^\circ$ ,  $\beta = \gamma = 90^\circ$ .

two orbitals, through bond 2-3. The analysis of this phenomenon has been given by us before<sup>11</sup> but it will be worthwhile to repeat it here.

Consider two orbitals separated by three  $\sigma$  bonds, in a cisoid geometry. Let us assume a weak through-space interaction so that the S and A combinations of these two approximately nonbonding orbitals are at roughly the same energy. We now mix in the 2-3  $\sigma$  level, which with respect to the twofold axis is symmetric, and the 2-3  $\sigma^*$  level, which is antisymmetric. The interaction diagram is shown in Figure 3. Only levels of like symmetry interact, and the nonbonding A level is clearly depressed below the destabilized nonbonding S. Note also that the nonbonding S level is 1-4 bonding, 1-2 antibonding, 2-3 bonding while the A level is 1-4 antibonding, 1-2 bonding, 2-3 antibonding. Switching two electrons from S to A, as happens at  $\alpha = 116^\circ$ , would be expected to weaken 1-4, strengthen 1-2, and weaken 2-3. This is precisely what may be observed in Figure 1, and thus our analysis of the level crossing in terms of a competition between direct and through-bond coupling is consistent with all the numerical results.

(11) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

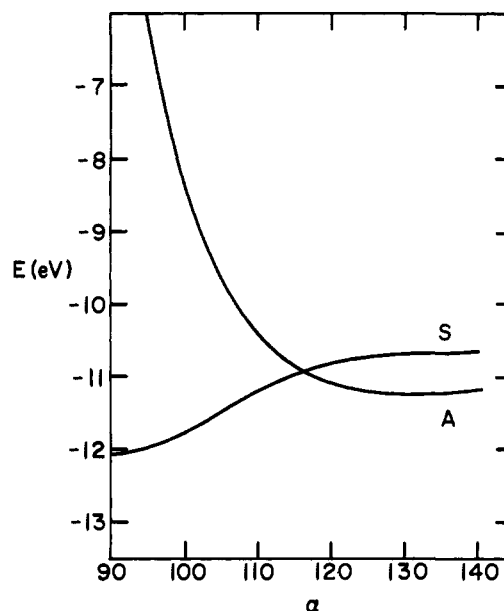


Figure 2. Energy of highest occupied and lowest unoccupied molecular orbitals of tetramethylene undergoing a simple 1-4 bond stretching.

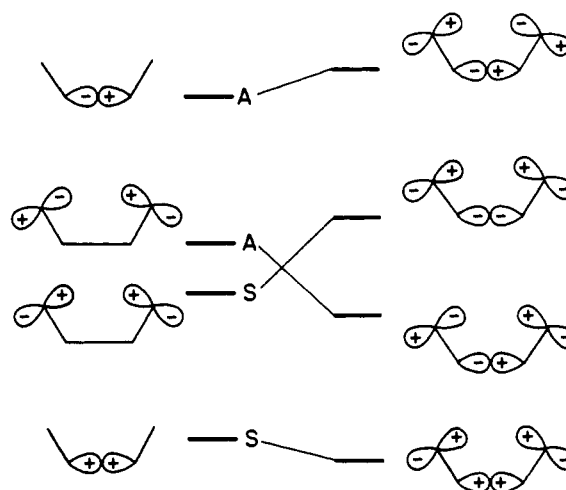


Figure 3. Interaction diagram for a tetramethylene with  $\theta = 180^\circ$ ,  $\beta = \gamma = 90^\circ$ , large  $\alpha$ . The radical orbitals are mixed with the  $\sigma$  and  $\sigma^*$  levels of the 2-3 bond.

