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Semiempirical MO Calculations on Symmetry Governed Reactions*

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Two symmetry governed reactions, the electrocyclic transformation of planar cyclopropyl cation to allyl cation and the dimerization of ethylene to cyclobutane, are examined using a modified INDO method. Results for the cyclopropyl-allyl cation reaction agree well with previously published *ab initio* results, and are much improved over previously published CNDO results. The symmetry-allowed disrotatory path is predicted to be significantly favored over the forbidden conrotatory transition. For the ethylene-cyclobutane system two surprising results are predicted within the constraints imposed upon the reaction path: first, that the entire reaction should occur within a small range in the separation of the two ethylene molecules as they approach one another, and second, that the symmetry-forbidden $[2_s + 2_s]$ addition should be slightly favored over the symmetry-allowed $[2_s + 2_a]$ addition. Since the Woodward-Hoffmann rules deal exclusively with changes in electronic energy, it is suggested that they should be applied with some caution to reactions in which changes in nuclear repulsion are quite large during the reaction process.

Key words: Cyclopropyl cation – Allyl cation – Ethylene dimerization – Cyclobutane – Symmetry governed reactions

1. Introduction

The publication of a series of communications in 1965 by Woodward and Hoffmann [1–3] and by Longuet-Higgins and Abrahamson [4] laid the groundwork for a comprehensive theory of concerted chemical reaction. Although the above authors argued on the basis of the energy of the highest occupied orbital of the reactant [1] or using correlation diagrams [2, 4], the same conclusions have been reached on the basis of perturbation theory [5–11], the valence bond method [12], and a symmetry argument concerning a Mobius twist in an olefinic ring [13]. Other pertinent references may be found in a paper by Woodward and Hoffmann [14].

The total energy of a molecular system may be partitioned as

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{nuclear}}$$

where $E_{\text{electronic}}$ includes the kinetic and potential energy of the electrons and E_{nuclear} is the nuclear-nuclear repulsion energy. The change in energy at any point during a reaction may be similarly partioned as

$$\Delta E_{\text{total}} = \Delta E_{\text{electronic}} + \Delta E_{\text{nuclear}} .$$

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* Dedicated to Professor H. Hartmann on his sixtieth birthday.

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Consider two possible concerted paths for a particular reaction, 1 and 2. We may further define

$$\begin{aligned}\Delta\Delta E_{\text{total}} &= \Delta\Delta E_{\text{electronic}} + \Delta\Delta E_{\text{nuclear}}\\ &= (\Delta E^1_{\text{electronic}} - \Delta E^2_{\text{electronic}})\\ &\quad + (\Delta E^1_{\text{nuclear}} - \Delta E^2_{\text{nuclear}})\,.\end{aligned}$$

Path 1 will be favored at any given point if $\Delta\Delta E_{\text{total}}$ is negative, while path 2 will be favored if $\Delta\Delta E_{\text{total}}$ is positive. All of the above-mentioned approaches to concerted reactions estimate the sign of $\Delta\Delta E_{\text{total}}$ by considering only $\Delta\Delta E_{\text{electronic}}$. Conclusions as to whether path 1 or 2 will be energetically favored will be valid only if $\Delta\Delta E_{\text{nuclear}}$ is not of opposite sign to and of greater absolute magnitude than $\Delta\Delta E_{\text{electronic}}$.

That ignoring $\Delta\Delta E_{\text{nuclear}}$ is generally justified is supported by the great amount of experimental data that has been explained [14]. We wish to sound a note of warning however; we believe that this implicit assumption is much better justified in reactions wherein differences in nuclear arrangements between the two paths are relatively minor, than in reactions wherein the differences are large. The possibility of symmetry-forbidden reactions being favored over symmetry-allowed reactions has also been discussed by Baldwin, Andrist, and Pinschmidt [15] and by Berson [16].

We have examined two simple concerted reactions, the intramolecular transformation of cyclopropyl cation to allyl cation and the intermolecular dimerization of ethylene to cyclobutane, using a modified INDO method described previously [17]. The calculations are in clear agreement with the Woodward-Hoffmann rules for the intramolecular electrocyclic reaction; for the intermolecular cycloaddition our calculations predict however that within the constraints we have imposed upon the reaction path the symmetry-forbidden reaction will be favored over the symmetry-allowed.

