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Modern valence-bond description of chemical reaction mechanisms: the 1,3-dipolar addition of fulminic acid to ethyne*

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Abstract. The electronic mechanism for the gas-phase 1,3-dipolar cycloaddition of fulminic acid (HCNO) to ethyne is studied through a combination of modern valence-bond theory in its spin-coupled (SC) form and intrinsic reaction coordinate calculations utilizing a complete-active-space self-consistent field wavefunction. It is shown that the concerted reaction follows a "heterolytic" route, during which three orbital pairs corresponding to three distinct bonds in the reactants (an in-plane π bond in ethyne, and a C—N and an N—O in-plane bond in HCNO) shift simultaneously to create the two new bonds closing the isoxazole ring and a nitrogen lone pair. The analysis of the SC wavefunction strongly suggests that the reacting system remains nonaromatic throughout the most important part of the cycloaddition process. This investigation provides the first demonstration of an alternative SC description of a bond rearrangement, achieved through the movement of singlet orbital pairs through space, during which at least one of the orbitals within a pair becomes completely detached from the atomic centre with which it is associated initially and ends up localized about another centre.

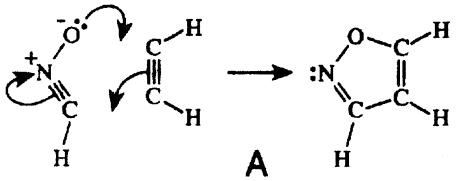
Key words: Spin-coupled approach – 1,3-Dipolar cycloadditions – Reaction mechanisms – Valence-bond theory

1 Introduction

The main aim of a number of experimental and theoretical studies of the mechanisms of 1,3-dipolar cycloadditions has been to establish whether these reactions proceed through a synchronous concerted mechanism, as suggested by Huisgen [1, 2], or follow a stepwise diradical pathway, consistent with the ideas of Firestone [3, 4]. To a large extent, the ensuing argument was effectively put to an end by McDouall et al. [5], who performed multiconfiguration self-consistent field (MCSCF) geometry optimizations for the reactants, products and transition structures (TS) along the concerted and nonconcerted pathways for three gas-phase 1,3-dipolar cycloadditions, namely those between fulminic acid (HCNO) and ethyne, HCNO and ethene, and nitrone (CH_2NHO) and ethene. The geometry optimizations were followed by large multireference configuration interaction calculations of the activation barriers which placed the concerted pathways for all three reactions significantly below the nonconcerted diradical alternatives. Additionally, the predicted concerted activation barriers were found to lie in the correct experimental range.

The results of McDouall et al. [5] indicate that in all three cyclic TS the two new bonds closing the cycle are partially formed to similar extents. This suggests that these simple examples of gas-phase 1,3-dipolar cycloadditions follow nearly synchronous pathways, much as the basic gas-phase Diels-Alder reaction between *cis*-butadiene and ethene.

An organic chemistry textbook would portray the mechanism of a 1,3-dipolar cycloaddition, say between HCNO and ethyne, and that of the Diels-Alder reaction in a very similar way:


A

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*Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

**Joseph Gerratt passed away on 16 October 1997

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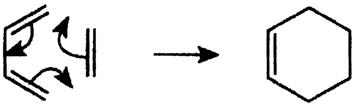
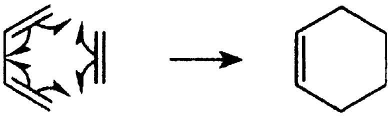


B

The full arrows in these schemes have their origins in the Lewis theory of valence, and although it is difficult to justify them within ab initio molecular orbital (MO) approaches, many practising chemists still find it convenient to think that the bonds are formed through movements of electron pairs as indicated by the arrows.

In a recent article [6] we showed, using modern ab initio valence-bond (VB) theory in its spin-coupled (SC) form [7–10], that scheme B, which illustrates the mechanism of the Diels-Alder reaction with full arrows, is not correct and that it is much more appropriate to use a picture in which half-arrows indicate the simultaneous breaking of the butadiene and ethene π bonds and the formation of the two new σ and one π bond within the cyclohexene ring:



