

MCSCF Gradient Calculation of Transition Structures in Organic Reactions

BY FERNANDO BERNARDI AND ANDREA BOTTONI

Istituto di Chimica Organica, Università di Bologna, Bologna, Italy

AND JOSEPH J. W. MCDOUALL AND MICHAEL A. ROBB*

Department of Chemistry, Queen Elizabeth College, London

AND H. BERNHARD SCHLEGEL

Department of Chemistry, Wayne State University, Detroit, Michigan, U.S.A.

Received 16th July, 1984

The applicability of MCSCF gradient methods to the calculation of transition structures and diradicaloid intermediates is discussed. It is shown how the diabatic surface model provides a useful criterion for the choice of the valence space in the MCSCF method and also provides useful qualitative information about the electronic rearrangement associated with various transition states. These ideas are then applied to the synchronous and asynchronous 1,3-dipolar cycloaddition of fulminic acid to acetylene.

One of the major development areas in quantum chemistry in recent years has involved the computation and characterization of the intermediates and transition structures for model organic reactions. Often these structures are diradicaloid in nature and are not described even qualitatively at the SCF level. The investigation of this type of species has been facilitated by the development of the MCSCF method [for a comprehensive review see ref. (1)] and gradient-optimization techniques. In recent work we have been involved in the development of MCSCF² gradient³ programs and in the subsequent analysis of the reaction profile using diabatic surfaces.⁴⁻⁷ In the present communication we shall attempt to present a methodological strategy that can be used to characterize potential surfaces that may contain diradicaloid structures. The application of this strategy will be illustrated with a study of transition structures occurring in the 1,3-dipolar cycloaddition of fulminic acid to acetylene.

The major difficulties in the application of MCSCF gradient methods to the computation of transition molecular structures lie (1) in the choice of configuration space of the MCSCF (*i.e.* the choice of the orbitals to be used in the CI expansion) and (2) in the determination of regions of the molecular potential surface in which to search for critical points. In this work we use a model for the description of saddle points based upon the surface of intersection of two diabatic surfaces (one associated with the reactants and one with products). Clearly, the reference CI expansion must be chosen so that each diabatic surface is represented equally well. The diabatic surfaces can be computed approximately using the methods discussed in ref. (4) and (5). The subsequent geometry optimization is then performed using the methods of ref. (3).

THEORETICAL METHODS

The standard methods for the optimization of molecular geometries (*e.g.* the Newton-Raphson method with updating of the Hessian as used in the GAUSSIAN 80 series of programs) work quite well for diradicaloid transition structures (saddle points) provided one uses MCSCF gradient³ methods. However, one must start the optimization procedure with a molecular structure where the force-constant matrix has one direction of negative curvature. Given the large number of molecular parameters in typical model organic reactions, the location of these regions of the molecular potential surface can be quite difficult. Further, it is obviously important not to make *a priori* assumptions about the nature of the reaction coordinate and thus miss possible transition structures.

In recent work we have developed an MCSCF procedure^{4,5} for the computation of a diabatic surface in which the adiabatic surface of the reaction is obtained from the interaction of two diabatic surfaces. The main feature of this procedure is that each diabatic surface is associated with the specific bonding situation of either the reactants or products and the transition structure lies on the surface of intersection of the two diabatic surfaces. In ref. (5) we have shown that the geometries of the transition structure of the cyanate-isocyanate rearrangement, the 1,2 sigmatropic shift in propene, the S_N2 reaction of H and CH_4 and the addition of singlet methylene to ethylene correlate very accurately with the intersection of appropriate diabatic curves. In the case of the sigmatropic shift we were able to locate the transition structure *a priori* from preliminary diabatic-surface calculations. The significant feature of this approach is that not only does it furnish us with an excellent starting transition structure, but also it provides some insight into the origin of the reaction barrier and conformational preference of possible reaction intermediates. The latter follows from the model used to define the diabatic surfaces themselves.^{4,5} We now give some brief discussion of this model.