The level crossing at  $\alpha = 116^\circ$  is a clear demarcation line between cyclobutane and an as yet undetermined species which we may call D. To the left of the level crossing in Figure 1 or 2 we have a distorted cyclobutane. It may have a stretched 1-4 bond, but it has an occupied S level and if released would collapse smoothly and along a path of uniformly decreasing energy to the equilibrium geometry of cyclobutane. The species D which we have to the right of the crossing is clearly not to be described as cyclobutane. It has a different electronic configuration,  $\cdots(A)^2$ . The total energy suggests that D is the tetramethylene diradical intermediate, with a preferred  $\alpha$  of  $\sim 125^\circ$ . However it may be that the rising energy at large  $\alpha$  is simply due to the strain at  $C_2$  and  $C_3$ , and that if we allowed simultaneous elongation of the 2-3 bond we could erase that barrier and proceed directly along a path of uniformly decreasing energy to two separate

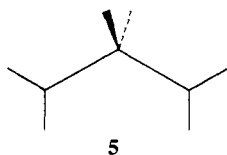
ethylenes. Support for this view is obtained from examining the occupied orbitals on the right of Figure 3. They differ in asymmetry and hybridization but are identical in nodal pattern with the bonding orbitals of two separate ethylenes.<sup>7</sup>

The discontinuity in total energy and the various overlap populations exhibited in Figure 1 will not survive the introduction of electron interaction. Configuration interaction will mix the configurations  $\dots(S)^2$  and  $\dots(A)^2$  which possess the same total symmetry, and the true wave function for the system will be

$$\psi = c_1(S)^2 + c_2(A)^2$$

with  $c_1 > c_2$  at small  $\alpha$ ,  $c_1 \sim c_2$  near the crossing, and  $c_1 < c_2$  at large  $\alpha$ . All the properties will be continuous, but their asymptotic behavior is correctly given by the pure configurations. The extended Hückel method is incapable of introducing electron interaction and so such interesting questions as whether the energy maximum near  $\alpha = 116^\circ$  will survive or turn into an inflection point must await better calculations.<sup>12</sup>

In our previous study of trimethylene<sup>2c</sup> we obtained a distinct potential energy minimum for a trimethylene intermediate in a so-called 0,0 conformation, **5**. It was



characterized by an antisymmetric, with respect to a vertical mirror plane, level at lower energy, as a consequence of hyperconjugative destabilization of the symmetric combination. This trimethylene intermediate thus preferred a conrotatory closure back to cyclopropane, but possessed a small barrier to that reclosure. We now searched our cyclobutane potential surface for a similar minimum.

Constraining  $\beta$  and  $\gamma$  to  $0^\circ$ ,  $\theta = 180^\circ$  we varied the  $C_1-C_2-C_3$  angle  $\alpha$ . A minimum was attained at  $\alpha = 120^\circ$  at an energy of 1.77 eV above cyclobutane. At the same  $\alpha$  and  $\theta$  the geometry with  $\beta = \gamma = 90^\circ$  was more stable by 0.13 eV. The 0,0 geometry was not a true minimum. While stable with respect to a disrotatory motion, it was not stable with respect to conrotatory closure at constant  $\alpha$ . We attribute the lack of stability of the tetramethylene 0,0 geometry, contrasted with the stability of the corresponding trimethylene, to two factors: first the better through-bond coupling of the two radical orbitals in trimethylene and the drastically worse steric situation at the terminal methylene hydrogens in tetramethylene.

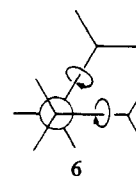
So far we have examined the pure stretching mode for breaking one bond. We next turn to a pure twisting motion, *i.e.*, a variation of  $\theta$  for a fixed  $\alpha$ . Whereas in the stretching mode  $\beta$  and  $\gamma$  remained at  $90^\circ$  throughout the motion, it soon became obvious that if  $\theta$  was varied we would need to optimize  $\beta$  and  $\gamma$  for each value of  $\theta$ . In the early stages of torsional motion away from the  $C'$  minimum particularly drastic variations of  $\beta$  and  $\gamma$  took place. Their sense was, however, pre-

(12) A lucid discussion of the very similar case of the cyclopropane-trimethylene surface is given by R. J. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, **73**, 1299 (1969).

