

Finally we note that the peptides studied in this paper are not sufficiently long to adopt a stable helical structure. This contention is supported by the similarity of the VCD spectra of the dimer and trimer of alanine. Consequently our interpretation of the data has focused on the local environment of the individual chiral centers and not upon any long-range helical effects as considered in the earlier theoretical models of vibrational optical activity.<sup>19</sup>

## V. Conclusions

We have demonstrated that VCD can combine the structural sensitivity of vibrational spectroscopy with the stereochemical and configurational sensitivity of chiroptical techniques. The new spectra are more sensitive to structural details than ordinary vibrational spectra, but currently they are more subtle and difficult to interpret. In this study we have approached the problem of interpretation on a qualitative basis by investigating a group of closely related simple molecules. The major features of the VCD spectra appear to be compatible with some simple interpretive arguments, but verification of these ideas must await further experimentation or theoretical computation.

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## Ground States of Molecules. 49.<sup>1</sup> MINDO/3 Study of the Retro-Diels–Alder Reaction of Cyclohexene

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**Abstract:** The retro-Diels–Alder reaction of cyclohexene to form ethylene and butadiene has been studied, using MINDO/3. The transition state is predicted to be very unsymmetric, corresponding to weakening of one of the two breaking CC bonds. The calculated entropy of activation agrees well with experiment and the calculated secondary isotope effects for 4,4-dideuteriocyclohexene and 4,4,5,5-tetradeuteriocyclohexene are similar to those measured for an analogous reaction by Taagepera and Thornton. Discrepancies between the conclusions reached here and those from recent ab-initio calculations are discussed.

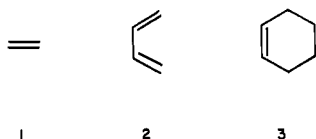
## Introduction

A major problem in studies of chemical reactions is to determine the timing of the bond breaking and bond forming processes that occur during them. The course of a reaction cannot be followed directly by any available experimental technique, so conclusions concerning mechanistic details of this kind can be drawn only very indirectly from experiment. This is an area where theoretical calculations would be especially useful, if they could be carried out by procedures able to give reliable results of sufficient accuracy.

One of the most striking examples is provided by the Diels–Alder reaction, whose detailed mechanism is still unknown after more than 40 years work by numerous investigations.<sup>3</sup> Opinion has vacillated concerning the timing of the formation of the two new bonds in reactions of this kind, from one extreme where the reaction is regarded as completely

synchronous to the other extreme where it is supposed to occur in steps via an intermediate biradical or zwitterion.<sup>3</sup> In recent years the former view seems to have been generally favored, partly as a result of the views expressed by Woodward and Hoffmann and partly on the basis of experimental studies of secondary deuterium isotope effects<sup>4</sup> and rates of reaction of anthracene derivatives.<sup>5</sup> However, none of these arguments are unequivocal.

Various attempts have been made from time to time to study the Diels–Alder reaction theoretically, but until recently the methods available have been far too inaccurate to lead to useful conclusions. Thus early CNDO<sup>6</sup> studies of the prototype reaction, ethylene (1) + 1,3-butadiene (2) → cyclohexene (3), predicted it to occur without activation. The situation has now changed with the development of computers able to handle RH (Roothaan–Hall; “ab initio SCF”)<sup>7</sup> calculations for systems of this size and of semiempirical procedures (MINDO/2;



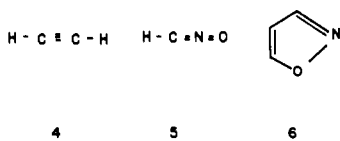
MINDO/3; MNDO)<sup>8</sup> able to give results of at least comparable accuracy.

The first calculation of this kind was one by McIver and Komornicki,<sup>9</sup> again on the basic reaction  $1 + 2 \rightarrow 3$ , using MINDO/2. By enforcing  $C_s$  symmetry throughout, they were able to find a stationary point on the potential surface corresponding to the transition state for completely synchronous addition. However diagonalization of the corresponding Hessian (force-constant) matrix showed it to have *two* negative eigenvalues, indicating that the point was not a transition state on the MINDO/2 potential surface.<sup>10</sup> The less negative root corresponded to an antisymmetric imaginary vibration, removing  $C_s$  symmetry and strengthening one of the new CC bonds while weakening the other. While the true transition state for the reaction was not located, McIver<sup>10</sup> generalized this conclusion by a symmetry-based argument, showing that in cases of this kind the transition state is very unlikely to have a symmetric structure. It can do so only if the off-diagonal force constants for stretching of the two relevant CC bonds in a valence force field model of the transition state are larger than the diagonal ones, which would be most unusual.

In 1974<sup>11</sup> we published a preliminary account of a detailed study of the same reaction, using the later MINDO/3<sup>8b</sup> method. As with MINDO/2, the symmetrical "transition state" had been found<sup>12</sup> to have two negative force constants. We were able to locate the true transition state<sup>11</sup> which proved to be very unsymmetrical, one of the new CC bonds being essentially completely formed while the other was still very long. The calculated activation energy for  $1 + 2 \rightarrow 3$  was in quite good agreement with experiment.

Our conclusions have recently been questioned by two groups of workers<sup>13,14</sup> who have claimed that their ab initio RH calculations predict the symmetrical structure to be a true transition state. One<sup>13</sup> of these studies was based on the use of single-configuration wave functions and could not therefore have dealt adequately with possible biradicaloid intermediates.<sup>11,15</sup> However, Townshend et al.<sup>14</sup> included  $3 \times 3$  CI at all the points they calculated on the potential surface. Minor but important differences between the results of these investigations were later resolved in a second paper by Burke et al.<sup>16</sup>

A similar discrepancy has recently arisen in studies of the analogous dipolar cycloaddition of acetylene (**4**) to fulminic acid (**5**) to form isoxazole (**6**).<sup>17</sup> Here our MNDO<sup>18</sup> calcula-



tions again predict a very unsymmetrical transition state for the reaction whereas Poppinger's RH studies indicate a far more symmetrical structure.<sup>17,19</sup> Here the discrepancy is real, because Poppinger carried out his calculations rigorously,<sup>19</sup> optimizing all variables and characterizing the transition state unequivocally by the McIver-Komornicki procedure.<sup>20</sup>

Basilevsky et al.<sup>21</sup> and Houk et al.<sup>22</sup> have recently discussed this dichotomy between the RH and semiempirical results. The latter authors in particular point out that unsymmetrical transition states are predicted by methods which neglect overlap (CNDO, INDO, NDDO) and symmetrical ones by methods where overlap is included (EH, RH). Their inclusion of EH results is, however, something of a red herring because their EH calculations were based on MINDO/3 geometries.

It is well recognized that the EH method leads to predicted bond lengths that are in serious disagreement with experiment (and so also with MINDO/3).

These criticisms are much less cogent than they may appear at first sight, as will presently be demonstrated. The Diels-Alder<sup>13,14</sup> calculations in particular are invalidated by technical shortcomings. Nevertheless we decided to reexamine the reaction of **1** with **2** in more detail, taking advantage of new techniques which have been developed here since our previous communication was submitted. For convenience, we in fact studied the retro-Diels-Alder conversion of **3** to (**1** + **2**). The MERPS (minimum energy reaction paths) for the forward and reverse reactions must of course lead to identical stationary points on the potential surface. We also used MINDO/3<sup>8b</sup> rather than the more recent (and apparently superior) MNDO<sup>8c</sup> procedure because MINDO/3 has been tested much more extensively and the results for a wide variety of reactions of hydrocarbons have been uniformly satisfactory. Here we report our results and discuss them in relation to experiment and those from the RH calculations.

