the water pools and then precipitate. The surfactant, excess reagents, and other reaction products are easily removed as described. The hydrophobic cluster molecules obtained are somewhat soluble in DMF, DMSO, or toluene/PEt_3, and completely soluble in pyridine.

Conclusion

In this paper we have described two of our extensions of known semiconductor colloid chemistry. The first is the use of bis(silyl)chalcogenide reagents in the arrested precipitation reaction. This has allowed for the fairly safe and convenient preparation of the chalcogenides (both as colloids and in bulk form) with liquid reagents. The second modification is more crucial. Using the controlled-growth ("living-polymer") process, culminating with the use of (organo)(silyl)selenides, we have been able to passivate the growing particle of the semiconductor solid and thereby isolate *molecular* particles of the solid-state infinite lattice. These particles are molecular in both size (10–100 Å) and solubility.

The solubility of these materials has been critical to our study of them. Since the compounds are quite stable and since they dissolve so readily we have been able to begin their detailed characterization using many of the analytical techniques of solution-phase chemistry.

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Registry No. AOT, 577-11-7; CdSe, 1306-24-7; $Se(TMS)_2$, 4099-46-1; PhSeTMS, 33861-17-5; $Te(TBDMS)_2$, 80594-86-1; heptane, 142-82-5.

MC–SCF Study of the Diels–Alder Reaction between Ethylene and Butadiene

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Abstract: In this paper we describe the results obtained in an MC–SCF STO-3G and 4-31G study of the cycloaddition reaction between butadiene (cis and trans) and ethylene. For this reaction it is possible to envisage three different mechanisms: a synchronous concerted approach, a nonsynchronous concerted approach, and a two-step process. At the STO-3G level we have found that the attack of ethylene on *cis*- or *trans*-butadiene involves three fragmentation transition states of diradicaloid nature associated with the syn–gauche, the trans, and the anti–gauche approach, which lead to three minima, again of diradicaloid nature, interconnected by two transition states of conformational origin. The attack on *cis*-butadiene involves also a fragmentation transition state of C_s symmetry associated with the concerted synchronous attack, which, however, is disfavored on energy basis, and the preferred paths are those associated with the nonsynchronous approaches. The 4-31G results provide a completely different mechanism, which agrees well with the experimental evidence. The main differences are (i) the three fragmentation transition states seem to disappear, so that the region of the potential energy surface associated with the gauche and trans approaches becomes very flat, and (ii) the C_s transition state is located at a slightly lower energy than the syn–gauche minimum. Therefore it appears that both synchronous and nonsynchronous paths exist and that the synchronous path is favored by ~2 kcal/mol.

1. Introduction

The Diels–Alder (DA) reaction is of great significance in the history of organic chemistry, from both an experimental and a theoretical point of view. However, despite the large number of experimental[7-9] and theoretical[2-6,9-22] studies, the mechanism of this reaction, even in the simple case of the reaction between butadiene and ethylene, is still in controversy. It is possible, in fact, to envisage three different mechanisms:[2-6] (i) a synchronous concerted approach, involving a cyclic aromatic transition state (TS) with the two new C–C bonds formed to equal extent; (ii) a two-stage asynchronous concerted mechanism in which there are two distinct stages to changes in the bonding, some mainly between the reactants and the single TS and the others mainly between the TS and products; (iii) a two-step process, which occurs in two kinetically distinct steps via a stable diradical intermediate.

In this paper we limit our attention only to the simple Diels–Alder reaction between butadiene and ethylene. Experimentally,

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[2] Woodward, R. B.; Katz, T. J. *Tetrahedron* **1959**, *5*, 70.

[3] (a) Dewar, M. J. S.; Griffin, A. C.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 6225. (b) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

[4] (a) Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203. (b) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

[5] Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771–5779.

[6] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–853.

[7] Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807, and references therein.

[8] Houk, K. N. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. 2, pp 181–271, and references therein.

[9] Bartlett, P. D.; Schueller, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 6071–6077.

[10] McIver, J. W., Jr. *Acc. Chem. Res.* **1974**, *7*, 72.

[11] (a) Basilevsky, M. V.; Tikhomirov, V. A.; Cheulov, I. E. *Theor. Chim. Acta* **1971**, *23*, 75. (b) Basilevsky, M. V.; Shamov, A. G.; Tikhomirov, V. A. *J. Am. Chem. Soc.* **1977**, *99*, 1369.

[12] Kikuchi, O. *Tetrahedron* **1971**, *27*, 2791.

[13] Jug, K.; Kruger, H. W. *Theor. Chim. Acta* **1979**, *52*, 19.

[14] Pancir, J. *J. Am. Chem. Soc.* **1982**, *104*, 7424.

[15] Herndon, W. C. *Chem. Rev.* **1972**, *72*, 157.

[16] (a) Burke, L. A.; Leroy, G.; Sana, M. *Theor. Chim. Acta* **1975**, *40*, 313. (b) Burke, L. A.; Leroy, G. *Theor. Chim. Acta* **1977**, *44*, 219.

