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Transition Regions in the Cope Rearrangement of 1,5-Hexadiene and Its Cyano Derivatives

Viktor N. Staroverov and Ernest R. Davidson*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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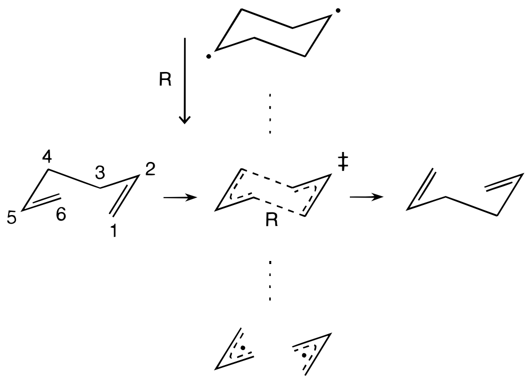
Abstract: Substituent effects on the mechanism of the Cope rearrangement were studied by computing C_{2h} (C_s) cuts through the potential energy surface (PES) for the reaction of 1,5-hexadiene and its di-, tri-, and tetracyano derivatives at the (U)B3LYP/6-31G* and (U)BPW91/6-31G* levels. The stabilization of substituted structures along the cuts is discussed in terms of the energies of isodesmic formation from allyl radicals and acetonitrile molecules. Cyano groups at C1, C3, and C5 provide a nearly additive stabilization of each point along the C_s cut even though their influence on the geometry is competitive. Evaluation of the density of effectively unpaired electrons at various geometries indicates that the radical character of a transition state (TS) is not altered by radical stabilizing substituents as such but depends solely on the interallylic bond length. Although the UB3LYP diyl intermediate for the parent compound is plausible when compared to the lowest triplet PES, neither MRPT2 at the UB3LYP geometries nor UDFT with the original Becke exchange (B) predict any intermediates. Similarly, for each of the three substituted compounds, the most believable (U)BPW91 model gives either one TS or one intermediate. Derivative 1,5-hexadienes with cyano groups at C1, C3, C5 or at C1, C3, C4, C6 rearrange by the same mechanism as the parent, i.e., through a mostly aromatic TS. However, 2,5-dicyano-1,5-hexadiene is found to react through an intermediate. It is suggested that B- rather than B3-type functionals should be used for sigmatropic rearrangements to avoid spurious stationary points.

Introduction

The Cope rearrangement is a generic reaction of 1,5-dienes which involves the [3,3] migration of a σ bond in the thermally activated molecule. In the recent past, the mechanism of the parent rearrangement was a contested point amid inconclusive experimental data[1] and conflicting evidence presented by semiempirical and approximate ab initio treatments.[2] One of the pathways reconcilable with kinetic experiments presupposes that the activated species is an "aromatic" transition state with a high extent of delocalization of electrons in which bond breaking and bond making occur simultaneously. The other viable point of view holds that bond breaking and bond making are consecutive steps separated by a diradical intermediate. In either case, it was agreed that the activated species has a four-center, chairlike geometry[3] of C_{2h} symmetry. Thus, the essential information about the mechanism of the Cope rearrangement can be obtained by studying a C_{2h} cut through the potential energy surface (PES) for this reaction. The interallylic distance R (i.e. $R = R_{\mathrm{C1-C6}} = R_{\mathrm{C3-C4}}$) serves as the natural coordinate along the C_{2h} cut which, at its lowest point, intersects with the reaction path. The increase of R indicates the change from cyclohexane-1,4-diyl through an aromatic system to bis-allyl. The variable nature of structures along the C_{2h} cut and the flatness of the PES in the neighboring region present a serious challenge to computational methods. In retrospect, it is clear that early calculations on the Cope rearrangement were often at variance with each other for a number of reasons including the insufficiency of representing the activated molecule with a single configuration, inadequate treatment of dynamic electron correlation, use of small basis sets, and excessive confidence in semiempirical procedures.



The most convincing evidence in favor of the aromatic transition state was obtained using second-order multireference perturbation theory (MRPT2) with a complete active space self-consistent field (CASSCF) reference wave function in CASPT2N[4] and MROPT2[5] formulations. Both CASPT2N[6] and MROPT2[7] calculations showed that along the C_{2h} cut there exists only one stationary point near $R = 1.85$ Å, and it is a saddle point, not a true minimum. Likewise, coupled cluster doubles (CCD) and quadratic configuration interaction with single and double excitations (QCISD), which introduce electron correlation to a

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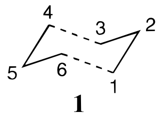
Hartree−Fock (HF) SCF wave function, gave a saddle point near $R = 1.87$ Å.[7] At about the same time, Wiest et al.[8] found that spin-restricted density functional theory (DFT) methods employing BLYP and B3LYP functionals with 6-31G* to 6-311+G** basis sets also predict transition states with R around 2 Å and activation enthalpies close to the experimental value. The aromatic character of these structures was confirmed by calculations of magnetic susceptibility exaltations[9] and the so-called density of effectively unpaired electrons.[10]

Cope rearrangements of substituted 1,5-hexadienes typically differ from the parent reaction by accelerated rates[11−13] meaning lower enthalpies of activation. The impact is particularly pronounced when the introduced groups are capable of resonance delocalization. The long-standing conceptual scheme for analyzing substituent effects, elaborated by Wehrli et al.[12] and Gajewski and Conrad,[13] regards the transition state as floating in a two-dimensional continuum between the two diradical extremes of the 1,4-diyl and bis-allyl. The problem with this scheme is that it discounts the possibility of a predominantly aromatic transition state with small contributions from the diradical valence bond electronic configurations. A more general approach, therefore, is to assume that coordinated radical-stabilizing perturbations of the unsubstituted transition state induce displacements in a *three-dimensional* continuum (two diradicals and the aromatic structure), presumably by altering the optimal ratio between the resonance contributors.

Recently, Doering and Wang[14,15] considered the possibility of another kind of transition state in which conflicting demands from substituents prevent each perturbation from realizing its full stabilizing potential, thus preserving the ratio between diradical resonance contributors. In a vivid description, the mutable C_{2h} transition state of the first kind has been termed by Doering "chameleonic". Correspondingly, the transition state of the second kind, imagined as a half diyl, half bis-allyl hybrid of C_s symmetry (with no aromatic contribution), has been called "centauric". Substituents also have been divided into two types according to the position: "active" located at C1, C3, C4, or C6 and "nodal" located at C2 or C5. Using the empirical lowering of activation enthalpies as the base, Doering and Wang concluded that the chameleonic model describes transition states in which both allylic moieties contain substituents of the same type, whereas the centauric model fits well, though not perfectly, transition states in which one allylic moiety is perturbed at active and the other at nodal sites.