Table I. Optimum  $\beta$  and  $\gamma$  for  $\alpha = 100^\circ$ ,  $\theta$  Varied

$\theta$ , deg	$\beta$ , deg	$\gamma$ , deg
180	90	90
170	82	98
160	73	107
150	65	115
140	58	122
120	41	139
100	64	44
80	79	101
60	71	109
40	70	110
20	77	103
0	90	90

dictable:  $\beta$  and  $\gamma$  varied in such a way as to restore, for a given  $\theta$ , as much 1-4 bonding as possible. One view of the combined motions is given in **6**. Table I



shows for a given  $\theta$  those values of  $\beta$  and  $\gamma$  which minimize the energy.  $\alpha$  is fixed at  $100^\circ$  in this search.

Note that a twofold symmetry axis ( $\beta = 180 - \gamma$ ) is maintained at all points except near  $\theta = 100^\circ$ . At  $\theta > 100^\circ$  the highest occupied level is S and we have a distorted cyclobutane. At  $\theta < 100^\circ$  the nonbonding A level is below the S. A level crossing at  $\theta \sim 100^\circ$  is indicated, but is in fact avoided by the molecule assuming an unsymmetric geometry. This unsymmetric conformation bridges softly the discontinuity in overlap populations that would otherwise have occurred at this point. This is demonstrated in Figure 4, which shows the variation in energy and overlap populations for the path described in Table I. The rationalization for the behavior of the overlap populations is identical with that discussed for the stretching motion. The through-bond coupling is relatively independent of the torsional angle  $\theta$ .<sup>11</sup>

We now proceed to the most general potential surface, where  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\theta$  are varied independently. Figure 5 shows contours of the energy as a function of the stretching and torsion variables  $\alpha$  and  $\theta$ . Each point on this surface corresponds to optimum  $\beta$  and  $\gamma$ , which generally parallel those given in Table I for a particular choice of  $\alpha$ . On either side of the dashed line in Figure 5 the system chooses to maintain a twofold rotation axis, with  $\beta = 180 - \gamma$ . The dashed line is the locus of points where the S-A level crossing should occur, but in fact asymmetrical choices of  $\beta$  and  $\gamma$  avoid this situation. This locus clearly demarcates the region where we may call the molecule a distorted cyclobutane. Outside we have an area where the 1-4 bond is broken and where the orbital shapes are approaching those of two separating ethylenes.

The lowest energy path between cyclobutane and the broken-bond species requires a combination of stretching and torsion. The height of the barrier for this process is approximately 1.4 eV or 32 kcal/mol. The observed<sup>5</sup> activation energy for cyclobutane pyrolysis is 62.5 kcal/mol. The calculation thus underestimates

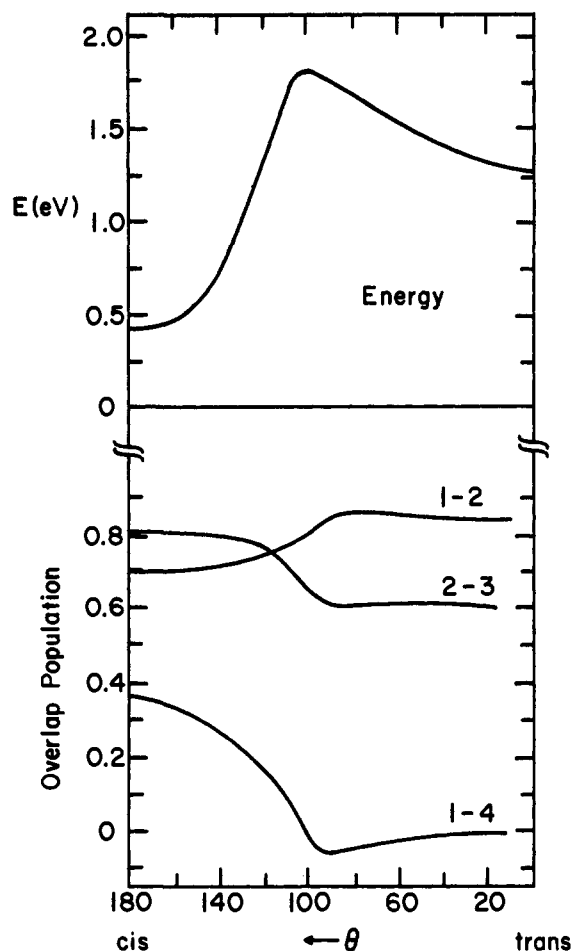


Figure 4. Energy (top) and overlap populations (bottom) for varying  $\theta$  at  $\alpha = 100^\circ$ .  $\beta$  and  $\gamma$  are optimized for each  $\theta$ , and representative values are shown in Table I.

