Ab Initio Calculation of the Equilibrium Structure and Coplanar Decomposition of Cyclobutane

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Abstract: Using a minimum basis set of Slater-type orbitals, the equilibrium structure of cyclobutane is determined. The calculated structure has C–C and C–H bond distances and HCH bond angles, which are within the limits of error for the experimentally measured values. The importance of methylene rocking in the puckered structure, shown in an earlier semiempirical calculation, is verified by the *ab initio* results. However, only a very small double minimum puckering potential is found. Force constants calculated for some of the important normal modes of vibration are too large by a factor of two. The orbital energies obtained agree very well with the measured photoelectron spectrum of cyclobutane. A potential surface for the coplanar (2s + 2s) rectangular decomposition of cyclobutane to form two ethylenes shows a potential barrier of 156 kcal/mol. The properties of this surface are discussed with reference to the Woodward–Hoffmann predictions.

Cyclobutane has a nonplanar structure, the elucidation of which has posed a rather difficult experimental problem. Several recent studies by different experimental methods[2–7] are now in agreement that the ring puckering angle is about 35°, and that the depth of the double minimum potential well for ring puckering is about 1.4 kcal/mol. The bond distances and bond angles may also be considered to be reasonably well established[3,6,8,9] and a vibrational analysis has been carried out to obtain the force constants for all normal modes of vibration.[10,11] Some semiempirical calculations[12] have added further details about the precise structure in examining atomic positions previously inaccessible to experimental measurement;[13] we discuss later our *ab initio* calculations which verify the importance of a particular methylene rocking mode in puckered cyclobutane.

In addition to the structure of cyclobutane, there has been much interest in its reactions, both thermal and photochemical. Thermally cyclobutane decomposes to give two molecules of ethylene,[14–16] and substituted cyclobutanes have been shown to undergo a geometrical isomerization to give the product in which a methylene group has rotated by 180° from its original position.[17] The photolysis of cyclobutane[18] yields ethylene as a major product, along with acetylene, propylene, ethane, and small quantities of other hydrocarbons. Much of the interest generated by the reactions of cyclobutane is associated with the mechanistic question of whether its reactions proceed *via* diradical or concerted pathways.[16,19] In addition, the reaction $C_4H_8 \rightarrow 2C_2H_4$ has played an important role in the illustration of the Woodward–Hoffmann rules of orbital symmetry control in concerted reactions.[20] A previous calculation by Hoffmann and coworkers[21] using the semiempirical extended Hückel theory explored the possibility of cyclobutane decomposition *via* the tetramethylene intermediate. This represents a more realistic path than that considered in the present article, although the *ab initio* method used in this paper is preferable as far as reliability of results.

Because of the interest in the structure of cyclobutane and its reactions, and in the Woodward–Hoffmann rules, we have undertaken an extensive *ab initio* study designed to explore the equilibrium structure of this molecule, its force constants, and its simplest possible decomposition path: the (2s + 2s) coplanar, rectangular path to give two ethylenes. Our calculations use a minimum basis set of Slater-type orbitals, with no intergral approximations. Calculation times are now sufficiently rapid to make possible the *ab initio* study of potential surfaces for the reactions of polyatomic molecules, and we obtain from our calculation an equilibrium structure for cyclobutane, a description of the (rectangu-

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[2] G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Amer. Chem. Soc.*, **75**, 5634 (1953).

[3] A. Almenningen, O. Bastiansen, and P. N. Skancke. *Acta Chem. Scand.*, **15**, 711 (1961); P. N. Skancke, Ph.D. Thesis, University of Oslo, 1960.

[4] D. A. Dows and N. Rich, *J. Chem. Phys.*, **47**, 333 (1967).

[5] T. Ueda and T. Shimanouchi, *ibid.*, **49**, 470 (1968).

[6] S. Meiboom and L. C. Snyder, *ibid.*, **52**, 3857 (1970). In this determination, the carbon–carbon distance was assumed. The derived C–H bond distance of 1.133 Å (when axial and equatorial bonds are assumed equal) is outside the normal range of values measured for saturated hydrocarbons and was not included in the "best" experimental structure. Note, however, that the nmr method gives information about the relative positions of protons which is not available by other means; in particular, a methylene rocking angle of 4° was found.

[7] J. M. R. Stone and I. M. Mills, *Mol. Phys.*, **18**, 631 (1970).

[8] J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, 20, 1703 (1952).

[9] R. C. Lord and B. P. Stoicheff, *Can. J. Phys.*, **40**, 725 (1962).

[10] R. C. Lord and I. Nakagawa, *J. Chem. Phys.*, **39**, 2951 (1963).

[11] D. Retzloff and J. Coull, *ibid.*, 47, 3927 (1967).

[12] J. S. Wright and L. Salem, *Chem. Commun.*, 1370 (1969).

[13] The possibility of nonequivalent C–H axial and equatorial bond lengths has been discussed by Meiboom and Snyder (ref 6) using their nmr data. However, the data are not sufficiently precise to allow any conclusions.

[14] R. W. Carr and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963).

[15] H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966).

[16] J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

[17] (a) R. Gerberich and W. D. Walters, *ibid.*, **83**, 3935, 4884 (1961); (b) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961); (c) J. A. Berson, D. C. Tompkins, and G. Jones, *J. Amer. Chem. Soc.*, **92**, 5799 (1970).

[18] R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, 43, 3814 (1965).

[19] (a) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (b) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (c) J. A. Berson, W. Bauer, and M. M. Campbell, *J. Amer. Chem. Soc.*, **92**, 7515 (1970).

[20] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[21] R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

Table I. Experimental Data on Cyclobutane Structure

Ref	R_{CC}, Å	R_{CH}, Å	∠HCH, deg	θ, deg	Barrier height, cm^{-1}	Method
8	1.568 ± 0.002	1.098 ± 0.04	114 ± 8	20 (+10, −20)		Electron diffraction
2					400	Ir, Raman
3	1.548 ± 0.003	1.092 ± 0.01	110	35		Electron diffraction, molecule puckered
9	1.558 ± 0.003					Raman
4				37 ± 6		Analysis of methylene rocking vibrations (ir)
5				34 ± 0.5	448	Near-ir spectrum
6	1.548	1.133	108.1	27		Nmr; all R_{CH} equal, assumed R_{CC} CH_2 rocking angle = 4°
7				35	503	Ir, Raman

lar) reaction path, and an estimate for the activation energy associated with this path. Our results show, as expected, that the qualitative discussion of Woodward and Hoffmann concerning this thermally "forbidden" reaction path is correct. In adding quantitative reliability to their arguments some interesting aspects are treated in detail, such as the significance of configuration interaction, the role of the "nonessential" orbitals, the "reaction coordinate," and the remarkable association between the potential surface and the dominant molecular configuration.