[17] Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190.

[18] Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

[19] Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4511.

[20] Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609.

[21] Houk, K. N.; Lin, Y. T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554–556.

[22] Ortega, M.; Oliva, A.; Lluch, J. M.; Bertran, J. *Chem. Phys. Lett.* **1983**, *102*, 317.

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the product of this reaction consists of cyclohexene (99.98%) and vinylcyclobutane (0.02%) with rate constants in the ratio of 5000 to 1 (7.6 kcal/mol at 450 K) for the mechanism leading to cyclohexene and to vinylcyclobutane.[9] Experimental evidence[21] has also recently been reported that is compatible only with a concerted mechanism for the formation of cyclohexene. At a theoretical level this cycloaddition is one of the textbook examples used in the illustration of the Woodward–Hoffmann rules,[6] which indicate that, in this case, a synchronous concerted mechanism is allowed.

Dewar, however, has consistently argued against this position on the basis of experimental evidence and semiempirical calculations.[3-5] The recent results reported in ref 5 replace the previous theoretical conclusions, being based on calculations performed with a more reliable procedure involving a UHF approach with 3 × 3 CI (HE-CI). In this paper Dewar et al. have studied the DA reactions of 1,3-butadiene with ethylene and its cyano derivatives and have reached the conclusion that the DA reactions of butadiene with cyano-substituted ethylenes are nonsynchronous, proceeding via biradical-like intermediates. However, these calculations cannot distinguish between two-step and two-stage mechanisms.

On the basis of these calculations, these authors suggest also that the mechanism of the prototypical DA reaction, i.e. that of butadiene with ethylene (which is the reaction studied in the present paper), remains uncertain, and whether or not this reaction is synchronous remains an open question. In this case the computational results suggest that the difference between the energies of the corresponding synchronous and nonsynchronous transition states is small.

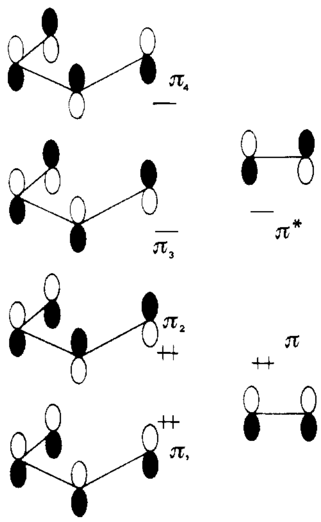
Apart from the semiempirical studies of Dewar et al.,[3-5] McIver,[10] Basilevsky et al.,[11] Kikuchi,[12] and Jug et al.,[13] there have been also a number of ab initio calculations on the mechanism of the prototypical Diels–Alder reaction. The first ab initio studies were those of Burke et al.[16] and Townshend et al.[17] Burke et al. have carried out extensive calculations on the concerted approach of this reaction at the SCF level using an STO-3G basis set and have also recalculated several points on the hypersurface using a medium-sized basis set (7s/3p). Townshend et al. have studied not only the concerted but also the two-step approach using an SCF treatment with limited CI at the STO-3G level and have recalculated the energy pathways with an extended 4-31G basis set. Both sets of results favored a synchronous concerted mechanism, but the methods used were criticized by Dewar et al.[3b] In fact, even though these studies already involved a very significant computational effort, they were performed without complete optimization and characterization of the critical points. In addition, those of Burke et al. did not include any configuration interaction, which is essential if a diradical-like species is to be described.

Recently, Houk et al.[20] have investigated the concerted approach at the SCF level using the STO-3G basis set and gradient techniques with optimization of all variables and have found in this case an authentic transition state. More recently Houk et al.[21] have carried out calculations to distinguish between synchronous and asynchronous concerted mechanisms using several theoretical levels (RHF/STO-3G, RHF/3-21G, and UHF-3-21G) with gradient optimizations and characterization of the critical points through the computation of the related Hessian matrices. In all cases they have found a C_s synchronous critical point, which is a transition state at the RHF level and a second-order saddle point at the UHF level. However, they pointed out that the UHF calculations are highly biased toward diradical character, since the wave function is approximately 50% triplet.

The effect of the inclusion of electron correlation by means of Moller–Plesset perturbation theory at the STO-3G SCF level has also been investigated,[22] and it has been found that this effect favored the asynchronous over the synchronous pathway, but because of various computational assumptions, these results are of limited significance.

In view of all these uncertainties in the ideas concerning the mechanism for the DA reaction, it was thought worthwhile to study with ab initio MC-SCF techniques the potential energy surface for the reaction of butadiene with ethylene, and in this paper, we report the results obtained in this study. Some preliminary results of this study have already been reported.[23]

Chart I



2. Computational Methods

The main aim in choosing the theoretical methods for performing these calculations was to try to ensure that as many as possible of the deficiencies apparent in the previous calculations were overcome. The following approach was adopted: (i) The calculations were carried out at the MC-SCF level[24] with minimal (STO-3G)[25] and extended (4-31G)[26] basis sets. (Integral and derivative calculations were performed with the GAUSSIAN 80 series of programs.[27]) (ii) Full optimization of all structures was carried out with MC-SCF gradient techniques.[28] (iii) Characterization of the critical points was done by diagonalizing the Hessian matrices computed by finite differences.

