H_4 protons and the frequency which was required to decouple H_2, H_5 protons.

Above 6° the bridging hydrogens and the H_1 and H_4 hydrogens undergo noticeable exchange averaging on the NMR time scale. Exchange appears to be complete at about 50° giving an experimental averaged resonance of τ 9.54. This is in good agreement with the weighted average (τ 9.50) of the individual resonances observed in the limiting spectrum at −63°. The exchange process could occur by means of twisting motions of the BH_2 groups to break hydrogen bridge bonds and place terminal hydrogens in bridging positions while bridging hydrogens move to terminal positions.[3] The essential invariance of the resonances assigned to H_2, H_5, H_3, and H_6 suggests that these hydrogens do not exchange rapidly on the ^1H NMR time scale.

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Supplementary Material Available: structure factors of $B_6H_{10}[P(CH_3)_3]_2$ (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 3375 (1967); (b) R. A. Geanangel and S. G. Shore, *ibid.*, **89**, 6771 (1967); (c) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967); (d) G. Kodama, U. Englehardt, C. Lafrenz, and R. W. Parry, *J. Am. Chem. Soc.*, **94**, 407 (1972); (e) H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *ibid.*, **91**, 2131 (1969); (f) H. D. Johnson, II, R. A. Geanangel and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).

(2) (a) G. L. Brubaker, M. L. Denniston, S. G. Shore, J. C. Carter, and F. Swicker, *J. Am. Chem. Soc.*, **92**, 7216 (1970); (b) M. L. Denniston, Ph.D. Thesis, The Ohio State University, 1970; (c) *Diss. Abstr., B*, **31**, 5237 (1971); (d) C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc. A*, 179 (1973).

(3) A. V. Fratini, G. W. Sullivan, M. L. Denniston, R. K. Hertz, and S. G. Shore, *J. Am. Chem. Soc.*, **96**, 3013 (1974).

(4) R. W. Rudolph and D. A. Thompson, *Inorg. Chem.*, **13**, 2779 (1974).

(5) (a) R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, in press; (b) R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971).

(6) K. Wade, *J. Chem. Soc. D.*, 792 (1971).

(7) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972).

(8) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Am. Chem. Soc.*, **95**, 6629 (1973).

(9) H. D. Johnson, II, V. T. Brice, and S. G. Shore, *Inorg. Chem.*, **12**, 689 (1973).

(10) R. Thomas and K. Eriks, *Inorg. Synth.*, **9**, 59 (1967).

(11) J. M. Stewart, F. A. Kundell, and J. C. Baldwing, "The XRAY System Version of 1972", Computer Science Center, University of Maryland, July 1970.

(12) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) See paragraph at end of paper regarding supplementary material.

(16) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", USAEC Report ORNL-3694, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(17) J. R. VanWaser, "Phosphorus and Its Compounds", Vol. I, Interscience, New York, N.Y., 1958, pp 32–43.

(18) (a) D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, **3**, 438 (1964); (b) J. B. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *ibid.*, **9**, 2170 (1970); (c) R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *J. Am. Chem. Soc.*, **92**, 3514 (1970).

(19) A. Stock, "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, N.Y., 1933.

(20) K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 559 (1972).

(21) R. J. Remmel, H. D. Johnson, II, I. S. Jaworiwsky, and S. G. Shore, *J. Am. Chem. Soc.*, **97**, 5395 (1975).

(22) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963, p 53.

(23) (a) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds", W. A. Benjamin, New York, N.Y., 1969; (b) S. G. Shore, in "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, N.Y., 1975, Chapter 3.

On the Stereochemistry of Polar 2 + 2 Cycloadditions

N. D. Epiotis,*[1a] R. L. Yates,[1a] D. Carlberg,[1a] and F. Bernardi*[1b]

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195, and the Istituto di Chimica Organica, Università di Bologna, 40136 Bologna, Italy. *Received January 23, 1975*

Abstract: Quantum mechanical calculations of the restricted Hartree-Fock (RHF) type on model polar 2 + 2 cycloaddition systems predict a transoid approach of the two cycloaddends. This contrasts with the results of experimental studies of polar 2 + 2 cycloadditions, all of which indicate a preferred cisoid approach of the two cycloaddends. These findings suggest that either the *overall* reaction sequence involving a transoid "approach" has a higher barrier than the reaction sequence involving a cisoid approach, forbidden in the Woodward-Hoffmann sense, or that a RHF level of theory is inadequate for the treatment of such reactions.

Polar 2 + 2 cycloadditions have been extensively studied in the past 20 years.[2] These reactions constitute a simple way of constructing functionalized four-member rings which can be further manipulated toward the desired end in the course of a synthesis. Mechanistic interest in these reactions has resurfaced very recently.[3a] At this point, there is sufficient experimental data available so that one can attempt an integration of the known facts into a coherent pattern that will constitute a good approximation of the mechanism of these reactions. In this paper we use theoretical arguments coupled with quantitative calculations at various levels of sophistication in order to interpret the available experimental data and gain insights into the mechanism of 2 + 2 cycloadditions. The calculations which have been employed include Mulliken-Wolfsberg-Helmholtz, abbreviated MWH, calculations,[3b] SCF-MO-CNDO/2 calculations,[4] and ab initio calculations using an STO-4G basis set.[5] These calculations are single determinant calculations of the restricted Hartree-Fock (RHF) type.

The Woodward-Hoffmann rules regarding the stereochemistry of pericyclic reactions stipulate that a thermal 2 + 2 cycloadditions will occur in a 2s + 2a fashion. Now, this stereochemical mode of union is sterically unfavorable, and, as a result, many chemists have reasoned that 2 + 2 cycloadditions will occur in a "stepwise" manner involving a diradical or dipolar intermediate wherein pericyclic bonding is absent. Herein lies the first important point which we wish to emphasize: *the initial hypotheses of many experimentalists who attempted to study the mechanism of 2 + 2 cycloadditions are based upon the one-determinantal*

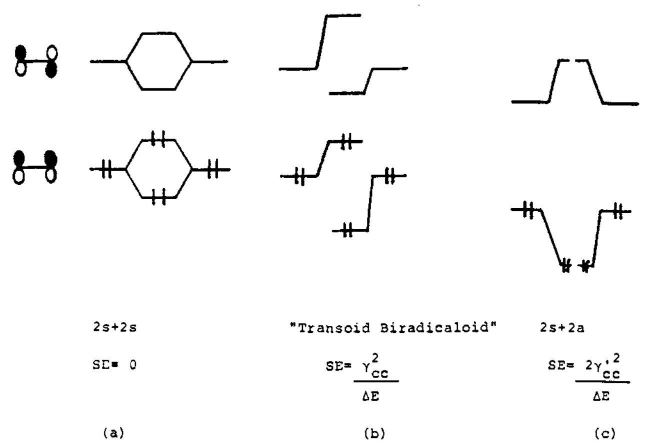


Figure 1. Interaction diagrams for the three stereochemical modes of union in the dimerization of ethylene: (a) 2s + 2s (b) "transoid biradical", and (c) 2s + 2a.