Almost immediately, Hrovat et al. followed up these reports with computational studies of cyano-, vinyl-,[16] and phenyl[17]-substituted 1,5-hexadienes. These workers performed optimizations of individual transition structures at the (U)B3LYP/6-31G* level and concluded that the stabilization effects are cooperative (positive deviations from additivity in the lowering of the activation energy) in the chameleonic model but competitive (negative deviations) in the centauric model. They also found that, for the parent rearrangement, the spin-unrestricted (UB3LYP) method predicts, in addition to the C_{2h} transition state, a stable diyl intermediate.[16] Besides, the calculations provided evidence for cooperative changes in the geometry of the chameleonic transition state, consistent with its mnemonic designation, and a near complete mutual cancellation of geometrical changes in the centauric model.

In this paper, we attack the substituent problem with a different approach relying on the isodesmic reaction method instead of the usual comparison of activation energies. Our results agree with, but elaborate on, the conclusions of Hrovat et al.[16] Without loss of generality, we restricted our consideration to just three cyano derivatives of 1,5-hexadiene (**1**) representing both chameleonic and centauric models: 2,5-dicyano-1,5-hexadiene (**2**), 1,3,5-tricyano-1,5-hexadiene (**3**), and 1,3,4,6-tetracyano-1,5-hexadiene (**4**). In addition to the traditional examination of energies and geometries, an attempt is made to analyze the impact of radical-stabilizing substituents on the radical character of transition structures in terms of the density of effectively unpaired electrons.



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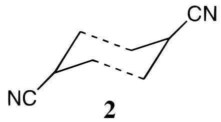

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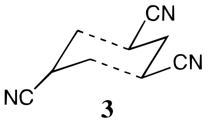

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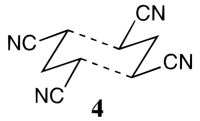

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In the succeeding sections, we raise the concern as to whether the (U)B3LYP theoretical model, despite its plausible predictions, is indeed appropriate for studying the Cope rearrangement. Because DFT in the spin-restricted Kohn−Sham formulation (RDFT) is unable to describe the PES for singlet diradicals, structures with suspected diradical character are sometimes computed with the broken symmetry, spin-unrestricted (UDFT) method. If different from RDFT, the UDFT result is taken as an indicator of the diradical character of the transition structure.[16−19] It turns out that the spin-restricted B3LYP method misses an entire stationary point in the diyl region of the UB3LYP PES for the parent Cope rearrangement.[16] Such a difference between restricted and unrestricted methods is by no means common, unless calculations are performed in the long

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(19) The test is based on the assumption that, for singlet diradicals, a broken symmetry, spin-unrestricted DFT gives a lower energy than the spin-restricted method. The corresponding magnitude of $\langle S^2 \rangle$ is thought of as a measure of the diradical character. Although this criterion sounds reasonable, it works only in DFT. Furthermore, there is no justification for the usual evaluation of $\langle S^2 \rangle$ in DFT.

bond region of the PES. Here we explore the RDFT vs UDFT dilemma by contrasting (U)B3LYP and MROPT2 cuts through the PES for the reaction. We also compare C_{2h} cuts through the singlet PES for the parent rearrangement and the triplet PES for its hypothetical photochemical counterpart. Finally, we study the role of density functionals in the behavior of the theoretical PES. The findings cast doubt upon the applicability of the UB3LYP method to the diyl-like structures.

Computational Methodology

Most geometry optimizations were carried out at the (U)B3LYP/6-31G* level under constraints of the highest possible symmetry (C_{2h} for **1**, **2**, and **4** and C_s for **3**) using Gaussian 98.[20] Cuts through the PES were obtained by varying the interallylic distance (R) and optimizing all other internal coordinates while holding R constant. In these calculations, default convergence criteria and the default integration grid were used. Stationary points were determined by full optimizations using tight convergence criteria (Opt=Tight) with the integration grid having 99 radial shells and 974 angular points per shell. Consequently, all the four decimal places in the values of R reported in this work are reliable. The reference state for MROPT2 calculations is a CAS generated by distributing 6 active electrons among 6 orbitals ($2a_g$,$2b_u$,b_g,a_u) including four orbitals describing the shifting π-bonds and two orbitals describing the shifting σ-bond. The total number of spin- and symmetry-adapted configurations with nonzero coefficients in the 6e$^-$/6 orbital CASSCF wave function is 52 for C_{2h} structures and 95 for C_s. The HONDO suite of programs[21] was used for this step. MROPT2 energies were computed with the second-order perturbation theory program developed by Kozlowski and Davidson[5] as part of the MELD code.[22] The density of effectively unpaired electrons, $u(\mathbf{r})$, was calculated from 6e$^-$/6 orbital CASSCF wave functions with the modified MELD code. The 6-31G* basis set was used in all instances.

Cyano Substituent Effects

Energy and Geometry. The usual way to study substituent effects on the Cope rearrangement consists of comparing the enthalpies of activation ($\Delta H^{\ddagger}$) for substituted 1,5-dienes. However useful, a perturbation of $\Delta H^{\ddagger}$ is not a direct measure of the substituent effect because substituents stabilize not only the transition structure but also the reactant. In principle, stabilization of the reactant can be taken into account in some manner, as was done by Doering and Wang[14,15] who corrected the experimental enthalpies of activation for conjugative interactions in the substituted olefinic compounds. Nevertheless, a comparison of individual transition states still does not separate the net stabilization caused by substituents at the unperturbed transition geometry from the stabilization owing to geometry relaxation.

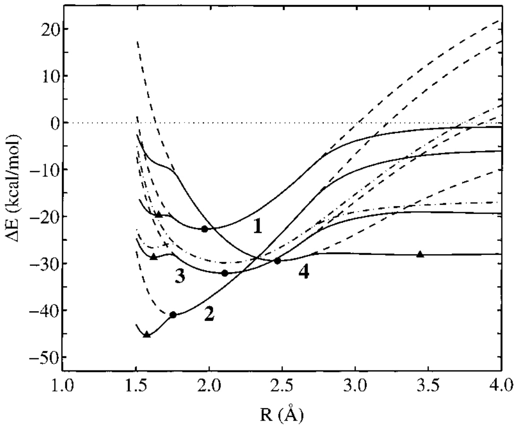

Figure 1. C_{2h} (C_s) cuts through the (U)B3LYP/6-31G* PES for Cope rearrangement structures **1**−**4**. ΔE is the isodesmic stabilization energy relative to ground-state allyl radicals and CH_3CN molecules. Solid lines represent UB3LYP results, dashed lines B3LYP. The dot-and-dash curve is the average of curves **2** and **4**. Circles mark transition states, triangles mark intermediates.