the activation barrier considerably. Even worse, it fails to predict the correct sign of the heat of the reaction, making two ethylenes more stable than cyclobutane. The deficiencies are typical of extended Hückel calculations, which nevertheless generally predict correctly the qualitative features of orbital interaction.

Are there any true local minima in the tetramethylene potential surface, other than cyclobutane? We have found two such minima, both in the "broken-bond" region. The first such minimum, referred to as G (for gauche), may be located in Figure 5. It occurs at  $\beta = \gamma = 90^\circ$ ,  $\alpha = 116^\circ$ ,  $\theta = 105^\circ$ , at 1.15 eV above cyclobutane. The second minimum is at  $\beta = \gamma = 90^\circ$ ,  $\alpha = 112^\circ$ ,  $\theta = 0^\circ$ , at 1.08 eV above cyclobutane. It will be referred to as T (for trans). The important overlap populations in G, T, a normal cyclobutane (C), and the closest approach to such when the terminal methylenes are trigonal (C') are compared in Table II.

Note the broken 1-4 bond, the lowered  $n(2-3)$ , and the raised  $n(1-2)$  in the G and T conformations. The absence of 1-4 bonding in G may be probed in still another manner. Fixing  $\alpha$  at  $116^\circ$  and  $\theta$  at  $105^\circ$  we allowed independent variation of  $\beta$  and  $\gamma$  over their entire range. The motivation for this was that considered as a distorted cyclobutane the G geometry might be expected to readjust the terminal methylene rotations to restore some bonding (see 6). This did not occur.

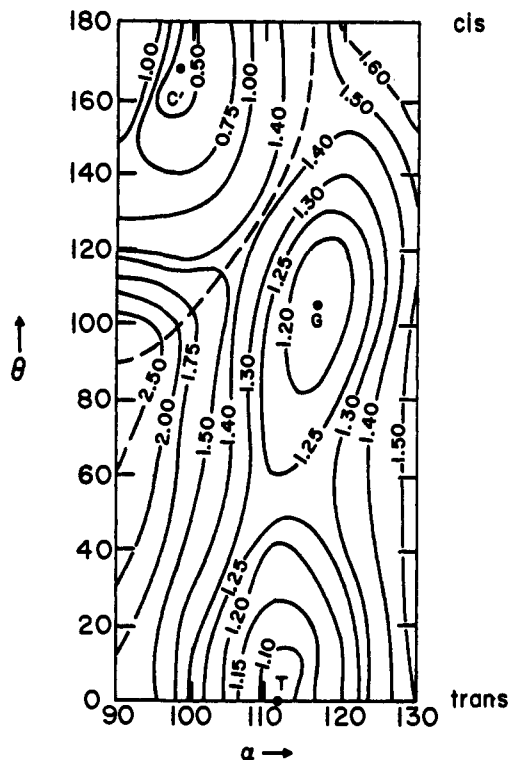


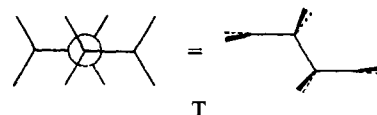
Figure 5. Potential energy surface for simultaneous variation of  $\alpha$  and  $\theta$  for optimum  $\beta$  and  $\gamma$ . The energies are in electron volts relative to a planar cyclobutane. The minima C', G, and T are subsequently discussed in the text. The dashed line is the locus of points at which S and A levels intersect, and at which a corollary discontinuity in all overlap populations occurs.