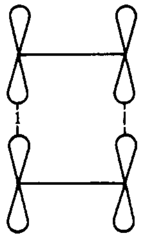
Woodward-Hoffmann theory of pericyclic reactions. For example, in the most recent experimental study of the mechanism of polar 2 + 2 cycloadditions,[3a] the authors introduce a series of three communications by the statement "Concerted [π^2s + π^2s] cycloadditions are forbidden by orbital symmetry. This ban is bypassed by reactions occurring via biradicals or zwitterions, as well as by the concerted process [π^2a + π^2s]." Recently, we have developed a treatment of the stereochemistry of thermal pericyclic reactions based upon standard two-electron configuration interaction (CI) theory[6] as well as a general theory of the rates, stereochemistry, and regiochemistry of thermal and photochemical pericyclic reactions based upon one-electron CI theory.[7] The conclusions of these theoretical studies may be summarized as follows. (a) CI can render Woodward-Hoffmann "forbidden" reactions effectively "allowed", e.g. *the terms "forbidden" and "allowed" are theory dependent* and have meaning only within the framework of the one-determinantal Woodward-Hoffmann treatment of pericyclic reactions. (b) CI can be relatively more important in polar than in nonpolar Woodward-Hoffmann "forbidden" reactions.[8] (c) CI is not as important in Woodward-Hoffmann "allowed" reactions. Actual CI calculations on model systems which support these qualitative ideas have already been published.[9] Accordingly, the mechanism of polar 2 + 2 cycloadditions should be reexamined in the light of the more general CI approaches.

Computational Details

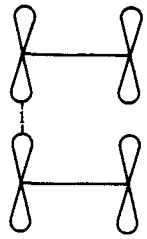
Three different types of computations were employed in this study, namely, Mulliken-Wolfsberg-Helmholtz (MWH), semi-empirical SCF-MO-CNDO/2, and ab initio calculations. The MWH and SCF-CNDO/2 calculations were performed on a CDC 6400 computer with already existing programs. The ab initio calculations utilized an STO-4G basis set and were carried out by means of the Gaussian 70 system of programs on a CDC 6600 computer. Due to the size of the molecules computed, no geometry optimization was attempted.

Results

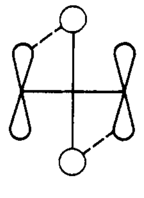
Before considering in detail the results of the various calculations, we should first review the general predictions of (effective) one-electron PMO theory regarding the stereochemistry of 2 + 2 cycloadditions.[10] Prior to undertaking this task, we wish to make some terminology clarifications. Specifically, there is an important distinction to be made between a terminology specifying the geometric arrangement of nuclei in space as two reactants approach each other and a terminology specifying the kind of bonding which obtains between the reactants. In this paper we shall use the terms "parallel", "perpendicular", and "transoid biradicaloid" in order to specify the three important geometries of approach of the two ethylenes, and the terms pericyclic and nonpericyclic in order to specify whether continuous bonding around the four uniting atomic centers is present or absent, respectively, in the geometry under consideration. The various possibilities are shown below:



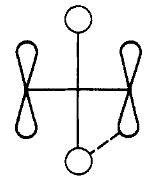
parallel
pericyclic
2s + 2s



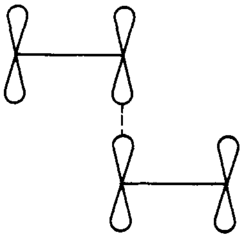
parallel
nonpericyclic



perpendicular
pericyclic
2s + 2a



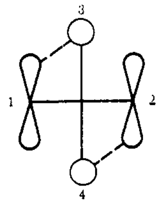
perpendicular
nonpericyclic

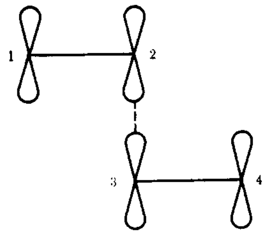


transoid
biradicaloid

The Woodward-Hoffmann notation 2s + 2s and 2s + 2a specifies simultaneously both geometry and bonding. However, many authors have used this notation to specify exclusively geometry. For example, theoretical chemists report that they have calculated the 2s + 2s and 2s + 2a transition states for the dimerization of ethylene while they actually mean that they have calculated the parallel and perpendicular transition state geometry with the actual type of bonding, e.g., pericyclic or nonpericyclic, to be determined from examination of the density matrix associated with the calculations.[11]

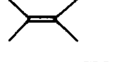
The relative stabilization of the three stereochemical modes of union can be readily determined by reference to the interaction diagrams of Figure 1. It can be seen that the "parallel" geometry is not stabilized and does not involve pericyclic bonding. Specifically, the pσ bond order between C_1 and C_3 and C_2 and C_4 is zero since there are two electrons occupying a bonding MO (BMO) and two electrons occupying an antibonding MO (ABMO). On the other hand, if one assumes that the resonance integrals γ_{13}', γ_{24}', and γ_{23} are all nearly equal, then the "perpendicular" geometry is stabilized twice as much as the "transoid biradicaloid" geometry and involves pericyclic bonding, e.g., it is a 2s + 2a geometry.



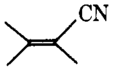


However, under the assumption that $\gamma_{13}' \simeq \gamma_{24}' \simeq \gamma_{23}$, steric effects will heavily favor the "transoid biradicaloid" geometry. As a result, the stereochemistry of 2 + 2 cycloaddition is expected to be one consistent with a transoid biradicaloid intermediate whenever steric effects heavily disfavor the 2s + 2a geometry of approach. In short, *one-electron PMO qualitative arguments rule out a preferred 2s + 2s mode of approach of the two cycloaddends.* Introduction of substituents of any kind on the two ethylenic moieties will alter the spacing of the interacting levels and magnitudes of the eigenvectors of the olefinic carbons but will not basically alter these conclusions which are, then, expected to be valid for polar 2 + 2 cycloadditions. This type of reasoning is implicit in the Woodward-Hoffmann rules and related treatments.

The ab initio calculation of an actual potential surface of a typical polar 2 + 2 cycloaddition is a formidable task. In such reactions, the two ethylenes are substituted by heteroatomic groups and the total number of basis set functions makes the calculations very costly. Thus, instead of computing the whole potential surface, one restricts his attention to important points of the potential surface, e.g., one calculates structures which are thought to represent transition states or intermediates.[12] The results of such studies coupled with experimental observations can be very useful in efforts to understand the mechanism of a reaction. We have chosen such an approach in our investigation of whether single determinant MO theory can account satisfactorily for the stereochemistry of polar 2 + 2 cycloadditions. The model reaction system was selected to be hydroxyethylene plus cyanoethylene:

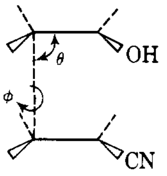


donor olefin

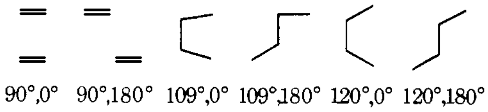


acceptor olefin

The structures which have been calculated are labeled according to the angle convention shown below:

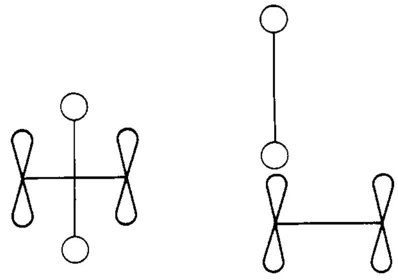


In the case of a "cisoid" approach where the two olefins lie on parallel planes, we define $\theta = 90°$ and $\phi = 0°$. We have computed the relative energies and overlap populations of the following structures:



I II III IV V VI

The energy difference between two structures of constant θ but different ϕ, e.g., $\theta = 0°$ vs. $\phi = 180°$, constitutes a criterion for the preferred geometry of approach of the two olefins. All calculated structures arise from initial bond formations between olefins lying in parallel planes. Structures like VII involving bond formation between olefins lying in perpendicular planes were not considered since previous calculations of the modified INDO[9] as well as the MINDO/3 variety[11] dealing with the dimerization of ethylene have shown the "perpendicular" geometry to be higher in energy than the "parallel" nonpericyclic geometry, apparently because of the severe steric repulsion obtaining in the "perpendicular" geometry. In our system, substituents should make such steric repulsion in the "perpendicular" geometry even more prohibitive and one can reasonably expect VII to lie higher in energy than I. Furthermore, we shall see that experimental evidence almost rules out a predominant 2s + 2a concerted mechanism in polar 2 + 2 cycloadditions. Intermediate structures of rotational angle ϕ equal to 90° as well as structures like VIII involving initial bond formation between two olefins lying in perpendicular planes were not considered since the energies of these structures relative to those of I-VI will not be crucial in the attempted correlation of theory and experiment. This last point will become self-evident after examination of the calculation results.

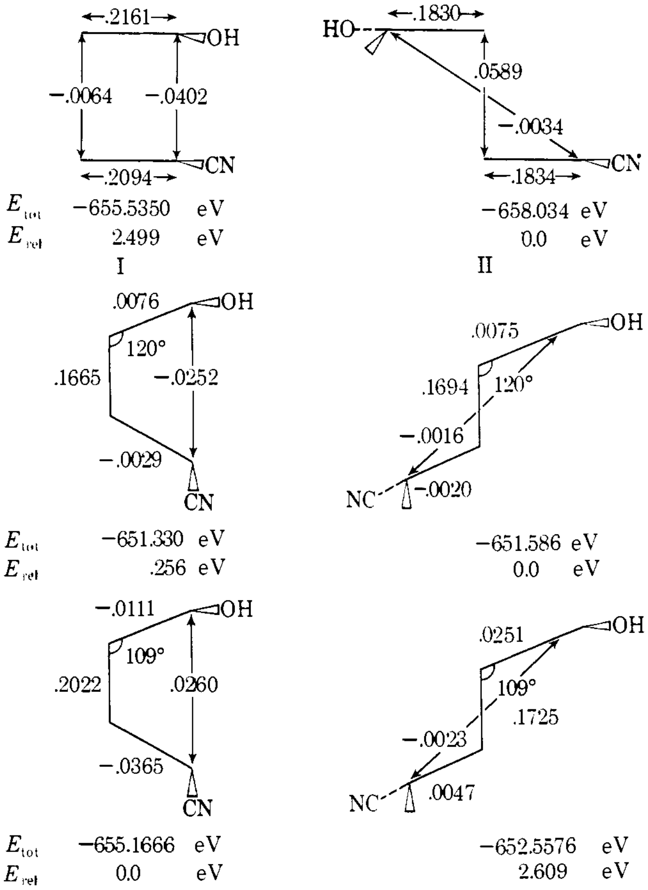


VII VIII

MWH Calculations

The results of the MWH calculations on I-VI are shown in Scheme I. The distance of approach of the two olefins has been taken to be 2.2 Å. The total energies as well as the pσ overlap populations of the various structures suggest that II occurs at the early stage of the reaction, III at a late stage of the reaction, and VI near the transition state. The early stage of the reaction is represented by structure I or II, e.g., two weakly interacting olefins. It can be seen that a trans approach is favored by 2.5 eV over a cis approach.

Scheme I. MWH Energies and Overlap Populations



The interaction of the two olefins approaching each other in a cis manner at the early stage of the reaction is antibonding along both pairs of union sites as can be readily seen from the $p\sigma$ overlap populations, −0.0064 and −0.0402. On the other hand, a trans approach leads to a strong bonding C_2-C_3 interaction ($p\sigma$ overlap population 0.0589) and a weak antibonding C_1-C_4 interaction ($p\sigma$ overlap population −0.0034). The antibonding interaction of the two olefins in I is understandable in terms of the interaction diagram of Figure 1a. Specifically if overlap is included in the analysis, as it is in the actual MWH calculation, the four-electron π-π interaction is destabilizing and the $p\sigma$ bond order along each pair of uniting centers negative. Furthermore, the interaction diagram is drawn for the case of the cycloaddition of two ethylenes while in our case we deal with the cycloaddition of two unsymmetrical olefins. As a result, the HOMO of one olefin can interact principally with the HOMO and minimally with the LUMO of the other olefin leading to unequal bonding along the two pairs of union sites.

The neighborhood of the transition state of the reaction is represented by structure V or VI since they both lie higher in energy than any of I, II, III, and IV. Structures V and VI both represent situations where a very weak through-space interaction between the p_z AO's of C_1 and C_4 obtains. These AO's are primarily interacting through the C_2-C_3 bond and their bond order is expected to be negative. This point has been adequately discussed by Hoffmann[13] and needs no further elaboration. The calculations show that the antibonding C_1-C_4 interaction is minimum in the trans geometry VI and maximum in the cis geometry V. As a result, VI is more stable than V by 0.25 eV.

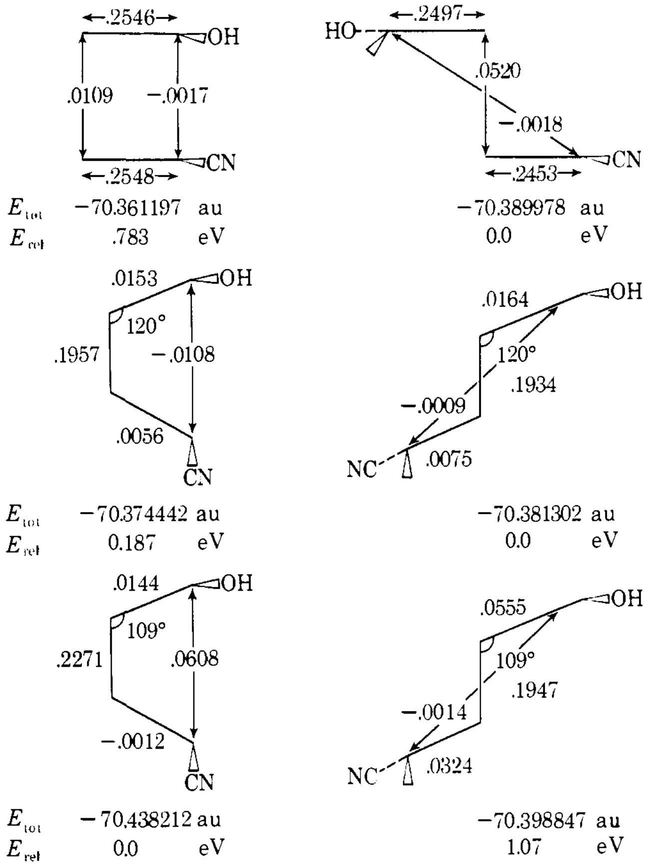
Finally, structures III or IV represent the late stage of the reaction. It is seen that III is nothing else but an unsymmetrically stretched cyclobutane ($p\sigma$ overlap populations 0.2022 and 0.0260) and, as expected, more stable than IV. Structure III represents a situation where a very strong through-space interaction between the p_z AO's of C_1 and C_4 dominates their interaction through the C_2-C_3 bond and leads to the cyclobutane-like features of III.