C

The SC study of the gas-phase Diels-Alder reaction [6] was performed on top of a minimum energy path (MEP) [11, 12] (also known as intrinsic reaction coordinate, IRC [13, 14]) calculated at the "six electrons in six orbitals" complete-active-space self-consistent field [CASSCF(6, 6)] level. Along a wide MEP interval centred on the TS, a SC wavefunction with six valence orbitals was found to recover most of the correlation energy (between 92.9% and 95.8%) of the CASSCF(6, 6) wavefunction, which justifies its use to obtain a qualitative model for the electronic reaction mechanism. Throughout the reaction, each of the nonorthogonal SC orbitals engaged in the bonds being broken and formed resembles a well-localized sp^x hybrid, which remains permanently attached to a single carbon atom. The bond-breaking and formation processes are reflected by easy-to-observe changes in the ways in which these orbitals are distorted towards one another and in their hybridization states, parallelled by corresponding variations in the overlaps between neighbouring orbitals, and by the evolution of the SC analogue of classical VB resonance: the active-space spin-coupling pattern. When the butadiene and ethene fragments are well apart, this pattern is dominated by a single Kekulé-type Rumer spin function, in which the singlet pairs involve the spins of the orbitals in the two butadiene and one ethene π bonds. Another Kekulé-type Rumer spin function, in which the spins of the orbitals in the three new cyclohexene bonds (two σ and one π) are coupled to singlets, takes precedence when the ring formation is near completion. At and around the TS, the two Kekulé-type Rumer spin functions have comparable weights, or are in "resonance". This and other analogies with the well-known SC description of benzene (similar orbital shapes, equalization of the overlaps between neighbouring orbitals) indicate clearly that the gas-phase Diels-Alder reaction passes through a geometry, very close to the TS, at which it is aromatic.

The aim of the present article is to apply the same set of theoretical tools – SC theory combined with CASSCF-level IRC calculations – in order to establish whether the electronic mechanism of gas-phase 1,3-dipolar cycloaddition of HCNO to ethyne is similar to that of the gas-phase Diels-Alder reaction, as one might be led to expect from the concerted, almost synchronous nature of the 1,3-dipolar cycloaddition. A first signal that this expectation could be wrong comes from a recollection of the highly unusual yet very neat SC descriptions of a series of 1,3-dipolar molecules, including diazomethane, HCNO and CH_2NHO [15, 16]. The classical VB representation of HCNO, for example, involves an unconvincing resonance between a number of zwitterionic and diradical structures, only one of which features in scheme A:

$$\mathrm{H{-}C{\equiv}\overset{+}{N}{-}\overset{-}{O}\leftrightarrow H{-}\overset{*}{C}{=}N{-}\overset{*}{O}\leftrightarrow H{-}\overset{-}{C}{=}\overset{+}{N}{=}O\leftrightarrow etc.}$$

SC theory clearly indicates that the central nitrogen atom in HCNO (and in the other 1,3-dipoles) is "hypervalent" or "hypercoordinate", in the sense that it takes part in more than four covalent bonds: an almost triple bond between carbon and nitrogen, a σ bond between nitrogen and oxygen, and a highly polar π bond between nitrogen and oxygen:

$$\mathrm{H{-}C{\equiv}N{=}O}$$

Obviously, it is very difficult to predict what will happen to this exotic bonding pattern when HCNO is approached by a dipolarophile (in our case, ethyne). The results reported in the present article came as a complete surprise to all three authors, who have years of experience with the application of SC theory to a wide range of chemical problems.

2 Computational procedure

Following McDouall et al. [5], we assumed that the 1, 3-dipolar cycloaddition of HCNO to ethyne follows a concerted pathway, along which the reacting system always remains planar (i.e. retains C_s symmetry). The wavefunction used by McDouall and coworkers is equivalent to a CASSCF(4,4)/4-31G construction, in which the active space consists of four orbitals, corresponding to the in-plane π HOMO and LUMO for each of the separated reactants. However, it is generally accepted that 1,3-dipolar cycloaddition reactions involve four π electrons from the 1,3-dipole and two from the dipolarophile (see, for example Ref. [17]). Moreover, a modern VB description of a 1,3-dipole based on just two active orbitals would lead to the incorrect conclusion of overwhelming diradical character and would miss out entirely the hypervalency of the central heavy atom. As a consequence, we decided to reoptimize the planar concerted TS for the $HCNO + C_2H_2$ cycloaddition using a CASSCF(6,6) wavefunction and a larger 6-31G* basis, and then to calculate the IRC at the same level of theory and to analyse the electronic mechanism of the reaction using a SC wavefunction with six valence orbitals defined in the same basis. We followed the IRC for 12 points from the TS in the direction of the reactants and for another 12 points in the direction of the product, all in steps of about 0.1 amu$^{1/2}$bohr. In order to assess the influence of further electron correlation (mostly dynamical) on the geometry of the TS, we also optimized its structure using the fourth-order restricted Møller-Plesset perturbation theory approach including single, double and quadruple substitutions [RMP4(SDQ)], again with the 6-31G* basis. The CASSCF- and RMP4(SDQ)-level TS locations were performed by means of GAUSSIAN94 [18], and for the IRC calculations we employed the algorithm of Gonzales and Schlegel [19, 20] implemented in that package.