### Procedure

The calculations were carried out by the standard MINDO/3 procedure, using the parameters previously reported.<sup>8b</sup>

The geometries of stable species were determined by minimizing the energy with respect to *all* geometrical variables, no assumptions of any kind being made.

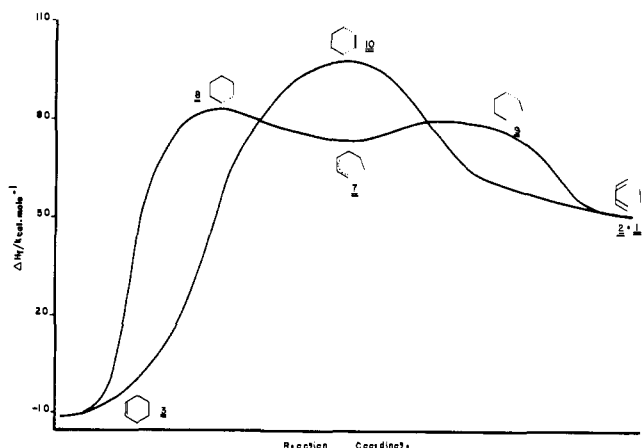
In the case of the reactant (**3**) and products (**1**, **2**), the calculations could be carried out by the usual spin-restricted version of MINDO/3, using the standard DFP (Davidon-Fletcher-Powell) procedure. Problems arose, however, in the intermediates studied here because of their biradical-like (biradicaloid) nature. In calculating such species, it is necessary to include  $CI_0$  (CI with the lowest doubly excited configuration) if a spin-restricted SCF MO treatment is used. Difficulties then arise, however, in calculating derivatives of the energy needed both for the DFP optimization and for the calculation of force constants and identification of stationary points by the McIver-Komornicki method. When  $CI_0$  is included, the bond order matrix is no longer stationary for variations in the geometry, so derivatives have to be found by finite difference between energies found by complete SCF calculations at each point. Two such calculations are therefore needed for each geometrical variable, i.e.,  $2N$  for a system with  $N$  geometrical variables. In the usual single-determinant procedure, only *one* SCF calculation is needed to estimate the  $N$  derivatives. Inclusion of  $CI_0$  therefore increases the amount of computing time by a large factor, and worse problems arise in calculating second derivatives.

These difficulties can be avoided by using a spin-unrestricted version of MINDO/3 (UMINDO/3).<sup>23,24</sup> Recent work here has shown that this leads to results similar to those given by the restricted version with  $CI_0$  and no problems arise in the calculation of derivatives. There are, however, two disadvantages in using the UHF method. First, the unrestricted wave function is not an eigenfunction of the total spin squared operator  $S^2$ . This can lead to appreciable mixing with the lowest triplet state whenever this state is close to the singlet ground state in energy. Unfortunately, reducing this problem by spin projection again leads to problems in calculating the first derivatives unless suitable coupling operators are used.<sup>25</sup> The second problem is that by assigning different spatial orbitals to different spins (DODS), one introduces a certain amount of electron correlation. Since MINDO/3 is parameterized to include an average correction for this quantity, the introduction of additional electron correlation leads to energies which are too low, by up to 25 kcal/mol in cases where  $\langle S^2 \rangle$  differs significantly from zero.

**Table I.** MINDO/3 Energies for Stationary Points in the Cyclohexene (3) to Butadiene (2) and Ethylene (1) Potential Surface

	3	8	7	9	2 + 1	10
$\Delta H_f^{\ddagger}/\text{RHF}^a$	-9.5	93.1	(118) <sup>f</sup>	(80.1) <sup>f</sup>	51.7	98.2
$\Delta H_f^{\ddagger}/\text{UHF}^b$	-9.5(0.0)	61.2(1.10)	48.5(1.18)	77.1(0.68)	51.7(0.0)	98.0(0.47)
$\Delta H_f^{\ddagger}/\text{RHF}-\text{CI}_0^c$	-12.8	69.9	59.8	79.3	45.4	95.9
$\Delta H_f^{\ddagger}(\text{corr})^d$	-10	84	74	80	52	98
$a^1b^{1e}$	0.000	0.063	-0.166	-0.013	0.000, 0.000	0.000
$a^2$	0.987	0.796	0.721	0.982	0.990, 0.986	0.983
$b^2$	-0.161	-0.602	-0.672	-0.190	-0.138, -0.166	-0.184

<sup>a</sup> kcal/mol. <sup>b</sup> Unrestricted Hartree-Fock method, kcal/mol. The expectation value of the operator  $S^2$  is shown in parentheses. <sup>c</sup> Using a  $3 \times 3$  CI based on the orbitals of the first excited singlet, in kcal/mol. <sup>d</sup>  $\text{CI}_0$  energies for 7 and 8 corrected by 14 kcal/mol (see text). <sup>e</sup> Coefficients of the CI matrix, where a and b represent configurations with occupancy of the HOMO and LUMO, respectively. <sup>f</sup> A single configuration RHF energy at the geometry found by the UHF method. In the RHF potential surface, these are not true stationary points.



**Figure 1.** Schematic UMINDO/3 potential surface for the conversion of cyclohexene (3) into ethylene (1) and *cis*-1,3-butadiene (2).

We therefore devised the following procedure which combines the advantages of both these methods.

The minimum energy reaction path (MERP) is first delineated by the usual reaction coordinate method, using UMINDO/3. Stationary points along the MERP are located approximately by inspection and their geometries are then refined by the McIver-Komornicki procedure.<sup>20</sup> The stationary points located in this way are then characterized by calculating and diagonalizing the Hessian (force constant) matrix, also following McIver and Komornicki.<sup>20</sup> The relevant stationary points are then relocated on the potential surface corresponding to MINDO/3  $\text{CI}_0$ . For reasons stated elsewhere, we found it more convenient to use a  $3 \times 3$  CI treatment based on MOs given by the "half-electron" method.<sup>26</sup> Extensive tests have shown this to give ground state energies virtually identical with those from a  $2 \times 2$  CI ( $\text{CI}_0$ ) treatment using closed shell MOs.<sup>27</sup> Most gratifyingly, the geometries so obtained were very similar to the UMINDO/3 ones while the energies were about 11 kcal/mol higher in the cases of biradicaloids.<sup>28</sup> Summarized in Table I are the single configuration MINDO/3, UMINDO/3, and MINDO/3  $\text{CI}_0$  energies for the stationary points located on the  $\text{C}_6\text{H}_{10}$  potential surface.

Recent work has shown that MINDO/3 can be used to calculate entropies of activation<sup>29</sup> as well as energies, and also isotope effects.<sup>30,31</sup> We extended these calculations to the retro-Diels-Alder reaction of 3. For this purpose we first obtained the vibrational frequencies of the various species by the method described in detail previously.<sup>32</sup> For cyclohexene, the restricted and unrestricted methods were equivalent (i.e.,  $\langle S^2 \rangle = 0$ ), whereas, for the transition states, the UHF method was used.