One assumes that for a reaction



the adiabatic surface can be described in terms of two sets of variables R_x and R_y . We also assume that we can model this reaction with two diabatic surfaces $E_x(R_x, R_y)$ and $E_y(R_x, R_y)$. The surface E_x correctly describes the energy minimum of the species x and represents the bonding situation of the species x at all regions of configuration space (including the minimum of the surface E_y). The definition of the two diabatic surfaces themselves involves (1) the use of fragment MCSCF orbitals of x and y and (2) a partition of the full valence CI space (CASSCF) into packets. Each packet consists of an isolated fragment configuration (either a Heitler-London or no-bond configuration in the language of valence-bond theory) plus all possible one-electron-transfer configurations. Thus, for example in the cycloaddition of two ethylenes, one packet (reactants) corresponds to two ethylene molecules in their ground states (a no-bond configuration) and the second (products) corresponds to two triplet excited ethylenes coupled to an overall singlet (a Heitler-London configuration). The truncation of each packet at one-electron-transfer configurations will clearly begin to break down at small interfragment separations where more than one electron transfer will become very important and other locally excited configurations will begin to make large contributions. However, the truncation at one-electron transfer has the feature that the packets are mutually exclusive and hence approximately orthogonal. With this definition at hand, one can compute a diabatic surface^{4,5} by performing an MCSCF calculation on each packet separately. The possible transition structures correspond to minima on the surface of intersection of these diabatic surfaces. It is

apparent that the surface of intersection of two diabatic surfaces is essentially a conformational hypersurface, thus the conformational minima (corresponding to various possible transition structures) allow a semi-classical analysis in terms of electrostatic, polarization, exchange repulsion and charge-transfer energies. In ref. (4) we have shown how this type of analysis can be performed for MCSCF wavefunctions.

APPLICATIONS

During the past two decades 1,3-dipolar cycloaddition reactions have become a general method for the synthesis of five-membered rings. However, there is considerable controversy concerning the reaction mechanism.^{8,9} There are two obvious alternatives, a synchronous mechanism involving two-bond cycloaddition *via* an aromatic transition state or an asynchronous mechanism involving the formation of a diradicaloid intermediate. In the latter case one must find two transition states corresponding to the formation of the first and second bonds. While a synchronous cyclic transition structure can be determined by SCF methods,^{10,11} the possibility of an extended diradical intermediate can only be investigated using methods that include at least the two configurations necessary to describe the diradical. Recently,¹² the addition of fulminic acid (1,3-dipole) to acetylene (dipolarophile) has been investigated using multireference CI methods. In these calculations a low-energy extended diradical intermediate was found. In the MCSCF calculations to be discussed here the synchronous and asynchronous processes can be treated with equal accuracy at the same level of theory.

This problem is of considerable theoretical interest. First, there are a very large number of possible 1,3-dipole/dipolarophile combinations with very different (computed) barriers for the synchronous process.¹³ Secondly, it should be apparent that the diabatic-surface method discussed above is capable of rationalizing the mechanistic controversy. In this formalism, the preference synchronous/asynchronous is simply related to the relative positions of the two possible minima of the surface of intersection of the two diabatic surfaces corresponding to reactants and products. These facts, in turn, can be rationalized using the methods described in ref. (4).

We shall begin our discussions with a qualitative discussion of the diabatic surface model as it applies to the 1,3-dipolar cycloaddition of fulminic acid to acetylene. Initially, we are concerned with the choice of the valence orbital space (*i.e.* those active orbitals whose occupancy must be allowed to have values other than 2 or 0 and which will form the basis of the CI expansion used in the MCSCF calculations). This discussion is most conveniently given in terms of the orbitals of the isolated fragments and formulated in a valence-bond type of language. The fulminic acid can be thought of as having two allyl-like systems of three π orbitals referred to as the in-plane π (incipient σ bonds) and out-of-plane π (incipient delocalized π orbitals) sets as the two fragments approach each other. Similarly, the acetylene has two sets of ethylene π orbitals which we shall refer to as the in-plane and out-of-plane set. The isolated fragments must have the orbital occupancy shown in fig. 1(a) for the in-plane and out-of-plane π systems. For the product isoxazole, the in-plane π -orbital occupancy must correspond to the promotion of one electron in each of the fragments from HOMO to LUMO. The unpaired electrons must be spin-coupled to a state of triplet spin within a fragment and these two triplet states subsequently spin-coupled to a singlet in order to describe two new σ bonds as a valence bond Heitler-London configuration. For the out-of-plane π system of the product isoxazole, the fragment π systems retain the configuration shown in fig. 1(a) (*i.e.* there is no requirement to uncouple and recouple the spins to describe the isoxazole π system).