Equilibrium Structure of Cyclobutane

The structure and conformation of cyclobutane have been studied by various methods, including electron diffraction,[3,8] ir-Raman spectra,[2,4,6,7,9] and nmr.[6] A summary of the experimental findings has been given by Meiboom and Snyder;[6] these data are presented below in Table I, together with some recent additions.

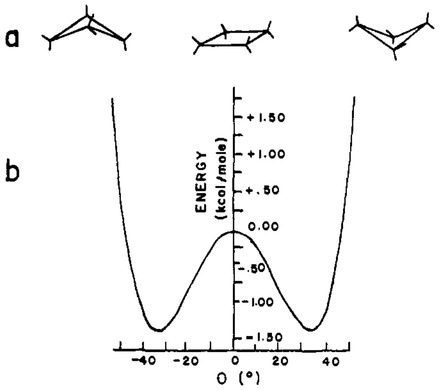

Figure 1. (a) Puckered and planar structures of cyclobutane. (b) Double minimum puckering potential.

As seen from Table I, cyclobutane has a puckered structure with a dihedral angle of about 35°. The conformational change due to ring puckering is shown in Figure 1a, where it is seen that the molecule flips between its puckered (D_{2d}) conformers *via* the planar (D_{4h}) molecule. Figure 1b shows the double minimum potential of Stone and Mills associated with the conformational change. They report a total barrier height of 1.44 kcal/mol for this potential, with the potential minimum occurring at a dihedral angle of 35 ± 5°, and find several bound vibrational levels within the well.[7]

The important geometric variables in D_{2d} cyclobutane are shown in Figure 2. Here θ, which characterizes the ring puckering, is the dihedral angle between C–C–C planes, Γ is the methylene rocking angle relative to the C–C–C plane which bisects a CH_2 group, α is the HCH angle, R_{CC} is the (unique) carbon–carbon bond distance, and $R_{CH(ax)}$ and $R_{CH(eq)}$ are the axial and equatorial C–H bond distances, respectively. This is the most general possible structure which will preserve D_{2d} symmetry. Until recently the possibility of methylene rocking and nonequivalent C–H distances has been neglected. Thus from the data in Table I, a reasonable representation of the experimental structure would seem to be: R_{CC} = 1.553 ± 0.005 Å, R_{CH} = 1.095 ± 0.01 Å, ∠HCH = 112 ± 4°, θ = 35 ± 5°.

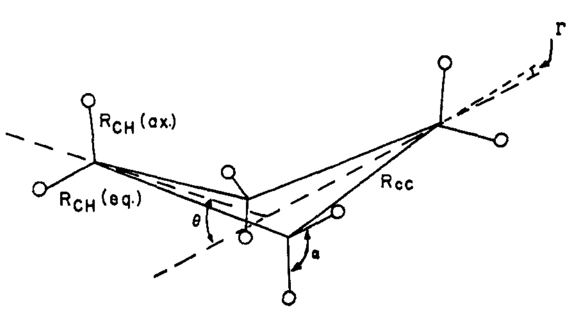

Figure 2. Geometric variables in puckered (D_{2d}) cyclobutane.

In addition to the experimental measurements quoted in Table I, there have been several empirical and semiempirical calculations of the cyclobutane structure. Among these we mention the Westheimer-type calculations of Allinger[22] and Wiberg,[23] the extended Hückel theory calculation of Hoffmann,[24] and the CNDO/2[25] study of Wright and Salem.[12] This latter study showed that a rocking of the methylene groups (Figure 2), so as to increase the staggering of adjacent hydrogens, was required in order to produce a double minimum puckering potential. In the *ab initio* structural study to follow, we test for both the possibility of methylene rocking and nonequivalent C–H bond lengths.

To establish a calculated geometry, we use the fact that a molecule of a given symmetry will allow nuclear

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(22) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, 90, 1199 (1968).

(23) K. B. Wiberg, *ibid.*, 87, 1070 (1965).

(24) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963).

(25) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, 43, S129, S136 (1967).

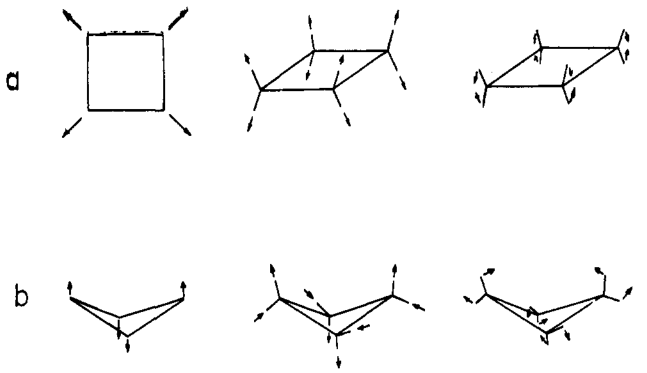

Figure 3. (a) Totally symmetric vibrational modes in D_{4h} symmetry. (b) Additional symmetric modes in D_{2d} symmetry.

relaxation along the totally symmetric coordinates until an energy minimum is reached (symmetry coordinates for nuclear motion are linear combinations of internal coordinates, such as bond stretching and angle bending motions). As shown by Lord and Nakagawa,[10] if cyclobutane is assumed to have D_{4h} symmetry then the totally symmetric (A_{1g}) coordinates for vibrational motion are the C–C symmetric stretch, the C–H symmetric stretch, and the symmetric HCH bend. These motions are shown below in Figure 3a. If the cyclobutane molecule has D_{2d} symmetry, however, then the B_{1u} species of D_{4h} symmetry now becomes totally symmetric, and we have in addition to the above three possibilities the ring puckering vibration, the antisymmetric C–H stretch, and the antisymmetric methylene rocking mode (Figure 3b).