Though the barriers to methylene group rotation are not large, the preferred conformation is definitely that with  $\beta = \gamma = 90^\circ$ . Through-bond coupling is very sensitive to deviation of  $\beta$  and  $\gamma$  from  $90^\circ$ , and we take our results to mean that in the G geometry there is no 1-4 bonding, and that the terminal methylene orientation is set by the desire for optimum through-bond coupling.

Table II. Overlap Populations and Energies for a Normal Cyclobutane (C), the Closest Approach to Such with the Constraints of Trigonal Methylenes (C'), and the Local trans and gauche Minima

Geometry	$\Delta E$ , eV	$n(1-4)$	$n(1-2)$	$n(2-3)$
C	0	0.708	0.708	0.708
C'	0.41	0.381	0.706	0.747
G	1.15	-0.023	0.871	0.627
T	1.08	0.001	0.865	0.625

The through-bond coupling is optimized in the trans (T) conformation. The 90,90 geometry is preferred



by 0.55 eV to the 0,90 geometry and by 0.58 eV to the 0,0 geometry. The latter conformation is not a local minimum but is unstable with respect to terminal methylene rotation. In the T conformation the A level is 0.64 eV below the S. This is a sizable inter-

action, but probably not one sufficient to guarantee a singlet ground state at that conformation.

The broken-bond conformations T and G are local minima (in the degrees of freedom allowed to them) for simple steric reasons, and not because of any peculiarities of orbital interaction. We probed this by varying  $\theta$  in a model *n*-butane with  $\alpha$  tetrahedral and staggered terminal methyl groups. Referred to a zero of energy at the trans conformation, the tetramethylene gauche conformation is at 0.07 eV, with a barrier of 0.23 eV intervening at  $\theta \sim 65^\circ$ . In *n*-butane the gauche conformation is at 0.06 eV above the trans, with a barrier of 0.15 eV. The behavior of tetramethylene and *n*-butane is parallel.

At various points along the potential surface we studied distortions of the trigonal methylene groups toward tetrahedral. No new minima emerged; the C' minimum preferred pyramidal distortion, while the T minimum remained trigonal.

The important question now faced us: are the T and G minima the sought after tetramethylene intermediates, or is it possible to fragment from T and G to two ethylenes along a path of uniformly decreasing energy? To answer this question we would have to study several new degrees of freedom: elongation of the C<sub>2</sub>-C<sub>3</sub> bond, shortening of C<sub>1</sub>-C<sub>2</sub> and C<sub>3</sub>-C<sub>4</sub>, and flattening of the CH<sub>2</sub> groups at C<sub>2</sub> and C<sub>3</sub> toward a locally planar geometry. The elongation of the C<sub>2</sub>-C<sub>3</sub> bond seems to be the most important of these motions, and we immediately run into the problem that extended Hückel methods, though reliable for angular potentials, are not trustworthy for determining atomic separations in molecules.

Though we were aware the results might be untrustworthy, we studied the simultaneous variation of two of the variables mentioned in the previous paragraph—the C<sub>2</sub>-C<sub>3</sub> bond distance and the CH<sub>2</sub> flap angle  $\varphi$  at C<sub>2</sub> and C<sub>3</sub>, defined in the drawing below



In the trans minimum  $\varphi = 56^\circ$  and for a fully relaxed ethylene  $\varphi = 0^\circ$ . For a given C<sub>2</sub>-C<sub>3</sub> distance the value of  $\varphi$  which minimized the energy decreased predictably. For example at 1.9 Å,  $\varphi = 40^\circ$ , at 2.4 Å,  $\varphi = 19^\circ$ . The energy decreased uniformly as the C<sub>2</sub>-C<sub>3</sub> bond was lengthened and  $\varphi$  was decreased. Similar behavior was obtained for the gauche minimum. Thus, the result of these calculations is that *G and T are not true minima but are unstable with respect to two separated ethylenes*. This is of course consistent with the fact that the molecular orbitals of G and T, just as those of the stretched tetramethylene shown in Figure 3, already resemble the orbitals of two ethylenes. We again would like to stress that our calculations, in view of their incorrect accounting of the thermochemistry of the reaction and their acknowledged deficiencies in predicting bond length changes, may not be reliable here; definitive conclusions must await better calculation than those we can do.