2. Method

We have previously derived [17] the following approximation for the off-diagonal core hamiltonian integral H_{ab} in zero-differential-overlap MO theories, based on an interpretation of the basis set as symmetrically orthogonalized [18] and on the commutator equation $[\underline{r}, h] = \underline{p}$, where $\underline{r}$ is the dipole operator, h is the hamiltonian operator, and $\underline{p}$ is the linear momentum operator:

$$H_{ab} = S_{ab}/2\left[\frac{K_A+K_B}{2}(H_{aa}+H_{bb}) + \frac{1}{1-S_{AB}^2}\,\frac{\varrho_B-\varrho_A}{\varrho_A+\varrho_B}(H_{aa}-H_{bb})\right] + \frac{1}{R}\,\frac{dS_{ab}}{dR}\,. \quad (1)$$

S_{ab} is the overlap integral between orbitals a and b, S_{AB} is the $s-s$ overlap between orbitals on A and B, H_{aa} and H_{bb} are the diagonal core hamiltonian elements, and R is the A–B distance, with orbital a centered on atom A and orbital b on atom B. ϱ_A and ϱ_B are slightly modified Schomaker-Stevenson single bond covalent radii [19], and K_A and K_B are adjustable parameters chosen to reproduce the binding energies of homonuclear diatomic molecules. Values used for ϱ_A

and K_4 may be found in Ref. [17]. Introduction of this formula into the INDO method [20] led to a striking improvement in bond energies and force constants and even to some improvement in bond lengths, ionization potentials, and dipole moments for a series of twenty-two first row diatomics.

Certain complicating factors arise in an extension to polyatomic systems. First, it is necessary to insure that three-center terms are treated properly in computing H_{ab}. All three-center terms are set equal to zero in the original INDO method. To be consistent, we also neglect three-center terms; we take H_{aa} and H_{bb} in (1) to include only nuclear attraction terms from atoms A and B. Second, certain terms neglected in the derivation of (1) become relatively more important at large distances. Jug [21] has shown that the absolute value of H_{ab} for non-nearest neighbors will generally be reduced compared to that calculated from (1) if these terms are included. In the interest of simplicity we have not differentiated between nearest and non-nearest neighbors. Such differentiation would pose problems of continuity in a chemical reaction as the roles of nearest and non-nearest neighbors reversed. Furthermore, the effects of higher terms on the total energy are very small. In problems where values of non-nearest neighbor H_{ab} terms would be expected to be crucial however (e.g. small changes in bond angles) our simplistic approach would probably not be adequate. Fortunately however the neglect of three-center terms and the neglect of higher terms in the derivation of (1) work in opposite directions, so that we can expect some cancellation of errors.

3. The Cyclopropyl-Allyl Cation Transformation

Extended Hückel calculations on the electrocyclic transformation of planar cyclopropyl cation to allyl cation have been performed by Kutzelnigg [22], MINDO/2 calculations by Dewar and Kirschner [23], modified CNDO/2 calculations by Clark and Smale [24], and small Gaussian basis set *ab initio* calculations by Clark and Armstrong [25]. After completion of this work, we learned of extensive *ab initio* studies by Merlet, Peyerimhoff, Buenker, and Shih [26] and by Radom, Hariharan, Pople, and Schleyer [27]. The two reaction modes are illustrated in Fig. 1. The conrotatory mode is symmetry-forbidden under the Woodward-Hoffmann rules while the disrotatory mode is allowed. In the conrotatory mode symmetry requires that the highest occupied orbital of cyclopropyl cation correlate with the lowest unoccupied orbital of allyl cation and *vice versa*, whereas in the disrotatory mode all occupied orbitals in the product correlate with occupied orbitals in the reactant (cf. Fig. 2).

The geometries assumed in the CNDO/2 [24] and *ab initio* [25] calculations are presented in Fig. 3. All bond lengths and angles were assumed to change linearly as a function of the angle of rotation of a line connecting H_2 and H_3 with respect to the plane of the carbon atoms. Calculations were performed at 15° intervals in this rotation.