The SC wavefunction with six valence orbitals for the system consisting of HCNO and ethyne can be represented as

$$\Psi^6_{00} = \hat{\mathscr{A}}\left[\left(\prod_{i=1}^{15}\varphi_i\alpha\varphi_i\beta\right)\left(\prod_{\mu=1}^{6}\psi_\mu\right)\Theta^6_{00}\right] \ . \qquad (1)$$

The six valence orbitals $\psi_1, \psi_2, \ldots, \psi_6$ (which we shall also call active or spin-coupled orbitals) are all singly occupied and nonorthogonal. The doubly occupied inactive orbitals holding the core electrons within Ψ^6_{00} are denoted by φ_i, while Θ^6_{00} stands for the active-space spin function which represents a general linear combination of all five unique spin-coupling schemes for a singlet system of six electrons:

$$\Theta^6_{00} = \sum_{k=1}^{5} C_{0k}\Theta^6_{00;k} \ . \qquad (2)$$

The zero subscripts of Ψ^6_{00}, Θ^6_{00} and $\Theta^6_{00;k}$ indicate the values of the total spin S and its z-projection, M, respectively ($S = M = 0$).

SC theory approximates the active and core orbitals, just as most MO-type approaches, by linear expansions in a suitable basis of atomic orbitals contributed by all atoms in the system. All the orbital and spin-coupling coefficients [C_{0k} in Eq. (2)] are determined variationally, by optimizing the energy expectation value corresponding to the wavefunction represented by Eq. (1). Most of the fully variational SC calculations described in the present article were performed with a very efficient new code (CASVB) [21, 22], available within the package MOLPRO [23], which exploits the invariance of CAS wavefunctions to nonsingular transformations of the active orbitals. An older SC code [24] was employed only at the TS and at both ends of the IRC segment, mainly in order to assist orbital plotting, and to confirm the validity of the unexpected forms of the solutions.

As we show in the next section, the active space spin-coupling pattern (Eq. 2) is dominated over the whole IRC interval by a single spin function, in which the spins of the valence orbitals are coupled to singlet pairs (slightly larger but still unimportant admixtures of other spin functions are observed only at and around the TS). A spin function of this type is present in all three systems of spin eigenfunctions (Kotani, Rumer and Serber) [25] which have been used most routinely in SC work. Contrary to the case of the Diels-Alder reaction [6], where use of the Rumer basis allowed us to draw an analogy between the SC picture and classical VB resonance, we found that none of these three spin bases introduces any particular interpretational advantages into the description of the 1,3-dipolar cycloaddition of HCNO to ethyne. All spin-coupling coefficients reported in Sec. 3 are expressed in the Kotani spin basis which is orthonormal, so that the weights of the individual spin functions making up Θ^6_{00} (see Eq. 2) are given simply by the squares of the corresponding spin-coupling coefficients, C^2_{0k}. The "perfect-pairing" mode is the one with $k = 5$.

3 Results and discussion

The CASSCF(6,6)/6-31G* geometry of the concerted TS for the gas-phase 1,3-dipolar cycloaddition of HCNO to ethyne is very similar to its CASSCF(4,4)/4-31G counterpart reported by McDouall et al. [5] (see Fig. 1). As we shall see later in this section, this is most probably due to the fact that two of the six valence SC orbitals are not directly involved in the formation of the new bonds between the reactants but remain almost entirely on the HCNO fragment throughout the reaction. Also shown in Fig. 1 is the geometry calculated at the RMP4(SDQ)/6-31G* level. This appears to be a reaction for which the TS geometry is not significantly altered by the inclusion of further electron correlation.

The Hartree-Fock, SC and CASSCF(6,6) energies at the TS and at the end points of the IRC segment studied in this paper (IRC = −1.19552 and +1.19526 amu$^{1/2}$bohr) are collected in Table 1 together with the corresponding SC and CASSCF correlation energies. The high percentage of CASSCF(6,6) correlation energy recovered by the SC wavefunction indicates that, from a

