3, **5**, **6**, and **7**, which cannot readily form carbocations, are also reactive.

Table II illustrates the relationship between reactivity and oxidation potential for a series of carboxylic acids. While **11** and **12** are fluorinated, **13** and **14** are recovered unchanged from the reaction mixture. In acetonitrile/tetraethylammonium fluoride solutions, the valence-band potential of TiO_2 is +1.0 V vs SCE;[22] protonation of the surface by **11–14** will cause a shift to more positive values. Therefore, the observed reactivity threshold of ca. +1.3 V is consistent with the location of the valence-band potential in this medium. Adjusting this threshold to more positive values, by deliberately protonating the semiconductor surface, or by using more oxidizing photocatalysts (e.g., SnO_2, which has a valence-band potential about 1 V more positive than that of TiO_2[29,30]), may significantly expand the range of molecules into which fluorine can be introduced by this method. Experiments along these lines are currently in progress.

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Ab Initio Calculations of the Effects of Cyano Substituents on the Cope Rearrangement

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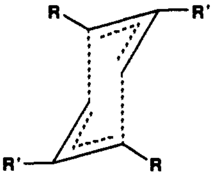
Multiconfiguration SCF (MCSCF) calculations, with the 3-21G basis set and a complete active space (CAS) wave function,[1] find the chair Cope rearrangement of 1,5-hexadiene[2] to proceed through an "aromatic" transition state (**1a**), in which bond making and bond breaking have proceeded synchronously. Although **1a** may be regarded as a resonance hybrid of two different diradical structures, **1b** and **1c**, a natural orbital analysis of the CAS-MCSCF wave function showed that the chair transition state has little diradical character.[1] In this communication we report the results of ab initio calculations on the effects of cyano groups on the transition state.

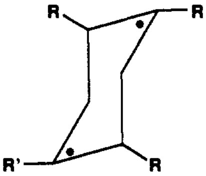
Table I. Interallylic Distances (R) and Energies (ΔE) above the Corresponding 1,5-Hexadienes for Chair Cope Transition States **1–3**, Calculated with the 3-21G Basis Set

transition state	R, Å			ΔE,[a] kcal/mol	
	SCF[b]	MP2[b]	partial CI[c]	SCF	FC-MP2
1	2.020	1.926	2.106	45.9[d]	28.3[e-g]
2	1.931	1.778	1.958	39.3	20.1[h]
3	2.093	2.015	2.213	44.8	26.7

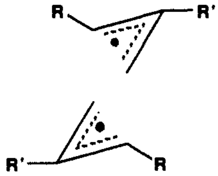
[a] Classical activation energies calculated at the SCF/3-21G geometries. Zero-point energy corrections necessary to calculate $\Delta H^{\ddagger}{}_0$ for **1–3** are, respectively, –0.2, –0.3, and –0.6 kcal/mol. [b] Full gradient optimization. [c] Optimization of only R with partial SD-CI (see text). [d] With 6-31G*, ΔE = 56.5 kcal/mol at the SCF level. [e] Using the MP2 optimized geometries for reactant and transition state, ΔE = 27.4 kcal/mol. [f] At the FC-MP4-SDTQ level, ΔE = 31.4 kcal/mol. With the 6-31G* basis set, ΔE = 31.0 kcal/mol at the FC–MP2 level and 38.7 kcal/mol at the FC-MP4-SDTQ level. [g] Experimentally, $\Delta H^{\ddagger}{}_{298}$ = 33.7 kcal/mol.[21] [h] Experimentally, $\Delta H^{\ddagger}{}_{298}$ = 23.3 kcal/mol for a monomethyl derivative.[4]



1a, R=R'=H
2a, R=H, R'=CN
3a, R=CN, R'=H



1b, R=R'=H
2b, R=H, R'=CN
3b, R=CN, R'=H



1c, R=R'=H
2c, R=H, R'=CN
3c, R=CN, R'=H

Experimental studies of the effects of cyano[3,4] and phenyl[5-7] groups have shown that both of these radical-stabilizing substituents accelerate the rate of the Cope rearrangement and are most effective when positioned at C-2 and C-5. Based on changes in the measured secondary kinetic isotope effects with substitution, Gajewski and Conrad have suggested that substituents can alter the structure of the transition state for the Cope rearrangement.[8] These authors proposed that substituents at C-2 and C-5 enhance bond making by selectively stabilizing structure **b**, relative to **c**. Similarly, substituents at C-3 and C-4 enhance bond breaking by stabilizing structure **c**, relative to **b**.[9]

In order to test the proposal of Gajewski and Conrad, we have located the transition states for the Cope rearrangement of two different dicyano-1,5-hexadienes, **2** and **3**. The transition states were located and the reactant geometries optimized by SCF calculations with the 3-21G basis set.[12] Vibrational analyses

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(9) Dewar and Jie have reported finding with AM1 that **1a** and **1b** represent two distinct transition states, whose relative energies can be altered by substituents.[10] Our attempts, with the versions of AM1 in AMPAC, MOPAC, and Gaussian 86, to find the "aromatic" C_{2h} chair transition state with R = 1.992 Å,[10] have been wholly unsuccessful and have invariably led back to the "biradicaloid" intermediate with R = 1.646 Å.[11] It should be noted that the AM1 "biradicaloid" transition states successfully reproduce the rate accelerations found experimentally[5] for phenyl substitutents at both C-2 (C-5) and C-3 (C-4).[11]
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established that each transition state had exactly one imaginary frequency. The energies of the reactants and transition states at the SCF optimized geometries[13] were recalculated with the inclusion of electron correlation at the MP2 level of theory,[14] and the transition-state geometries were reoptimized at this level of theory. These calculations were performed with the Gaussian 86 package of ab initio programs.[15] The SCF and frozen core MP2 (FC-MP2) activation energies, calculated at the SCF 3-21G optimized geometries, are given in Table I, along with the SCF and MP2 optimized, interallylic, C–C bond lengths (*R*) in each transition state.