Table 1. Interallylic Distances, Absolute Energies, Energies of Isodesmic Formation from Allyl Radicals and CH_3CN Molecules (ΔE), and Lowest Vibrational Frequencies for the Stationary Points on C_{2h} Cuts through the PES for the Cope Rearrangement of 1,5-hexadiene (**1**) and Its 2,5-Dicyano (**2**), 1,3,5-Tricyano (**3**), and 1,3,4,6-Tetracyano (**4**) Derivatives, Computed at the (U)B3LYP/6-31G* Level

substitution pattern	R_{C1-C6}[a] (Å)	$E_{(U)B3LYP}$ p(hartree)	$\langle S^2\rangle$[b]	$\Delta E_{(U)B3LYP}$[b] (kcal/mol)	$\nu(a_u)$[b] (cm^{-1})
1	1.9661	−234.556928	0.	−22.7	*i*569.5
	1.6518	−234.552131	0.66	−19.8	206.3
2	1.7524[c]	−419.059057	0.	−41.0	*i*128.1
	1.5741	−419.066072	0.94	−45.4	40.4
3	2.1062	−511.281464	0.	−32.1	*i*527.6
	1.6181	−511.276106	0.84	−28.7	53.9
4	2.4670	−603.513727	0.	−29.4	*i*249.6
	3.4429	−603.511697	1.00	−28.1	6.7

[a] Optimized at the Opt=Tight, Int(Grid=99974) level. [b] Computed using the 99/974 grid with the SCF=Tight option. [c] Exists only on the spin-restricted PES.

For these reasons, we decided to evaluate substituent effects in structures **1**−**4** in terms of the energies of "isodesmic" formation at arbitrary points along the C_{2h} cut of the PES, according to the following equation

$$2CH_2{=}CH{-}CH_2^{\bullet} + nCH_3CN \rightarrow [C_6H_{10-n}(CN)_n]^* + nCH_4$$

where n = 0, 2, 3, and 4 for structures **1**, **2**, **3**, and **4**, respectively. The isodesmic formation (or stabilization) energy, ΔE, is defined as the energy of recombination of the reference system (two allyl radicals and n CH_3CN molecules in their ground-state equilibrium geometries) into a point (geometry) on the PES of $C_6H_{10-n}(CN)_n$ along with as many ground-state CH_4 molecules as necessary to conserve the number of atoms. Since we want to examine ΔE as a function of the interallylic distance $R = R_{C1-C6} = R_{C3-C4}$, we shall omit zero-point energy corrections and heat capacity contributions.

Figure 1 depicts C_{2h} (C_s for **3**) cuts through the (U)B3LYP/6-31G* surfaces of isodesmic stabilization energies ΔE for structures **1**−**4**. Properties of the stationary points located on these curves are summarized in Table 1. The C_{2h} cut for the parent Cope rearrangement (**1**) in the symmetry and spin-restricted description (B3LYP) has a single stationary point: a transition state at $R^{\ddagger} = 1.9661$ Å. The broken symmetry, spin-unrestricted (UB3LYP) curve differs from B3LYP in two respects. At large R, as expected, only the UB3LYP curve has a correct asymptotic behavior. More interesting is the fact that at the other extreme

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of the interallylic distances, the UB3LYP curve passes through a shallow but, nevertheless, easily detectable minimum at $R = 1.6518$ Å,[23] even as the B3LYP curve rapidly and monotonically increases. Transition state **1** on the (U)B3LYP cut has the stabilization energy $\Delta E = -22.7$ kcal/mol. For comparison, the experimental stabilization energy of the parent transition state relative to two allyls is estimated at $\Delta E = -30.1$ kcal/mol.[25] Note that although the B3LYP stabilization energy is rather poor, the same B3LYP method predicts the activation energy of 1,5-hexadiene with good accuracy.[8]

In structure **2**, "nodal" cyano groups at C2 and C5 stabilize every point along the C_{2h} cut but do so more effectively at short interallylic distances.[28] Transition state **2**, which exsists only on the spin-restricted cut near the bifurcation point, contracts to the interallylic bond length of $R^{\ddagger} = 1.7524$ Å (Table 1). At this geometry, it is almost twice as stable as the unsubstituted transition state. The spin-unrestricted optimization of **2** predicts an even more stable intermediate with $R = 1.5741$ Å, which is quite close to the standard C−C bond length of 1.54 Å expected in cyclohexane-1,4-diyl.

The four cyano groups at C1, C3, C4, and C6 in structure **4** jointly stabilize the bis-allyl resonance contributor. The outcome is a considerably looser transition state with $R^{\ddagger} = 2.4670$ Å and stabilization $\Delta E = -29.4$ kcal/mol, which is only 6.7 kcal/mol stronger than ΔE for the parent transition state **1**. Although the B3LYP and UB3LYP curves for **4** also bifurcate near $R = 1.75$ Å, this time there is no stationary point on the UB3LYP branch. However, we found an extremely shallow minimum on the other side of the UB3LYP curve located at $R = 3.4429$ Å. While this stationary point may well be an artifact, it fits in perfectly with the overall picture as a stabilized bis-allyl.

When the entire curves for **2** and **4** are compared, it is seen that the stabilization of *tight* structures by cyano groups at "nodal" positions (C2 and C5) is considerably stronger than the stabilization at "active" positions (C1, C3, C4, and C6). For *loose* structures, however, it is the active substituents that are much more effective in lowering the energy. Thus, perturbations of the allylic moieties by substituents of the same type alter dramatically the entire PES in the transition region. In view of the fact that such C_{2h} structures can change from cyclohexane-1,4-diyl to bis-allyl, depending on the pattern and chemical composition of substituents, the Doering's term "chameleonic" seems very appropriate.

A different picture arises in the case of structure **3**. Here the two cyano groups at C1 and C3 distort the interallylic distance and the C1−C2−C3 allylic moiety toward a looser bis-allyl geometry while the cyano group at C5 strives to shorten R and pull the C4−C5−C6 moiety toward the 1,4-diyl (hence, the name "centauric"). As a tradeoff, the interallylic distance in transition state **3** ($R^{\ddagger} = 2.1062$ Å) is almost precisely the average of R values in **2** and **4**. The stabilization energy of transition state **3** is also the average of vertical stabilization energies for **2** and **4**. Similar observations can be made about the interallylic distance and stabilization energy of diyl intermediate **3** at $R = 1.6181$ Å. In fact, the entire stabilization energy curve **3** is very nearly the average of curves **2** and **4**, which is shown in Figure 1 as a dot-and-dash line. This suggests that, at a fixed R, each cyano group in **3** does realize its full stabilizing potential, contrary to what might be concluded by comparing **2**, **3**, and **4** at their respective optimized values of R. It is also well worth noting that the C_s cut through the PES for centauric **3**, but not chameleonic **2** or **4**, closely resembles the C_{2h} cut for parent **1**, the only difference being a greater overall stabilization of the substituted structure. Thus, in agreement with Hrovat et al.,[16] we find that cyano substituents in a centauric transition state jointly stabilize each point on the PES even as they impose conflicting demands on the molecular geometry.