The various optimizations were performed with CASSCF wave functions with CI expansions derived from four electrons in four orbitals (CAS1) and six electrons in six orbitals (CAS2). For the addition of 1,3-butadiene and ethylene, the molecular orbitals were constructed from the noninteracting species butadiene and ethylene (see Chart I). Thus, in the CAS1-type computations, the valence space includes four electrons and four orbitals, the π_2 and π_3 MO's of butadiene and the π and π^* MO's of ethylene, while in the CAS2-type computations the valence space includes six electrons and six orbitals, all four π MO's of butadiene and again the two π MO's of ethylene. Both types of valence spaces are appropriate for the motions investigated here.

It is important to justify the procedure used from the outset and to discuss possible shortcomings. In previous work[29,30] we have shown that the MC-SCF method with the STO-3G basis gives a good qualitative picture of the surface. For example, in our recent study of 1–3 dipolar cycloadditions,[30] the number and nature of the various critical points on the synchronous and nonsynchronous pathways were in good agreement at the STO-3G and 4-31G levels. However, the stability of diradicaloid structures is overestimated with the STO-3G basis set. Thus, we have good reason to expect that the general features of the surface and the critical geometries will be qualitatively correct at the STO-3G level. However, we expect that diradicaloid minima may become very shallow or even disappear with extended bases. Thus, we have proceeded by exploring the surface in great detail at the STO-3G level, recognizing that the relative energetics of diradicaloid structures may be qualitatively

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(23) Bernardi, F.; Bottoni, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1051–1052.

(24) (a) Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795–1812. (b) Robb, M. A.; Eade, R. H. A. *NATO Adv. Study Inst. Ser., Ser. C* **1981**, *67*, 21–54.

(25) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–2664.

(26) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.

(27) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; De Frees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*(No. 406).

(28) Schlegel, H. B.; Robb, M. A. *Chem. Phys. Lett.* **1982**, *93*, 43–46.

(29) Bernardi, F.; Bottoni, A.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260–2264.

(30) McDouall, J. J. W.; Robb, M. A.; Niazi, U.; Bernardi, F.; Schlegel, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 4642.

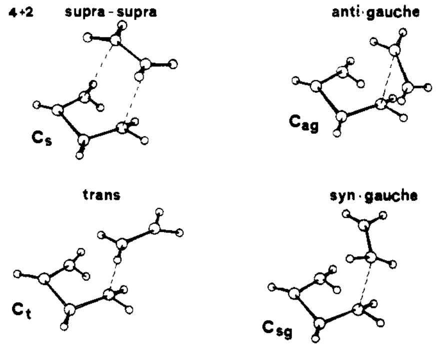


Figure 1. 4 + 2 supra–supra synchronous approach of C_s symmetry, the anti-gauche (C_{ag}), trans (C_t), and syn–gauche (C_{sg}) approaches between *cis*-butadiene and ethylene.

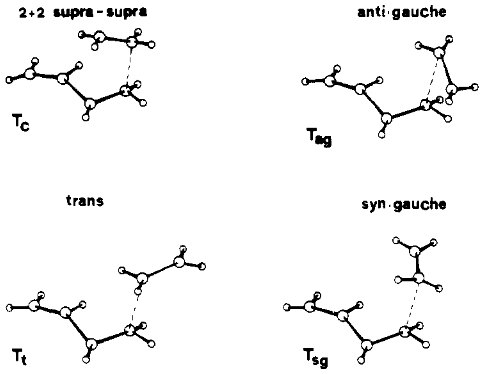


Figure 2. 2 + 2 supra–supra approach (T_c), the anti–gauche (T_{ag}), trans (T_t), and syn–gauche (T_{sg}) approaches between *trans*-butadiene and ethylene.

incorrect. The most interesting regions of the surface can then be explored with extended basis sets.

In the present study we have investigated the following reaction paths, which are expected to be relevant on the basis of either the Woodward–Hoffmann rules or previous computations: (i) a 4 + 2 supra–supra synchronous approach, (ii) a syn–gauche, a trans, and an anti–gauche approach, and (iii) a 2 + 2 supra–supra approach.

In order to obtain information also on the influence of conformation on diene reactivity, the gauche and trans approaches have been computed with respect to the *cis*- and *trans*-butadiene. The various approaches to the cis and trans isomers are shown in Figures 1 and 2, respectively.