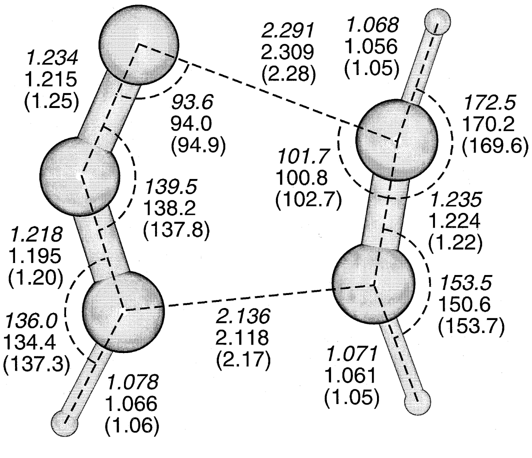


Fig. 1. Geometry of the transition structure (TS) for the gas-phase 1,3-dipolar cycloaddition of fulminic acid (HCNO) to ethyne. CASSCF(6,6)/6-31G* (*middle*) and RMP4(SDQ)/6-31G* (*top*, in *italics*) values from the current work, and CASSCF(4,4)/4-31G values (*bottom*, in *parentheses*), taken from Ref. [5]. Bond lengths in Å, angles in degrees

quantitative viewpoint, the SC ansatz with six valence orbitals comes very close to the CASSCF(6,6) construction. This fact allows us to make use of the interpretational advantages of SC theory in order to describe the changes in the electronic structure of the reacting system.

Further (dynamical) electron correlation does not have a significant effect on the TS geometry or on the dominant component of the wavefunction, but does modify the height of the activation barrier, calculated as the difference between the energy of the TS and the energy corresponding to the optimized geometry of the reacting system at infinite separation between the reactants. The CASSCF(6,6)/6-31G* activation barrier, 24.9 kcal mol^{-1}, is close to the CASSCF(4,4)/4-31G value of 26.0 kcal mol^{-1} [5]. However, CASMP2 calculations on top of the CASSCF(6,6)/6-31G* wavefunctions at the CASSCF(6,6)/6-31G* geometries, using the orthogonal valence bond second-order Møller-Plesset MCSCF perturbation theory construction [26] implemented in GAUSSIAN94, reduce the barrier height to 12.2 kcal mol^{-1}. The RMP4(SDQ)/6-31G* activation barrier was found to be 16.7 kcal mol^{-1}.

As the HCNO and ethyne molecules approach each other, the six SC orbitals pass smoothly from shapes characteristic of weakly interacting HCNO and ethyne fragments (see the rightmost column in Fig. 2, which corresponds to IRC ≈ -1.2 amu$^{1/2}$bohr) to shapes consistent with the bonding in the final product, isoxazole (see the leftmost column in Fig. 2, which shows the orbitals at IRC ≈ 1.2 amu$^{1/2}$bohr). This is a trivial statement so far as orbitals ψ_1, ψ_3 and, to some extent, ψ_4 and ψ_6 are concerned: the variations in the shapes of these orbitals starting from an IRC point well before the TS, through the TS, and finishing at an IRC point well after the TS (moving from right to left in Fig. 2) are in good agreement with previous SC descriptions of bond-breaking and bond-making processes [6, 28–32]. As a rule, during processes of this type, each SC orbital remains distinctly associated with a single atom and distorts in a perceptible but by no means extreme fashion in order to leave existing bonding interactions and to enter into new ones. The transition from a bonding scheme appropriate for reactants to a bonding scheme more suited to products is signalled by abrupt changes in some SC orbital overlaps and in the way in which the spins of the corresponding SC orbitals are coupled together to achieve the required overall value of the total spin S. These changes have always been observed to occur within a very narrow interval of internuclear separations (along an IRC segment of approximately 0.2 amu$^{1/2}$bohr in the case of the Diels-Alder reaction [6]).

None of the previous SC studies of bond-breaking and bond-formation processes has produced anything even remotely related to the changes in the shapes of orbitals ψ_2 and ψ_5 along the IRC for the reaction between HCNO and ethyne and, in particular, their forms at the TS where each of these two orbitals has a distinct three-centre character. In fact, our first reaction to the shapes of these orbitals at the TS was disbelief and we had to perform a very careful analysis of the changes in the bonding pattern during the whole cycloaddition process in order to convince ourselves of the correctness of the results.

Let us follow the details of this analysis, starting from the case of well-separated fragments (see the rightmost column of orbitals in Fig. 2). It is obvious that orbitals ψ_2 and ψ_4 make up the in-plane ethyne π bond. A comparison of the shapes of orbitals ψ_1, ψ_3, ψ_5 and ψ_6 to the contour plots for the SC orbitals in linear HCNO [16] shows that orbitals ψ_3 and ψ_6 correspond to a C–N bond (which would be a π bond in the linear conformation), and orbitals ψ_1 and ψ_5 are engaged in a polar N–O bond. In order to verify that this bonding scheme is