Thus, to search for a minimum energy in D_{4h} symmetry we need to examine three coordinates, whereas to find the minimum in D_{2d} there are no less than six.

Method of Calculation

For the calculations we use a minimum basis set of exponential orbitals. The program used was written by Dr. R. M. Stevens of Harvard University and has been discussed in several recent articles.[26,27] It makes efficient use of molecular symmetry to reduce integral evaluation times. Carbon and hydrogen exponents were fixed at their (near) optimum values of $1s_C$ = 5.68, $2s_C$ = $2p_C$ = 1.72, $1s_H$ = 1.20.

Results

Beginning with a geometry search in D_{4h} symmetry we assumed as starting point the structure having R_{CC} = 1.556 Å, R_{CH} = 1.095 Å, ∠HCH = 108°. Successive parabolic minimization in the order R_{CH}, R_{CC}, α (= ∠HCH) gave as a final calculated (D_{4h}) structure R_{CC} = 1.550 Å, R_{CH} = 1.092 Å, α = 108.2°, and a total energy of $E = -155.8370$ au. This D_{4h} geometry can reasonably be considered to be within the limits of error of the experimental geometry derived from Table I. It is of course no surprise that approximate Hartree–Fock calculations give good bond distances and bond angles in complex molecules. This result has been abundantly verified in the literature.[28,29]

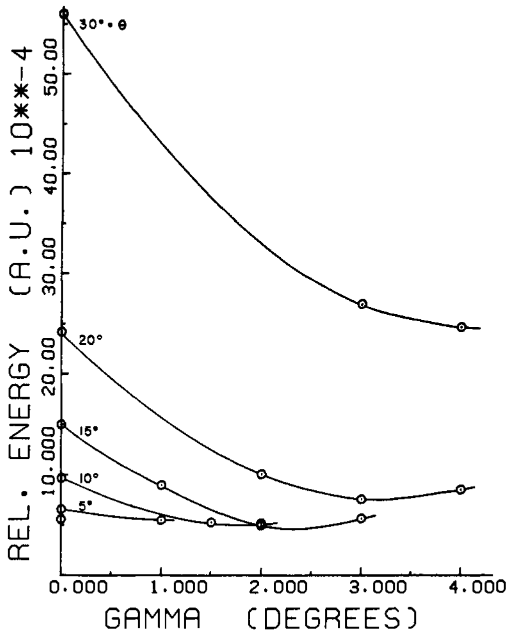

Figure 4. Variation of total energy as a function of dihedral angle θ and rocking angle Γ. The energy zero corresponds to -155.8475 au, and the distance between the larger division marks on the energy axis is 0.001 au.

The search for a minimum energy was continued, this time using D_{2d} symmetry. For several chosen values of the dihedral angle θ, parabolic minimization was carried out along the symmetry coordinates in the order Γ, CC symmetric stretch, CH symmetric stretch, CH antisymmetric stretch, and HCH symmetric angle bending. (Incremental values were 0.01 Å for bond distances, 1° for angles.) At θ = 20°, the only coordinate variation which lowered the energy of the puckered structure was the methylene *rocking motion* Γ, in agreement with the CNDO/2 result of Wright and Salem.[12] Thus at other values of θ, Γ was considered to be the only significant variable. Keeping R_{CC}, R_{CH}, and α constant and computing the total energy for various values of θ and Γ gives the energy curves shown in Figure 4.

Figure 4 shows the variation in energy along lines of constant θ. Inspection of the figure shows evidence of only a very small potential well for ring puckering. For planar cyclobutane (θ = 0°), $E = -155.83694$ au. As θ increases without methylene rocking the total energy goes up. Introduction of methylene rocking (following down the θ curves to their minima) shows that the lowest total energy is reached at θ = 15°, Γ = 2.4°, where $E = -155.83705$ au. This represents an energy lowering of only 0.0001 au or 0.06 kcal/mol at θ = 15°, a result which is clearly in disagreement both with experiment (θ = 35°, ΔE = 1.44 kcal/mol)[7] and with our previous semiempirical calculation (θ = 20°, ΔE = 0.3 kcal/mol).[12]

Why does our present calculation fail to find the potential well? It may be due to the fact that the puckering motion corresponds to the ring of carbon atoms passing through an *inversion-type barrier*. At least in the case of ammonia, an inversion barrier is

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(26) E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, **51**, 5229 (1969).

(27) R. M. Stevens, *ibid.*, **52**, 1397 (1970). A calculation of cyclobutane in D_{4h} symmetry requires 20 min on the IBM 360/75; in C_{2v} symmetry this requires 30 min.

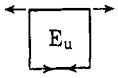
(28) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261, 2276 (1967); W. H. Fink, D. C. Pan, and L. C. Allen, *ibid.*, **47**, 895 (1967).

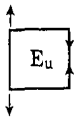
(29) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **52**, 4064 (1970).

poorly treated by small basis set calculations.[30] An addition of d orbitals used as polarization functions remedies the defect in the ammonia barrier[31] and may also be significant here. We believe we have demonstrated, in any case, the importance of including methylene rocking in the calculation.

Force Constants

A complete analysis of the normal modes of vibration in cyclobutane has been given by Lord and Nakagawa.[10] Based on the ir and Raman spectra of C_4H_8 and C_4D_8 and certain assumptions (due to lack of data), they assign force constants for all symmetry coordinates. Using the same normalization factors and our closely spaced parabolic calculations (see ref 29 for a discussion of important details in the calculation of force constants), we can compare our calculated harmonic force constants to those of Lord and Nakagawa. Calculations are given for the ring breathing and C–H symmetric stretch (Figure 3a) and also the B_{1g} and E_u modes (shown below). The latter two are important in the discussion of the concerted rectangular decomposition and the two-step decomposition, respectively.[32]





Starting from the D_{4h} structure, force constants were obtained by allowing small displacements (Δr = 0.02 Å) along the symmetry coordinates of Lord and Nakagawa[10] (see their paper for definitions).

$$Q(A_{1g}) = (1/2)(\Delta R_{12} + \Delta R_{23} + \Delta R_{34} + \Delta R_{41}) \quad \text{(ring breathing)}$$

$$Q(B_{1g}) = (1/2)(\Delta R_{12} - \Delta R_{23} + \Delta R_{34} - \Delta R_{41}) \quad \text{(ring deformation)}$$

$$Q(E_u) = (1/\sqrt{2})(\Delta R_{12} - \Delta R_{34}) \quad \text{(ring deformation)}^{32}$$

$$Q(A_{1g}) = (1/\sqrt{8})\Delta[(r_1 + r_1') + (r_2 + r_2') + (r_3 + r_3') + (r_4 + r_4')] \quad \text{(CH symmetric stretch)}$$

A comparison of experimental and theoretical values is shown below.