From the preceding argument it should be obvious that (in terms of the fragment

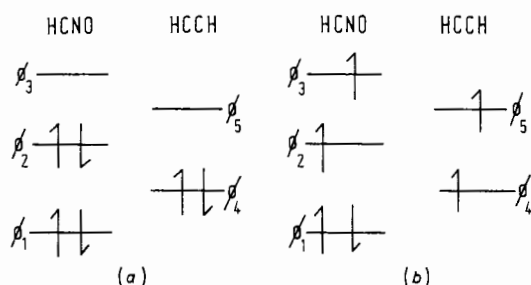


Fig. 1. (a) No-bond and (b) Heitler–London configurations for the singlet–singlet and triplet–triplet diabatic surface for the addition of fulminic acid to acetylene.

orbitals) one requires a valence space consisting of four in-plane π orbitals (the HOMO and LUMO of each fragment) in order to describe the product, the transition state and the reactants with equal accuracy. Thus the valence space to be used in the MCSCF calculations should contain these four σ orbitals at least. Furthermore, the product isoxazole, the intermediate diradical and the transition state for the formation of the second bond should be dominated by the diabatic surface associated with the Heitler–London configuration (for the in-plane π orbitals) shown in fig. 1(b). We shall refer to this surface henceforth as the triplet–triplet surface. On the other hand, the reactants (fulminic acid and acetylene) must be dominated by the diabatic surface associated with the no-bond configuration (for the in-plane π system) corresponding to the configuration shown in fig. 1(a). We shall refer to this surface in subsequent discussions as the singlet–singlet diabatic surface. The transition structures for the synchronous formation of isoxazole and for the formation of the first σ bond in the asynchronous process should be associated with the intersection of these two diabatic surfaces.

We can now outline our computational strategy for the characterization of the critical points on the surface for the cycloaddition of fulminic acid to acetylene. The orbitals for the initial MCSCF calculation for each geometry optimization were obtained from MCSCF calculations on the isolated fragments. These orbitals were then orthogonalized as follows: (1) the core orbitals (doubly occupied in all reference CI configurations), the valence orbitals and the virtual orbitals were each symmetrically orthogonalized within each set and (2) the valence orbitals were then Schmidt orthogonalized to the core and the virtual orbitals subsequently Schmidt orthogonalized to the core and then to the valence orbitals. This procedure unambiguously defines the valence-orbital set. Note that the SCF orbitals are not suitable as starting orbitals because the virtual orbitals tend to be very diffuse with extended basis sets and the appropriate weakly occupied orbitals do not usually correspond to the lowest-energy occupied orbitals of an SCF calculation. All of our geometry optimizations are then carried out with a full CI in the space of the four in-plane π orbitals (corresponding to HOMO and LUMO of each fragment). In order to improve the energetics, MCSCF calculations were also carried out (at the geometry just obtained) with a valence space that consisted of the HOMO–LUMO out-of-plane π orbitals as well corresponding to eight valence orbitals and 1764 configurations. This calculation should account for some of the dynamic correlation of the delocalized π system.

The calculations were carried out at the STO-3G and 4-31G basis set level. At the STO-3G level each critical point was characterized by computing the hessian (by finite difference) in the subspace consisting of the interfragment geometrical parameters and

the CNO angle of fulminic acid, which was strongly coupled to these variables. This hessian was then updated numerically in the 4-31G geometry optimizations.