At the STO-3G level the Hessian matrix was computed in a subset of variables (see Figure 3) containing the bond lengths C_3–C_4, C_4–C_5, and C_5–C_6, the angles $H'_4C_4C_3$, $H_4C_4C_3$, $C_3C_4C_5$, $C_4C_5C_6$, $H'_5C_5C_6$, and $H_5C_5C_6$, and the dihedral angles $H'_4C_4C_3Y$, $H_4C_4C_3Y$, $C_6C_5C_4C_3$, $H'_5C_5C_6C_4$, $H_5C_5C_6C_4$, $H'_6C_6C_5C_4$, and $H_6C_6C_5C_4$. In the 4-31G basis, the Hessian matrix was obtained by updating the STO-3G Hessian matrix during the optimization.

3. Results and Discussion

The various critical points located on the reaction surface at the three computational levels CAS1 STO-3G, CAS2 STO-3G, and CAS1 4-31G are listed in Table I together with the corresponding energy values. Either total energies (E_T) or energy differences (ΔE) relative to the two trans minima found in the case of *cis*- and *trans*-butadiene are reported.

A complete tabulation of the optimized geometrical parameters for the various structures obtained at the CAS1 STO-3G and 4-31G computational levels is collected in Tables II–IV in the supplementary material. The notation used to define the internal coordinates is shown in Figure 3, while in Figure 4, the rotational energy profile for the various diradical structures is given. Schematic representations of the geometries of the relevant critical points are given in Figures 5–9.

3.1. CAS1 STO-3G Results. A critical point of C_s symmetry corresponding to the concerted approach between *cis*-butadiene and ethylene has been located. After diagonalization of the Hessian matrix constructed in the manner discussed previously, we have found only one negative eigenvalue, which shows that this point is a real transition state (first-order saddle point) involving the synchronous formation of the two new carbon–carbon bonds C_1–C_6 and C_4–C_5. This negative eigenvalue is associated with a transition vector, which corresponds to a symmetric motion of the system, and is dominated by the distance *R* (see Figure 3a), which describes the approaching of the two molecules. Furthermore, this first-order saddle point lies considerably higher in energy with respect to the region of the diradical species

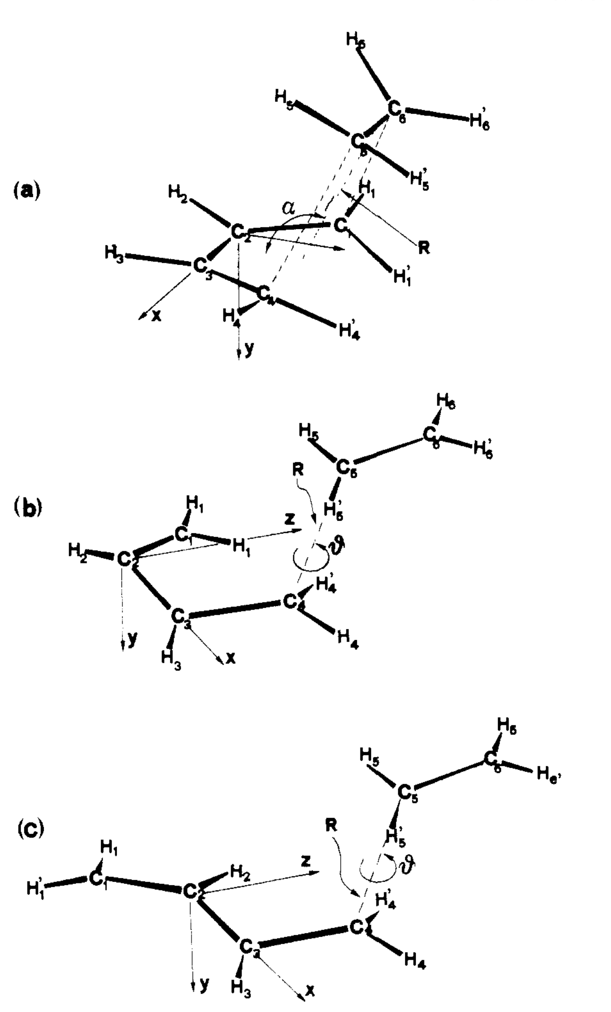


Figure 3. Notations used to define the various geometrical parameters for the three model examples: (a) 4 + 2 synchronous attack of C_s symmetry, (b) trans approach between *cis*-butadiene and ethylene, and (c) trans approach between *trans*-butadiene and ethylene.

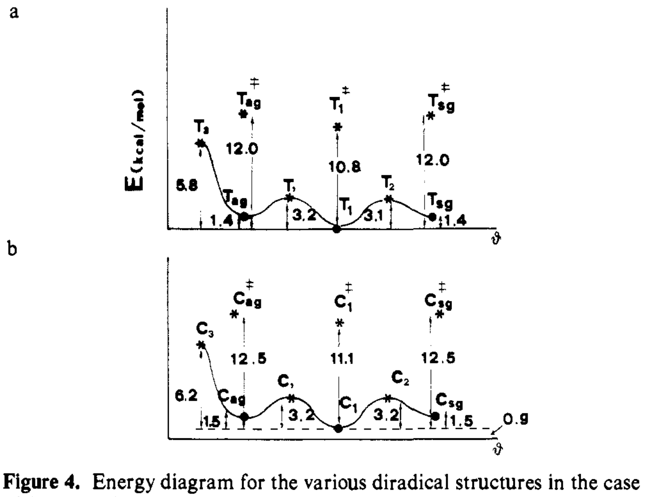
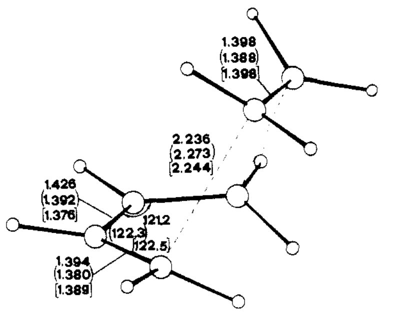