Radical Character. It is logical at this point to ask the following question: Do radical stabilizing substituents perturb transition structures by altering the amount of the radical character or merely by causing changes in the geometry? In an earlier publication,[10] we showed that the density of effectively unpaired electrons $u(\mathbf{r})$ provides a meaningful and useful measure of the radical character of Cope rearrangement structures. If it is permissible to compare the distributions of effectively unpaired electrons in systems of different size, we can obtain the answer by computing the density $u(\mathbf{r})$ at the UB3LYP geometries of transition states and diradical intermediates **1**−**4**, using 6e$^-$/6 orbital CASSCF wave functions.[29] To separate the net effect of substituents at a fixed geometry from the effect of geometrical changes, we performed calculations of $u(\mathbf{r})$ twice for each species: (i) in structures **2**−**4** in which the six-membered ring and all unsubstituted hydrogen atoms were frozen at the optimized geometry of transition state (intermediate) **1**, while the cyano groups were allowed to relax, and (ii) in the fully optimized transition states (intermediates) **2**−**4**. By this means, calculations of $u(\mathbf{r})$ for partially optimized structures pick out variations of the radical character caused by cyano substituents alone, while calculations for the fully optimized structures reflect the combined effect of cyano groups and structural relaxation. In each case, we also evaluated the total number of effectively unpaired electrons, defined as $n = \int u(\mathbf{r})\, d\mathbf{r}$, and Mulliken atomic populations of $u(\mathbf{r})$.[30]

Figures 2 and 3 show how the introduction of cyano groups into the frozen six-membered ring influences the distribution and total number n of effectively unpaired electrons. A small

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(23) This minimum, first reported by Hrovat et al.,[16] corresponds to cyclohexane-1,4-diyl with the pseudoaxial orientation of hydrogens at C2 and C5. The pseudoaxial conformation remains preferable at the B3LYP/6-31G* level down to $R = 1.52$ Å when it switches to pseudoequatorial. Both forms can be optimized only near $R = 1.52$ Å. Curiously, at the CASSCF/6-31G* level, the pseudoaxial and pseudoequatorial forms give rise to two distinct stable intermediates.[24]

(24) Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 9756−9759.

(25) Obtained by subtracting 4.2 kcal/mol, the change in zero-point energies (ZPE) and thermal enthalpy corrections estimated at the (U)B3LYP/6-31G* level, from the "experimental" *enthalpy* of stabilization relative to two allyls, $\Delta H_{298} = -25.9$ kcal/mol. The latter is based on the enthalpy of activation of 1,5-hexadiene, $\Delta H^{\ddagger}_{298} = +33.8$ kcal/mol (determined from the actually measured[26] $\Delta H^{\ddagger}_{500} = +\,33.5$ kcal/mol by computing thermal corrections at the B3LYP/6-31G* level), and the most recent experimental values for the enthalpies of formation of 1,5-hexadiene ($\Delta H^{\ddagger}_{298} = +\,20.1$ kcal/mol) and the allyl radical ($\Delta H^{\ddagger}_{298} = +39.9$ kcal/mol).[27] Note that the ZPE and thermal corrections to the stabilization enthalpy ΔH are considerably greater than the similar corrections to the enthalpy of activation ($\Delta H^{\ddagger}_{298} = \Delta E^{\ddagger}_{e} - 1.2$ kcal/mol).

(26) Doering, W. v. E.; Toscano, V. G.; Beasly, G. H. *Tetrahedron* **1971**, *27*, 5299−5306.

(27) Roth, W. R.; Bauer, F.; Beitat, A.; Ebbrecht, T.; Wüstefeld, M. *Chem. Ber.* **1991**, *124*, 1453−1460.

(28) In agreement with the findings of Hrovat et al.,[16] our unpublished calculation of the C_{2h} cut through the PES for 2-cyano-1,5-hexadiene shows that the stabilization of **2** is less than twice the stabilization of the corresponding monosubstituted structure at each value of R.

(29) The density of effectively unpaired electrons is defined by the equation $u(\mathbf{r}) = 2\rho(\mathbf{r}) - \int \rho(\mathbf{r},\mathbf{r}')\, \rho(\mathbf{r}',\mathbf{r})\, d\mathbf{r}'$, where $\rho(\mathbf{r})$ is the charge density and $\rho(\mathbf{r},\mathbf{r}')$ is the reduced density matrix. As a generalization of the uncompensated spin density, the function $u(\mathbf{r})$ describes the radical character of molecules of any spin multiplicity including singlets. In RHF or spin-restricted DFT for a singlet state, $\rho(\mathbf{r},\mathbf{r}')$ is twice an idempotent operator, so $u(\mathbf{r}) \equiv 0$. This is why $\rho(\mathbf{r},\mathbf{r}')$ has to be generated from a CI wave function.

(30) For singlet wave functions, Mulliken atomic populations of $u(\mathbf{r})$ are identical with Mayer's free valences: (a) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 73−84. (b) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 477−483.

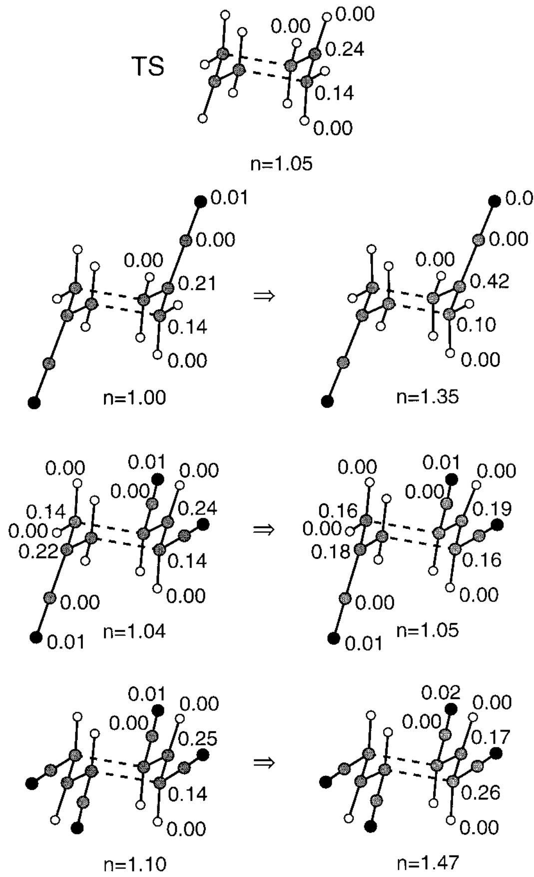

Figure 2. Atomic populations of effectively unpaired electrons in B3LYP transition states (TS) **1**−**4**. Left side: Partially optimized structures (the six-membered rings and unsubstituted hydrogens are frozen at the TS geometry of **1**). Right side: Fully relaxed structures. Actual geometries are shown in all cases. The density *u*(**r**) is from CASSCF wave functions computed at the (U)B3LYP geometries; *n* is the total number of effectively unpaired electrons.