In fig. 2(a)–(f) we illustrate the geometries of the critical points located by the procedure described above. Table 1 contains the geometrical parameters of fulminic acid and acetylene obtained at the same level of theory. The absolute and relative energetics are summarized in table 2. It can be seen that there is a cyclic transition state [fig. 2(b)] for the synchronous two-bond addition to give isoxazole [fig. 2(a)], an extended diradicaloid transition state [fig. 2(c)] for the formation of the first bond leading to a diradical intermediate, which exists in a *trans* form [fig. 2(d)] or a *cis* form [fig. 2(e)], and a second diradicaloid transition state [fig. 2(f)], which connects the *cis* form of the diradical intermediate [fig. 2(e)] with the product isoxazole. It can be seen that the STO-3G geometries are in quite good agreement with the 4-31G results, indicating that the STO-3G basis is capable of giving a good qualitative description of the surface. The geometry of the cyclic synchronous transition state is in good agreement with that obtained in ref. (11) at the SCF level in the same basis. This is to be expected since this species is well described at the SCF level.

The description of the diradicaloid region of the surface obtained in the present work is slightly different from that obtained in ref. (12) and deserves some comment. The geometry of the diradicaloid transition state [fig. 2(c)] that connects reactants and the diradical intermediate is in qualitative agreement with the structure obtained in ref. (12) at the UHF and 3X3 CI level (in the 4-31G basis). The major difference is that the interfragment C(3)–C(1) distance is considerably shorter in the present computations. However, in the present calculations we find two different structures for the diradical intermediate, a *trans* form [fig. 2(d)] and at slightly lower energy a *cis* form [fig. 2(e)], that differ only in the arrangement of the C–C–H angles in the acetylene fragment. In the present work we have also searched for a *cis* form of the transition state shown in fig. 2(c). Since the calculation was clearly converging to the *trans* form it was abandoned. Thus it seems likely that the transition state for the formation of the first bond connects the reactants with the *cis* form [fig. 2(e)] of the diradical intermediate, and the *trans* form [fig. 2(d)] represents a subsidiary minimum accessible *via* inversion at C(2). The *cis* form of the diradical intermediate [fig. 2(e)] is again in good agreement with the structure found in ref. (12), where an improved estimate (obtained from large-scale multireference CI calculations) for the transition structure for the asynchronous process (formation of the first bond) was obtained by interpolating geometries along a path connecting the *cis* form of the intermediate and the transition structure located at the SCF + 3X3 CI level. An interpolation based on the *trans* form would have yielded a structure in better agreement with the present fully optimized transition state. Finally, a transition structure has been obtained for the formation of the second bond in the asynchronous process [fig. 2(f)]. This lies energetically below the transition structure for the formation of the first bond in the asynchronous process.

The total and relative (to reactants) energies are given in table 2 along with the CI results obtained from ref. (11) and (12) for comparison. It can be seen that the relative energetics for the synchronous process are in good agreement with those obtained from ref. (11) using a CI treatment that included replacements from two a' and three a'' orbitals. The MCSCF reaction barrier (synchronous process) of 26–28 kcal mol⁻¹ will be lowered by the inclusion of correlation in more a' orbitals.^{11, 12} However, it must be stressed that one must be careful in comparing CI calculations for the synchronous and diradicaloid regions of the surface. In the diradicaloid region of the surface SCF orbitals are far from optimum for use in the CI expansion even if a multireference expansion is used. Thus one must be certain that one is describing both regions of