CNDO/2 Calculations

The results of the CNDO/2 calculations on I-VI are shown in Scheme II. The distance of approach of the two olefins has been taken to be 2.2 Å. Here, the total energies as well as the $p\sigma$ overlap populations of the various structures suggest that either II or VI are representative of the early stage of the reaction while III is representative of the late stage of the reaction.

In its early stage, the reaction can be represented by II or VI. It can be seen that II is more stable than I by 0.78 eV, in qualitative agreement with the MWH calculations. The interaction of the two olefins approaching each other in a cis manner as in I is antibonding along one pair of union sites and bonding along the other. This arises from the interaction of the π HOMO of one olefin with both the π HOMO (maximally) and π LUMO (minimally) of the other olefin due to the lack of symmetry in the two olefins and the zero differential overlap approximation of the CNDO/2 calculation. Rotation by 180° converts the cis to a trans approach (II) and improves the C_2-C_3 $p\sigma$ bonding while leaving the C_1-C_4 antibonding interaction unchanged. The early stage of the reaction can also be represented by VI which is found to be more stable than V by 0.19 eV by virtue of relieving the antibonding C_1-C_4 $p\sigma$ interaction. Finally, the late stage of the reaction is represented by III, an unsymmetrically stretched cyclobutane. In short, there is a qualitative agreement between the MWH and the CNDO/2 calculations in terms of their energy prediction in all cases.

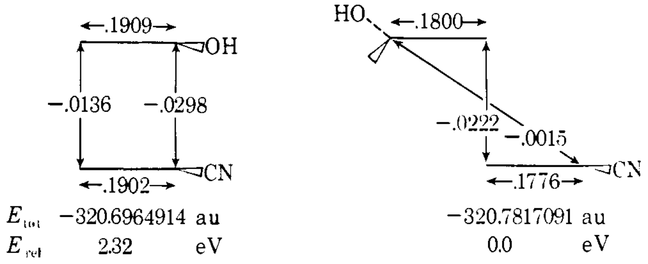
Scheme II. CNDO/2 Energies and Overlap Populations



Ab Initio (STO-4G) Calculations

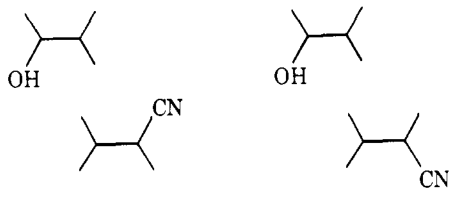
The ab initio calculations were restricted to structures I and II since the computational time required becomes nearly prohibitive for "large" systems like the one we have attempted to study. The results are shown in Scheme III. It can be seen that the ab initio results are qualitatively similar to the MWH results. Once again, the trans approach is favored over the cis approach by 2.32 eV (at a 2.2 Å distance of approach). This was found to be true for three different distances of approach and, in fact, the energy difference between I and II increased as the distance between the two olefins decreased.

Scheme III. Ab Initio STO-4G Energies and Overlap Populations



d, Å	E(I) − E(II), kcal/mol
2.0	103.48
2.2	53.49
2.4	26.93

A final point remains to be made. Specifically, the calculations were all carried out assuming that the substituents on the olefins have a syn relationship in geometry I. Ab initio calculations show that the energy difference between I(syn) and I(anti) as well as that between II(syn) and II(anti) is too small compared with the energy difference between I and II. A typical calculation result is provided below.

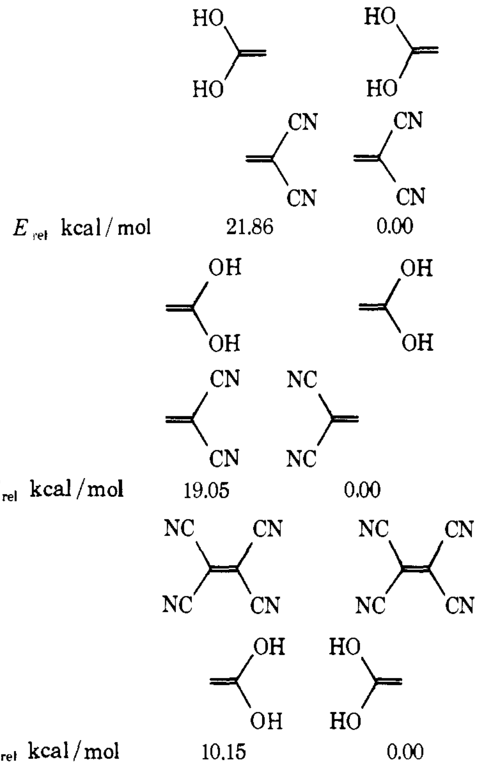


II (syn) − 320.7817

II (anti) − 320.7811

In other words, the energy difference between II(syn) and II(anti) is only 0.36 kcal/mol as compared to a difference of 53.49 kcal/mol between I(syn) and II(syn). Thus, the choice of the stereochemical relationship between the substituents CN and OH does not affect our general conclusions.

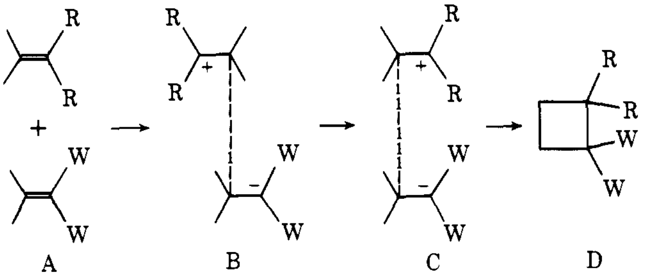
The objection may be raised that our model reaction system does not truly represent a "polar" 2 + 2 cycloaddition. Consequently, we have calculated cisoid and transoid structures which represent an early stage of the reaction for highly substituted donor and acceptor olefins. The results of CNDO/2 computations, for which the distance of approach of the two olefins is the same as before, are shown below:



As can be seen, the transoid geometry is more stable than the corresponding cisoid geometry in each case and, hence, we can be confident that our previous analysis is valid.