Type	Symmetry	Calcd, mdyn/Å	Exptl, mdyn/Å
CH stretch	A_{1g}	8.24	4.70
CC stretch	A_{1g}	8.39	4.24
CC stretch	B_{1g}	5.45	3.66
CC stretch	E_u	4.58	1.39

The force constants are seen to be too large by approximately a factor of 2. Absolute values show a similarity with the *ab initio* results of Newton *et al.*,[29] where for the symmetric stretching modes in ethane they find k_{CH} = 7.3 mdyn/Å (expt 5.1) and k_{CC} = 6.5 mdyn/Å (expt 4.5). Since approximate Hartree–Fock calculations overestimate force constants, the potential surface for distortion of cyclobutane from its equilibrium position is such that the energy change required to distort the molecule along a reaction path (*e.g.*, the B_{1g} or E_u modes) will be too large. This would lead to activation energies which are too large, unless there is a compensation due to the overestimation of cubic (anharmonic) force constants. Before discussing calculation of a reaction path, we give further details on the electronic structure of cyclobutane.

Molecular Orbitals of Cyclobutane

We present here the SCF results for square, planar cyclobutane at its optimum geometry: R_{CC} = 1.550 Å, R_{CH} = 1.092 Å, α = 108.2°. To discuss the molecular orbital results for this structure, we define global Cartesian coordinates and local atomic axes as shown in Figure 5. These orientations, together with the D_{4h} character table given by Herzberg,[33] define the symmetry orbitals from which the MO's are constructed. Although the MO's obtained contain a certain amount of mixing between σ_{CH_2} and σ_{CC} symmetry orbitals, they are labeled according to the pure semilocalized orbitals given by Salem and Wright.[34] Molecular orbital types, orbital symmetries, and orbital energies are listed in Table II for occupied and virtual orbitals.

Inspection of Table II shows that the π_{CH_2} orbitals are interspersed among the σ_{CC} and σ_{CH_2} orbitals. The highest occupied orbital ($3e_u$) is a "mixed" orbital, containing both σ_{CH_2} and σ_{CC} character. The lowest vacant orbital ($2a_{2u}$) is a $\pi^*_{CH_2}$ orbital and is not clearly separated from other low-lying σ^* orbitals ($4e_u$, $4a_{1g}$). The photoelectron spectrum of cyclobutane has recently been recorded and assigned by Heilbronner and coworkers and communicated to us.[35] These results

Table II. Molecular Orbitals of D_{4h} Cyclobutane

Orbital symmetry	Orbital type	Orbital energy, eV	Exptl, eV[a]
$1a_{1g}$	1s	−304.850	
$1e_u$	1s	−304.849	
$1b_{2g}$	1s	−304.847	
$2a_{1g}$	σ_{CC}	−29.539	
$2e_u$	Mixed	−23.678	
$2b_{2g}$	Mixed	−19.504	
$1a_{2u}$	π_{CH_2}	−17.287	−18.2
$3a_{1g}$	σ_{CH_2}	−16.712	−15.9
$1e_g$	π_{CH_2}	−14.133	−13.4, −13.6
$1b_{1g}$	σ_{CC}	−12.715	−12.5
$1b_{1u}$	π_{CH_2}	−11.624	−11.7
$3e_u$	Mixed, mostly σ_{CC}	−11.050	−10.7, −11.3
$2a_{2u}$	$\pi^*_{CH_2}$	+13.972	(Unoccupied)
$4e_u$	σ^*_{CC}	+15.194	
$4a_{1g}$	$\sigma^*_{CH_2}$	+16.699	
$1a_{2g}$	σ^*_{CC}	+17.036	
$2e_g$	$\pi^*_{CH_2}$	+18.895	
$5e_u$	$\sigma^*_{CH_2}$	+19.289	
$3b_{2g}$	$\sigma^*_{CH_2}$	+19.926	
$2b_{1u}$	$\pi^*_{CH_2}$	+23.567	
$4b_{2g}$	σ^*_{CC}	+24.005	

[a] See ref 35.

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(30) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **45**, 888 (1966).

(31) A. Rauk, L. C. Allen, and E. Clementi, *ibid.*, **52**, 4133 (1970).

(32) The actual motion is slightly more complicated due to a wagging of the CH_2 groups accompanying the trapezoidal distortion. See ref 10.

(33) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, Van Nostrand, New York, N. Y., 1945.

(34) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

(35) (a) E. Heilbronner, personal communication; (b) P. Bischof, E. Haselbach, and E. Heilbronner, *Angew. Chem., Int. Ed. Engl.*, **9**, 953 (1970).

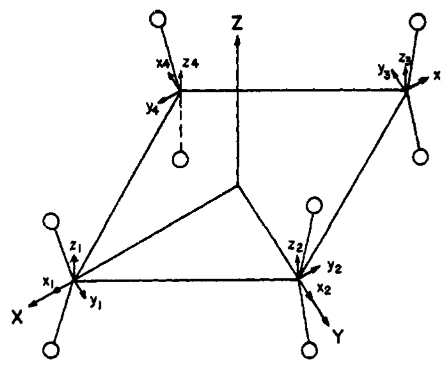

Figure 5. Coordinate system for cyclobutane in D_{4h} symmetry.

are given for comparison in the last column of Table II. Using Koopman's theorem, the agreement between the calculated orbital energies and the experimental vertical ionization potentials is remarkable.