Molecular entropies were calculated from the calculated geometries and vibrational frequencies in the manner previously described.<sup>29</sup>

The calculation of kinetic isotope effects in the rigid-rotor-harmonic-oscillator (RRHO) approach involves evaluating the ratios of the suitable translational, rotational, and vibrational partition functions for the two isotopic species.<sup>33</sup> We have demonstrated previously<sup>30</sup> that the MINDO/3 method gives very good predictions of isotopic frequency shifts, suggesting that the solution of the partition functions should give reasonable results. The standard form of the Bigeleisen equation was used.

$$\frac{K_1}{K_2} \cdot \frac{S_2 S_1^\ddagger}{S_1 S_2^\ddagger} \cdot \frac{\kappa_2}{\kappa_1} = \text{HRR} = \frac{\nu_1^\ddagger}{\nu_2^\ddagger} \cdot \text{VP} \cdot \text{EXC} \cdot \text{ZPE} \quad (1)$$

$$\text{VP} = \prod \frac{u_{2i}^{3n-6}}{u_{1i}^{3n-6}} / \prod \frac{u_{2i}^{3n-7}}{u_{1i}^{3n-7}}$$

$$\text{EXC} = \prod \frac{1 + e^{-u_{1i}}}{1 + e^{-u_{2i}}} / \prod \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}}$$

$$\text{ZPE} = \frac{\exp \left[ \sum \frac{3n-6}{2} (u_{1i} - u_{2i}) \right]}{\exp \left[ \sum \frac{3n-7}{2} (u_{1i} - u_{2i}) \right]}$$

where  $S$  is a symmetry number,  $\kappa$  a transmission coefficient, and  $u_i = h\nu_i/KT$ . Subscripts 1 and 2 refer to light and heavy isotopes, respectively.

## Results and Discussion

### (a) Location of Stationary Points on the Potential Surface.

We initially studied the retro-Diels-Alder reaction of 3 using the restricted version of MINDO/3 with the  $\text{C}_3\text{C}_4$  bond length as the reaction coordinate. The transition state located in this way was refined and characterized (one negative force constant) by the McIver-Komornicki procedure. Its calculated heat of formation (Table I) corresponded to an activation energy of 102.6 kcal/mol. The structure was, as expected, unsymmetrical, the lengths of the nascent CC bonds being 1.65 and 2.75 Å.

We have combined the kinetic results of Barnard and Parrott<sup>34</sup> with the older data of Uchiyama et al.<sup>35</sup> to obtain a value of  $63.95 \pm 1.42$  kcal/mol for  $\Delta H^\ddagger$  (99% confidence limit), using the Eyring equation (see paragraph at end of text regarding supplementary material). This value is very much less than the MINDO/3 one, part of the discrepancy being due, as we had previously reported, to the biradicaloid nature of species corresponding to the relevant parts of the potential surface. This became apparent when we recalculated the reaction, using UMINDO/3.

The UMINDO/3 potential surface (Figure 1) differed qualitatively from that given by restricted MINDO/3, the reaction now being predicted to take place in two distinct steps,

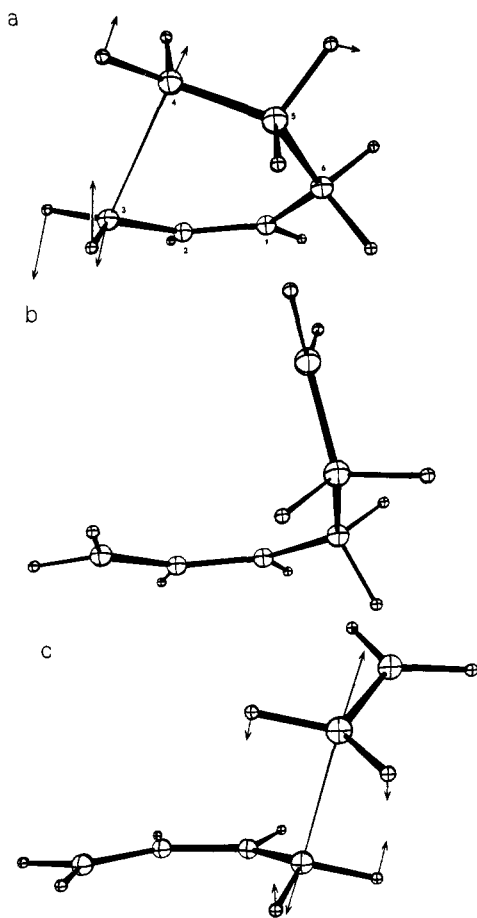
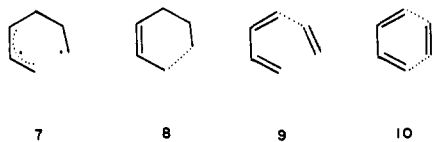


Figure 2. ORTEP plots of (a) the transition state **8**, (b) the biradicaloid intermediate **7**, and (c) the transition state **9** on the UMINDO/3 potential surface for the conversion of **3** into **1 + 2**. The atoms are numbered according to the cyclohexene ring system. Arrows illustrate the form of the normal mode corresponding to the reaction coordinate.

via a stable intermediate biradicaloid **7**. The heats of formation calculated for the reactant (**3**), products (**1 + 2**), **7**, and the two transition states **8** ( $3 \rightarrow 7$ ) and **9** ( $7 \rightarrow 1 + 2$ ) are listed in Table



I. The symmetric structure **10**, corresponding to synchronous formation of both bonds, was also located. The calculated Hessian matrix for **7** had no negative eigenvalues, indicating it to be a true minimum on the potential surface, **8** and **9** each had just one negative eigenvalue, confirming their identification as transition states, and **10** had two negative eigenvalues. ORTEP plots for **7**, **8**, and **9** are shown in Figure 2, together with illustrations of the eigenvectors of the negative Hessian eigenvalues calculated for the species **8** and **9**. These should correspond to the reaction coordinate in each case and it will be seen that they do have the forms expected for the reactions in question. ORTEP plots illustrating the forms of the two negative eigenvalues calculated for the Hessian matrix of **10** are shown in Figure 3.

When the geometries of **7**, **8**, and **9** were recalculated using MINDO/3 with  $CI_0$ , little change occurred, but the energies, as usual, were higher (Table I). A comparison of the calculated UMINDO/3 bond lengths for **3**, **7**, and **9** with those reported by Townshend et al.<sup>14</sup> using the STO-3G basis set with  $3 \times 3$  CI is shown in Table II and an analogous comparison of the

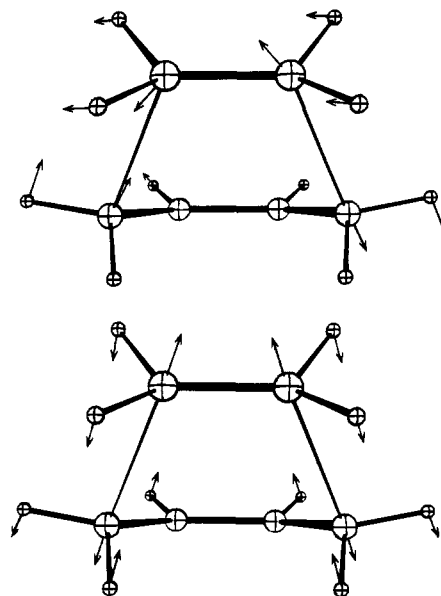


Figure 3. ORTEP plots of the stationary point **10**, illustrating the eigenvectors of the two negative eigenvalues of the Hessian matrix calculated for this species using the UMINDO/3 method.

geometry of the symmetric structure **10** with that calculated by Townshend et al.<sup>14</sup> and Burke and Leroy<sup>16</sup> is presented in Table III. The agreement between the MINDO/3 and the ab initio results is fairly good, the differences being no greater than the differences between the two reported ab initio geometries for **10** (Table III).