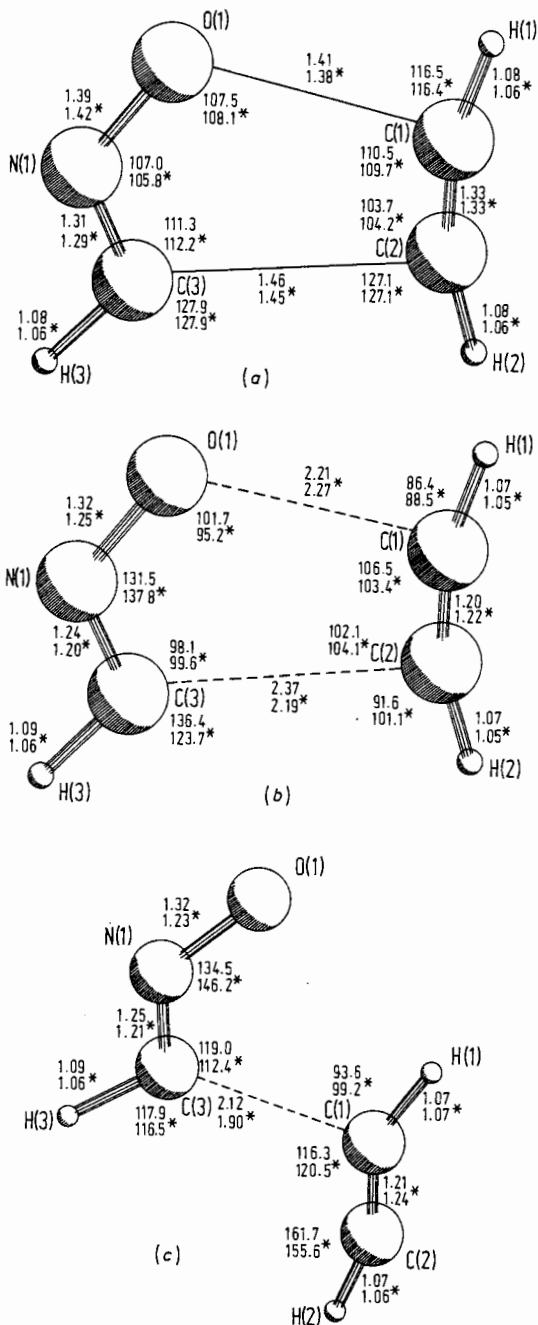


Fig. 2. Optimized geometries computed at MCSCF/STO-3G (no superscript) and MCSCF/4-31G (asterisk): (a) isoxazole, (b) synchronous cyclic transition leading from fulminic acid and acetylene to isoxazole, (c) asynchronous transition state corresponding to the formation of the first bond (*i.e.* connecting reactants and the *trans* diradical intermediate), (d) *trans* diradical intermediate, (e) *cis* diradical intermediate and (f) asynchronous transition state connecting the *cis* diradical intermediate to the product isoxazole.