Since the CNDO/2 calculations predict cyclopropyl cation to be less stable than allyl cation by more than 400 kcal/mole, in contrast to the experimental value of ~25 kcal/mole [28], we shall not review the results in any detail. The *ab initio* calculations predict cyclopropyl cation to be less stable by 64 kcal/mole.

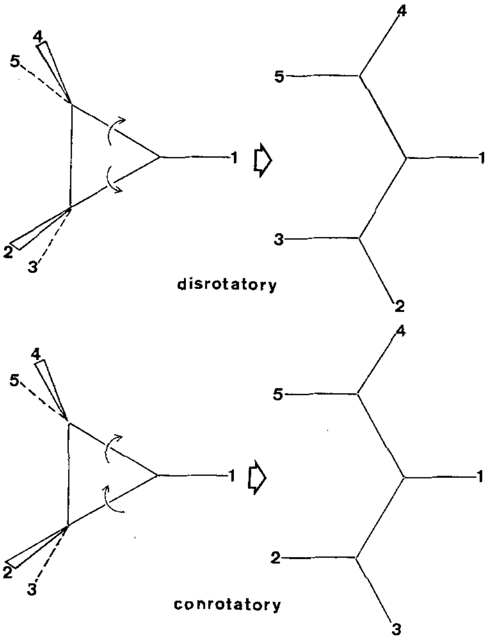


Fig. 1. The disrotatory and conrotatory modes for the electrocyclic transformation of planar cyclopropyl cation to allyl cation

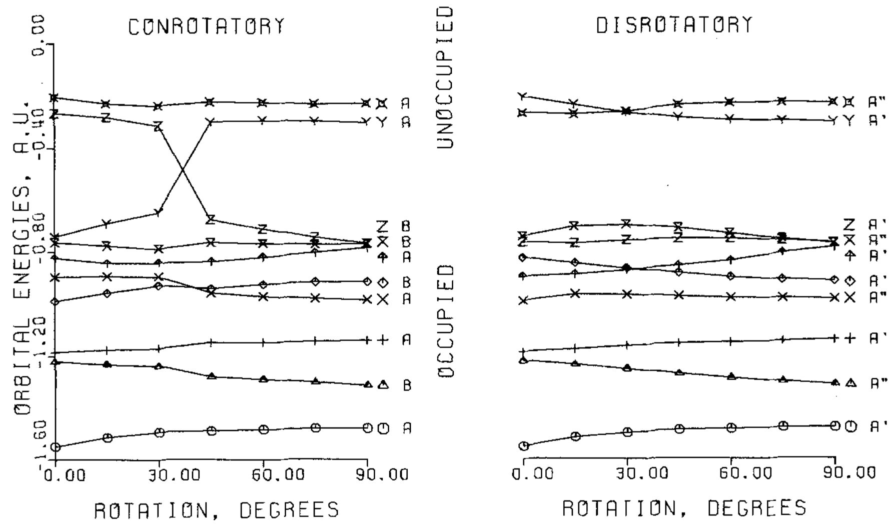


Fig. 2. Correlation diagrams for the conrotatory and disrotatory modes of the cyclopropyl-allyl cation transformation, as calculated using our modified INDO method. Orbitals are labeled with respect to the axis of symmetry for the conrotatory mode and with respect to the plane of symmetry for the disrotatory mode

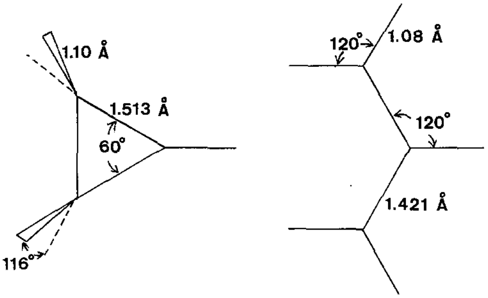


Fig. 3. The geometries assumed by Clark and Smale[24] and by Clark and Armstrong[25] for cyclopropyl and allyl cations. In each cation all C–H and C–C distances have been taken as identical

Energy plots for the *ab initio* calculation are presented in Fig. 4, showing a sizable barrier of ~53 kcal/mole for the conrotatory mode but none at all for the disrotatory mode.