Coplanar (2s + 2s) Decomposition of Cyclobutane

The rectangular coplanar decomposition of cyclobutane to form two ethylenes has served as an important example in the discussion by Woodward and Hoffmann of orbital symmetry control in organic reactions and is now a well-known example of a thermally forbidden, photochemically allowed reaction. As shown by Woodward and Hoffmann,[20] the important characteristic of this reaction path is an orbital crossing and the resultant rise in energy at the transition state. Our intention here is to present an *ab initio* calculation of this reaction path to test the predictions of Woodward and Hoffmann, to see whether any new features emerge, and to compare to the experimental activation energy of 62.5 kcal/mol[14] for the reaction $C_4H_8 \rightarrow 2C_2H_4$.

The correlation diagram used by Woodward and Hoffmann[20] is shown in Figure 6. The notation SA, for instance, refers to a pair of localized orbitals symmetric with respect to plane P_1 and antisymmetric with respect to plane P_2.

We indicate also in Figure 6 the group-theoretic notation for rectangular C_4H_8 in the D_{2h} symmetry group.[36]

From the diagram it is clear that as we go from the ground state of cyclobutane to that of two ethylenes there is a region of the potential surface in which two electronic configurations will be important. With respect to cyclobutane, the first is a σ_{CC} (AS, or b_{3u}) orbital which correlates directly with an excited π^* orbital in ethylene, while the second is a σ^*_{CC} (SA, or b_{2u}) orbital which correlates with a π orbital in ethylene. In D_{2h} notation, the configuration of (undistorted) cyclobutane is $(1a_g)^2(1b_{2u})^2(1b_{3u})^2(1b_{1g})^2(2a_g)^2(2b_{2u})^2$ $(2b_{3u})^2(2b_{1g})^2(1b_{1u})^2(3a_g)^2(1b_{2g})^2(1b_{3g})^2(4a_g)^2(1a_u)^2(3b_{2u})^2$ $(3b_{3u})^2$, with the low-lying virtual orbitals following in the order $(2b_{1u})^0(4b_{2u})^0(4b_{3u})^0$.... From the comparison with Table II it is evident that the symmetry types in D_{4h} are related to those in D_{2h} (see Chart I).

Referring again to Figure 6, as the transition state is approached the $3b_{3u}$ orbital (AS) rises in energy and crosses the $4b_{2u}$ (SA) orbital. For convenience, we shall refer to the cyclobutane-like configuration... $(3b_{3u})^2(4b_{2u})^0$ as ψ_{AS}, and the configuration which resembles two ethylenes ...$(3b_{3u})^0(4b_{2u})^2$ as ψ_{SA}. In searching the potential surface for the rectangular decomposition, it was decided to limit the configuration interaction to states built from these two configurations. This is the minimum number to be considered in an accurate calculation. The state function ψ is then constructed from one of the configurations, ψ_{AS} for example, by considering a double excitation to its lowest lying virtual orbital. Diagonalizing the CI Hamiltonian then gives two state functions, $\Psi_I(AS)$ and $\Psi_{II}(AS)$, which are the ground and doubly excited states of the system. [The notation $\Psi_I(AS)$ implies the lower energy state function formed from the AS configuration. Alternatively, one could use the SA configuration and its virtual orbitals to construct the state functions, obtaining $\Psi_I(SA)$ and $\Psi_{II}(SA)$.] Since at an arbitrary point on the potential surface it is not evident which configuration will give the lowest CI energy, SCF calculations were done at every point for both configurations. In fact, it was found that in the "cyclobutane region" a state function based on ψ_{AS} gave a lower state energy, while in the "two ethylenes region" ψ_{AS} was better. The precise meaning of "cyclobutane region" will be discussed later.

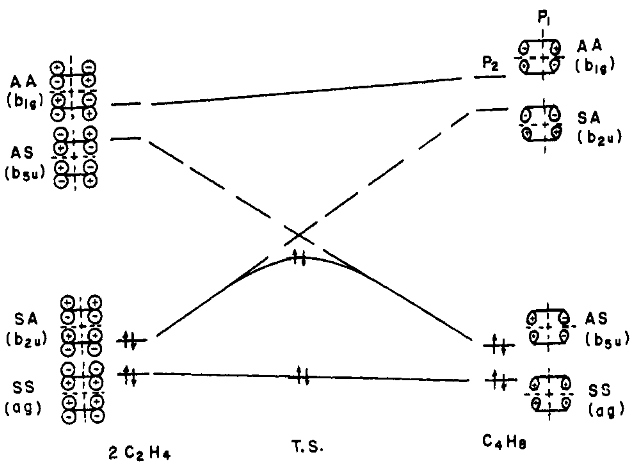

Figure 6. Woodward–Hoffmann correlation diagram for the coplanar approach of two ethylene molecules.

Chart I

D_{4h}	D_{2h}
a_{1g} b_{1g}	a_g
a_{1u} b_{1u}	a_u
a_{2g} b_{2g}	b_{1g}
a_{2u} b_{2u}	b_{1u}
e_g	b_{2g} b_{3g}
e_u	b_{2u} b_{3u}

Given a closed-shell Slater determinant (the SCF result) and a double excitation to one of its virtual

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(36) The D_{2h} group is taken from G. Herzberg, ref 33. To define the symmetry orbitals used, the local orientation of the p orbitals used at each carbon is always parallel to the global *xyz* axes.

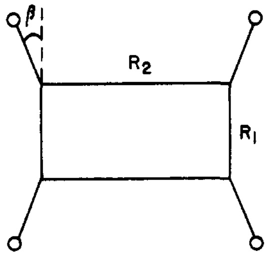

Figure 7. Geometric variables in rectangular (D_{2h}) symmetry.

orbitals, standard CI formulas give

$$\Delta E = 2(\epsilon_j - \epsilon_i) + J_{ii} + J_{jj} - 4J_{ij} + 2K_{ij}$$

where ΔE = excitation energy, ϵ_i = energy of ith occupied orbital ϕ_i, and ϵ_j = energy of jth virtual orbital ϕ_j with the usual definitions of Coulomb and exchange integrals (over MO's). Solution of

$$\begin{vmatrix} -\lambda & K_{ij} \\ K_{ij} & \Delta E - \lambda \end{vmatrix} = 0$$

then gives the two roots λ, which are to be added to the SCF single configuration energy, to obtain the ground state Ψ_{I} and doubly excited state Ψ_{II} and their corresponding energies E_{I} and E_{II}.