Problems arise in calculating the energies of biradicals by MINDO/3, both in the restricted version with  $CI_0$  and in UMINDO/3, due to an overestimation of the effects of electron correlation. In MINDO/3, the parameters are chosen by fitting experimental data for molecules, in particular their heats of formation. MINDO/3 therefore includes a built-in correction for electron correlation, corresponding to the average correlation energy of electrons in normal closed shell molecules. Since the use of  $CI_0$  on UMINDO/3 explicitly takes into account the correlation energy for the two "unpaired" electrons in a biradicaloid, use of these procedures should give energies too negative by the average electron-pair correlation energy included in MINDO/3, since this is then counted twice over. Tests have shown<sup>36</sup> that the energies for biradicaloid species given by MINDO/3 with  $CI_0$  and UMINDO/3 are too negative by (on average) 14 and 25 kcal/mol, respectively, values similar to those estimated by Clementi and others<sup>37</sup> for the electron-pair correlation energies in atoms and small molecules. This important problem will be discussed in detail elsewhere. Our present conclusion is that the best estimate of the heat of formation of a given molecular species is given by the restricted (MINDO/3) value without  $CI_0$  if the values with  $CI_0$  and UMINDO/3 are not lower than it is by 14 or 25 kcal/mol, respectively, and otherwise by the MINDO/3  $CI_0$  value plus 14 kcal/mol, or the UMINDO/3 value plus 25 kcal/mol. Correspondingly corrected heats of formation are listed in the fourth row of Table I. These values predict  $\Delta H_{298}^\ddagger$  for  $3 \rightarrow 2 + 1$  to be 94 kcal/mol and  $\Delta H_{298}^\ddagger$  for  $2 + 1 \rightarrow 3$  to be 32 kcal/mol. Whereas the experimental value for the former (64 kcal/mol)<sup>34,35</sup> is rather smaller than the MINDO/3 value, the experimental estimate for the latter<sup>38</sup> is in much better agreement.

The decrease in energy on inclusion of  $CI_0$  or use of UMINDO/3 is a measure of the degree of biradical character. In the case of "normal" molecules inclusion of  $CI_0$  usually lowers the energy by only 2–5 kcal/mol. Use of UMINDO/3 in such cases merely reproduces the restricted solution, the two sets

**Table II.** Comparison of the Optimized UMINDO/3 and STO-3G Bond Lengths for the Species **3**, **7** ( $D_a$ ),<sup>a</sup> and **9** ( $T_a$ )<sup>a</sup>

bond	<b>3</b>		<b>7</b>		<b>9</b>	
	UMINDO/3	STO-3G	UMINDO/3	STO-3G	UMINDO/3	STO-3G
C <sub>1,2</sub> <sup>b</sup>	1.35	1.35	1.40	1.39	1.44	1.45
C <sub>2,3</sub>	1.50	1.53	1.37	1.36	1.35	1.34
C <sub>3,4</sub>	1.52	1.54	4.05	4.81	5.29	4.91
C <sub>4,5</sub>	1.52	1.56	1.46	1.53	1.35	1.40
C <sub>5,6</sub>	1.52	1.54	1.51	1.55	2.06	1.96
C <sub>6,1</sub>	1.50	1.53	1.48	1.43	1.38	1.41

<sup>a</sup> Structures as labeled in ref 14. <sup>b</sup> Numbering of the atoms follows that of cyclohexene.

**Table III.** Comparison of the Optimized UMINDO/3 and STO-3G Bond Lengths for the Stationary Point **10**

bond	UMINDO/3	STO-3G <sup>a</sup>	STO-3G/3 × 3 CI <sup>b</sup>
C <sub>1,2</sub>	1.425	1.41	1.36
C <sub>2,3</sub>	1.38	1.38	1.40
C <sub>3,4</sub>	2.19	2.26	2.21
C <sub>4,5</sub>	1.37	1.38	1.40

<sup>a</sup> From ref 16. <sup>b</sup> From ref 14.

of MOs ( $\alpha$  and  $\beta$  spin) being identical. As the biradical character increases, the lowering of energy due to CI<sub>0</sub> likewise increases and UMINDO/3 begins to deviate from the restricted treatment. The point at which a system should be described as a biradicaloid rather than a normal molecule is of course arbitrary. In MINDO/3, it seems natural to draw the dividing line at the point where inclusion of CI<sub>0</sub> lowers the energy by more than 14 kcal/mol so that the "corrected" value falls below that given by MINDO/3 without CI<sub>0</sub>.<sup>39</sup>

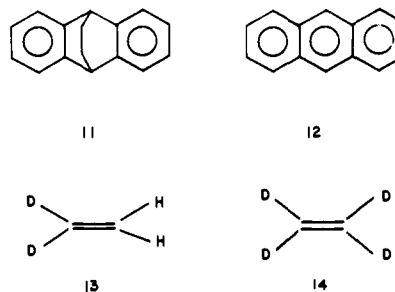
The results in Table I then imply that **1**, **2**, **3**, and the transition state (**9**) for conversion of (**1** + **2**) into **7** are "normal" molecular species while **7** and **8** are biradicaloid. Note that **7** is predicted to represent a significant dip in the potential surface, separated from (**1** + **2**) by an appreciable barrier (6 kcal/mol). The barrier to rotation about the CC bond in **7** derived from the ethylene (**1**) would be expected to be small and indeed is only 2 kcal/mol according to MINDO/3. If therefore our potential surface is correct, the Diels-Alder reaction **1** + **2** → **3** should take place with loss of configuration of the dienophile **2**. Indeed, one would expect butadiene to catalyze cis-trans isomerism in the latter. While Diels-Alder reactions normally take place by stereospecific cis addition to the dienophile,<sup>40</sup> no one as yet seems to have studied the parent reaction of **1** with **2**. It is quite possible that substituents may alter the shape of the potential surface, effectively eliminating the intermediate. On the other hand, calculations of energies of biradicaloid species by the rules indicated above are necessarily much less reliable than those for normal molecules because so few heats of formation for biradicaloid species are available to check them. In any case, experimental studies are in progress here to establish the stereochemistry of the (**1** + **2** → **3**) cycloaddition. Finally, it should be emphasized that the uncertainties concerning the corrections to be applied to energies calculated by the UMINDO/3 method, or when using CI<sub>0</sub>, in no way affect our main conclusion, that the transition state for the overall reaction is very unsymmetrical, corresponding to closure of the second bond in a biradicaloid intermediate (which may, or may not, be a stable species).