The *ab initio* work of Merlet *et al.* [26] and the MINDO/2 calculations of Kirschner and Dewar [23, 29] both predict that rotation of the two methylene groups is abrupt in the forbidden conrotatory mode and gradual in the allowed disrotatory mode. Kirschner and Dewar [29, 30] have further raised the very interesting question of "chemical hysterisis". They suggest that the conrotatory reaction follows different paths for the forward and reverse reactions. Rather than consider these complexities, we have chosen to follow a modified version of the simple path assumed by Clark and Smale [24] and by Clark and Armstrong [25] for the following reasons:

1. Partitioning of $\Delta\Delta E_{\text{total}}$ into $\Delta\Delta E_{\text{electronic}}$ and $\Delta\Delta E_{\text{nuclear}}$ is much more attractive if the paths for the disrotatory and conrotatory modes are as similar as possible.

2. We wish to demonstrate the efficacy of our modified INDO method [17]. We feel that this can best be done by comparison with minimal or small basis set *ab initio* calculations, such as the work of Clark and Armstrong [25], and with CNDO or INDO calculations, such as the work of Clark and Smale [24].

We repeated the calculations at the same geometries as in Fig. 3 using our modified INDO method. Although the results were far superior to the CNDO/2 calculations, disturbing minima appeared in both the forbidden and allowed paths, and an incorrect ordering of the energies of the two species was predicted, with cyclopropyl cation more stable by 12 kcal/mole.

In an effort to remedy the situation, a partial optimization of the geometries of the two cations was effected. The C–H bond distance was set equal to the calculated equilibrium distance in the CH molecule, 1.195 Å [17]. All bond angles were kept as in Fig. 3, and the C–C distances were varied so as to minimize the energy. This gave a C–C distance of 1.665 Å in cyclopropyl cation and of 1.560 Å in allyl cation. All bond distances and angles were again varied linearly as a function of the angle of rotation. An energy plot is given in Fig. 5.

Also included in Fig. 5 are the results of a configuration interaction calculation for the conrotatory mode involving single and double excitations from the highest occupied to the lowest unoccupied orbital. It is well known that changes in cor-

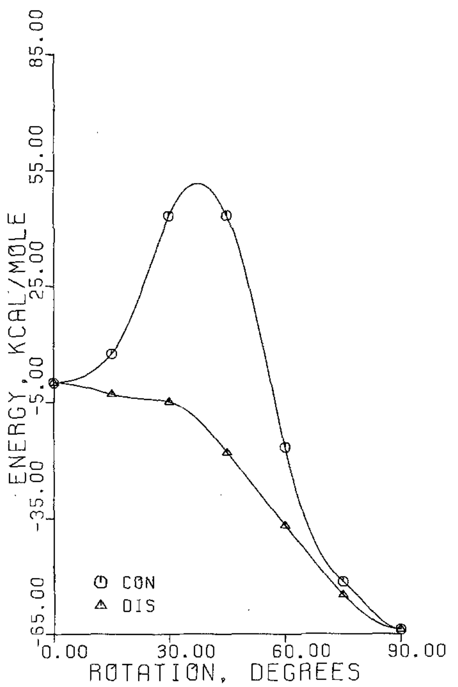


Fig. 4

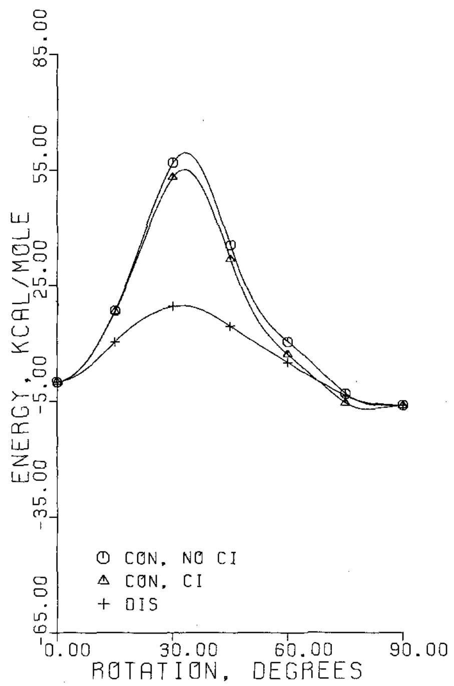


Fig. 5

Fig. 4. Plot of energy *vs.* angle of rotation for the conrotatory and disrotatory modes for the *ab initio* results of Clark and Armstrong[25]. The energy of cyclopropyl cation is taken as 0. In this and in all other energy *vs.* reaction coordinate plots presented in the work, curves have been generated by fitting the indicated points to polynomials in piecewise sections, and values between points are therefore not exact. Effects of orbital crossings are not shown