Figure 4. Energy diagram for the various diradical structures in the case of (a) *trans*-butadiene and (b) *cis*-butadiene. The reference value used is the energy of the T_t minimum. The symbol ‡ is used to distinguish the various fragmentation transition states from the corresponding minima.

Table I. Total Energy Values (E_T) and Energy Differences (ΔE_T) of the Critical Points Found in the Cycloaddition Reaction between Butadiene and Ethylene

	STO-3G CAS1		STO-3G CAS2		4-31G CAS1	
critical points[a]	E_T[b]	ΔE[c]	E_T[b]	ΔE[c]	E_T[b]	ΔE[c]
C_{ag} TS	-230.117 47	13.1	-230.162 44	2.4		
C_{ag} M	-230.136 06	1.4			(-232.598 49)[d]	4.3
C_t TS	-230.120 49	11.2	-230.166 31	0.0	(-232.605 30)[d]	0.0
C_t M	-230.138 27	0.0				
C_{sg} TS	-230.119 80	11.6	-230.165 86	0.3	(-232.604 96)[d]	0.2
C_{sg} M	-230.135 95	1.5			-232.603 86	0.9
					(-232.601 17)[d]	(2.6)
C_1 TS	-230.133 22	3.2				
C_2 TS	-230.133 32	3.1				
C_3 TS	-230.128 34	6.2			(-232.590 18)[d]	(9.5)
C_s TS	-230.106 43	19.9	-230.162 54	2.4	-232.607 41	-1.3
					(-232.606 75)[d]	(-0.9)
T_{ag} TS	-230.120 53	12.0				
T_{ag} M	-230.137 55	1.4			(-232.602 23)[d]	
T_t TS	-230.122 45	10.8				
T_t M	-230.139 70	0.0			(-232.602 23)[d]	
T_{sg} TS	-230.120 63	11.9				
T_{sg} M	-230.137 54	1.3				
T_1	-230.134 63	3.2				
T_2	-230.134 73	3.1				
T_3	-230.130 46	5.8				
T_c SOSP	-230.113 78	16.3				
reactants	-230.149 95[e]	-7.3	-230.21846[f]	-32.7	-232.658 29[e]	-33.3

[a] M denotes a minimum, TS, a transition state, and SOSP, a second-order saddle point. [b] Atomic units. [c] Kilocalories per mole. [d] Energy value coresponding to the CAS1 STO-3G optimized geometry. [e] Computations at SCF STO-3G optimized geometries. [f] Computations at MC-SCF STO-3G optimized geometries.



C_s

Figure 5. CAS1 STO-3G, CAS2 STO-3G, and CAS1 4-31G optimized geometries for the C_s TS. The CAS1 geometries are in parentheses (STO-3G) and square brackets (4-31G). Lengths are in angstroms and angles in degrees.

C_{sg}

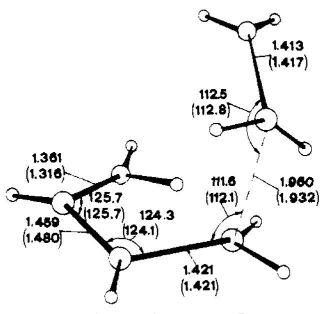
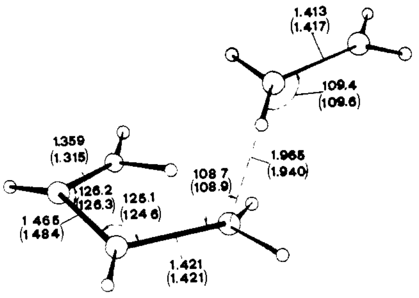


Figure 6. CAS1 (parentheses) and CAS2 STO-3G optimized geometries of the C_{sg} TS.

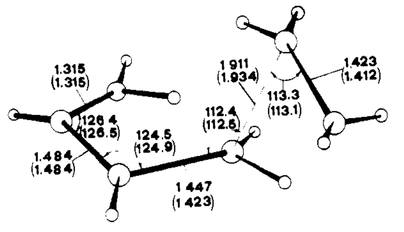
corresponding to the gauche and trans approaches. The relevant optimized geometrical parameters of the C_s transition state are reported in Figure 5.