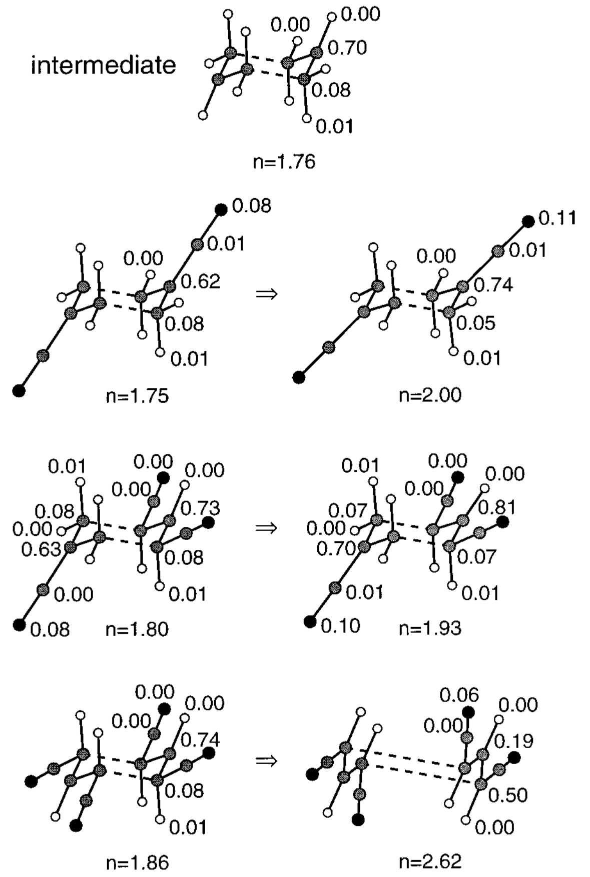

Figure 3. Same as in Figure 2 for the UB3LYP diradical intermediates **1**−**4**.

decrease of *n* is observed in the partially optimized transition state **2** as well as in intermediate **2**, because the more electronegative nitrogen atoms of "nodal" cyano groups induce a nonnegligible depletion of unpaired electron populations on C2 and C5.[31] In contrast, cyano substituents at C1, C3, C4, and C6 in the partially optimized transition state **4** and intermediate **4** slightly increase the total number of effectively unpaired electrons, but only marginally affect their distribution between the core carbons. This observation is consistent with the weaker stabilizing capacity of "active" substituents.[16] In either case, cyano groups do not alter the general pattern set by the parent structure. In the partially optimized "centauric" structures **3**, changes of *u*(**r**) are also minimal. Furthermore, populations of effectively unpaired electrons on C1, C3, C4, and C6 in **3** are very similar, as are the numbers for C2 and C5, even though only half the carbons of each type are substituted. This convincingly shows that "radical stabilizing" groups scarcely affect the extent of the radical character at a fixed position of the ring nuclei.

Relaxation of the six-membered-carbon ring leads to tighter structures **2** and looser **4**. As is apparent from Figures 2 and 3, both the contraction of **2** and the loosening of **4** result in an increase of the number of effectively unpaired electrons and their redistribution in the ring, reflecting the growing importance of diradical resonance contributors. Relative to "chameleonic" **2** and **4**, structural changes in the "centauric" **3** are minor and result in lesser variations of *u*(**r**) (Figures 2 and 3). Perturbations of the radical character in **3** are also pictured in Figures 4 and 5. These show contour plots of *u*(**r**) in partially and completely optimized transition states and intermediates as compared with the unsubstituted compound. From the above observations one is led to believe that in *any* fully optimized substituted structure there would be about as many effectively unpaired electrons as there are in the unsubstituted structure with the same value of *R*. Thus, cyano groups by themselves do not alter the radical character of transition structures but rather cause changes in the molecular geometry, and it is the geometry that determines the nature of the wave function.

Existence of the Diradical Intermediate

Every point on the PES for the Cope rearrangement is described with a singlet wave function. Calculations of singlet states are usually subject to the constraint that spin-up and spin-down electrons occupy orbitals of identical symmetry and form. In one-determinantal methods such as Hartree−Fock SCF and DFT, this restriction leads to an incorrect behavior of singlet PES at stretched bond lengths. The best way to eliminate the defect is to use a configuration interaction (CI) wave function which has the advantage that it preserves the correct spin density. Unfortunately, the CI approach is not readily extendable to DFT.

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[31] Following an insightful suggestion of Hrovat and Borden, we have also computed *u*(**r**) for transition structures **2** using the 10 e^-/10 orbital CASSCF wave function which includes contributions from the two nodal cyano groups. In the extended CASSCF description, Mulliken populations of effectively unpaired electrons on the CN groups are no longer negligible, as expected due to the naturally large correlation effects in the CN group itself. Nevertheless, despite the marked increase of the total number of effectively unpaired electrons as a result of enlarging the CAS, the populations on the ring carbons exhibit very small changes (see the Supporting Information).

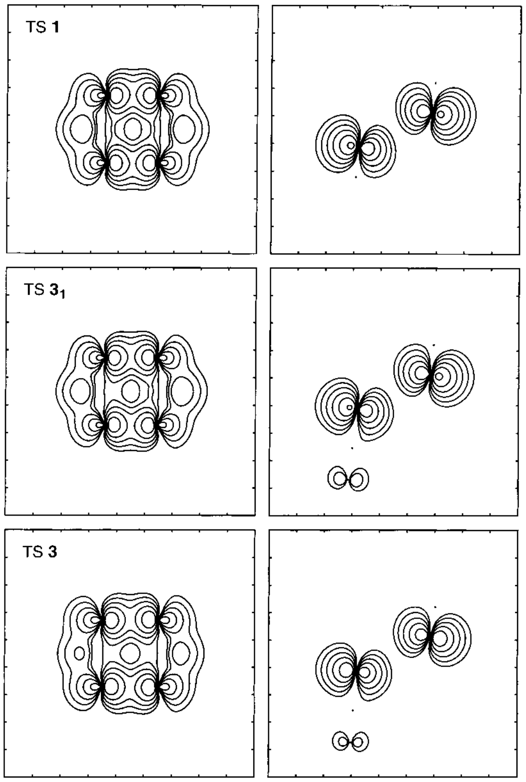

Figure 4. Effects of cyano substituents at C1, C3, and C5 on the density of effectively unpaired electrons $u(\mathbf{r})$ in B3LYP transition states (TS). Upper panels: Fully optimized TS **1** ($R^{\ddagger} = 1.9661$ Å). Middle panels: Partially optimized TS $\mathbf{3_1}$ (the six-membered carbon ring is frozen at the geometry of TS **1**). Lower panels: Fully optimized TS **3** ($R^{\ddagger} = 2.1062$ Å). The plots are in the C1−C3−C4−C6 plane (left panels) and in the perpendicular mirror plane drawn through C2 and C5 (right panels). Contours start at 0.001 e/a_0^3. Densities of successive levels differ by a factor of $10^{1/3}$. Tick marks are 1 Å apart.

A compromise, suitable for both SCF and DFT, is to release the spin constraint imposed on the single configuration solution at the price of allowing the spin density to be totally wrong.