Fig. 5. Plot of energy *vs.* angle of rotation for the conrotatory mode with and without configuration interaction and for the disrotatory mode, using our modified INDO method and partially optimized geometries. The energy of cyclopropyl cation is taken as 0

relation energy are important in molecular dissociation; the simplest example of this is the dissociation of H_2 to products whose energy is the average of the energies of $(H^+ + H^-)$ and of $(2H^\cdot)$. It is apparent from Fig. 2 that in the conrotatory mode a C–C σ bond is being broken prior to the orbital crossing point, and that the π system of allyl cation is being formed subsequent to the orbital crossing point. These two processes do not occur simultaneously for a symmetry-forbidden reaction within the orbital approximation (i.e., in a single determinantal wave function). The highest occupied orbital is either of A or of B symmetry and never a combination of the two. As the σ bond ruptures, there will be an increase in correlation energy, peaking at the orbital crossing point. There is no such increase for a symmetry-allowed reaction. In the disrotatory transformation shown in Fig. 2 all occupied orbitals in the reactant correlate with occupied orbitals in the product. Bond breaking and forming can consequently occur simultaneously, and there is little change in correlation during the process.

The results shown in Fig. 5 are encouraging. The geometry optimization has removed the minima in the two modes, and the correct order of stability is pre-

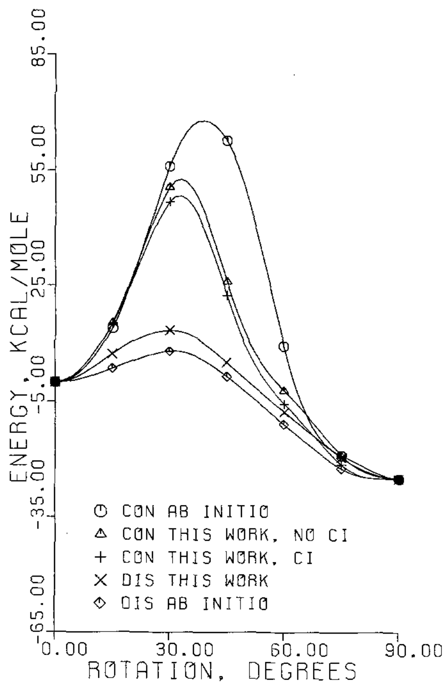


Fig. 6. Plot of energy *vs.* angle of rotation for the curves of Figs. 4 and 5 after scaling to the experimental energy difference of 25 kcal/mole between cyclopropyl cation and allyl cation. The energy of cyclopropyl cation is taken as 0

dicted, with allyl cation more stable by 6 kcal/mole. The barrier for the conrotatory mode is calculated as ~59 kcal/mole and is lowered to ~55 kcal/mole by the configuration interaction calculation. A barrier for the disrotatory mode of ~20 kcal/mole is predicted. We have adopted a somewhat arbitrary procedure to compare our calculations with the *ab initio* results. For both calculations we have added or subtracted an energy increment to the calculated energy of allyl cation so that the experimental difference of 25 kcal/mole is duplicated, and have added or subtracted $\theta/90$ of this increment to each point along the reaction path, where θ is the angle of rotation. Figure 6 is the resultant. Despite the arbitrariness of this procedure, it does seem to indicate that a maximum in the disrotatory mode is not inconsistent with the *ab initio* results. The same conclusions would apply to the work of Radom *et al.* [27], which predicted cyclopropyl cation to be more stable than allyl cation by 39 kcal/mole and predicted no energy barrier for the disrotatory mode. Dewar and Kirschner [23] and Merlet *et al.* [26] predict an energy barrier for the disrotatory mode. The former cite experimental [31] evidence that this may indeed be the case.