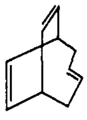
Discussion

We have presented a general qualitative PMO argument and the results of three different types of calculations dealing with the stereochemistry of approach of an electron donor and an electron acceptor olefin. *All of these approaches predict that two olefins substituted with groups of opposite electronic character will approach each other in a trans manner.* Accordingly, one may be inclined to think that the best mechanism of a polar cycloaddition can be written as follows:



The calculations clearly demonstrate that, at the one determinant level, there is no special coulombic attraction between the donor and acceptor olefins, postulated by many experimentalists,[14] which could force a cis approach. In a general sense, the calculations have shown that *the general PMO prediction of trans approach of two olefins is valid at the RHF level irrespective of the type of substituents borne by the two olefins.* This is a key finding for it suggests that *nonpolar and polar cycloadditions will be mechanistically similar.* However, *the experimental facts are in stark disagreement with this prediction.*

Thermal 2 + 2 cyclodimerizations are examples of 2 + 2 cycloadditions which fall in the extreme nonpolar end of the reactivity spectrum. The regioselectivity of 2 + 2 thermal cyclodimerizations is consistent with a biradical mechanism.[15] In this and all subsequent sections, the term "biradical mechanism" signifies a mechanism where pericyclic bonding between the reactants is absent until the very late stage of the reaction. The stereochemistry of 2 + 2 thermal cyclodimerizations has been extensively studied. The thermal 2 + 2 cyclodimerization of VII has been thought to occur in a concerted 2s + 2a manner.[16] However, the 2 + 2 thermal cyclodimerization of VIII has been studied by Padwa and his coworkers and found to be consistent with a biradical mechanism.[17]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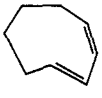
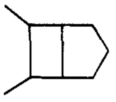

VIII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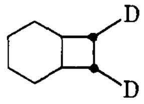

X

The stereochemistry of extreme nonpolar 2 + 2 cycloadditions and cycloreversions has been studied by various workers and has been found, in most cases, to be consistent with a diradical mechanism since extensive stereochemical loss accompanied these reactions. The decomposition of the cis and trans isomers of 6,7-dimethylbicyclo[3.2.0]heptane (IX) is nonstereoselective[18] and the experimental results are quite similar to those obtained for the decomposition of the cis and trans isomers of 1,2-dimethylcyclobutane.[19] The cycloaddition of tetrafluoroethylene and 1,2-dideuterioethylene was found to yield cyclobutane products and the observed stereochemistry was consistent with a diradical mechanism.[20] Finally, the pyrolysis of X yields *trans*-1,2-dideuterioethylene as the major isomer but the proportions of the trans isomer formed are larger than the thermodynamic value.[21] In addition, it should be mentioned that the kinetic parameters of cyclobutane decomposition were shown to be both qualitatively and quantitatively consistent with the biradical mechanism.[22] In short, it appears that regiochemical, stereochemical, and kinetic criteria favor a diradical mechanism for most thermal 2 + 2 cycloadditions or cycloreversions which are found at the *extreme* nonpolar end of the reactivity spectrum.

Table I. Stereochemistry of Polar Cycloadditions

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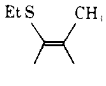
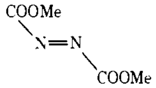
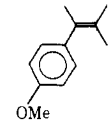
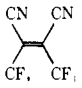
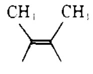
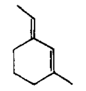
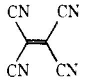
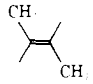
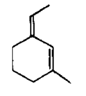
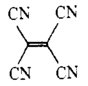
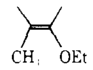
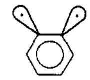
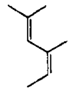
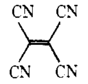
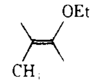
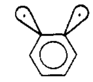
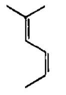
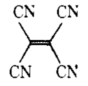
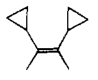
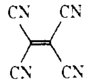
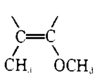
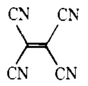
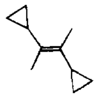
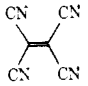
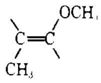
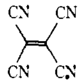
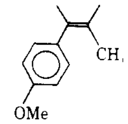
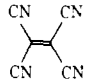
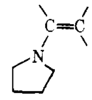
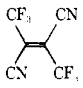
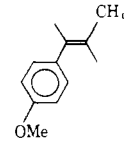
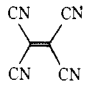
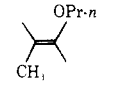
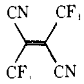
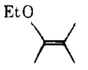
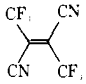
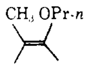
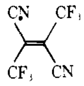
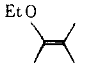
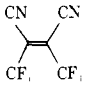
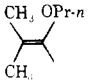
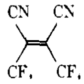
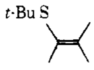
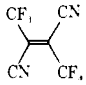
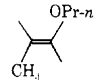
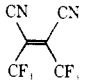
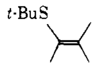
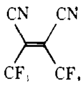
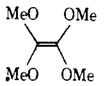
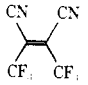
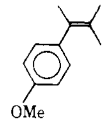
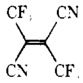
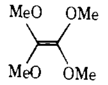
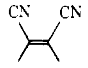
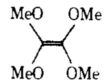
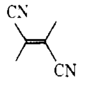
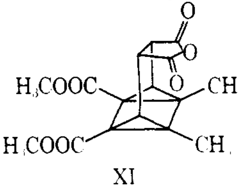
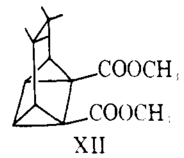
		100	*a*			100	*f*
	SO_3	100	*b*			100	*e*
	SO_3	100	*b*			100	*e*
		94	*c*			100	*e*
		79.2	*c*			72.3	*e*
		>90	*d*			95 (PhH) 94 (CH_2Cl_2) 91 ($(CH_3)_2CO$) 84 (CH_3CN)	*h*
		>90	*d*			97 (PhH) 95 (CH_2Cl_2) 91 ($CH_3COOCH_2CH_3$) 82 (CH_3CN)	*h*
		85–90 (PhH) 72 (CH_2Cl_2) 51 (CH_3CN)	*e*			100	*f*
		100 (PhH, CH_2Cl_2, CH_3CN)	*e*			100	*f*
		100	*f*			46.2	*f*
		100	*f*			59.5	*f*
		100	*f*			100	*f*
		100	*f*			100	*g*
		100	*f*			100	*i*
						100	*i*

[a] J. Firl and S. Sommer, *Tetrahedron Lett.*, 4713 (1972). [b] M. Nagayama, O. Okumura, S. Noda, and A. Mori, *Chem. Commun.*, 841 (1973). [c] H. H. Wasserman, A. J. Solodar, and L. S. Keller, *Tetrahedron Lett.*, 5597 (1968). In the case of the trans isomer a high component of ene reactions was observed. [d] S. Nishida, I. Moritani, and T. Taraji, *J. Org. Chem.*, 38, 1878 (1973). [e] See ref 2c. [f] See ref 27. [g] R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 80, 823 (1968). [h] See ref 2. [i] R. W. Hoffmann, V. Bressel, J. Gelhaus, and H. Hansen, *Chem. Ber.*, 104, 873 (1971).