(b) **Entropies.** The uncertainty in the energies calculated by MINDO/3 CI<sub>0</sub> and UMINDO/3 for the biradicaloid species **7** and **8** is inconvenient because it makes it difficult to tell which of the two transition states (**8** and **9**) is the higher in energy and hence the transition state for the overall reaction. The values in Table I imply that **8** plays this role; however, the fact that our calculated enthalpy of activation is too high suggests that

we may have overestimated the energy of **8** and that that of **9** may in fact be higher. In order to obtain further information concerning this, we have calculated the entropies of **3**, **8**, and **9**, using the standard procedures described elsewhere.<sup>29</sup> The calculated absolute entropy of **3** at 600 K was 100.4 cal K<sup>-1</sup> mol<sup>-1</sup>, in excellent agreement with experiment<sup>41</sup> (100.04 cal K<sup>-1</sup> mol<sup>-1</sup>). The calculated entropies of activation for **8** and **9** were, respectively, 9.0 and 17.2 cal K<sup>-1</sup> mol<sup>-1</sup> at 600 K and 9.3 and 18.0 cal K<sup>-1</sup> mol<sup>-1</sup> at 1000 K. Analysis of the data recently reported for the range 1000–1190 K by Barnard and Parrott,<sup>34</sup> and for the range 800–900 K by Uchiyama et al.,<sup>35</sup> led to a value of 6.74 ± 1.46 cal K<sup>-1</sup> mol<sup>-1</sup> (99% confidence limit). Comparison with the calculated values suggests very strongly that **8** is indeed the transition state for the overall reaction, as the values in Table I predict. Admittedly the calculated entropy for **9** may be too large because the rigid rotor approximation is not strictly valid for species with low frequency torsional vibrations. However, it seems unlikely that the error exceeds 3 cal K<sup>-1</sup> mol<sup>-1</sup>. A similar though smaller error would also be expected for **8**. Our calculated value is indeed greater than the experimental value by a little more than the likely maximum error in the latter.

(c) **Kinetic Isotope Effects.** Another test of our predictions can be obtained by comparing the calculated and observed changes in the rate with isotopic substitution, in particular of hydrogen by deuterium. While neither the parent reaction of **1** with **2** to form **3**, nor its converse, have as yet been studied in this way, data are available for the retro-Diels-Alder reactions of a number of derivatives of **3** and have been the basis of arguments in favor of symmetrical transition states.<sup>4</sup>

An example of this is provided by the work of Thornton and Taagepera<sup>4</sup> on the retro-Diels-Alder conversion of dibenzobicyclo[2.2.2]octadiene (**11**) to anthracene (**12**) and ethylene



(**1**), based on a comparison of the rates measured for the parent compound, and for geminal dideuterio and tetra-deuterio derivatives leading respectively to **13** and **14**. If the transition state is symmetrical, the rate constants for the three reactions ( $K_0$ ,  $K_2$ ,  $K_4$ , respectively) should obey the relation

$$K_2 = (K_0 K_4)^{1/2} \quad (2)$$

If, however, the rate-determining step involves formation of only *one* of the new bonds (e.g., **3** → **7**, or **7** → **1** + **2**), then it might be expected that

$$K_2 = 1/2(K_0 + K_4) \quad (3)$$

**Table IV.** Harmonic Rate Ratios Calculated for  $-d_0$ ,  $-4,4-d_2$ ,  $-5,5-d_2$ , and  $-4,4,5,5-d_4$  Cyclohexene and the Corresponding Transition State (**8**) at 493 K

	$\nu_D/\nu_H$	VP	EXC	ZPE	HRR	$k_D/k_H$	lit
$-d_4/-d_0$	0.98849	1.00341	1.18669	0.69640	0.81969	0.81969	$0.852 \pm 0.007^a$
$-4,4-d_2/-d_0$	0.99191	1.00672	1.15579	0.74697	0.86211	0.43106 <sup>b</sup>	
$-5,5-d_2/-d_0$	0.99637	0.99516	1.02702	0.93496	0.95211	0.47605 <sup>b</sup>	
						0.907113	$0.924 \pm 0.005^a$

<sup>a</sup> For the reverse Diels–Alder reaction of dibenzobicyclo[2.2.2]octadiene, cf. ref 4. <sup>b</sup> After multiplication by the appropriate symmetry numbers.

Thornton and Taagepera concluded that their results were more consistent with the geometrical mean (eq 2) than the arithmetical mean (eq 3) and similar conclusions have been reported for other retro-Diels–Alder processes. Thornton and Taagepera have reviewed this work, showing that the rate ratio per deuterium atom ( $K_H/K_D$ ) varies little, having an average value of 1.08 at 50 °C.

We calculated the corresponding kinetic isotope effects for the conversion of **3** and its 4,4-dideuterio, 5,5-dideuterio, and 4,4,5,5-tetradeuterio derivatives into **2** and **1**, **13**, or **14** (Table IV). The rate ratios were obtained from the calculated vibration frequencies for the various species and the corresponding transition states (**8**), using the Bigeleisen equation (1). The total relative isotopic rate for the dideuterio derivative was obtained by summing the individual relative rate constants for the 4,4- and 5,5-dideuterio cyclohexenes. This is justifiable since the two processes are indistinguishable so far as the electronic motions are concerned, in the Born–Oppenheimer approximation. The average value for each ( $K_H/K_D$ ) contribution was 1.108 at 50 °C, in good agreement with the mean value given by Thornton and Taagepera.<sup>4</sup>

Thornton and Taagepera<sup>4</sup> used the argument given above to define a mechanistic index  $\chi$  (eq 4), normalized between the extremes of eq 2 and 3 and purportedly a measure of the degree of synchronicity of the reaction:

$$\chi = \frac{K_2 - (K_0K_4)^{1/2}}{1/2(K_0 + K_4) - (K_0K_4)^{1/2}} \quad (4)$$

Their experimental results for the retro-Diels–Alder reaction of **11** led to the value

$$\chi = 0.04 \pm 0.21 \text{ (SD)} \quad (5)$$

For a sample of 12, the 95% (one sided) confidence limit is 0.04 + 0.37. Thornton and Taagepera concluded on this basis that the reaction must be more or less synchronous and that a two-step mechanism could be eliminated from consideration.

This argument rests, however, on the assumption that eq 3 must hold in the case of a single-ended reaction where only one bond is partly formed in the transition state. Our calculations are inconsistent with this. Although **8** is highly unsymmetrical, one of the new CC bonds being completely formed in it, the isotope effects calculated for the dideuterio derivative of **3** ( $K_2/K_0 = 0.907$ , obsd<sup>4</sup> 0.924) and the tetradeuterio derivative ( $K_4/K_0 = 0.820$ , obsd<sup>4</sup> 0.852) are very similar to the experimental ratios for **11** and lead to a value for  $\chi$  (0.39) that is within the 95% confidence limit of the value calculated by Thornton and Taagepera.<sup>4</sup>

Although these results do not of course prove the transition state to be unsymmetrical, they clearly weaken the arguments for a symmetrical structure on the basis of isotope effects. The use of kinetic isotope effects in the study of reaction mechanisms has until now been based on qualitative, and indeed largely intuitive, ideas concerning the results to be expected in terms of a given reaction mechanism. Combination of such measurements with MINDO/3 calculations should provide a much more powerful and reliable criterion.

We also carried out calculations for the Diels–Alder reactions of **2** with **1** and **14**, finding a  $K_H/K_D$  ratio at 298 K close to unity (0.993). The few measurements of kinetic isotope effects that have been carried out for Diels–Alder reactions in the usual (forward) direction also give values close to or less than unity.<sup>4</sup> The fact that the secondary deuterium isotope effects are so small for the forward reaction, and yet large for the reverse one, indicates that the transition state must be effectively reactant-like in structure. This is surprising, because one would intuitively have thought that **8** would be more closely related to cyclohexene (**3**) than to (**1** + **2**).

### Comparison with Other Theoretical Calculations

As we have already noted, our earlier conclusions<sup>11</sup> concerning the mechanism of the archetypal Diels–Alder reaction (**1** + **2** → **3**) are in direct disagreement with those drawn from two ab-initio RH investigations.<sup>13,14,16</sup> The work reported here does nothing to resolve this. On the contrary, the present detailed MINDO/3 study supports our earlier one<sup>11</sup> in predicting the transition state to be quite unsymmetrical, corresponding to cyclization of an intermediate biradicaloid. Indeed, there is even a strong indication that the latter may correspond to a local minimum on the potential surface.