Table 1. Total Hartree-Fock (HF), Spin-coupled (SC), complete-active-space self-consistent field (CASSCF) and correlation energies (ΔE^{corr}) for 1,3-dipolar cycloaddition of HCNO to ethyne evaluated at the transition structure (TS) and at the two ends of the intrinsic reaction coordinate (IRC) segment studied in this paper. All energies in hartree. Values in brackets following ΔE^{corr}(SC) indicate the percentage of the corresponding CASSCF correlation energy recovered by the single-configuration SC wavefunction

Quantity	IRC = −1.19552	TS (IRC = 0)	IRC = +1.19556
E(HF)	−244.40593	−244.38968	−244.40223
E(SC)	−244.48669	−244.46790	−244.47915
E(CASSCF)	−244.49046	−244.47258	−244.48183
ΔE^{corr}(SC)	−0.08076 (95.5%)	−0.07822 (94.4%)	−0.07692 (96.6%)
ΔE^{corr}(CASSCF)	−0.08453	−0.08290	−0.07960

Table 2. Weights $(C_{0k}{'})^2$ of the Kotani spin functions making up $\Theta_{00}^{6\,\prime}$ (see Eq. 4) at the TS and at the two ends of the CASSCF(6,6) IRC segment studied in this paper. $(S_1S_2\ldots S_5)$ stands for the sequence of partial resultant spins obtained after combining the spins of the first $1, 2, \ldots, 5$ electrons (for further details see Ref. [33])

k	$(S_1S_2\ldots S_5)$	IRC = −1.19552	TS (IRC = 0)	IRC = +1.19556
1	$(\frac{1}{2}\,1\,\frac{3}{2}\,1\,\frac{1}{2})$	0.02514	0.03859	0.00157
2	$(\frac{1}{2}\,1\,\frac{1}{2}\,1\,\frac{1}{2})$	0.00492	0.02654	0.00197
3	$(\frac{1}{2}\,0\,\frac{1}{2}\,1\,\frac{1}{2})$	0.00704	0.02165	0.01578
4	$(\frac{1}{2}\,1\,\frac{1}{2}\,0\,\frac{1}{2})$	0.00524	0.12191	0.00984
5	$(\frac{1}{2}\,0\,\frac{1}{2}\,0\,\frac{1}{2})$	0.95766	0.79131	0.97084