Neither restricted nor unrestricted Hartree−Fock (RHF and UHF) are useful methods for studying the Cope rearrangement, because they exclude electron correlation effects. At the same time, DFT in the Kohn−Sham formulation is quite robust when using a modern density functional, even though it is also a one-determinantal description of the associated noninteracting system. In RDFT, a C_{2h} cut through the PES still does not go to the correct dissociation limit (the energy of two allyl radicals) but the situation is remedied by going to UDFT. Davidson[32] discussed the spin stability of RHF and RDFT solutions along a C_{2h} cut of the PES for the Cope rearrangement of 1,5-hexadiene and found that the RHF calculation is always unstable, that is, UHF always gives a lower energy. Interestingly, B3LYP and B3PW91 calculations proved to be stable over a large range of interallylic distances.

Along the C_{2h} cut through the PES for the parent Cope rearrangement, shown again in Figure 6, the (U)B3LYP/6-31G* Kohn−Sham determinant is stable from $R = 1.75$ to 2.7 Å. Although at long interallylic distances the B3LYP and UB3LYP curves are distinguished only by the expected difference in their asymptotic form, for $R < 1.75$ Å they differ qualitatively in that the UB3LYP curve has a minimum at $R = 1.6518$ Å, whereas the spin-restricted curve has none. The nature of the UB3LYP stationary point was verified by frequency calculations. An imaginary vibration frequency first appears to the right of the minimum at about $R = 1.67$ Å.

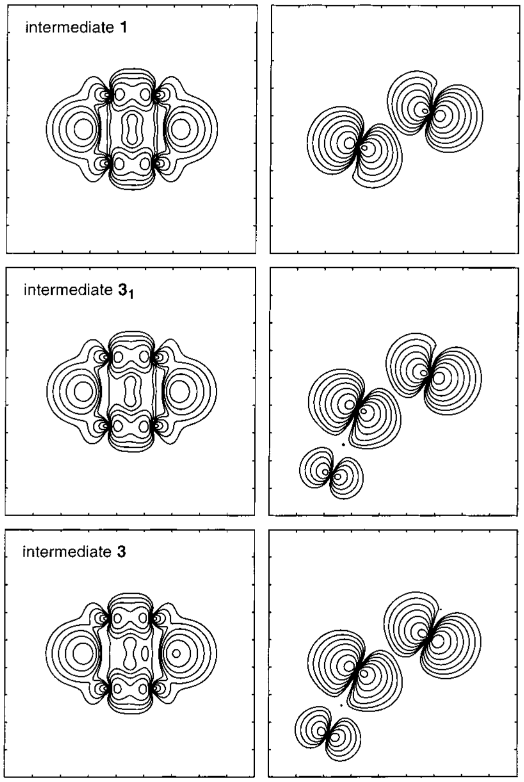

Figure 5. Effects of cyano substituents at C1, C3, and C5 on the density of effectively unpaired electrons $u(\mathbf{r})$ in UB3LYP diyl intermediates. Upper panels: Fully optimized intermediate **1** ($R^{\ddagger} =$ 1.6518 Å). Middle panels: Partially optimized intermediate $\mathbf{3_1}$ (the six-membered carbon ring is frozen at the geometry of intermediate **1**). Lower panels: Fully optimized intermediate **3** ($R^{\ddagger} = 1.6181$ Å). Plotting conventions as in Figure 4.

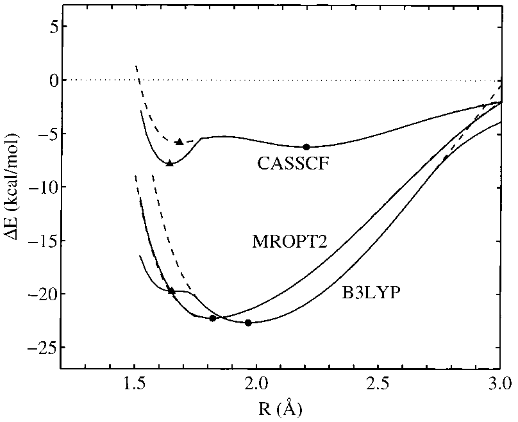

Figure 6. CASSCF and MROPT2 energies along a C_{2h} cut through the (U)B3LYP/6-31G* PES for the Cope rearrangement of 1,5-hexadiene. ΔE is the stabilization energy relative to two isolated allyls. Solid lines are computed at the UB3LYP optimized geometries, dashed lines at B3LYP optimized geometries. Circles mark transition states, triangles mark intermediates.

To decide which of the B3LYP and UB3LYP predictions is true, we computed CASSCF and MROPT2 energies at the UB3LYP and B3LYP geometries along the C_{2h} cut.[33] The results appear in Figure 6. The 6e$^-$/6 orbital CASSCF wave function is known to provide a faulty description of the transition region for the Cope rearrangement, as it predicts both a loose transition

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(32) (a) Davidson, E. R. *Int. J. Quantum Chem.* **1998**, *69*, 241−245. (b) Davidson, E. R. *Chem. Phys. Lett.* **1998**, *284*, 301−307.

state at $R^{\ddagger} = 2.189$ Å *and* a diradical intermediate at $R = 1.641$ Å, the diyl having a slightly lower energy.[24] These two structures are still present on the CASSCF curve at $R^{\ddagger} = 2.20$ Å and $R = 1.64$ Å, even though CASSCF energies are now computed at UB3LYP optimized geometries. In fact, the tendency of CASSCF to favor the diyl is so strong that even at the symmetry and spin-restricted B3LYP geometries it predicts a minimum with $R = 1.68$ Å, while there is no such minimum on the B3LYP curve itself. At the higher MROPT2 level, however, the short-R minimum disappears without a trace, and the transition state moves to $R^{\ddagger} = 1.82$ Å, similarly to what was first observed in CASPT2N[6] and MROPT2[7] calculations at CASSCF optimized geometries. Furthermore, the stabilization energy gap between B3LYP and UB3LYP geometries vanishes at the MROPT2 level in both the diyl and bis-allyl extremes. Apart from a displacement by roughly 0.1 Å toward shorter interallylic distances, the MROPT2 curve mimics the B3LYP result almost unerringly all the way from tight geometries up to about $R = 2.7$ Å, where the spin-symmetry problem comes into play. This suggests that it is the UB3LYP rather than B3LYP method that provides an incorrect description of the PES in the 1,4-diyl region. The question whether spurious diyl intermediates would arise in calculations with other density functionals is discussed below.

Comparison of Singlet and Triplet PES

The simplest wave function describing the PES for the parent Cope rearrangement is a single Slater determinant (a Kohn−Sham determinant in DFT)

$$^{1}\Psi_{0} = |...7a_{g}^{2}5a_{u}^{2}7b_{u}^{2}|$$

Along the reaction path, the participating molecular orbitals of the reactant pass smoothly into the molecular orbitals of the product. Because the overall $^{1}A_{g}$ symmetry of the determinant $^{1}\Psi_{0}$ is conserved, the reaction is allowed by Woodward−Hoffmann rules.