4. The Dimerization of Ethylene

Calculations on the ethylene dimerization are more complicated. Since the starting point for the reaction is two ethylene molecules at infinity, no smooth

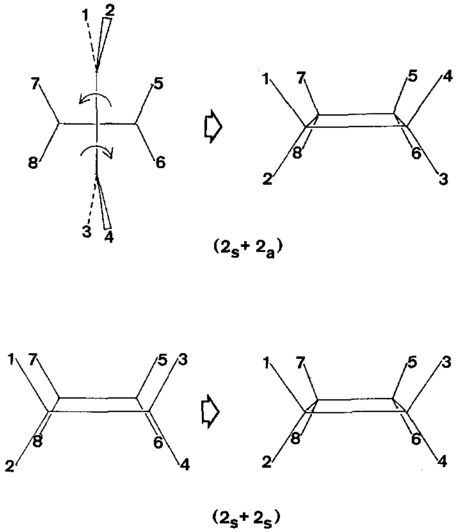
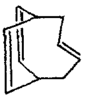
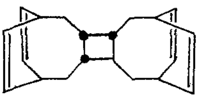


Fig. 7. The $[2_s+2_s]$ and $[2_s+2_a]$ modes for the reaction 2 ethylene → cyclobutane

linear transition in geometry to cyclobutane is possible. There are two modes of reaction of interest, the symmetry-forbidden $[2_s+2_s]$ and the symmetry-allowed $[2_s+2_a]$. These are illustrated in Fig. 7. The $[2_s+2_s]$ reaction involves a simple approach of the two ethylene molecules keeping all four carbons coplanar, while the $[2_s+2_a]$ requires a complicated twisting of one of the ethylene molecules. To our knowledge, experimental evidence for unstrained thermal $[2_s+2_a]$ cycloadditions is still lacking. Woodward and Hoffmann [14] cite the fact that pyrolysis of *cis*- or *trans*-dimethylcyclobutane yields a mixture of *cis*- and *trans*-butenes [32] as possible evidence, but admit that the experimental evidence [33] seems to favor a diradical mechanism rather than a concerted process. In the same work, Woodward and Hoffmann cite an example of a strained $[2_s+2_a]$ cycloaddition, the spontaneous dimerization of olefin I to II [34], but point out that the twisting of the double bond about its axis will cause the $[2_s+2_a]$ path to be distinctly favored. The spontaneous dimerization of *cis, trans*-cycloocta-1,5-diene (III) yields predominantly the symmetry-forbidden *trans, trans (syn)* product (IV) [35]. The ratio of forbidden to allowed product is 11:4, indicating that even in this strained system the $[2_s+2_a]$ concerted mode is not a favorable path.



I



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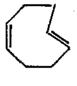
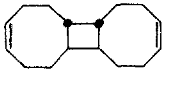


III



IV

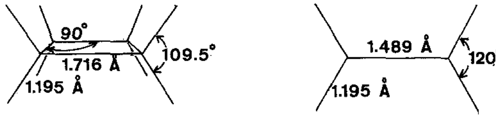


Fig. 8. Partially optimized geometries for ethylene and cyclobutane, as calculated by our modified INDO method

An *ab initio* surface for the $[2_s + 2_s]$ mode has been reported by Wright and Salem [36] and an Extended Hückel surface for a non-concerted tetramethylene mechanism by Hoffmann and coworkers [37]. Fischer and Kollmar [38] report that CNDO/2 calculations predict cyclobutane to be 360 kcal/mole more stable than two ethylene molecules, in contrast to the experimental value of 16 kcal/mole. Based on our experience with geometry optimization in the cyclopropyl-allyl cation transformation, we optimized the C–C bond distances in ethylene and cyclobutane, taking all C–H distances as 1.195 Å. We have taken cyclobutane as planar; *ab initio* results [36] predict an energy difference of only 1.44 kcal/mole relative to the equilibrium puckered structure, so that this should cause no serious errors. The resulting geometries are given in Fig. 8. Using these geometries, cyclobutane was predicted to be 24 kcal/mole more stable than two ethylene molecules, in good agreement with experiment and with the *ab initio* [36] result of 27 kcal/mole. We assumed a linear change in all other bond lengths and angles as a function of the ethylene C–C bond distances, which were constrained to be equal and were varied so as to minimize the energy at each point in the separation of the two ethylene molecules. Surprisingly, the calculations predict that to a very good approximation (~ 1 kcal/mole) the system may be regarded as two undistorted ethylene molecules at a separation greater than 2.1 Å and as a cyclobutane with two of its C–C bonds stretched at less than 2.0 Å. In other words, all changes in the geometry of the two ethylene molecules may be regarded as occuring within a very small range. The $[2_s + 2_s]$ surface reported by Wright and Salem [35] also displays this division into ethylene and cyclobutane regions. Since this was found to be the case for both the $[2_s + 2_s]$ and for the $[2_s + 2_a]$ mode only this simplified surface will be reported.