The ab initio studies,<sup>13,14</sup> on the other hand, were claimed to support a symmetrical structure for the transition state, corresponding to a completely synchronous reaction. While one<sup>14</sup> of them agreed with MINDO/3 in predicting the existence of a local minimum on the potential surface corresponding to an intermediate of biradical-like type, this was claimed not to lie on the main reaction path, being separated from it by an intervening ridge.

This discrepancy may, however, be merely an artifact of the inadequate manner in which the ab initio calculations were carried out. Thus Burke and Leroy could not in any case have located a low energy path involving biradicaloid species because they did not include CI, and the procedure employed by Townshend et al.<sup>14</sup> (i.e., the RH method using a small basis set with very limited CI) would also be expected to underestimate the relative stabilities of biradical-like species. However, even if the procedure used by the latter authors had been entirely accurate, their conclusions would still have been invalidated by the inadequate techniques used by them to locate and characterize stationary points on the potential surface.

(1) Calculations of molecular geometries by cyclic variation of coordinates is acceptable only for very small molecules unless independent checks are applied to establish that convergence has been reached. Failure to do this can lead to large errors. In the present case these would moreover have been likely to be greater for the unsymmetrical biradicaloid intermediate than for the symmetrical “transition state” since the former involves more independent variables. This would lead to too small a difference in energy between the two species and so could well account for the ab-initio value being smaller than the MINDO/3 one.

(2) Use of assumed values for geometrical variables in order to simplify geometry optimization is also unacceptable and can likewise lead to large errors in calculated energies. Townshend et al. used assumed values for 17 of the 42 independent vari-

ables. Here again the errors would be greater for the unsymmetrical species since more independent variables are involved.

(3) Similar criticisms apply to the procedure used by Townshend et al. to locate the symmetrical transition state, i.e., calculation of sections of the potential surface obtained by varying one coordinate at a time.

(4) Even if the reported symmetrical structure was a stationary point on the potential surface, there is no evidence that it was a saddle point and not, as in MINDO/3, a maximum in two dimensions. The "tests" applied by the authors in this connection were wholly inadequate.

(5) The most crucial point in Townshend et al.'s entire argument, concerning the existence of a ridge between the symmetrical "transition state" and the biradical intermediate, rested on a *single* calculation of an arbitrary path across the potential surface linking the two and on the fact that this one arbitrary path had a maximum 2 kcal/mol higher energy than the "transition state".

In short, there is no reason to suppose that if Townshend et al. had carried out their study properly, with rigorous location and characterization of stationary points, their conclusions would not have agreed with ours.

As we have also already noted, a similar discrepancy exists between MNDO and ab initio RH<sup>19</sup> calculations in the case of the dipolar cycloaddition of acetylene to fulminic acid. Here the ab initio calculation, by Poppinger,<sup>19</sup> was carried out properly, the transition state being located and characterized by the McIver-Komornicki<sup>20</sup> procedure. Since it corresponded to an almost synchronous process, the two forming bonds in it being similar in length, it is very unlikely that there could be alternative paths involving unsymmetrical transition states. Here therefore is a clear conflict between the two procedures, although the differences in energy between the MNDO transition states and the symmetrical structure were not large.

Houk et al.<sup>22</sup> have suggested that the neglect of bicentric overlap in MINDO/3 and MNDO may lead them to underestimate the stabilities of symmetrical transition states, leading instead to transition states that are unsymmetrical. They noted that the EH method, where overlap is included, tends to favor symmetrical structures for transition states, but that this tendency is reversed if overlap is neglected. They also noted that other semiempirical treatments in which overlap is neglected, e.g., CNDO, also tend to favor unsymmetrical structures, like MINDO/3 and MNDO.

This argument, however, neglects a basic difference between MINDO-type treatments and conventional semiempirical methods. The former are parametrized to reproduce experimental data, i.e., the results that would be obtained by accurate solution of the relevant Schrödinger equations. The parametrization therefore compensates for errors of all kinds, including those inherent in the RH method itself, due to use of incomplete basis sets and to neglect of electron correlation. The success of MINDO/3 indicates that the compensation for the errors resulting from neglect of monocentric overlap is very successful, although these errors are likely to be large since the neglect of monocentric overlap is unjustifiable and is known to lead to large errors in calculated energies. Since the neglect of bicentric overlap in MNDO is justifiable as a first approximation and indeed has a much smaller effect on the total energy, it seems likely that any errors due to it will have been effectively compensated in MNDO.

On the other hand, the use of small basis sets and neglect of electron correlation are known to lead to very large errors in the heats of atomization of molecules, calculated by the RH method. Analogous errors are to be expected in comparisons of the energies of the reactants and the transition state in a reaction since the transition state contains weakened bonds. Indeed, Schaefer<sup>42</sup> has shown that it is necessary to use very

large basis sets and extensive CI if satisfactory results are to be obtained in calculations for even very simple reactions. MINDO/3 and MNDO apparently compensate adequately for these factors via the parametrization, judging by their success in predicting both heats of formation of stable species and activation parameters. Since Poppinger used a minimum basis set (STO-3G) without CI, any discrepancy between his results and the MNDO ones is therefore more likely to be due to these factors than to any shortcomings of MNDO.

### Mechanism of the Reaction

It is generally accepted that the Diels-Alder reaction must follow one of two alternative paths, the first being a synchronous pericyclic process and the other a two-step or two-stage one where an intermediate biradical-like or zwitterionic intermediate is involved. It has been generally assumed that in the latter case the rate-determining step must be the formation of this intermediate, its collapse to product being rapid. The mechanism predicted by MINDO/3 introduces a third alternative, i.e., a two-step or two-stage mechanism where the rate-determining step is the conversion of the intermediate to the cyclic product, rather than its formation. This implies the rather startling conclusion, that collapse of a singlet biradical by internal combination may require very significant activation even when no stress or strain effects are involved. While the existence of such a barrier is contrary to most current ideas, the fault lies in the erroneous assumption that a singlet biradical must show reactivity similar to that of a pair of analogous isolated single radicals. This should be the case only if the radical centers in the biradical are far apart in space and isolated from one another by sufficient intervening bonds. Otherwise the radical centers will interact to give a closed shell species of lower reactivity, although this may still be a species that is represented better as a biradical than by any alternative classical valence structure, i.e., a biradicaloid.<sup>43</sup>

However, since the MINDO/3 mechanism seems to run counter to established ideas and conclusions claimed to follow from the available experimental evidence, we must first establish its credentials as a source of information to be taken seriously.

First, it should be pointed out that it is impossible to observe the course of a reaction by available experimental techniques. Our ideas concerning reaction mechanisms derive from circuitous reasoning based, e.g., on changes in the rate of reaction with changes in the reactants, these being interpreted with the aid of qualitative and largely phenomenological theories of the way in which the rate of a given reaction should change with reactant structure. Arguments of this kind are at best negative and even then seldom conclusive. It is nearly always possible to explain the experimental data in a variety of ways by making suitable assumptions. The choice ultimately has to be based on the "reasonableness" of the assumptions that have to be made, this being assessed on the basis of existing theory. The result is a tendency to select mechanisms that conform to existing theory and hence in turn seem to support it. The appearance is, however, an illusion because the theory itself was originally based on equally inconclusive evidence, a situation which only occasionally comes to light when, as in the notorious case of the 2-norbornyl cation, there is a head-on clash between opposing views concerning the reasonableness of alternative assumptions.