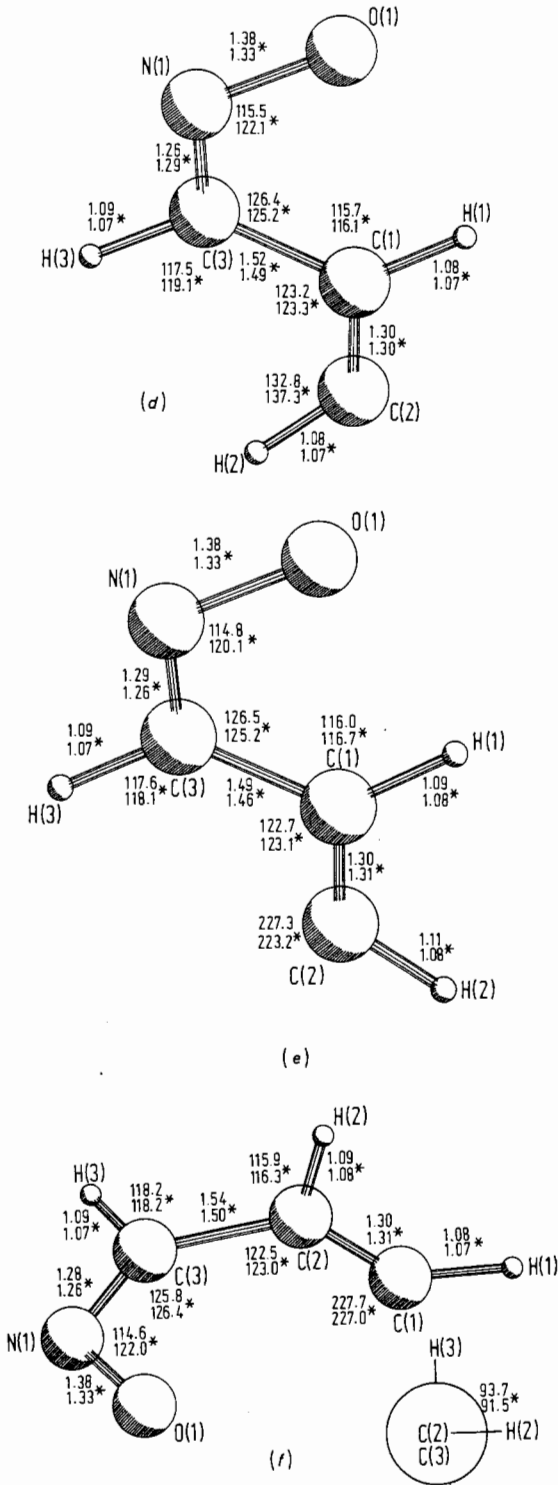


Fig. 2. For description see facing page.

Table 1. Optimized geometries computed at MCSCF/STO-3G and MCSCF/4-31G for fulminic acid (HCNO) and acetylene (HCCH) (atoms labelled as in fig. 2)

molecule	bond	bond length/Å	
		STO-3G	4-31G
HCNO	C(3)—H(3)	1.06	1.05
	C(3)—N(1)	1.17	1.14
	N(1)—O(1)	1.29	1.26
HCCH	C(1)—H(1)	1.07	1.05
	C(1)—C(2)	1.18	1.20

Table 2. Total and relative energies for the reaction of fulminic acid with acetylene

structure	MCSCF ^a STO-3G	MCSCF ^a 4-31G	MCSCF ^b 4-31G	ref. (11) ^c	ref. (12) ^d
total energies/hartree ^e					
HCCH + HCNO	-241.3130	-244.1360	-244.2394	-244.5444	-244.6181
cyclic synchronous TS ^f [fig. 2(b)]	-241.3056	-244.0952	-244.1941	-244.5062	-244.5973
asynchronous first TS ^f [fig. 2(c)]	-241.2950	-244.0871	-244.1841	—	-244.6031
<i>trans</i> diradical intermediate [fig. 2(d)]	-241.3715	-244.1214	-244.2005	—	—
<i>cis</i> diradical intermediate [fig. 2(e)]	-241.3746	-244.1246	-244.1977	—	-244.6081
asynchronous second TS ^f [fig. 2(f)]	-241.3636	-244.1123	—	—	—
isoxazole [fig. 2(a)]	-241.5211	-244.2426	-244.3150	—	—
relative energies/kcal mol ⁻¹					
HCCH + HCNO	0.0	0.0	0.0	0.0	0.0
cyclic synchronous TS ^f [fig. 2(b)]	4.6	26.0	28.4	24.0	13.0
asynchronous first TS ^f [fig. 2(c)]	11.3	30.7	34.7	—	9.39
<i>trans</i> diradical intermediate [fig. 2(d)]	-36.6	9.1	24.4	—	—
<i>cis</i> diradical intermediate [fig. 2(e)]	-38.6	7.2	26.2	—	8.20
asynchronous second TS ^f [fig. 2(f)]	-31.7	14.9	—	—	—
isoxazole [fig. 2(a)]	-130.6	-66.9	-47.4	-69.1	-63.4

^a Full CI (CASSCF) in four a' orbitals and four electrons. ^b Full CI (CASSCF) in four a' and four a'' orbitals and eight electrons. ^c CI using SCF orbitals all single and double excitations from two a' and three a'' orbitals. ^d CI (two reference second-order Moller-Plesset) using SCF orbitals. ^e 1 hartree = 2625 kJ mol⁻¹. ^f Transition state.

the surface with equal accuracy. The MCSCF energetics clearly do not include any true dynamic correlation. Thus the exothermicity and the reaction barriers will not be accurately reproduced. Nevertheless, the valence space has been chosen in this work so that the region of the synchronous transition structure and the region of the diradicaloid structures are described with equivalent accuracy. Thus one has some confidence in the relative energetics of the high-energy regions of the synchronous as against asynchronous pathways.