While $^{1}\Psi_{0}$ dominates in the range of medium interallylic distances, it becomes inadequate at the diradical extremes. At long R, when the transition structure is essentially a complex of two weakly interacting allyl radicals, the simplest qualitatively correct description involves two configurations of equal weight

$$^{1}\Psi_{\text{bis-allyl}} = |...7a_{g}^{2}5a_{u}^{2}7b_{u}^{2}| - |...7a_{g}^{2}5b_{g}^{2}7b_{u}^{2}|$$

At short interallylic distances, the molecule is a 1,4-diyl with the wave function

$$^{1}\Psi_{\text{diyl}} = |...7a_{g}^{2}5a_{u}^{2}7b_{u}^{2}| - \lambda|...7a_{g}^{2}5a_{u}^{2}8a_{g}^{2}|$$

where λ is close to one. A reasonable wave function for all interallylic distances must, therefore, include at least the three configurations used in constructing wave functions $^{1}\Psi_{0}$, $^{1}\Psi_{\text{bis-allyl}}$, and $^{1}\Psi_{\text{diyl}}$ (the 6e^{-}/6 orbital CASSCF function satisfies this requirement).

The determinant $^{1}\Psi_{0}$, however deficient at both diradical extremes, remains the lowest energy solution out of all one-determinantal descriptions along the C_{2h} cut. The situation is quite different for a C_{2h} cut through the triplet PES of a hypothetical photochemical Cope rearrangement. The triplet PES is the first excited solution above the singlet. Kohn−Sham determinants for the 1,4-diyl and bis-allyl differ by the symmetries of singly occupied orbitals,

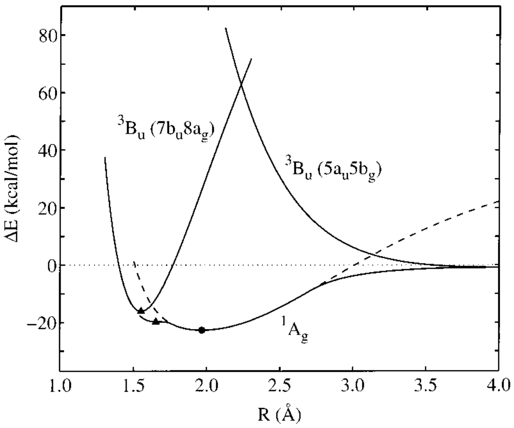

Figure 7. C_{2h} cuts through the singlet and triplet (U)B3LYP/6-31G* PES for the Cope rearrangement of 1,5-hexadiene. ΔE is the stabilization energy relative to two allyls. Singly occupied orbitals in the triplet Kohn−Sham determinants are indicated in parentheses. Solid lines represent UB3LYP results, dashed lines B3LYP. Circles mark transition states, triangles mark intermediates.

$$^{3}\Psi_{\text{diyl}} = |...5a_{u}^{2}7a_{g}^{2}7b_{u}8a_{g}|$$

$$^{3}\Psi_{\text{bis-allyl}} = |...7a_{g}^{2}7b_{u}^{2}5a_{u}5b_{g}|$$

so the 1,4-diyl and bis-allyl DFT descriptions belong to different PES (Figure 7). The deep minimum at $R = 1.55$ Å corresponding to the triplet diradical has the energy and geometry similar to those of the UB3LYP singlet cyclohexane-1,4-diyl. The triplet complex of two allyl radicals represented by the second curve is unstable and undergoes dissociation. The apparent intersection of PES for $^{3}\Psi_{\text{diyl}}$ and $^{3}\Psi_{\text{bis-allyl}}$ in Figure 7 is not a true crossing point but rather a projected one because the geometries of the diyl and bis-allyl at this R are not the same. Because the overall symmetry of determinants $^{3}\Psi_{\text{diyl}}$ and $^{3}\Psi_{\text{bis-allyl}}$ is accidentally the same ($^{3}B_{u}$), a CASSCF calculation would have produced a smooth PES connecting the limiting configurations.

Our calculations with B(3)LYP and B(3)PW91 density functionals show that, although stabilization energies of the triplet intermediate vary with the method in a wide range from −9.0 (BLYP/6-31G*) to −23.6 kcal/mol (B3PW91/6-31G*), the vertical singlet−triplet gap at the triplet PES minimum remains remarkably constant at about 1.0 kcal/mol. Such a small value is a strong indication of the diradicaloid character of tight Cope rearrangement structures.

The Role of Density Functionals

A glance at the current literature reveals that most DFT calculations of molecules are performed with the semiempirical Becke-style three-parameter hybrid density functional B3LYP[34] which combines exact Fock and empirical Becke exchange with a local Vosko−Wilk−Nusair (VWN) correlation functional corrected by the nonlocal correlation of Lee, Yang, and Parr (LYP). The popularity of the B3LYP method is based on its remarkable success in predicting accurate geometries for a wide range of molecules. It is reasonable to expect that, in its spin-unrestricted modification, the B3LYP method should also

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(33) The CASSCF wave function includes all the important configurations needed to describe the PES for the Cope rearrangement, but lacks correlation between the active and inactive electrons (i.e. dynamic correlation). For pericyclic reactions, inclusion of dynamic correlation is necessary to obtain qualitatively correct PES: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67−75. The CASSCF wave function is still an excellent reference state for perturbation theory calculations.

(34) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

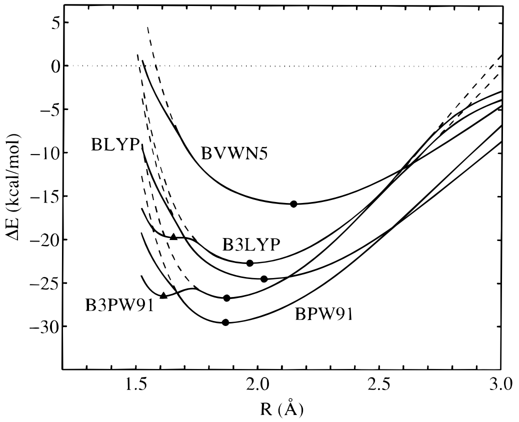

Figure 8. C_{2h} cuts through the PES for the Cope rearrangement of 1,5-hexadiene computed with various density functionals using the 6-31G* basis set. Solid lines represent broken symmetry, spin-unrestricted results; dashed lines are from spin-restricted calculations. Circles mark transition states, triangles mark intermediates.

Table 2. Interallylic Distances, Absolute Energies, Energies of Formation from Two Allyls (ΔE), and Lowest Vibrational Frequencies for the Stationary Points on a C_{2h} Cut through the PES for the Cope Rearrangement of 1,5-Hexadiene, Computed with Various Density Functionals and the 6-31G* Basis

method	$R_{\mathrm{C1-C6}}$[a] (Å)	E[b] (hartree)	$\langle S^2\rangle$[b]	ΔE[b,c] (kcal/mol)	$\nu(a_u)$[b] (cm^{-1})
(U)BLYP[d]	2.0215	−234.419222	0.	−24.5	*i*499.0
(U)B3PW91	1.8770	−234.470601	0.	−26.7	*i*517.0
	1.6108	−234.470242	0.79	−26.5	203.7
(U)BPW91	1.8750	−234.520498	0.	−29.6	*i*431.8
(U)BVWN5	2.1359	−235.816114	0.	−15.9	*i*487.4

[a] Optimized at the Opt=Tight, Int(Grid=99974) level. [b] Computed using the 99/974 grid with the SCF=Tight option. [c] Expected experimental value is −30.1 kcal/mol.[25] [d] (U)B3LYP results appear in Table 1.

produce reliable PES for diradicals. Against this background, the qualitative disagreement between the UB3LYP method and multireference perturbation theories (MROPT2, CASPT2N) regarding the existence of the 1,4-diyl intermediate on the PES for the Cope rearrangement comes as a surprise.