We present a plot of energy vs. the separation of the two ethylene molecules for the two modes in Fig. 9. Again, a configuration interaction calculation was performed for the symmetry-forbidden mode, involving single and double excitations from the highest occupied to the lowest unoccupied orbital. Despite the fact that the $[2_s + 2_s]$ reaction is symmetry-forbidden while the $[2_s + 2_a]$ is symmetry-allowed, the $[2_s + 2_s]$ path is predicted to be preferred at a separation of greater than 2.0 Å. At at separation of less than 2.0 Å the two modes are equivalent within the approximate paths considered here. Although the $[2_s + 2_a]$ path at 2.1 Å lies less than 2 kcal/mole above the $[2_s + 2_s]$ path for the single determinantal calculation, it lies a full 12 kcal/mole above the path including configuration interaction. Changes in correlation energy seem to be more important here than in the cyclopropyl-allyl cation system. Configuration interaction lowered the barrier in the symmetry-forbidden mode 10 kcal/mole for the dimerization of ethylene and only 4 kcal/mole for the cyclopropyl-cation transformation. It is possible that this may be generally true for addition reactions compared to electro-

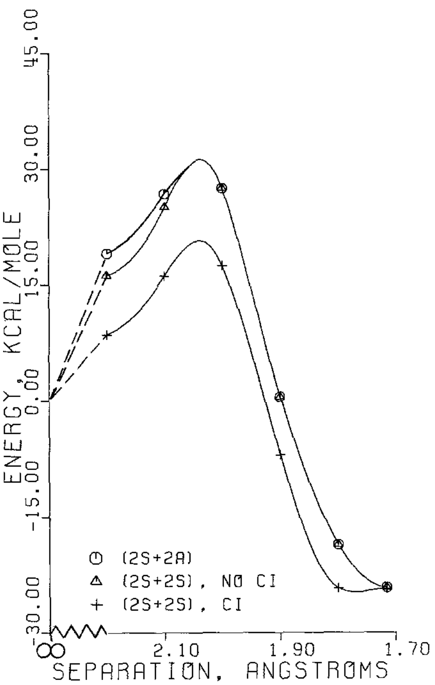


Fig. 9. Plot of energy *vs.* separation of the two ethylene molecules for the $[2_s+2_s]$ mode with and without configuration interaction and for the $[2_s+2_a]$ mode, using our modified INDO method. The energy of two ethylene molecules at infinity is taken as 0