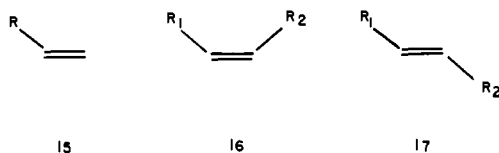
This is unfortunate because it means that there are virtually no reactions with transition states of known structure that can be used to test the ability of theoretical procedures to calculate potential surfaces and hence reaction mechanisms. The only course is to ensure that a procedure reproduces the properties of numerous stable molecules (i.e., minima on the potential surface), and also activation parameters of a variety of reac-

tions. It must also avoid predicting mechanisms that are definitely refuted by experiment. These tests have been applied to MINDO/3 and the results for hydrocarbons have been satisfactory. Problems have arisen in the case of heteroatoms due to known failings of the INDO approximation. While MNDO avoids the latter and seems likely to prove generally superior to MINDO/3, it has not yet been tested so thoroughly by calculations for reactions (over 200 to date in the case of MINDO/3). As already noted, this is why we decided to use MINDO/3 in the present connection. While we would be the last to claim that calculations of this kind can lead to incontrovertible conclusions at the present time, we feel that their performance (which has been well documented) justifies their claim to be taken seriously in connections such as this, both in their own right and as a guide to further experiment.

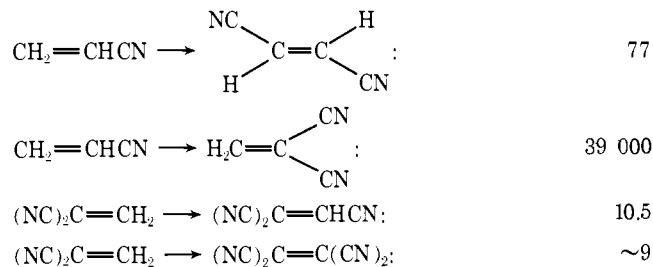
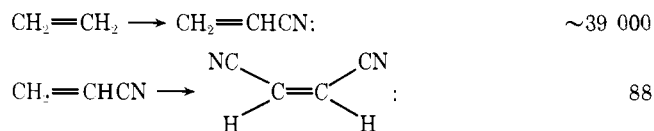
Turning now to the experimental evidence; there has been a strong bias over the last decade to interpret this in terms of a synchronous mechanism because of the almost hypnotic effect of the Woodward-Hoffmann rules. Most of the evidence is in fact either inconclusive or points in the opposite direction, as the following brief survey will show.

**Substituent Effects.** Evidence derived from substituent effects falls into three categories. Firstly, effects on the rate; secondly, effects on regioselectivity; thirdly, effects on stereochemistry.

The evidence from rates of reaction of substituted dienes and dienophiles seems to provide prima facie evidence for a very unsymmetrical structure for the Diels-Alder transition state. The clearest example comes from an argument by Dewar (see ref 43), based on a comparison of the rates of reaction of a given diene with ethylene (1), a monosubstituted ethylene (15), and the corresponding cis (16) and trans (17) 1,2-disubstituted

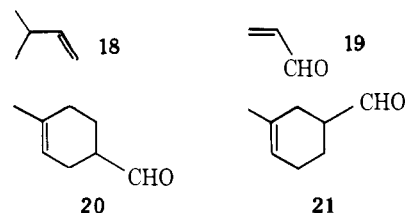


ethylenes. If the reactions are synchronous, the effects of the substituents should be additive (apart from possible steric effects in 17 which should manifest themselves by a difference in rate between 16 and 17). The ratio of rates for ethylene to a monosubstituted ethylene, and a monosubstituted to a disubstituted ethylene, should then be the same. If on the other hand the reaction is of two-step or two-stage type, one of the new bonds in the transition state being much weaker than the other, then the effects of substituents at different positions in ethylene should differ; the ratio of rates of reaction for the monosubstituted ethylene and ethylene being large and that for the disubstituted and monosubstituted ethylenes small. Dewar and Pyron<sup>5</sup> presented data showing that the latter pattern holds but the best example, to which they referred but which they did not quote, comes from the detailed studies by Sauer et al.<sup>44</sup> who measured the rates of reaction of cyclopentadiene with all the cyanoethylenes and listed relative rates measured, or estimated, in dioxane at 20 °C. Unfortunately the rate of reaction of cyclopentadiene with ethylene has not been reported but a rough estimate can be obtained from data for the ethylene-butadiene reaction<sup>45</sup> together with the assumption that the ratio of rates of Diels-Alder reactions of cyclopentadiene and butadiene is independent of substrate.<sup>46</sup> Estimating this from data for reactions of maleic anhydride,<sup>5,49</sup> we arrive at the following ratios of rates:



The results certainly seem to imply that the transition states for the unsymmetrical dienophiles must be very unsymmetric. It is of course still possible that the symmetric dienophiles may react in a synchronous manner, but such behavior would be unusual. The available evidence seems to suggest that transition states for a series of related reactions have similar structures. One would not, for example, expect linear free energy relationships to be so prevalent if this were not the case.

The second line of evidence comes from studies of the regioselectivity of addition of unsymmetrical dienes to unsymmetrical dienophiles. It has long been recognized that the experimental data can again be satisfactorily interpreted in terms of biradical intermediates, the isomer formed being the one in which the substituents stabilize the intermediate biradical most effectively. Thus isoprene (18) and acrolein (19) combine to form 20 rather than 21<sup>47</sup> because in the former case both



substituents (CH<sub>3</sub>, CHO) are at active positions in the intermediate biradical. The fact that Diels-Alder reactions are especially facile if they involve combination of species carrying substituents of opposite type (i.e., electron releasing on one and electron withdrawing on the other) can also be explained in this way in terms of polarization of the delocalized electrons in the transition state leading to the biradical; cf. the alternation effect in vinyl copolymerization.<sup>48</sup>

The regioselectivity in the latter case can be explained in terms of mutual conjugation<sup>49</sup> between the substituents in an aromatic pericyclic transition state, isoconjugate with benzene. Thus in such a transition state for (18 + 19 → 20), the (-I) methyl and (+E) formyl group would be "para" to one another. It is however, difficult to explain on this basis the fact that similar "ortho/para" orientation is observed where the substituents are both of similar type, e.g., both COOR (+E).

The third line of evidence comes from studies of the stereochemistry of reactions involving 1,2-disubstituted dienophiles or 1,4-disubstituted dienes.<sup>40</sup> Addition invariably takes place cis, a fact which is most simply explained if the reactions are synchronous pericyclic ones. Problems arise for any mechanism which postulates a biradical-like intermediate in such cases unless the collapse to product is extremely rapid or unless rotation about the ethylenic CC bond in the intermediate is inhibited. Neither is the case in the MINDO/3 mechanism for the ethylene-butadiene reaction but then neither is the stereochemistry of this reaction known. We are indeed studying it at the present time. The reactions that have been studied have all involved the combination of nucleophilic dienes with electrophilic dienophiles, where rearrangement of the intermediate would be inhibited both by the special resonance effects indicated above and by electrostatic attractions between the resulting charges on the diene and dienophile. It is also entirely possible that substituents may alter the shape of the potential



surface, reducing or even removing the minimum corresponding to the intermediate biradicaloid. Calculations for such systems would obviously be of much interest but we have not yet been able to undertake them.