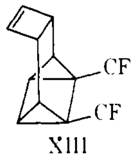
Polar cycloadditions and cycloreversions have been studied extensively. Data collected in Table I clearly indicate that these reactions are highly stereoselective, or, even stereospecific in certain cases. These results are in contrast to the stereochemical results obtained in the case of nonpolar cycloadditions. The facility of polar and nonpolar 2 + 2 cycloadditions is also markedly different. Indeed, polar 2 + 2 cycloadditions can be accomplished at room temperature, while nonpolar cycloadditions occur only at very high temperatures.[23] A final interesting illustration of the special nature of 2 + 2 polar cycloadditions is provided by studies



XI



XII



XIII

which show that XIII decomposes slowly at 80°,[24] XII has a half-life of 12 min at 19°,[25] and XI has a half-life of 3 min at 20°.[26] In other words, increasing the polar character of the cycloreversion leads to faster decomposition rates. An impressive result was the determination of the kinetic parameters for the decomposition of XI.[26] It was found that $\Delta H^\ddagger$ for XI was very much lower than $\Delta H^\ddagger$ for the decomposition of quadricyclane to norbornadiene. Even more impressive was the finding that $\Delta S^\ddagger$ for XI was very similar to $\Delta S^\ddagger$ for the rearrangement of *cis*-divinylcyclobutane, a presumably concerted reaction. Many other examples of facile intramolecular polar 2 + 2 cycloadditions can be found in the literature.

The experimental results discussed above clearly demonstrate that there is a mechanistic dichotomy between polar and nonpolar cycloadditions, *a conclusion which is in apparent contradiction with the prediction of the RHF calculations.* Furthermore, the mechanism written on the basis of the one-determinant calculation cannot account for the high stereoselectivity or, in cases, stereospecificity of the polar 2 + 2 cycloadditions. A trans approach of the donor and acceptor olefins is expected to give rise to loss of stereochemistry of the starting olefins since rotation about the C_1-C_2 and C_3-C_4 bonds in structure B will compete with bond rotation about the C_2-C_3 bond and eventual closure of structure C to product. To quote the authors of a pioneer paper in the study of the stereochemistry of polar cycloadditions:[27] "The stereospecificity observed in some cases makes a two-step reaction mechanism unlikely in a form characterized by an intermediate in which the reactant molecules approach each other largely endwise, . . .".

What is the origin of this apparent disparity between theory and experiment? A plausible interpretation is that the transoid approach is indeed favored over the cisoid approach irrespective of the type of quantum mechanical calculation employed but bond rotation necessary to convert the transoid biradicaloid B to a cisoid biradicaloid intermediate C, which can subsequently close to the four membered ring, involves a substantial activation energy. As a result, the activation energy for the overall reaction sequence A → B → C → D is higher than that for the reaction sequence which proceeds on the energy path involving a cisoid approach. Since barriers to rotation are not extremely high, the implication of the calculations is that a cisoid approach involves a low activation energy, i.e., a "2s + 2s" polar cycloaddition is not "forbidden".

Can we integrate the results of the calculations reported here as well as the experimental results within a simple framework?

A satisfactory theoretical interpretation of the mechanism of 2 + 2 cycloadditions should be able to account for the following experimental trends, in addition to accommodating the implications of our calculations. (a) Nonpolar 2 + 2 cycloadditions are slow reactions while polar 2 + 2 cycloadditions are extremely fast. (b) Nonpolar 2 + 2 cycloadditions are nonstereoselective while polar 2 + 2 cycloadditions are highly stereoselective or even stereospecific. (c) Nonpolar and polar 2 + 2 cycloadditions proceed with head-to-head regioselectivity. These trends are nicely accounted for by the LCFC-CI approach, which we recently delineated.[7a] This approach forms the basis for the construction of qualitative energy surfaces which show how barriers and intermediates arise.[7b]

Figure 2 shows the energy surfaces for 2s + 2s nonpolar and polar cycloadditions. The following trends are immediately obvious.

(a) A nonpolar 2s + 2s cycloaddition involves a high barrier which occurs at short intermolecular distances, i.e., a late transition state. On the other hand, a polar 2s + 2s reaction involves a lower barrier which occurs at long intermolecular distances, e.g., an early transition state. This result harmonizes with Hammond's postulate.[28]

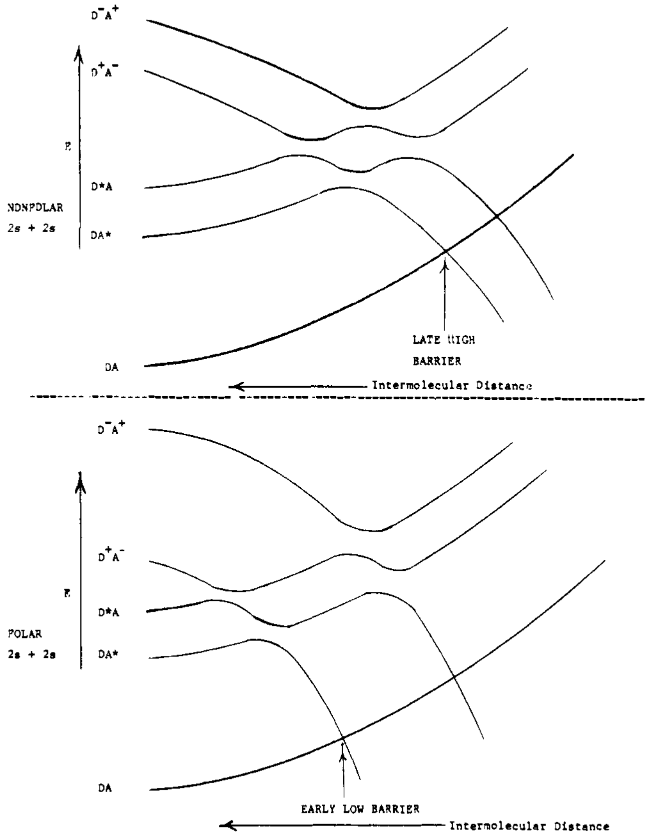


Figure 2. State correlation diagrams for 2s + 2s nonpolar and polar cycloadditions. The energies of the basis set configurations are given by the following equations:

$$E(\mathrm{DA}) = S,$$

$$E(\mathrm{D^+A^-}) = I_\mathrm{D} - A_\mathrm{A} + C,$$

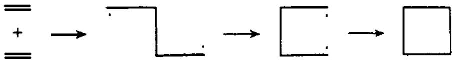
$$E(\mathrm{D^-A^+}) = I_\mathrm{A} - A_\mathrm{D} + C,$$

$$E(\mathrm{DA^*}) = h\nu(\mathrm{A} \rightarrow \mathrm{A^*}) + S,$$

$$E(\mathrm{D^*A}) = h\nu(\mathrm{D} \rightarrow \mathrm{D^*}) + S,$$

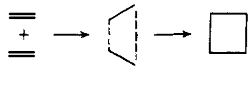
where S is a function accounting for the nonbonded repulsion as a function of intermolecular distance. I_D and I_A are the ionization potentials of the donor and acceptor olefins, respectively, and A_A and A_D are the electron affinities of the acceptor and donor olefins, respectively. At infinite separation, the electrostatic attractive term, C, is zero but becomes progressively more negative as the intermolecular distance decreases. Crossing avoidance is determined with respect to an effective one electron Hamiltonian. Systems are assumed symmetrical.