The region of the diradical species has also been completely investigated, and the results are summarized in Figure 4, which shows some similarities with Figure 1a of ref 5. For either the *cis*-butadiene or the *trans*-butadiene, we have found three minima, corresponding to an anti-gauche (C_{ag} M, T_{ag} M), a trans (C_t M,



C_t

Figure 7. CAS1 (parentheses) and CAS2 STO-3G optimized geometries of the C_t TS.



Cag

Figure 8. CAS1 (parentheses) and CAS2 STO-3G optimized geometries of the C_{ag} TS.

C_{sg}

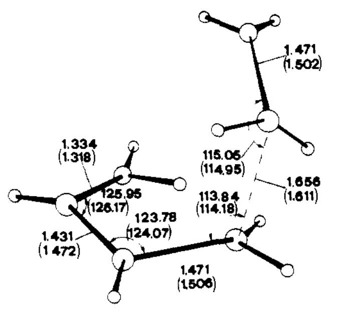


Figure 9. STO-3G CAS1 (parentheses) and 4-31G CAS1 optimized geometries of the C_{sg} M.

T_t M), and a syn–gauche (C_{sg} M, T_{sg} M) approach. The energy differences between the three minima in both cases are quite small, with the trans minimum at a slightly lower energy (~1.5 kcal/mol) than the syn–gauche and the anti–gauche minima. It is also found that the T_t minimum is more stable by ~1 kcal/mol than the C_t minimum. For each minimum we have also located a corresponding fragmentation transition state, i.e. a C_{ag} TS and T_{ag} TS for the anti–gauche approach, a C_t TS and T_t TS for the trans approach, and finally a C_{sg} TS and T_{sg} TS for the syn–gauche approach. Also, the various transition structures are very close in energy with barriers of the order of 11–12 kcal/mol with respect to the corresponding minima. In both cases the trans approach is slightly favored with respect to the others by ~1.2–1.4 kcal/mol.

Note that the structures are true diradicals. Thus, for the C_{sg} TS, $r(C_4–C_5) = 1.96$ Å, and $r(C_1–C_6) = 3.46$ Å, which are similar to those reported by Dewar in ref 5.

For all the structures, which were supposed to be a minimum, the diagonalization of the Hessian matrix showed only positive eigenvalues. On the other hand, the diagonalization of the matrices associated with the transition states was characterized, as required, by only one negative eigenvalue, with the corresponding transition vector dominated in every case by the approaching distance R (see parts a and b of Figure 3).

All the structures are characterized by a value of the dihedral angle ϑ, which describes the relative position of the ethylene and butadiene fragments with respect to the rotation around the $C_4–C_5$ direction (see parts a and b of Figure 3). The value of $\vartheta = 0°$ is taken to correspond to the situation when the $C_5–C_6$ bond eclipses the $C_3–C_4$ bond. The distinctive value of ϑ is between 70° and 80° in the case of the anti–gauche approach, close to 180° for the trans approach, and between 280° and 285° in the case of the anti–gauche approach.

In addition to the structures previously described, we have also found, for both the *cis*-butadiene and *trans*-butadiene surfaces, two more critical points that we have indicated as C_1, C_2 and T_1, T_2, respectively. These species, always diradical in nature, correspond to values of the dihedral angle ϑ that are intermediate between the corresponding values for C_{ag} M and C_t M (C_1), T_{ag} M and T_t M (T_1), C_t M and C_{sg} M (C_2), and T_t M and T_{sg} M (T_2). The Hessian matrix was always characterized by only one negative eigenvalue. The corresponding eigenvector is dominated by the rotation angle ϑ, showing that C_1, C_2 and T_1, T_2 are conformational transition states connecting the various minima, as shown in Figure 4.

We have also investigated the ring closure from the syn–gauche minimum to cyclohexene and found that this process occurs without almost any barrier. That the absence of a significant barrier is real and not a failure of the very full search procedures used (which is, inevitably, still a possibility) is supported by the fact that the potential surface was found to be extremely flat in the region of the syn–gauche minimum. On the other hand, the ring closure from the anti–gauche minimum to vinylcyclobutane involves a barrier of 6.2 kcal/mol in the case of *cis*-butadiene and 5.8 kcal/mol in the case of *trans*-butadiene. The two related transition states, denoted as C_3 and T_3, both have diradical character and correspond to values of the dihedral angle ϑ of −4.5° for C_3 and ~−1° for T_3. In both cases the potential surface was found to be extremely flat for values of ϑ in the range $-15° \leqslant \vartheta \leqslant 30°$.

In the case of the *trans*-butadiene, we have also investigated a 2 + 2 supra–supra approach. This type of approach between the two molecules, which corresponds to a value of ϑ equal to zero, is illustrated in Figure 2. Also, in this case, we have located a critical point of diradical type that we have indicated with the symbol T_c (c = cis). We have found that the related Hessian matrix has two negative eigenvalues showing that the T_c structure is a second-order saddle point (SOSP), i.e. a point on the potential surface characterized by two directions of negative curvature. Even if this point has no chemical significance, it is of interest to look at the shape of the transition vectors corresponding to the two negative eigenvalues. While the first transition vector (the lower one) is dominated by the approaching distance R and preserves the local plane of symmetry $C_3C_4C_5C_6$, the second eigenvector (the higher one) corresponds to the rotation around C_4C_5; i.e., it is associated to a motion that breaks this local plane.