Method. For the calculation, the basis set used is again a minimal basis set of Slater-type orbitals. The orbital exponents used for cyclobutane were retained throughout: $1s_{\text{C}} = 5.68$, $2s_{\text{C}} = 2p_{\text{C}} = 1.72$, $1s_{\text{H}} = 1.20$.

In reducing the number of geometric variables to be studied in our search of the potential surface, we were aided by the following considerations. (1) The (calculated) energy minimum for the HCH angle in cyclobutane is 108° and in ethylene is 116°. Since the energy is a slowly varying function of angle, we fixed the HCH angle at 112°. (At the cyclobutane extremum this introduces an error of only 0.002 au, for ethylene the error is 0.001 au.) (2) The R_{CH} distance remains approximately constant, being calculated to be 1.092 Å in C_4H_8 and becoming 1.086 in C_2H_4.[37] Since no erratic stretchings of the CH bond would be expected, an intermediate value of 1.089 Å was assumed. This also introduces a very small error (as can be verified by inspection of the calculated R_{CH} force constant).

There are three remaining variables of importance in D_{2h} symmetry. They are shown in Figure 7 which is a top view of the planar cyclobutane molecule which has undergone a rectangular distortion. In cyclobutane, $R_1 = R_2 = 1.550$ Å (calcd), $\beta = 45°$. In two ethylenes at large separation $R_1 = 1.334$ Å, $R_2 = \infty$, $\beta = 0$. For some regions of the potential surface, at each (R_1, R_2) pair several values of β were taken to find the minimum energy. When clear patterns had emerged, best interpolated values of β were used to arrive at the final potential surface given in Figure 8. The contours of this surface are based on the calculation of 50 *ab initio* points and on a detailed study of the surface using the CNDO/2 method as reparameterized by Fischer and Kollmar.[38] At the lower left corner lies cyclobutane, in the bottom of a flat potential well. Its CI energy is −155.839 au (thus the 2 × 2 CI is negligible, since cyclobutane without this CI has energy −155.837 au). The upper right corner, with $R_1 = 1.34$, R_2 = large, $\beta = 0$ represents two ethylenes, at energy −155.80 au. (This is a 2 × 2 CI calculation based on the $(\pi)^2$ function. Mixing with the doubly excited π^* is important and lowers the energy by 0.04 au over the single configuration function.) The end points, C_4H_8 and C_2H_4, contain no uncertainty in that they represent calculated minima in all (single configuration) relevant degrees of freedom. Moving away from cyclobutane along the dashed line, contours of increasing energy are crossed until a saddle point is encountered at energy −155.590 au (this number actually represents an upper bound to the energy of the barrier due to the difficulty of locating exactly the saddle point, the rough minimization of β, and the assumptions in R_{CH} and HCH angle, but it should be within 0.01 au of the correct value) for $R_1 = 1.42$ Å, $R_2 = 2.21$ Å, and $\beta = 15°$. This is the transition state for the rectangular decomposition. At the transition state, the excitation energy ΔE is approximately zero, *i.e.*, the configurations ψ_{AS} and ψ_{SA} give the same total energy and can thus be considered equally valid descriptions of the transition state. The locus of points for which $\Delta E = 0$ is shown by a dotted line. This line has the very interesting characteristic that it represents the *ridge* along a mountain range (energetically speaking) separating cyclobutane from two ethylenes. On the cyclobutane side of this ridge, the best single configuration description of the system uses the cyclobutane configuration, ψ_{AS}, and the lowest energy CI function for the ground state uses ψ_{AS} and its virtual orbitals. Using ψ_{AS}, the excitation energy

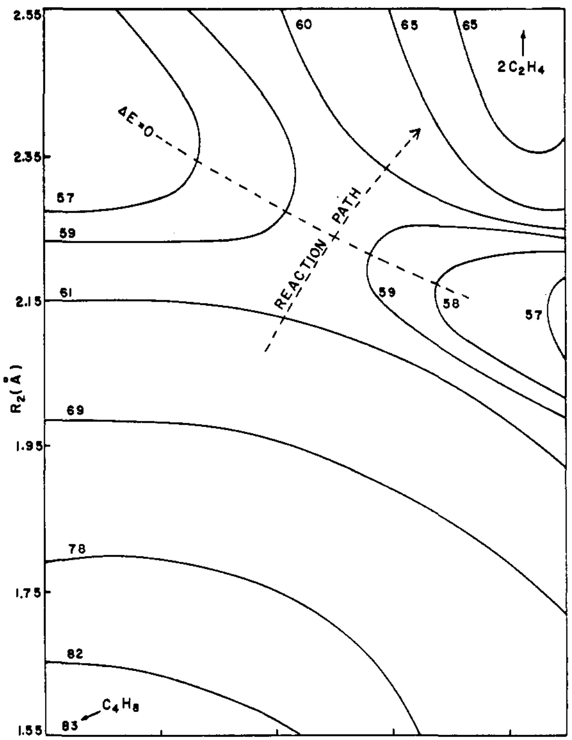

Figure 8. *Ab initio* potential surface for the rectangular decomposition.

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[37] Minimization of energy with respect to geometry for C_2H_4, using exponents as for cyclobutane, gave $R_{\text{CC}} = 1.322$, $R_{\text{CH}} = 1.086$, ∠HCH = 116°, and a total energy of −77.859 au. This compares well with the result of Switkes, Stevens, and Lipscomb[26] who found $E = -77.856$ at the experimental geometry.

[38] H. Fischer and H. Kollmar, *Theor. Chim. Acta*, 13, 213 (1969).