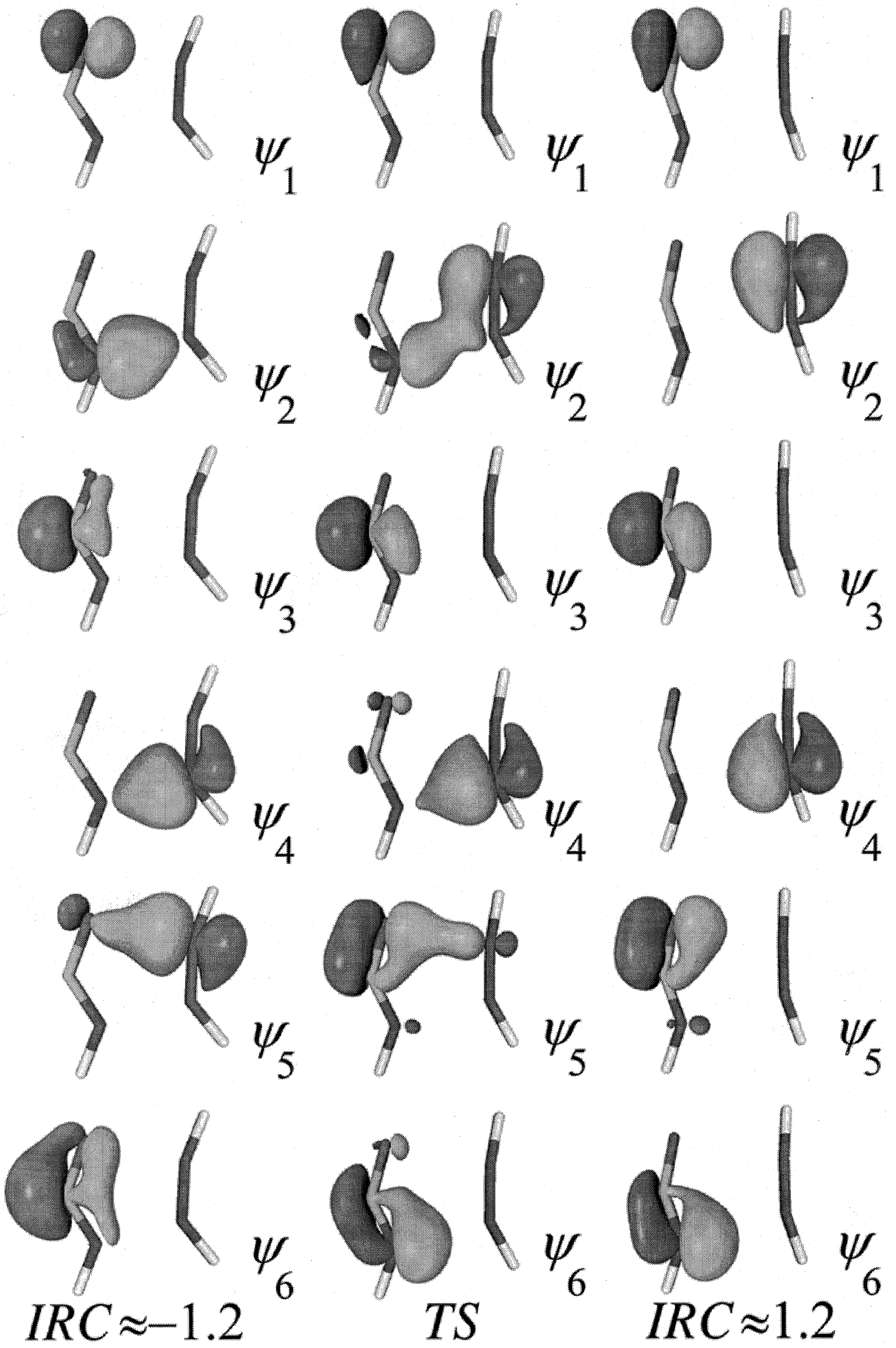


Fig. 2. Valence orbitals $\psi_1, \psi_2, \ldots, \psi_6$ from the spin-coupled wavefunction for gas-phase 1,3-dipolar cycloaddition of HCNO to ethyne at intrinsic reaction coordinate (IRC) = -1.19552 amu$^{1/2}$bohr, the *TS* (IRC = 0) and IRC = $+1.19556$ amu$^{1/2}$ bohr. Three-dimensional isovalue surfaces corresponding to $\psi_\mu = \pm 0.1$, drawn from virtual reality modelling language files produced by MOLDEN [27]

also reflected in the spin-coupling pattern within the wavefunction represented by Eq. (1), it is necessary to reorder the orbitals so as to arrange the orbitals involved in the three bonds in pairs

$$\begin{aligned}\Psi^6_{00} &= \hat{\mathscr{A}}\left[(\text{core})\psi_1\psi_2\psi_3\psi_4\psi_5\psi_6\Theta^6_{00}\right]\\ &= \hat{\mathscr{A}}\left[(\text{core})\psi_2\psi_4\psi_6\psi_3\psi_5\psi_1\Theta^{6\ \prime}_{00}\right] \qquad (3)\end{aligned}$$

where

$$\Theta^{6\ \prime}_{00} = \sum_{k=1}^{5} C_{0k}{}'\Theta^6_{00;k} \qquad (4)$$

The spin function $\Theta^{6\ \prime}_{00}$ corresponding to the reordered orbital set is largely dominated by the "perfect-pairing" spin function in which the spins of the pairs of orbitals (ψ_2, ψ_4), (ψ_6, ψ_3) and (ψ_5, ψ_1) are coupled to singlets (see the rightmost column of numbers in Table 2; the values of the coefficients $C_{0k}{}'$ in Table 2 were obtained using the

Table 3. Overlap integrals between the SC orbitals at IRC = +1.19526 amu$^{1/2}$bohr (top values in *boxes*), at the TS (middle values in *boxes*), and at IRC = −1.19552 amu$^{1/2}$bohr (bottom values in *boxes*)

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
ψ_1	1	0.144 0.307 −0.034	0.209 0.242 0.215	0.101 0.339 −0.040	0.786 0.739 0.519	0.181 0.320 0.465
ψ_2		1	0.061 0.440 0.224	0.703 0.804 0.740	0.168 0.419 0.133	0.176 0.710 0.237
ψ_3			1	0.111 0.455 0.125	0.486 0.558 0.192	0.659 0.744 0.845
ψ_4				1	0.003 0.326 0.274	0.295 0.607 0.022
ψ_5					1	0.070 0.316 0.150
ψ_6						1

program SPINS described in Ref. [33]). Another ordering of the three orbital pairs and of the orbitals within pairs would produce slightly different values for the weights of spin functions $\Theta^6_{00;1}$–$\Theta^6_{00;4}$, but the weight of the "perfect-pairing" spin function $\Theta^6_{00;5}$ would remain exactly the same.

The overlaps between the SC orbitals in the rightmost column of Fig. 2 are given by the top values within the boxes in Table 3. The numbers corresponding to orbitals on the HCNO fragment (ψ_1, ψ_3, ψ_5 and ψ_6) are in good agreement with the overlaps between the four SC orbitals for linear HCNO reported in Ref. [16].