3.2. CAS2 STO-3G Results. In order to assess whether the CAS1 valence space is appropriate to describe this potential energy surface, we have performed a geometry optimization of C_s, C_{ag}, C_t, and C_{sg} TS using the CAS2 computational level where the valence space includes six electrons and six orbitals, the latter being the four π MO's of butadiene and the two π MO's of ethylene. The relevant geometrical parameters optimized at the CAS2 level together with the corresponding values computed at the CAS1 level are shown in Figures 5–8, and the related energy values are listed in Table I. It can be seen that the geometries of these four species are much the same in the CAS1 and CAS2 approximations, the major difference being that for the syn–gauche and trans structures the forming single bonds are slightly longer and that the lengths of the two carbon–carbon bonds away from this are slightly more distorted from their butadiene values than in the CAS1 ones. In contrast, the two forming single bonds in the synchronous species are shortened at the CAS2 level, while the butadiene part of the transition structure has carbon–carbon bonds that are slightly less nearly equal in length.

Also, at the CAS2 level the energies of the three diradical TS are very close, with relative energy differences very similar to those computed at the CAS1 level. The only significant difference is found in the comparison with the synchronous TS, whose energy at the CAS2 level remains again higher than those of the diradical TS, but the difference is significantly reduced (from 8.82 to 2.36 kcal/mol with respect to the C_t TS).

Therefore, these results indicate that the CAS1 valence space is adequate, particularly for the geometry optimization.

3.3. CAS1 4-31G Results. Also, at this level a stationary point of C_s symmetry has been found, and diagonalization of the updated Hessian matrix has shown it to be a first-order saddle point. The geometrical parameters vary only slightly from the values computed at the STO-3G level, as shown in Figure 5. Accordingly, the energy lowering in passing from the 4-31G energy value computed at the STO-3G geometry to the 4-31G energy value computed at the 4-31G geometry is only 0.4 kcal/mol.

We have also investigated the other various reaction paths for the case of *cis*-butadiene. In spite of extensive searches, no fragmentation transition states for the gauche and trans approaches could be located. On the other hand, optimization of the structure corresponding to the C_{sg} minimum has led again to a critical point (a minimum on the basis of the updated Hessian matrix) whose energy is listed in Table I and whose geometry is shown in Figure 9. The changes with respect to the STO-3G geometry are minor, and the energy lowering associated with these changes is again very small (1.69 kcal/mol). This minimum is also slightly higher than the structures corresponding to the C_{sg} and C_t STO-3G transition states, as shown by the 4-31G energy values computed at the STO-3G geometries listed in Table I.

Thus, in passing from the STO-3G to the 4-31G MC-SCF results, we have found that the region of the potential surface associated with the gauche and trans approaches becomes very flat and that the STO-3G structure in the region of the various diradical minima are quite accurate. Both these trends are in accord with the results found in the MC-SCF study of the thermal cycloaddition of two ethylenes.[29] Consequently, we have carried out 4-31G computations using the STO-3G geometries on some important points of the surface. In particular, we have computed the energy values of the anti–gauche minimum (C_{ag} M) and of the conformational transition state C_3 to obtain information about the energetics involved in the process of ring closure to vinylcyclobutane. Furthermore, we have also computed the energy of the trans minimum for attack on *trans*-butadiene (T_t M) in order to obtain information on the relative energies for attack on *cis*- and *trans*-butadiene.

An important piece of information provided by the 4-31G computations is that the C_s transition state is located at a slightly lower energy than the C_{sg} minimum. The present results seem also to suggest that the nonsynchronous mechanism involving the

C_{sg} minimum is a two-stage concerted one, this because the intermediate diradical, if it exists, is very short lived since the barrier to its conversion to cyclohexene, as shown at the STO-3G level, is very small. Therefore, on the basis of these results, it appears that both synchronous and nonsynchronous paths exist and that the synchronous concerted path is favored by ~2 kcal/mol.

In addition there is also a third reaction mechanism that from the C_{ag} intermediate leads to vinylcyclobutane through a transition state of conformational origin. The present results do not allow us to assess clearly whether this mechanism is a two-stage or a two-step one. However, the rate-determining step seems to be associated with the formation of the second bond. The related barrier on the basis of 4-31G computations at STO-3G geometries is of the order of 5.2 kcal/mol, and this path is disfavored with respect to the synchronous concerted path by ~11 kcal/mol. The attack on *trans*-butadiene should involve again a mechanism of the latter type, leading again to vinylcyclobutane, and the mechanism should be disfavored by a similar amount with respect to the energetically more favorable concerted synchronous mechanism, which proceeds through the C_s transition state.