On the basis of these considerations, it is reasonable that a nonpolar cycloaddition will occur via a transoid biradicaloid intermediate as shown below.[29]

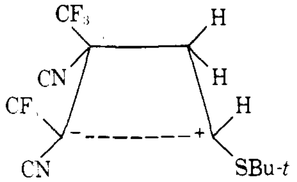


This conclusion will be valid only if the activation energy for the overall reaction is smaller than the activation energy for the 2s + 2s mechanism, which, as we have seen, involves a very high barrier.

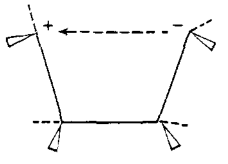
On the other hand, polar cycloadditions will occur in an *effective* 2s + 2s pericyclic manner which can be depicted as follows



(b) Prior to the crossing of the barrier, there is no pericyclic bonding between the two reactants. In the nonpolar case, the two reactants achieve pericyclic bonding at a very short distance of approach. Accordingly, bond rotation can occur prior to this point. By contrast, in the polar case, the two reactants achieve pericyclic bonding at a long distance, i.e., these reactions are *effectively pericyclic 2s + 2s reactions*. As we have already seen, experimental results are, in most cases, in agreement with this prediction (Table I). In fact, various structures of the alleged dipolar intermediate written by experimentalists in order to rationalize the observed stereoselectivity of polar cycloadditions amount to nothing else but a pictorial, implicit specification of a 2s + 2s pericyclic complex. Examples are given below.



ref 27

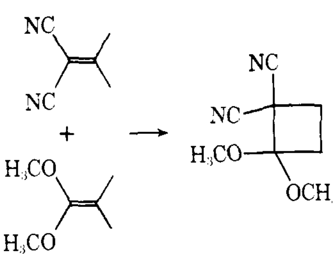


ref 2b

The energy profile for the polar cycloaddition, which is forbidden in the Woodward-Hoffmann sense but effectively "allowed" at the level of the LCFC-CI theory, may resemble the one shown in Figure 3, where the high minimum represents a pericyclic structure which would correspond to the "dipolar intermediate" of experimental parlance. We remark here that even reactions "allowed" in the Woodward-Hoffmann sense can display a high minimum as recent calculations and arguments suggest.[11b]

The similarity between a pericyclic 2 + 2 polar cycloaddition which exhibits an energy dip in the energy profile and the much studied solvolytic reaction which yields a "tight" ion pair which can subsequently be transformed to a solvent separated ion pair is illustrated in Figure 3. We suggest that trapping the intermediate involved in a polar cycloaddition or any other reaction does *not* contribute evidence against the pericyclicity of the reaction but only provides information about the shape of the potential energy surface.[30]

(c) The regioselectivity of a nonpolar 2 + 2 cycloaddition which proceeds via a biradicaloid intermediate is expected to be the one which affords maximal stabilization of the intermediate, i.e., head to head. On the other hand, the regioselectivity of a polar 2 + 2 cycloaddition will be the one which maximizes the $\langle D^+A^-|H|DA\rangle$ and $\langle D^+A^-|H|DA^*\rangle$ matrix elements. In typical donor-acceptor pairs as the one shown below, the predicted regioselectivity is head to head.



An alternative possibility which cannot be neglected concerns the validity of the theoretical methodology employed in our calculations, i.e., single determinant MO calculations performed within the RHF constraint. This approach is known to lead to difficulties when bonds are broken or formed as a result of the reaction. It would be of interest to test single determinant MO theory at the unrestricted Hartree-Fock (UHF) level on reactions "forbidden" in the Woodward-Hoffmann sense.

Going beyond the Hartree-Fock approximation, one may argue that only a multideterminantal approach could give a correct description of reaction paths. The theoretical chemist is already familiar with examples of breakdown of the RHF model and some of them have been alluded to in a recent survey of quantum mechanical results.[31] However, the relative stability order of molecules or transition states "aromatic" > "nonaromatic" > "antiaromatic" has manifested itself in all calculations which have included configuration interaction.[32] In our case, a cisoid approach corresponds to an "antiaromatic" situation and a transoid approach to a "nonaromatic" situation.

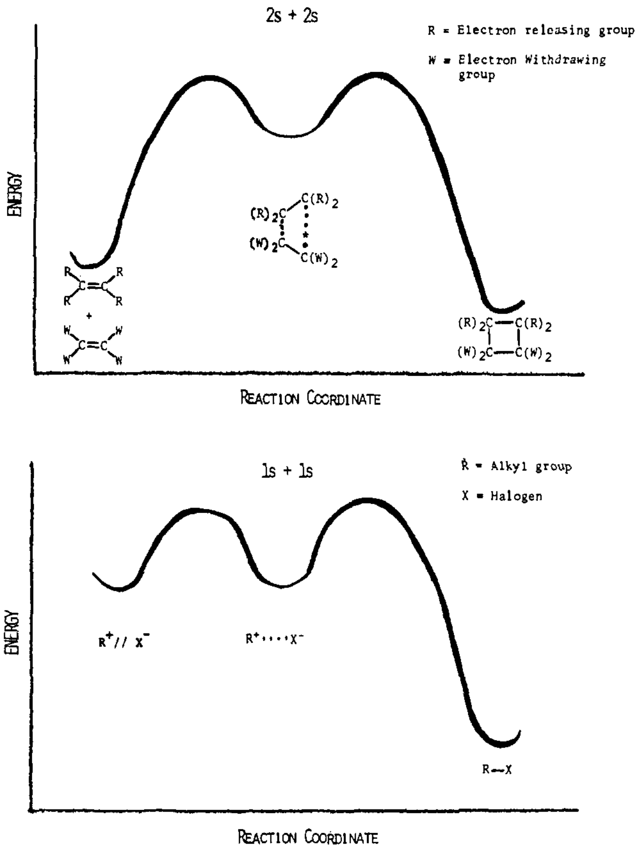


Figure 3. Energy profiles for a 2s + 2s polar cycloaddition and the solvolytic reaction of an alkyl halide, RX.

In view of the above considerations, we believe that our interpretation of the mechanism of polar 2 + 2 cycloadditions and, in general, polar Woodward-Hoffmann "forbidden" reactions is the best way to reconcile the experimental results and the theoretical calculations. However, the possibility that a single determinant UHF approach or a multideterminantal approach could render the cisoid approach lower in energy than the transoid approach remains present. Obviously, theoretical studies in that direction would be most welcome.