Before we leave the general potential surface we note that we tested for the presence of minima other than C', G, and T by an automatic minimization procedure in which all four degrees of freedom were varied. The

starting points for the minimization were a random set of some twenty choices for  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\theta$ , including some anomalous geometries analogous to the  $\theta = 100^\circ$  point in Table I as well as some geometries chosen to approximate a hypothetical  $2_s + 2_a$  pathway.<sup>7</sup> In each case the variables converged to either C',<sup>13</sup> G, or T, and no new minima were located. We believe that the four degrees of freedom we allow are not sufficient to show up the symmetry-allowed  $2_s + 2_a$  path, *i.e.*, the constraints we impose wash out traces of this concerted fragmentation. We plan to explore a more liberal set of constraints to compare the energetics of the allowed concerted path with the nonconcerted one studied in this paper.

## Conclusion and Consequences

Outside a clearly demarcated region of a distorted cyclobutane we find only two local minima, both with a 1-4 bond broken. These appear not to be absolute minima but seem to be unstable with respect to decomposition to two ethylenes. Thus our potential surface appears to have only two real minima on it—cyclobutane and two ethylenes.<sup>14</sup>

Where then is that kinetically useful intermediate, the tetramethylene diradical? If by the term "intermediate" is here meant a true unstable molecule, a minimum in the many-dimensional potential energy surface, then if our calculations are correct *there is no such species*. Our computations do show a large region of coordinate space where the energy of a ring-opened C<sub>4</sub>H<sub>6</sub> does not vary much with  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\theta$ , and no doubt with other degrees of freedom as well. In the context of modern trajectory calculations<sup>15</sup> we believe that a consequence of such a large flat region of the potential energy surface is that molecules would, on the average, be spending relatively long times ( $>10^{-12}$  sec) exploring this surface. In its effects on the rate constant, in the possibilities it offers for interception and diversion, we think that such a flat region will be operationally indistinguishable from a true minimum.<sup>16</sup> A new word is necessary to describe such a species and we suggest the use of the term *twixtyl*<sup>17</sup> for a molecule or a range of molecular conformations which is not a minimum in a potential energy surface but which operationally behaves as a true intermediate.

If our results are confirmed by the better calculations, which certainly must and will be done on this problem,<sup>18</sup>

(13) Some of the runs did not actually reach C', but stopped in the very flat valley (see Figure 5) at  $\alpha = 100^\circ, 150^\circ < \theta < 180^\circ$ . In this valley the energy varies by only  $\sim 0.01$  eV, but the actual minimum is at the point indicated in Figure 5.

(14) The absolute number of minima is, of course, a function of the number of degrees of freedom made available. If we varied other degrees of freedom than we did, we surely would encounter all the stable and unstable isomers and fragmentation products of C<sub>4</sub>H<sub>6</sub>—*e.g.*, the butanes, methylcyclopropane, propylmethylene, two acetylenes, and two hydrogen molecules, etc.

(15) P. J. Kuntz, M. H. Mok, and J. C. Polanyi, *J. Chem. Phys.*, **50**, 4623 (1969); L. M. Raff and M. Karplus, *ibid.*, **44**, 1212 (1966); D. L. Bunker and N. C. Blais, *ibid.*, **41**, 2377 (1964), and related work by these research groups.

(16) We also believe that the same flat region can account for the observed geometrical isomerization of cyclobutanes (ref 5 and 6). Over a large portion of the surface it costs very little in energy to rotate a single methylene group by  $90^\circ$  from its equilibrium position.

(17) From the aphetic English 'twixt. This usage was enthusiastically approved by an *ad hoc* committee on nonconcerted reactions, consisting of L. A. Paquette, J. Meinwald, and M. J. Goldstein, meeting in Ithaca, N. Y., on March 2, 1970.