It is important to realize that although the shapes of the SC orbitals ψ_2 and ψ_5 at the TS (see the middle column of orbitals in Fig. 2) have undergone significant changes in comparison to the earlier stage of the reaction (depicted by the rightmost column of orbitals in Fig. 2), these changes have not been accompanied by a major recoupling of the spins of the SC orbitals. In fact, if we retain the orbital order from the final expression in Eq. (3), the spin-coupling pattern at the TS is still dominated by the "perfect-pairing" spin function $\Theta^6_{00;5}$, although its weight has decreased from about 97% at IRC $\approx$ 1.2 amu$^{1/2}$bohr to about 79% at the TS (see the middle column of numbers in Table 2). This shows that the orbital pairs (ψ_2, ψ_4), (ψ_6, ψ_3) and (ψ_5, ψ_1) observed when the reactants are well-separated, are retained to a large extent within the SC wavefunction at the TS.

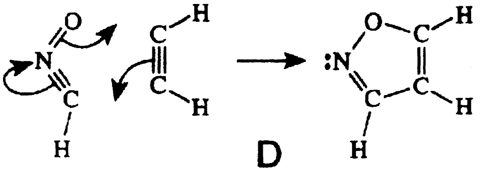
At the TS, SC orbital ψ_2, which was initially one of two orbitals involved in the in-plane ethyne π bond, resembles a linear combination of two sp^x hybrids: one at its "original" ethyne carbon and another at the HCNO carbon. The other orbital within this pair, ψ_4, does not change so dramatically, but its shape at the TS suggests that it is getting ready to participate in a new σ bond with an orbital at the HCNO carbon. SC orbitals ψ_6 and ψ_3, which described one of the C–N bonds at IRC $\approx$ 1.2 amu$^{1/2}$bohr, are not much altered on the way to the TS. They do show, however, a slight tendency to shift over the nitrogen atom. At the TS, SC orbital ψ_5, like ψ_4, attains a shape resembling a mixture of two sp^x hybrids, one of which is at its "original" location (the oxygen atom) and the other one is at the opposite ethyne carbon. At the TS, the second orbital in this pair, ψ_2, becomes a little more localized about the oxygen atom.

As the middle column of Fig. 2 suggests, most of the SC orbitals at the TS share the same region of space. Accordingly, all the overlap integral values are higher than at IRC $\approx$ 1.2 amu$^{1/2}$bohr (see the middle numbers within the boxes in Table 3). However, the largest overlaps continue to be those between orbitals for which the corresponding spins are coupled to singlets by the "perfect-pairing" spin function. This observation lends additional support to the conclusion that the orbital pairs within the separated reactants are retained at the TS. The large orbital overlaps at the TS offer better opportunities for classical VB "resonance", which explains the decrease in the weight of the "perfect-pairing" spin function at the TS.

At IRC ≈ -1.2 amu$^{1/2}$bohr, the formation of the isoxazole ring is almost complete, and it is much easier to deduce the functions served by the six SC orbitals (see the leftmost column in Fig. 2). Orbital ψ_2 is no longer a mixture of two sp^x hybrids: the contribution centred about the ethyne carbon, with which this orbital used to be associated in the limit of separated reactants, has disappeared and we are left with a conventional σ SC orbital localized about the HCNO carbon. Together with ψ_4, this orbital describes one of the new σ bonds closing the ring. The second new σ bond involves orbitals ψ_5 and ψ_1, the first of which has lost most of its connection with its parent oxygen atom and now resides almost entirely on the opposite ethyne carbon. The shape of ψ_1 has become even more similar to an oxygen $2p$ orbital, which suggests that the hybridization state of the oxygen in isoxazole is probably close to sp^2. Finally, orbitals ψ_3 and ψ_6 appear to be engaged in a nitrogen lone pair, partially polarized towards the oxygen atom. This bonding scheme is confirmed by the spin-coupling pattern corresponding to the orbital reordering introduced in Eq. (3): the leftmost column of numbers in Table 2 shows that this spin-coupling pattern is heavily dominated (about 96%) by the "perfect-pairing" spin function. The overlaps between the SC orbitals (see the bottom values in the boxes in Table 3) also indicate that the main bonding interactions, just as at previous points along the IRC, correspond to the orbital pairs (ψ_2, ψ_4), (ψ_6, ψ_3) and (ψ_5, ψ_1).