Note Added in Proof. Since the submission of this manuscript, explicit potential surface calculations (J. Michl, *Pure and Appl. Chem.* **41,** 507 (1975); A. Devaquet, *ibid.* **41,** 455 (1975)) on 2 + 2 cycloaddition model systems have provided striking support for (a) the validity of the LCFC-CI approach in constructing qualitative potential energy surfaces, and (b) the validity of our analysis of any thermal or photochemical reaction based on such diagrams. These new ideas are fully developed in a monograph entitled "Theory of Organic Reactions", currently in preparation, as well as in upcoming papers by one of the authors (N.D.E.).

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References and Notes

(1) (a) University of Washington; (b) Università di Bologna.

(2) For reviews dealing with preparative and mechanistic aspects of $2 + 2$ polar cycloadditions, see: (a) R. Huisgen, R. Grashey, and T. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, N.Y., 1964; (b) R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969); (c) P. D. Bartlett, *Q. Rev., Chem. Soc.*, **24**, 473 (1970). For theoretical discussions, see: W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).

(3) (a) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5054, 5055, 5056 (1973). (b) For a thorough review of this type of calculation, see S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1972, Chapter 4.

(4) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

(6) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 1191, 1200, 1206, 1214 (1973).

(7) (a) N. D. Epiotis, *J. Am. Chem. Soc.*, **94**, 1924, 1935, 1941, 1946 (1972); N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, **13**, 751 (1974). (b) A detailed discussion of the construction of these diagrams which have evolved from the work reported in ref 7a, and how they can be applied to diverse thermal and photo-chemical reactions will be given in a monograph and a series of future papers by one of the authors (N.D.E.).

(8) This is true for cycloadditions and electrocyclic ring closures.

(9) (a) L. M. Raff and R. N. Porter, *J. Chem. Phys.*, **51**, 4701 (1969); (b) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *J. Am. Chem. Soc.*, **93**, 5055 (1971); (c) R. C. Bingham and M. J. S. Dewar, *ibid.*, **94**, 9107 (1972); (d) P. Coffey and K. Jug, *Theor. Chim. Acta*, **34**, 213 (1974).

(10) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.

(11) (a) Reference 9d; (b) J. W. McIver, Jr., *Acc. Chem. Res.*, **7**, 72 (1974).

(12) For one of the latest manipulations of this computational philosophy, see: W. J. Hehre, L. Salem, and M. R. Willcott, *J. Am. Chem. Soc.*, **96**, 4330 (1974).

(13) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **93**, 7091 (1971).

(14) For example, see ref 1.

(15) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 5624 (1973), and references therein.

(16) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357, 4723 (1967).

(17) A. Padwa, W. Koen, J. Masaracchia, C. L. Osborn, and D. J. Trecker, *J. Am. Chem. Soc.*, **93**, 3633 (1971).

(18) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969).

(19) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

(20) P. D. Bartlett, G. M. Cohen, S. P. Elliott, K. Hummel, R. A. Minus, C. M. Sharts, and J. Y. Fukunaga, *J. Am. Chem. Soc.*, **94**, 2899 (1972). The energies of the π HOMO and LUMO of tetrafluoroethylene are similar to those of ethylene. Hence, the electronic stabilization of the $2s + 2a$ transition state in the cycloaddition of tetrafluoroethylene and ethylene is very much similar to that of the $2s + 2a$ transition state in the cyclodimerization of two ethylenes.

(21) J. E. Baldwin and P. W. Ford, *J. Am. Chem. Soc.*, **91**, 7192 (1969).

(22) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); *Int. J. Chem. Kinet.*, **1**, 221 (1969). See also: E. N. Cain and R. K. Solly, *J. Am. Chem. Soc.*, **94**, 3830 (1972).

(23) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962); J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962).

(24) R. S. H. Liu, *Tetrahedron Lett.*, 1409 (1969).

(25) H. Prinzbach, W. Eberbach, and G. Philippassian, *Angew. Chem., Int. Ed. Engl.*, 7, 887 (1968).

(26) S. F. Nelsen and J. P. Gillespie, *Tetrahedron Lett.*, 3259 (1969).

(27) S. Proskow, H. E. Simmons, and T. L. Cairns, *J. Am. Chem. Soc.*, **88**, 5254 (1966).

(28) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(29) This point is now under intensive theoretical scrutiny.

(30) R. Huisgen, R. Schug, and G. Steiner, *Angew. Chem., Int. Ed. Engl.*, **13**, 30, 31, (1974).

(31) H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules", Addison-Wesley, Reading, Mass., 1972.

(32) (a) K. Hsu, R. J. Buenker, and S. P. Peyerimhoff, *J. Am. Chem. Soc.*, **93**, 2117 (1971); K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *ibid.*, **94**, 5639 (1972); (b) M. J. S. Dewar and S. Kirschner, *ibid.*, **96**, 5246, 6809 (1974); (c) G. A. Segal, *ibid.*, **96**, 7892 (1974); (d) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *ibid.*, **93**, 5005 (1971). The LCFC-CI approach of ref 7a also predicts the same relative stability order.

Overlap Repulsion as an Important Contributor to Aromaticity

Nicolaos D. Epiotis* and Ronald L. Yates

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195. *Received April 16, 1975*

Abstract: A Hückel aromatic molecule can be viewed in terms of one-electron MO theory as a system in which stabilizing orbital interactions are maximized and destabilizing overlap repulsions are minimized relative to a nonaromatic analogue. This latter conclusion is opposite to intuitive expectations and currently held viewpoints and it suggests yet another important factor which may favor "crowded" over "uncrowded" geometries. The results of semiempirical and ab initio calculations as well as experimental results drawn from the literature are presented to support the conclusions reached by an orbital symmetry based approach.

Simple perturbation theory arguments lead to the prediction that the π stabilization energies of the union of pentadienyl with methyl to form benzene or hexatriene are: benzene, $\delta E = 4a\beta$; hexatriene, $\delta E = 2a\beta$, where the a's are AO coefficients in the pentadienyl NBMO and β is a standard resonance integral. According to this analysis, benzene is more stable than hexatriene and the difference in stability can be equated to what is traditionally referred to as "resonance energy".[1] In this work, we show that the greater stability of a Hückel aromatic cyclic molecule relative to its nonaromatic noncyclic analogue is only partly the result of greater stabilization of the cyclic geometry, and that *overlap repulsion, contrary to any intuitive expectations, can destabilize the cyclic form less than the noncyclic one!*

We have chosen to compare five diverse Hückel aromatic systems with their nonaromatic analogues and investigate by one-electron MO (OEMO) theory the origin of π Hückel aromaticity in these systems. The comparisons involve: (a) benzene vs. *trans*-1,3,5-hexatriene in its extended conformation; (b) *cis*- vs. *trans*-1,2-difluoroethylene; (c) the methyl rotational barrier in *cis*- vs. *trans*-1-fluoropropene; (d) the staggered and eclipsed conformations of dimethyl ether; (e) *cis*- vs. *trans*-2-butene in the staggered conformation. In all cases experimental results and ab initio calcu-