(18) A thorough *ab initio* study of this surface has been undertaken by L. Salem and collaborators.

then the implications for mechanistic studies are startling, and we will have to completely reexamine our definition of diradical intermediates and our simplistic view of nonconcerted reactions.<sup>19</sup>

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(19) Another area where we may have to face an intermediate simulated by a flat-topped potential surface is in some nonclassical carbonium ions.

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## Heat Capacities of Organic Compounds in Solution. II. Some Tetraalkylammonium Bromides<sup>1</sup>

Edward M. Arnett\* and James J. Campion

Contribution from the University of Pittsburgh  
and Mellon Institute of Carnegie-Mellon University,  
Pittsburgh, Pennsylvania 15213. Received October 9, 1969

**Abstract:** Partial molar heat capacities of solution  $\Delta C_{p_2}^\circ$  are reported for a series of tetraalkylammonium bromides. The process is transfer from the pure solid state to high dilution in water as measured by the integral heat method of Criss and Cobble. Heats of solution are shown to be extremely dependent upon the hydrophobic structure of the ion and upon the temperature. This gives warning against interpreting heats of solution for compounds of this type at a single temperature in simple terms. The corresponding heat capacity of solution for tetra-*n*-butylammonium bromide in ethanol is reported and results contrasting to those in water are discussed.

For a variety of good reasons, tetraalkylammonium salts occupy a special position in the development of modern solution theory. As a result they have been subjected to unusually extensive and systematic scrutiny by a battery of physical methods, with particular emphasis on their behavior in aqueous solution.<sup>2</sup> This combined effort has been described by Franks<sup>3</sup> as "a textbook example of how . . . water-solute interactions should be studied."

The very large partial molal heat capacity  $\bar{C}_{p_2}$  of tetra-*n*-butylammonium bromide in aqueous solution reported by Frank and Wen<sup>4</sup> and recently confirmed by Ackerman<sup>5</sup> is often cited as powerful evidence that nonpolar groups enhance a degree of temperature-dependent structuredness on water molecules close to them. In our previous paper<sup>6</sup> concerning the determination of heat capacities of solution for a series of alcohols in water,<sup>7</sup> we described the application of Criss and Cobble<sup>8</sup> "integral heat of solution" method. A simple solution calorimeter described by us<sup>9</sup> was

used to measure the temperature coefficient of the partial molal heat of solution ( $\Delta \bar{H}_s$ ) for the solute from a pure liquid or solid state to high dilution in water. It, therefore, gives directly the difference in heat capacity ( $\Delta C_{p_2}^\circ$ ) between the heat capacity of the pure solute [as a liquid ( $C_p^L$ ) or gas ( $C_p^G$ ) or solid ( $C_p^S$ )], and that of its partial molal heat capacity at infinite dilution,  $\bar{C}_{p_2}$ . This is defined formally as

$$\Delta C_{p_2}^\circ = \bar{C}_{p_2} - C_{p_2}^{L, G, \text{ or } S} \quad (1)$$

In this paper, we will describe the result of applying this method to a series of crystalline tetraalkylammonium bromides in water at temperatures mostly between 10 and 50°. Our results may be compared with those from a similar study (published since the present paper was first submitted) by Sarma, Mohanty, and Ahluwalia,<sup>10</sup> which covers a wider series of salts but which was limited to two temperatures. Their paper also provides a bibliographical entrée to the field.

### Experimental Section

**Preparation and Purification of Chemicals.** With the exception of tetraisoamylammonium bromide [(*i*-Am)<sub>4</sub>NBr], the tetraalkylammonium bromides and other reactants were of Eastman White Label quality. Tetramethylammonium bromide (Me<sub>4</sub>NBr) was recrystallized once from water. Tetraethylammonium bromide (Et<sub>4</sub>NBr) was recrystallized once from isopropyl alcohol. Tetra-*n*-propylammonium bromide (Pr<sub>4</sub>NBr), tetra-*n*-butylammonium bromide (Bu<sub>4</sub>NBr), and [(*i*-Am)<sub>4</sub>NBr] were recrystallized once from a chloroform-ether mixture (10-15 volumes of ether added to the chloroform).

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\* To whom correspondence should be addressed.

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