From the MCSCF results presented in table 2 it can be seen that the transition state for the synchronous process is predicted to be lower than for the first step of the asynchronous process at all levels of computation. Furthermore, the second transition state in the asynchronous processes lies at a lower energy than the first and the second barrier is predicted to be quite small. Thus both the synchronous and asynchronous processes could be consistent with retention of stereochemical information (in the case of substituted adducts given the same relative orientation of approach).

Finally we turn to an *a posteriori* rationalization of some of these results in terms of the diabatic-surface model. This is instructive because it is indicative of the success of the model when used to locate transition structures *a priori* and it also complements the qualitative discussion given previously. In fig. 3–5 we give cross-sections through the diabatic surfaces chosen to pass through the cyclic synchronous transition structure (fig. 3), the first asynchronous structure (fig. 4) and the *trans* diradical

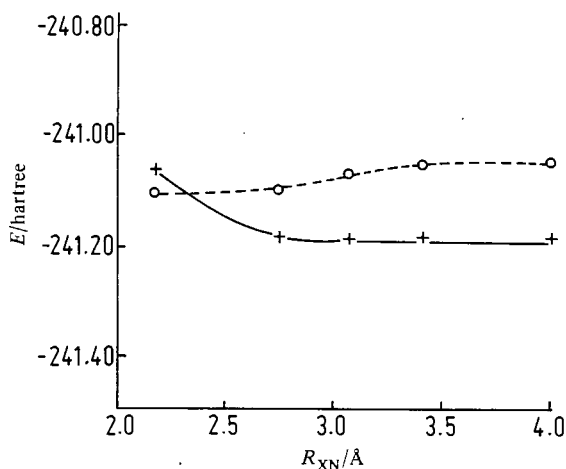


Fig. 3. Diabatic surface cross-section passing through the synchronous cyclic transition state: (—) singlet-singlet, (---) triplet-triplet.

intermediate minimum (fig. 5). The figure in each case shows the diabatic energies obtained along the coordinate (R_{XN}) corresponding to a rigid dissociation along the line connecting N(1) of the fulminic acid fragment and the centre of the C(1)—C(2) bond. In fig. 3 (cyclic synchronous transition state) one observes that the singlet-singlet diabatic curve is very flat and begins to become repulsive only in the region of the transition state ($R_{XN} = 2.74 \text{ Å}$) itself. In contrast, in fig. 4 (corresponding to the first diradicaloid transition structure) the singlet-singlet diabatic surface quickly becomes repulsive and intersects the attractive triplet-triplet surface in the region of the transition structure ($R_{XN} = 3.41 \text{ Å}$). The intersection of the singlet-singlet and triplet-triplet surfaces in the synchronous process occurs in a region where the truncation at one-electron transfer is no longer valid. However, in fig. 5 (diradical intermediate)

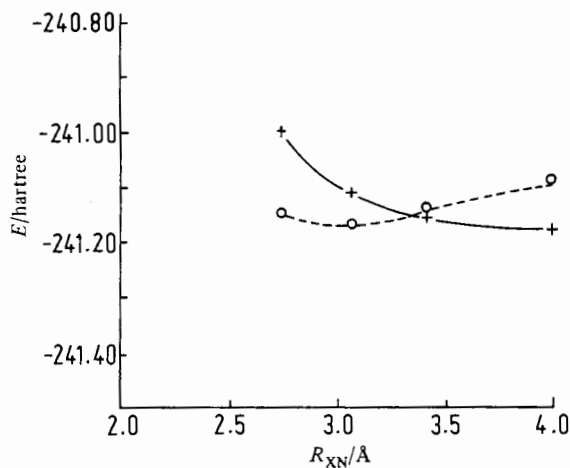


Fig. 4. Diabatic surface cross-section passing through the asynchronous transition state for the formation of the first bond: (—) singlet-singlet, (---) triplet-triplet.