Table III. Orbital Energies along the Reaction Coordinate (au)

Cyclobutane			Transition state[a]		2 ethylenes		
	$1a_g$	-11.204	$1a_g$	$-11.194\ (-11.174)$	$1a_g$	-11.215	
	$1b_{2u}$	-11.204	$1b_{2u}$	$-11.194\ (-11.174)$	$1b_{2u}$	-11.215	
	$1b_{3u}$		$1b_{3u}$	$-11.193\ (-11.173)$	$1b_{3u}$	-11.213	
	$1b_{1g}$	-11.204	$1b_{1g}$	$-11.193\ (-11.173)$	$1b_{1g}$	-11.213	
	$2a_g$	-1.085	$2a_g$	$-1.002\ (-0.989)$	$2a_g$	-1.000	
	$2b_{2u}$	-0.870	$2b_{2u}$	$-0.927\ (-0.924)$	$2b_{2u}$		
	$2b_{3u}$		$2b_{3u}$	$-0.792\ (-0.782)$	$2b_{3u}$	-0.759	
	$2b_{1g}$	-0.717	$2b_{1g}$	$-0.736\ (-0.732)$	$2b_{1g}$		
π_{CH_2}	$1b_{1u}$	-0.635	$1b_{1u}$	$-0.608\ (-0.602)$	$1b_{1u}$	-0.614	σ_{CH}
σ_{CH_2}	$3a_g$	-0.614	$1b_{3g}$	$-0.568\ (-0.562)$	$1b_{3g}$		
π_{CH_2}	$1b_{2g}$	-0.519	$3a_g$	$-0.556\ (-0.547)$	$3a_g$	-0.548	σ_{CC}
	$1b_{3g}$		$3b_{2u}$	$-0.513\ (-0.504)$	$3b_{2u}$		
SS	$4a_g$	-0.467	$1b_{2g}$	$-0.485\ (-0.482)$	$1b_{2g}$	-0.472	σ_{CH}
π_{CH_2}	$1a_u$	-0.427	$1a_u$	$-0.453\ (-0.450)$	$1a_u$		
σ_{CC}	$3b_{2u}$	-0.406	$4a_g$	$-0.379\ (-0.395)$	$4a_{4g}$	-0.349	SS (π)
AS	$3b_{3u}$		$3b_{3u}$	$-0.143\ (+0.158)$	$4b_{2u}$		SA
$\pi^*_{CH_2}$	$2b_{1u}$	$+0.513$	$4b_{2u}$	$+0.144\ (-0.160)$	$3b_{3u}$	$+0.291$	AS (π^*)
SA	$4b_{2u}$	$+0.558$	$3b_{1g}$	$+0.380\ (+0.393)$	$3b_{1g}$		AA
	$4b_{3u}$		$2b_{1u}$	$+0.566\ (+0.574)$	$2b_{1u}$	$+0.593$	σ^*_{CH}
$\sigma^*_{CH_2}$	$5a_g$	$+0.613$	$2b_{3g}$	$+0.611\ (+0.619)$	$2b_{3g}$		
AA	$3b_{1g}$	$+0.626$	$4b_{3u}$	$+0.630\ (+0.643)$	$5a_g$	$+0.666$	σ^*_{CH}
	$2b_{2g}$	$+0.694$	$5a_g$	$+0.639\ (+0.639)$	$5b_{2u}$		
	$2b_{3g}$		$4b_{1g}$	$+0.679\ (+0.686)$	$4b_{3u}$	$+0.672$	σ^*_{CC}
	$5b_{2u}$	$+0.708$	$5b_{2u}$	$+0.695\ (+0.692)$	$4b_{1g}$		
	$5b_{3u}$		$2b_{2g}$	$+0.826\ (+0.837)$	$2b_{2g}$	$+0.912$	
	$4b_{1g}$	$+0.732$	$5b_{3u}$	$+0.826\ (+0.846)$	$2a_u$		
	$2a_u$	$+0.866$	$2a_u$	$+0.862\ (+0.872)$	$5b_{3u}$	$+0.956$	
	$5b_{1g}$	$+0.882$	$5b_{1g}$	$+0.872\ (+0.892)$	$5b_{1g}$		

[a] $R_1 = 1.42$ Å, $R_2 = 2.21$ Å, $\beta = 15°$.

ΔE for the double excitation goes from very large and positive ($\Delta E = +1.25$ au) at cyclobutane, to 0 at the transition state, to large and negative at two ethylenes ($E = -0.62$ au). Across the ridge, one falls downhill to two ethylenes and the best single configuration description is then ψ_{SA}. In MO terms, if for any point on the potential surface the configuration of two ethylenes becomes of lower energy than the cyclobutane configuration, then the system will decompose to two ethylenes. Thus one can say that to one side of this ridge the system is still cyclobutane, but once crossed it becomes two ethylenes. This is a multidimensional argument which corresponds to the orbital crossing expressed in the Woodward–Hoffmann diagram (Figure 6). A similar discussion has been given by Hoffmann, *et al.*,[21] for the two-step (tetramethylene) pathway.

At the beginning of this search of the potential surface, it was thought that the only way to find the transition state was to do a complete *n*-dimensional scan of the potential surface ($n = 3$ in this case) to locate the saddle point. This is because no optimization techniques can be used to search for saddle points; in fact, this is precisely what they avoid. However, from our potential surface it is seen that along the locus of points $\Delta E = 0$ lies a minimum, and this minimum lies very near the transition state. Thus an arbitrary search for the transition state of a Woodward–Hoffmann forbidden concerted pathway could be transformed into the following, much simplified procedure:[39] (1) Search for a point on the potential surface which has $\Delta E = 0$. (2) Do parabolic coordinate variations about this point, such that the condition $\Delta E = 0$ is preserved, and the energy decreases.

Thus one follows this path to the transition state. This corresponds to sliding down a ridge to the saddle point, while being constrained to stay on the ridge. Experience now gained in this laboratory on diverse reaction surfaces and the studies of Hoffmann and coworkers shows that if an orbital crossing is necessary to go from reactant to product, then the region of orbital crossing will very likely be at or near the transition state. This is easily understood in that the energy lowering due to CI is a maximum precisely in this region.