This overall mechanism, suggested on the basis of the 4-31G MC-SCF results and of a critical analysis of the STO-3G MC-SCF results, also agrees well with the available experimental evidence for this simple Diels–Alder reaction.

We examine now in detail the main structural features of the two important structures involved in this mechanism, i.e. the C_s transition state and the C_{sg} minimum.

The main features of the results obtained for the C_s TS (see Figure 5) are that the forming carbon–carbon distance is quite long (2.2 Å) and that the carbon–carbon distances of the two fragments are strongly distorted: the ethylene and butadiene double bonds have all lengthened by about 0.04 Å, and the butadiene single bond has shortened by about 0.07 Å, with a tendency toward equalization of these bonds. The details of these results also reveal some additional remarkable features that confirm the stereochemical implications discussed by Brown and Houk at the SCF level.[20]

The results obtained for the C_{sg} minimum are illustrated in Figure 9. In this case we can notice that one bond is almost completely formed (C_4–C_5 with a bond length of ~1.6 Å) and that the formation of this bond has caused a very significant lengthening of the two adjacent C–C bonds (C_3–C_4 and C_5–C_6), a shortening of the butadiene single bond C_2–C_3, while the C_1–C_2 butadiene bond has remained almost unchanged at its double-bond value. Another interesting feature is that the two terminal methylene groups are almost one above the other and therefore in a position suitable for starting the process of formation of the second bond.

4. Conclusions

In this paper we have described the results obtained in an MC-SCF study at the minimal STO-3G level and the extended 4-31G level of the cycloaddition reaction between butadiene (cis and trans) and ethylene. At the STO-3G level we have found that the attack of ethylene on *cis*-butadiene involves four fragmentation transition states, i.e. a transition state of C_s symmetry associated with the concerted synchronous attack and three transition states of diradicaloid nature associated with the syn–gauche, the trans, and the anti–gauche approach, which lead to three minima, again of diradicaloid nature. These three minima are interconnected by two transition states of conformational origin. From the syn–gauche minimum one can have ring closure to cyclohexene almost without any barrier, while from the anti–gauche minimum, one can have also ring closure to vinylcyclobutane with a barrier of about 6 kcal/mol. The attack on *trans*-butadiene, which leads only to vinylcyclobutane, involves again three transition states of diradicaloid nature and three minima interconnected by two transition states of conformational origin. The barrier to ring closure to vinylcyclobutane is again of ~6 kcal/mol.

The synchronous concerted path is disfavored on energy basis, and the preferred paths are those associated with the nonsynchronous approaches. The rate-determining step for the attack on either *cis*- or *trans*-butadiene is the formation of the first bond, and the reaction should occur mainly through a trans approach, with the attack on *trans*-butadiene slightly favored. Therefore, at the STO-3G level, the rate-determining step is associated with the fragmentation transition states, which have very similar energy values in the various cases. Consequently, these results suggest that the rate of formation of cyclohexene (via attack on *cis*-butadiene) and vinylcyclobutane (via attack on *cis*- and *trans*-butadiene) are similar, in contrast with the experimental results, which indicate that the mechanism leading to cyclohexene is favored by ~7 kcal/mol with respect to that leading to vinylcyclobutane.

The 4-31G results provide a completely different mechanism, which agrees now very well with the experimentals results. The main differences are (i) the three fragmentation transition states seem to disappear, so that the region of the potential energy surface associated with the gauche and trans approaches becomes very flat; and (ii) the C_s transition state is located at a slightly lower energy than the syn–gauche minimum.

Therefore, on the basis of the 4-31G results, it appears that both synchronous and nonsynchronous paths exist, with the synchronous path favored by 2 kcal/mol. Of course the energy difference of 2 kcal/mol is not very significant at this level. However, as we have shown in our study of 1–3 dipolar cycloadditions,[30] the addition of dynamic electron correlation will favor the synchronous path so that this difference will be increased at high levels of theory. On the other hand, this may be partly offset by the fact that the entropy of the diradical region will be larger than that of the region of the synchronous transition structure. The nonsynchronous paths can lead to cyclohexene via a syn–gauche attack on *cis*-butadiene or to vinylcyclobutane via an anti–gauche attack on *cis*-butadiene or all three types of nonsynchronous attack on *trans*-butadiene. In all cases the rate-determining step is the formation of the second C–C bond, and therefore the ring closure to cyclohexene is favored by about 7 kcal/mol with respect to that of vinylcyclobutane. Consequently, the synchronous concerted approach is favored by about 10 kcal/mol over the mechanism leading to vinylcyclobutane, in good accord with the experimental results.

These results suggest also that the preference for the synchronous mechanism can be easily modified by substituents with large steric effects in favor of an asynchronous two-stage mechanism, since repulsive effects should be smaller in the case of a two-stage mechanism than in the case of a synchronous mechanism, in agreement with Dewar's suggestions.[5]

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Supplementary Material Available: Tables of optimized geometrical parameters for the various structures obtained at the CAS1 STO-3G and 4-31G computational levels (Tables II–IV) (8 pages). Ordering information is given on any current masthead page.