**Secondary Isotope Effects.** Studies of deuterium isotope effects had been cited as evidence for a symmetrical transition state in several Diels–Alder reactions. As we have already pointed out, our MINDO/3 calculations show this argument to be inconclusive since similar rate ratios are predicted by MINDO/3 on the basis of a very unsymmetrical transition state.

**Arguments Based on the AH Technique.**<sup>5</sup> This approach was based on studies of the relative rates of Diels–Alder reactions of maleic anhydride with anthracene and its various benzo derivatives. It is well recognized that the rates of electrophilic substitution in alternate hydrocarbons (AH) can be predicted rather accurately in terms of localization energies calculated by the PMO method<sup>50</sup> and it can also be shown that the rate of a synchronous 1,4 Diels–Alder cycloaddition should run parallel to the sum of the two corresponding localization energies, i.e., the 1,4-bislocalization energy.<sup>51</sup>

If the rate-determining step in the Diels–Alder reaction is the formation of an intermediate biradical, its rate should run parallel to the localization energy of the most reactive position in the diene (here the 9 or 10 position). If synchronous, it should run parallel to a sum of the two corresponding localization energies. The observed rates seemed on this basis to support a synchronous mechanism.<sup>5</sup>

This argument, however, rests on the assumption that the first bond-forming process is rate determining, leading to a biradical intermediate which collapses rapidly to the product.<sup>44</sup> If the rate-determining step is in fact the cyclization of this biradical, as our calculations indicate to be the case for the corresponding reaction of butadiene (2), then the overall rate should depend on the reactivities of *both* the 9 and 10 positions; for the concentration of the intermediate will be greater, the greater the reactivity of the position first attacked, while the rate of the second step will depend on the reactivity of the other meso position.

**Entropy of Activation.** Numerous attempts have been made to distinguish between synchronous and nonsynchronous paths for the prototype Diels–Alder reaction,  $1 + 2 \rightarrow 3$ , by comparing the observed entropy of activation with values calculated for the two different transition states. Since these depend on pure guesses concerning the vibration frequencies of the latter, it is not surprising to find that both mechanisms have found support in this way from their proponents (cf. ref. 45, 52 and 53). As noted above, MINDO/3 leads to a good estimate of the entropy of activation for the reverse reaction, provided that the transition state for the overall reaction is that corresponding to the first step (i.e.,  $3 \rightarrow$  biradicaloid intermediate). It is of course impossible to calculate the corresponding value for the symmetrical synchronous path because the highest point in this is not a saddlepoint but rather a maximum in two variables. Such a species would have two normal modes with imaginary vibration frequencies, corresponding to translation along the two coordinates, so its entropy could bear no relation to that of a symmetrical transition state (if such exists). It would certainly be of interest to calculate the entropy of the latter by some procedure which predicts such a species, if indeed a procedure exists which leads to this result and is also capable of reproducing vibration frequencies with sufficient accuracy.

## Summary and Conclusions

While we would be the last to claim that the work reported here has led to unambiguous conclusions concerning the mechanism of the Diels–Alder reaction, we feel it has clearly indicated that the current view of it as a synchronous pericyclic

process is by no means well based. Indeed, seen at face value, the available experimental evidence seems to point rather strongly to very unsymmetrical transition states in the reactions of unsymmetrical dienophiles with dienes and hence to the strong implication that the same is true in other cases as well.

Our MINDO/3 calculations provide strong support for this conclusion, within the admitted uncertainties attached to any theoretical procedure at the present time. Indeed, MINDO/3 predicts, though less emphatically, that the reaction between ethylene and butadiene involves a stable biradicaloid intermediate whose collapse to cyclohexene is the rate-determining step. It may well be possible to confirm this prediction by experiments now in progress. If it proves to be correct, the effects on organic theory would be far reaching.

As regards other theoretical studies; those for the Diels–Alder reaction have been carried out either by methods with no claim to quantitative accuracy or by procedures open to technical criticisms so severe that no meaningful mechanistic conclusions can be drawn from them. There is some evidence that MINDO/3 may disfavor synchronous cyclic transition states relative to the unsymmetrical ones involved in corresponding two-step or two-stage processes, in comparison with minimum basis set RH calculations. The latter are, however, known to be liable to very large errors so it is impossible to tell which of the two is nearer to the truth. Our work in any case stresses the need for full geometry optimization and proper location and identification of transition states in theoretical studies of this kind.

Finally, the work reported here represents, to our knowledge, the first case where theoretical calculations of entropies of activation and kinetic isotope effects have been used as aids in establishing the mechanism of a reaction. Calculations of this kind in conjunction with experiment, should provide a powerful diagnostic tool.

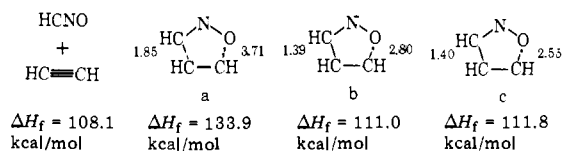
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**Supplementary Material Available:** Tables containing an analysis of the kinetic data in terms of the Eyring equation, calculated vibrational frequencies for 3, 8, and the corresponding  $-4,4-d_2$ ,  $-5,5-d_2$  and  $-4,4,5,5-d_4$  species, and optimized Cartesian coordinate for 1–3 and 7–10 (10 pages). Ordering information is available on any current masthead page.

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 (39) An alternative, and complementary, criterion is to inspect either the value of  $\langle S^2 \rangle$  given by the UMINDO/3 method or the eigenvectors of the CI matrix when using CI. Biradicaloids normally have values for  $\langle S^2 \rangle$  which are greater than 1.0 or have nearly equal contributions from the two closed shell configurations  $a^2$  and  $b^2$  (see Table I).  
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## The Electronic States of Ni<sub>2</sub> and Ni<sub>2</sub><sup>+</sup>

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**Abstract:** Extensive generalized valence bond (GVB) and configuration interaction calculations (POL-CI) have been carried out for the lowest states of Ni<sub>2</sub> and Ni<sub>2</sub><sup>+</sup> for bond lengths from 1.6 to 4.0 Å. The six lowest states of Ni<sub>2</sub> are found to be essentially degenerate with an average equilibrium bond length  $R_e = 2.04$  Å and  $D_e = 2.92$  eV. A  $4\Sigma_u^-$  ground state is found for the ion with a bond length  $R_e = 1.96$  Å and dissociation energy  $D_e = 4.14$  eV. The bonding of Ni is dominated by the interactions of the 4s orbitals on each Ni with each Ni of Ni<sub>2</sub> corresponding to a  $(4s)^1(3d)^9$  configuration. The lowest states lead to singly occupied  $\delta$  orbitals on each center with other 3d occupations leading to 100 electronic states within about 1.0 eV of the ground state.

### I. Introduction

The diatomic molecules formed of the first-row transition elements represent a potential source of information relevant to the study of organometallic complexes, surface chemistry, and solid-state physics. Unfortunately, isolation of these molecules from the bulk metal is very difficult to do in a manner that allows proper characterization. Experimental data

to date on these molecules are scarce<sup>1-3</sup> and quite inconclusive.

Until recently, high-quality theoretical studies of these molecules were not feasible. With the development of sound effective potential techniques the size of the problem has been greatly reduced. As a first step toward calculations on larger clusters of Ni atoms, we have carried out a study of the bonding