The evolution of the SC wavefunction along the IRC for 1,3-dipolar cycloaddition of HCNO to ethyne does not exhibit either of the two most important features of the usual SC description of a bond-breaking/bond-making process: the reaction progress is not accompanied by abrupt changes in the coupling of the spins of the SC orbitals or in the overlaps between these orbitals. In fact, the curves showing the weights of the different spin eigenfunctions within $\Theta^{6'}_{00}$ (see Eq. 4) and of the SC overlap integrals as functions of the IRC are so mundane that we decided against including them in the paper.

The key to understanding the SC model for the electronic mechanism of the reaction between HCNO and ethyne is the observation that the orbital pairs (ψ_2, ψ_4), (ψ_6, ψ_3) and (ψ_5, ψ_1) are preserved along the whole segment of the reaction path during which the bonding in the system switches from a reactants-type to a product-type. However, these three orbital pairs are not firmly associated with pairs of atoms: they "move" and realize different bonds at different stages of the reaction. The orbital pair (ψ_2, ψ_4) which well before the TS describes the ethyne in-plane π bond ends up involved in one of the σ bonds closing the isoxazole ring. The other new σ bond is made up of orbital pair (ψ_5, ψ_1) which has its origins in the polar in-plane N—O bond in HCNO. The pair that shifts least of all is (ψ_6, ψ_3): starting as a C—N bond in HCNO, it ends up as the nitrogen lone pair in isoxazole. These three orbital relocations can be expressed in a simplified way as



D

The only difference between this scheme and the "textbook-style" scheme A in the Introduction is in the more realistic description of the 1,3-dipole furnished by SC theory.

4 Conclusions

Although the gas-phase 1,3-dipolar cycloaddition of HCNO to ethyne and the gas-phase Diels-Alder reaction are both six-electron pericyclic reactions, and most organic chemistry textbooks would represent them in very much the same way (see schemes A and B in the Introduction), the SC models for the electronic mechanisms of these reactions, derived in this work and in Ref. [6], respectively, suggest that they have somewhat less in common than many chemists might expect.

The gas-phase Diels-Alder cycloaddition is best represented by a "homolytic" mechanism (see scheme C in the Introduction) in which the half-arrows indicate that the three π bonds present in the reactants do break during the reaction and the spins associated with the orbitals describing these bonds recouple in a different way to form two new σ and one π bond in the product. On the contrary, the gas-phase concerted 1,3-dipolar cycloaddition of HCNO to ethyne follows a "heterolytic" route (see scheme D in Sec. 3), during which three orbital pairs corresponding to three distinct bonds in the reactants shift simultaneously to create two new bonds and a lone pair in the product. As we showed in Ref. [6], the Diels-Alder reaction passes through an aromatic TS, at which the electronic structure of the reacting system strongly resembles certain features of that of benzene. The "heterolytic" nature of the 1,3-dipolar cycloaddition described in the present work, as opposed to the "homolytic" character of the Diels-Alder reaction, creates almost no opportunity for competition between different spin-coupling patterns which, as an analogue to classical VB resonance, is the central moment in the SC description of aromatic systems. Indeed, our results indicate that the reacting system consisting of HCNO and ethyne should be considered as nonaromatic along a sufficiently long IRC segment connecting the reactants to isoxasole and passing through the TS.

It has become customary to consider the SC approach as a modern extension of classical VB theory (see, for example, Refs. [7–10]), which is also reflected in the title of the present article. Yet the SC description of the electronic mechanism of the gas-phase 1,3-dipolar cycloaddition of HCNO to ethyne departs from one of the basic principles of classical VB theory, and most of its extensions, according to which each of the orbitals used to construct the wavefunction should be distinctly associated with a single atomic centre. SC orbitals spreading over more than one centre have been observed in previous SC work: two well-known examples are provided by the antipairs in certain antiaromatic systems such as square cyclobutadiene [34] and by the B–H–B bridges and closed BBB bonds in boranes [35]. However, the present investigation provides the first demonstration of an alternative SC description of a bond rearrangement, achieved through the movement of singlet orbital pairs through space, during which at least one of the orbitals within a pair becomes completely detached from the atomic centre with which it is associated initially and ends up localized about another centre. The ability of the SC wavefunction to produce a description of this type follows from a purely MO element in its construction: the SC orbitals are, in fact, singly occupied nonorthogonal MOs. A more orthodox modern VB approach, insisting on strict localization of the orbitals such as, for example, the "breathing orbitals" VB method of Hiberty et al. [36] would need a number of additional ionic structures in order to compensate for the insufficient flexibility of the orbitals at intermediate stages of the pair shifts (consider, for example, the TS). The resulting wavefunction would be no easier to interpret than a standard MO *ansatz* of a comparable quality [e.g. a CASSCF(6,6) construction]. The simple and easy-to-visualize elegance of the SC model would certainly be lost.

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