Once the reaction path is established along the potential surface, there is much interesting information to be obtained from it. The *reaction coordinate* corresponds to following this path, *i.e.*, moving along the deepest part of the valley which leads to the saddle point. Table III gives the orbital energies for reactant, transition state, and product, together with their D_{2h} symmetry species and chemical type. For the transition state, orbital energies are given for configuration ψ_{AS} and in parentheses for ψ_{SA}.[40] It can be seen in the transition state that except for the highest occupied and lowest vacant orbitals, the rest of the MO's are essentially unchanged in the two configurations. This is no doubt due to the large energy gap separating them from the "frontier" orbitals $3b_{3u}$ and $4b_{2u}$. Since Table III gives the symmetry species of two widely separated ethylenes (third column in the Table), orbital symmetry correlations can be followed by moving from left to right across the table, while following the individual symmetry species. Although there are significant variations in orbital energies among many of the orbitals, the most dramatic variation occurs with the $3b_{3u}$ and $4b_{2u}$ orbitals. A plot of these orbital

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(39) The actual transition state for the reaction will generally correspond to a much lower energy two-step pathway.

(40) The notation used here can be confusing, since AS refers both to an orbital type ($3b_{3u}$) and to the configuration ψ_{AS} which contains the doubly occupied $3b_{3u}$ orbital.

energies as a function of reaction coordinate would reveal the characteristic orbital crossing discussed by Woodward and Hoffmann.[20] The $4b_{2u}$ (SA) orbital, for instance, changes in energy from −0.35 au in two ethylenes, to −0.16 au at the transition state, to +0.56 au in cyclobutane. The change of this MO (and the corresponding $3b_{3u}$ orbital) is clearly the dominant feature of the orbital correlation diagram and will make the principal contribution to the activation energy for the rectangular decomposition.

To discuss the variation in state energies along the reaction path, we add two intermediate points: one has R_1 = 1.44 Å, R_2 = 1.95 Å, β = 30°, and is therefore closer to cyclobutane; the other has R_1 = 1.33 Å, R_2 = 2.45 Å, β = 0°, which is a structure approaching two ethylenes. For representational purposes, a simplified reaction coordinate is used; namely, the $P\sigma\sigma$ overlap between two approaching (undistorted) ethylenes.[41] From the energies of these two points and those of cyclobutane, the transition state, and two ethylenes, we obtain the configuration and state correlation diagrams shown in Figure 9. The two configurations in the diagram are labeled ψ_{AS} and ψ_{SA}. Referring to cyclobutane (right-hand side of diagram), the single configuration ψ_{AS} has energy $E = -155.837$ au. The ground (Ψ_I) and doubly excited (Ψ_{II}) *states* formed from this configuration have energies −155.839 and −154.583 au, respectively. Proceeding toward two ethylenes, at the transition state we find $\psi_{AS} = \psi_{SA} = -155.50$ au, $\Psi_I = 155.59$ au, and $\Psi_{II} = -155.41$ au. For an isolated ethylene molecule $\psi_{SA} = -77.859$ au, $\psi_{AS} = -77.237$ au (this is the *doubly* excited $(\pi^*)^2$ state, where both electrons in a π orbital have been promoted), $\Psi_I = -77.8977$ au and $\Psi_{II} = -77.1966$ au. The Ψ_I indicated in Figure 9 is thus twice −77.8977 or −155.795 au, whereas Ψ_{II} is given by −77.8977 − 77.1966 = 155.094 au. The stabilization due to configuration interaction at the transition state is seen to be large, about 0.09 au or 56 kcal/mol when compared to the energy of the intended crossing at the AS–SA intersection.

Seen from the side of two ethylenes, the potential barrier of 0.205 au (5.57 eV or 128 kcal/mol) agrees well with the Woodward–Hoffmann prediction that the activation energy for the reaction $2C_2H_4 \rightarrow C_4H_8$ along this path is about the energy needed to raise two π electrons to a nonbonding level, or 5 eV.

For the reaction in the reverse direction, $C_4H_8 \rightarrow 2C_2H_4$, we find a barrier height of (+155.839 − 155.590) = 0.249 au, or 156 kcal/mol. To obtain an activation energy, zero point differences should be corrected. Vibrational frequencies for cyclobutane are known[10] (and also for ethylene[33]) and could be estimated for the transition state using the methods of Benson.[19b] However, since the total zero point energy of cyclobutane is only 0.214 au and many vibrational modes in the transition state would change their values only slightly relative to cyclobutane, inclusion of ZPE would constitute only a small refinement to the calculated barrier height. Thus for the reaction $C_4H_8 \rightarrow 2C_2H_4$ along the rectangular decomposition path, our calculated activation energy is 156 kcal/mol.

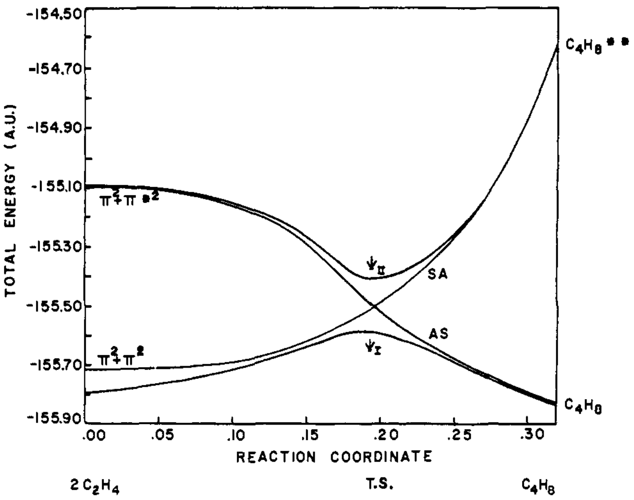

Figure 9. Configuration and state correlation diagram from the *ab initio* calculation.

The experimental results of Walters, *et al.*,[14] and of Frey[15] show an activation energy of about 62 kcal/mol for the thermal (400°) decomposition of cyclobutane. This shows rather convincingly that the reaction does not proceed along a rectangular decomposition path, a fact which has been known experimentally for some time. Whether the reaction actually proceeds in two steps *via* a biradical tetramethylene or in a concerted 2s + 2a fashion is currently of much interest. We hope to be able to distinguish by this type of calculation which is the real reaction path, and further studies to this effect are in progress.

Acknowledgment. The authors thank Dr. R. M. Stevens for providing them with the *ab initio* program used for the calculations and the CNRS for a generous grant of computer time at Orsay.

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(41) This coordinate has been used in previous studies of the approach of two ethylene molecules. See L. Salem and A. Devaquet, *J. Amer. Chem. Soc.*, 90, 543 (1968).