Because of the flatness of the potential surface for the transition state along *R*, the optimized value of *R* can vary significantly with the type of calculation. For example, as first found by Dewar and Healey,[16] the MP2 3-21G value for *R* in **1**[17] (Table I) is 0.16 Å shorter than the CAS-MCSCF value.[1] In order to investigate the effect of electron correlation on the optimized transition-state geometries for **1–3**, using a variational instead of a perturbational technique, partial CI calculations were performed at three different values of *R*. All other geometry parameters were optimized at the SCF level (in C_{2h} symmetry for **1** and **2** and in C_i symmetry for **3**) at each value of *R*. The CI calculations involved all single and double excitations into the virtual orbitals (51 in **1** and 71 in **2** and **3**) from all the MOs (four in **1** and five in **2** and **3**) with appreciable contributions from p AOs oriented parallel to the interallylic C–C bonds. The three CI energies for each transition state were then fitted to a quadratic potential in *R*, and the minimum was found. These partial CI calculations were performed by using MELD,[19] and the resulting values of *R* for **1–3** are also contained in Table I.

As shown in Table I, the optimized values of *R* for the three transition states are consistent with the hypothesis that the relative size of the contributions of diradical structures **b** and **c** depend on the position of the radical-stabilizing cyano groups in **1–3**. Despite the differences in the absolute values of *R* obtained by the three different types of calculations, the trends in the values of *R* are the same. All three methods find that transition state **2** has the smallest value of *R* and that transition state **3** has the largest. Because the potential surface for the Cope rearrangement is quite flat along the coordinate *R*, the interallylic bond length in the chair transition state varies strongly (by about 0.25 Å at the MP2 and partial CI levels) with the positions of the cyano substituents.

The energies in Table I are in agreement with the experimental finding[3-7] that a pair of substituents is more effective at C-2 and C-5 than at the four other carbons in stabilizing the transition state for the Cope rearrangement. The FC-MP2 value of 8.2 kcal/mol for the lowering of the activation energy by the cyano substituents at C-2 and C-5 in **2** is in reasonable agreement with the experimental value of 10.4 kcal/mol for a methyl derivative of **2**.[4] After correction for zero-point energy differences, the ratio between the FC-MP2 values for the activation-energy lowering by the cyano substituents at C-1 and C-4 in **3** and at C-2 and C-5 in **2** is 0.24. This compares quite well with the experimental ratio of 0.28 for pairs of phenyl substituents at these two sets of carbons.[7]

Although cyano substituents at C-2 and C-5 substantially stabilize the Cope transition state and, in agreement with the inference drawn by Conrad and Gajewski, cause its geometry to alter in the direction expected for diradical structure **2b**, it is to be emphasized that **2** is not a diradical. This is indicated by the optimized values of *R* for **2** and confirmed by analysis of its CI wave function. The ratio of the squares of the two largest coefficients in the CI wave function for **2** is only 0.024, which is approximately 40 times less than the ratio of near unity that is expected in a true diradical.[20]

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Supplementary Material Available: Structures showing SCF optimized geometries for transition states **1–3** and for the corresponding 1,5-hexadiene reactants and MP2 optimized geometries for **1–3** (9 pages). Ordering information is given on any current masthead page.

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Solvent-Induced Ring Inversion in Protonated 2,3-Dihydro-1*H*-1,4-benzodiazepines

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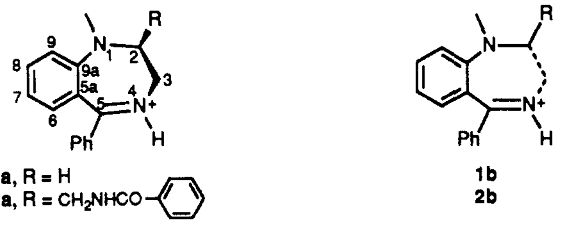
The conformation of the seven-membered ring in protonated 2,3-dihydro-1*H*-1,4-benzodiazepines is boat- or twist-boat-like in the solid state;[2] little is known about the conformations in solution. Ring inversion **1a** ⇌ **1b**, which occurs easily in the case of the unprotonated species,[3] interconverts enantiomers, making the observation of this process in principle amenable to chiroptical methods. We have found CD spectroscopic evidence that proves that the molecular geometry of 2-substituted derivatives is extremely dependent on solvent polarity including what we assume is a complete inversion of the seven-membered ring conformation.



1a, R = H
2a, R = CH_2NHCO–
1b
2b

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