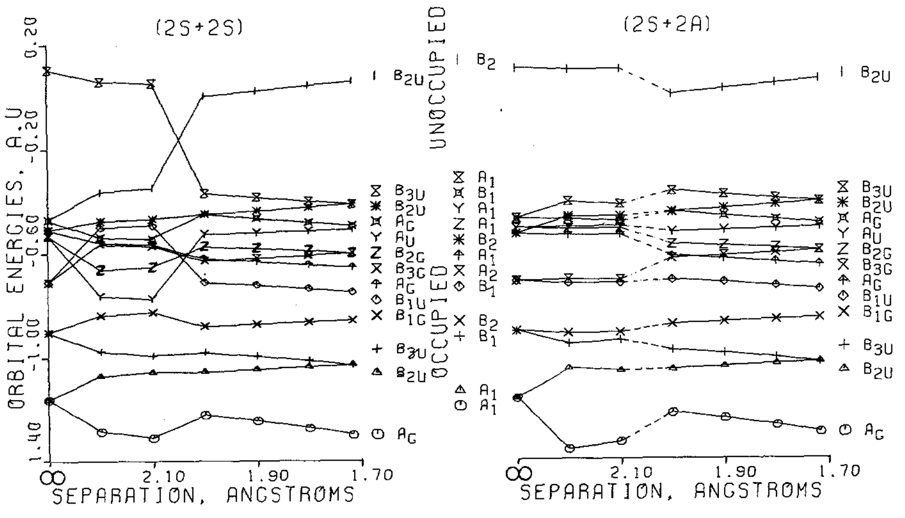


Fig. 10. Correlation diagram for the $[2_s+2_s]$ and $[2_s+2_a]$ modes, as calculated using our modified INDO method. For the $[2_s+2_s]$ mode orbitals are labeled according to D_{2h} symmetry. Since the symmetry is broken during reaction by the $[2_s+2_a]$ mode, no correlation diagram may strictly be constructed. Within the approximate paths we have examined here however, C_{2v} symmetry is maintained at separations greater than 2.1 Å and D_{2h} symmetry at separations less than 2.0 Å

Table 1

Cyclopropyl → allyl cation			2 ethylene → cyclobutane		
θ deg.	$\Delta\Delta E_{\text{electronic}}$ kcal/mole	$\Delta\Delta E_{\text{core repulsion}}$ kcal/mole	R Å	$\Delta\Delta E_{\text{electronic}}$ kcal/mole	$\Delta\Delta E_{\text{core repulsion}}$ kcal/mole
0	0	0	∞	0	0
15	−13.58	+ 7.39	2.2	−414.29	+417.14
30	−52.64	+14.70	2.1	−407.76	+409.46
45	−39.38	+18.44	2.0	0	0
60	−18.05	+12.60	1.9	0	0
75	− 3.72	+ 3.12	1.8	0	0
90	0	0	1.716	0	0

$\Delta\Delta E$ is defined as $(\Delta E^{\text{disrotatory}} - \Delta E^{\text{conrotatory}})$ for the cyclopropyl-allyl cation transformation and as $(\Delta E[2_s + 2_a] - \Delta E[2_s + 2_s])$ for the ethylene-cyclobutane system.

cyclic reactions. The geometric changes are greater in an addition reaction, and bond breaking may go farther before bond forming begins.

We present a correlation diagram for the dimerization of ethylene in Fig. 10. It is apparent that $\Delta\Delta E_{\text{electronic}}$ as defined in the introduction to this work should favor the $[2_s + 2_a]$ mode. We present in Table 1 $\Delta\Delta E_{\text{electronic}}$ and $\Delta\Delta E_{\text{core repulsion}}$ for both the electrocyclic and the cycloaddition reactions, where $\Delta\Delta E_{\text{core repulsion}}$ includes inner shell electrons in our valence electron calculations. Although $\Delta\Delta E_{\text{electronic}}$ favors the $[2_s + 2_a]$ path by more than 400 kcal/mole at a separation of 2.1 Å, this is more than compensated by $\Delta\Delta E_{\text{core repulsion}}$. The large values of $\Delta\Delta E_{\text{electronic}}$ and $\Delta\Delta E_{\text{core repulsion}}$ for the cyclopropyl-allyl cation transformation should be compared to the relatively small values for the dimerization of ethylene. We believe this supports our suggestion that focusing exclusively on $\Delta\Delta E_{\text{electronic}}$ may be of questionable validity if the nuclear configurations differ greatly between the two paths.

5. Conclusions

We wish to summarize briefly the conclusions we draw from this work:

a) That the agreement between the *ab initio* results of Clark and Armstrong [25] and the calculations of this work, and the marked improvement over CNDO/2 results [24], support the use of formula (1) in zero-differential-overlap methods.

b) That configuration interaction or some other method of accounting for electronic correlation is necessary for symmetry-forbidden reactions, particularly for cycloaddition reactions.

c) That conclusions drawn concerning a preference for one path in a concerted reaction over another may not be valid if there are major differences in nuclear configuration between the two paths.

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