There are strong grounds[6,7] to believe MROPT2 rather than the UB3LYP method and to assume that the spurious intermediate is due to a shortcoming of the UB3LYP functional. To determine whether the defect is contained in the exchange or correlation part of the UB3LYP functional, we computed C_{2h} cuts through the spin-restricted and spin-unrestricted PES for the parent reaction using various combinations of Becke's hybrid exchange and the original Becke exchange (B) with correlation functionals of Lee, Yang, and Parr (LYP), Perdew and Wang (PW91), as well as Vosko, Wilk, and Nusair (VWN).

Figure 8 demonstrates that, although spin-restricted and spin-unrestricted DFT calculations with *any* functional differ at $R < 1.75$ and > 2.5 Å, cyclohexane-1,4-diyl intermediates appear on the PES only when the method employs a B3-type functional regardless of the correlation components. Outside of the 1,4-diyl range there are no qualitative distinctions between the methods. Table 2 shows that the B3LYP, BLYP, and B3PW91 functionals all underestimate the stabilization of the transition state relative to a pair of allyls. The BPW91 functional yields not only a reasonable stabilization ΔE but also a very good estimate of the interallylic distance, $R = 1.8750$ Å (the actual value is commonly placed near 1.87 Å). The BVWN5 method stands out as less successful because the VWN(5) functional considerably overestimates the correlation energy.

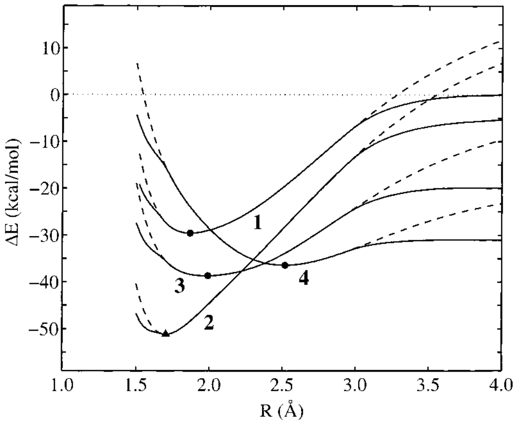

Figure 9. Same as in Figure 1, but using the (U)BPW91/6-31G* method.

The fact that spin-restricted DFT is stable to spin symmetry breaking over the important range of R from 1.75 to about 2.5 Å is interesting by itself,[32] especially since the RHF SCF wave function is always unstable. As far as the stability of spin symmetry is concerned, this property of RHF suggests a plausible explanation to the exceptional role of Becke-style hybrid exchange in predicting the additional stationary point. Indeed, the RHF energy can be regarded as a density functional which includes the exact Fock exchange but no correlation. Unlike the original B functional,[35] the hybrids B3LYP[34] and B3PW91[36] contain a portion of the exact Fock exchange. Hence, an SCF Kohn−Sham determinant obtained with a B3-type density functional should be more prone to spin symmetry breaking than the Kohn−Sham determinant generated without resorting to exact exchange.

To determine whether B- and B3-type functionals predict qualitatively different PES for cyano-substituted systems as well, we recomputed C_{2h} cuts for structures **2**−**4** using the (U)BPW91/6-31G* method. The curves, shown in Figure 9, have no minima on the UBPW91 branches, which supports our surmise that all of the UB3LYP diradical intermediates **1**−**4** are spurious. Both BPW91 and UBPW91 methods give but one stationary point for each of the four compounds. Remarkably, the stationary point for **2** ($R = 1.7047$ Å) is not a transition state but rather an intermediate (although not quite a diyl, because the interallylic distance is still too large and $\langle S^2\rangle = 0$). This peculiarity of 2,5-dicyano-1,5-hexadiene is in line with the very recent finding of Hrovat et al.[17] that the nonhybrid density functional (U)BLYP predicts an intermediate (though not a diradical) in the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene. The question whether this remains true for other substituents invites further investigation.

Conclusions

C_{2h} (C_s) cuts through the PES juxtaposed by the isodesmic reaction method illustrate changes in the mechanism of substituted Cope rearrangements in a more expressive fashion than single-point calculations. Radical stabilizing substituents at C2 and C5 or at C1, C3, C4, and C6 provide nearly additive stabilization of the energy and drive the geometry toward one of the two diradical extremes, cyclohexane-1,4-diyl and bis-allyl. A mixed-type substitution at C1, C3, and C5 (the "centauric" model) also leads to nearly additive stabilization of the energy but its influence on the geometry is competitive.

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(35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.
(36) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

Similar conclusions have been reached by Hrovat et al.[16] by considering the activation energies.

The distribution of effectively unpaired electrons is almost unaffected by the introduction of radical stabilizing groups at the frozen geometry of the carbon ring. The number of effectively unpaired electrons varies substantially only when the ring is allowed to relax. Therefore, substituents by themselves do not alter the ratio between resonance contributors in a transition state but rather cause changes in the geometry, and it is the structural relaxation that changes the nature of the wave function.

On the theoretical PES for the parent compound, a diyl intermediate appears only when Becke-style hybrid (B3) density functionals are used. Neither MROPT2 at UB3LYP optimized geometries nor UDFT with the original Becke exchange (e.g. UBLYP) yield any stationary points other than the aromatic transition state. Similarly, the UB3LYP diradicals of cyano derivatives of 1,5-hexadiene disappear at the UBPW91 level. The only remaining stationary point may be either a transition state or an essentially aromatic intermediate. Hence, UB3LYP diradical intermediates in the Cope rearrangement are spurious (as are the CASSCF intermediates).

Assuming that the (U)BPW91 method gives the best approximation to the true PES for the reaction, 1,5-hexadienes substituted at C1, C3, C5 or at C1, C3, C4, C6 undergo the Cope rearrangement by the same mechanism as the parent compound, that is, through a single transition state. However, 2,5-dicyano-1,5-hexadiene appears to rearrange through an intermediate.

Given the erroneous behavior of UB3LYP in the short-*R* region, we recommend that empirical density functionals without the admixture of exact exchange be more frequently used in calculations of sigmatropic rearrangements. Among the functionals we tested on the Cope rearrangement, (U)BPW91 gives the most believable results.

Acknowledgment. This work was supported by the National Science Foundation under grant CHE-9613944. We thank Professor Weston T. Borden for comments and suggestions made during the preparation of the manuscript.

Supporting Information Available: *Z*-matrices of stationary points and Mulliken populations of effectively unpaired electrons from 10e$^-$/10 orbital CASSCF wave functions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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