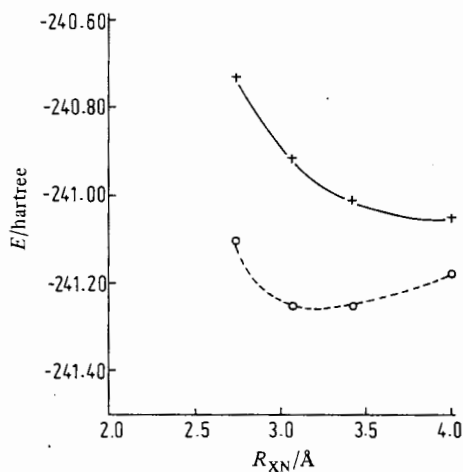


Fig. 5. Diabatic surface cross-section passing through the *trans* diradical intermediate: (—) singlet-singlet, (---) triplet-triplet.

the geometry of the fragments is now such that the triplet-triplet diabatic surface lies below than the singlet-singlet for all values of the interfragment separation. Thus the synchronous transition state and the first asynchronous transition state correspond to regions of intersection of the diabatic surfaces. However, the second asynchronous transition state (from the diradical intermediate to isoxazole) lies (like the diradical intermediate itself) on the triplet-triplet diabatic surface. The synchronous two-bond cycloaddition appears to be feasible in this situation because of the fact that the singlet-singlet diabatic surface is not strongly repulsive due to the stabilization of the extended π system.

CONCLUSIONS

It is clear that SCF methods cannot provide an adequate description of both the synchronous and asynchronous pathways for 1,3-dipolar cycloaddition reactions whereas MCSCF methods will provide an accurate description of both processes. For the asynchronous process MCSCF is necessary both to describe the avoided intersection of the singlet-singlet and triplet-triplet surfaces and because the intermediate is diradicaloid. The use of the diabatic surface model provides a useful scheme on which to base one's selection of the valence space and also provides some *a posteriori* rationalization of the topology of the surface.

Note added in proof: We have also located (at the STO-3G level) the transition state connecting the *cis* [fig. 2(e)] and *trans* [fig. 2(f)] diradical intermediates. The energy of this transition state is 7.5 kcal mol⁻¹ above that of the *trans* intermediate.

All computations were run on the CDC 7600 or the CRAY 1S computers at the University of London national computing centre and on the VAX 11/750 at Queen Elizabeth College. The cooperation of both computer centres is gratefully acknowledged. The MCSCF gradient programs have been installed as part of the GAUSSIAN 80¹⁴ suite of codes. We also acknowledge the financial support of NATO under grant no. RG 096.81. A. B. thanks the Royal Society for the award of a visiting fellowship.

- ¹ J. Olsen, D. L. Yeager and P. Jorgensen, *Adv. Chem. Phys.*, 1983, **55**, 1.
- ² R. H. A. Eade and M. A. Robb, *Chem. Phys. Lett.*, 1981, **83**, 362.
- ³ H. B. Schlegel and M. A. Robb, *Chem. Phys. Lett.*, 1982, **93**, 43.
- ⁴ F. Bernardi and M. A. Robb, *Mol. Phys.*, 1983, **48**, 1345.
- ⁵ F. Bernardi and M. A. Robb, *J. Am. Chem. Soc.*, 1984, **105**, 54.
- ⁶ F. Bernardi, M. A. Robb, H. B. Schlegel and G. Tonachini, *J. Am. Chem. Soc.*, 1984, **106**, 1198.
- ⁷ F. Bernardi, A. Bottoni and M. A. Robb, *Theor. Chim. Acta*, 1984, **64**, 259.
- ⁸ R. Huisgen, *Angew. Chem.*, 1963, **2**, 565.
- ⁹ R. A. Firestone, *J. Org. Chem.*, 1968, **33**, 2285.
- ¹⁰ D. Poppinger, *Aust. J. Chem.*, 1976, **29**, 465.
- ¹¹ A. Komornicki, J. D. Goddard and H. F. Schaefer, *J. Am. Chem. Soc.*, 1980, **102**, 1763.
- ¹² P. C. Hiberty, G. Ohanessian and H. B. Schlegel, *J. Am. Chem. Soc.*, 1983, **105**, 719.
- ¹³ M. Sana and G. Leroy, *J. Mol. Struct.*, 1982, **89**, 147.
- ¹⁴ GAUSSIAN 80: J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn and J. A. Pople, *Quantum Chemistry Program Exchange*, 1981, **13**, 406.