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The Cope Rearrangement Revisited Again. Results of ab Initio Calculations beyond the CASSCF Level

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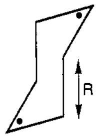
Abstract: Calculations on the chair and boat Cope rearrangements have been performed at the CASPT2N level of theory, in which second-order perturbation theory is used to provide electron correlation beyond that included at the CASSCF level. Unlike previous CASSCF calculations with the 6-31G* basis set, CASPT2N calculations with 6-31G*, 6-311G**, and 6-311G(2d,2p) all find a single stationary point of C_{2h} symmetry for the chair and C_{2v} symmetry for the boat, which corresponds to the transition state for a reaction in which bond making and bond breaking are synchronous. The CASPT2N energetics are in much better agreement with experiment than are those computed at the CASSCF/6-31G* level, as is the CASPT2N finding that the Cope rearrangement is concerted and does not involve the formation of a diradical intermediate.

Semiempirical and *ab initio* electronic structure calculations have been performed in order to elucidate the mechanisms of pericyclic reactions, particularly the Cope rearrangement.[1,2] The central mechanistic question in this reaction has been whether the rearrangement of 1,5-hexadiene involves the formation of chair cyclohexane-1,4-diyl (**1**) as a discrete intermediate[3a] or whether the reaction is concerted and passes through a six-electron, "aromatic" transition state (**2**) in which bond making and bond breaking are synchronous.[3b]



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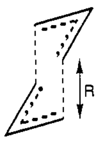

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The first calculations on the Cope rearrangement were semiempirical MINDO/2[5] and MINDO/3[6] calculations. Both sets of calculations found only one reaction pathway, passing through **1** as an intermediate. The findings of his MINDO/3 calculations led Dewar to propose that, in general, pericyclic reactions cannot involve synchronous bond making and bond breaking.[7]

Subsequent AM1 calculations by Dewar initially appeared to support this contention, since only a diradicaloid intermediate (**1**) was found.[8a] However, further investigations of the AM1 potential surface led to the claim by Dewar that a concerted, aromatic transition state (**2**) had also been located for the chair Cope rearrangement.[8b] Following the discovery that this purported C_{2h} transition state was not a stationary point (all first derivatives of the energy were not zero),[9] it was reidentified by Dewar as a point of inflection.[1b] Nevertheless, AM1 calculations on the boat Cope rearrangement[8b] and on the Cope rearrangements of 3,3-dicyano-1,5-hexadiene,[10] semibullvalene,[11] and bullvalene[11] all found two discrete C_{2h} stationary points, a minimum for **1** and a saddle point for **2**.

The AM1 results have led Dewar back to the two-reaction path mechanism for the Cope rearrangement,[1b] which he first espoused 20 years earlier, on the basis of experiments performed in his laboratory.[12a] Kinetic studies by Dewar and Wade found that phenyl groups at either C_2 or C_3 of 1,5-hexadiene accelerate the Cope rearrangement. This result led Dewar to propose the existence of two different transition states, one stabilized by phenyl groups at $C_{2(5)}$ and the other by phenyl groups at $C_{3(4)}$.

However, additional kinetic experiments by Dewar and Wade showed that in the Cope rearrangement of 2,4-diphenyl-1,5-hexadiene, the rate accelerations found in the two monophenyl-1,5-hexadienes are multiplicative.[12b] This experimental result indicates that a single transition state is being stabilized by phenyl groups at $C_{2(5)}$ and $C_{3(4)}$. Coupled with the results of Dewar's MINDO/3 calculations,[6] this experimental finding led Dewar to abandon the two-path mechanism, to which he has now returned on the basis of his AM1 calculations.[1b,8b,10,11]

The description of the mechanism of the Cope rearrangement that has been provided by *ab initio* calculations has also proven to be time-dependent. Calculations with the 3-21G basis set found a C_{2h} diradical intermediate (**1**) when only one pair of electrons was correlated but an aromatic C_{2h} transition state (**2**) when correlation was provided via CI for all six of the electrons that are "active" in this rearrangement.[13] The finding of an aromatic transition state for the Cope rearrangement was confirmed by complete active space (CAS)SCF/3-21G calculations, which

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(1) Reviews: (a) Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Ann. Rev. Phys. Chem.* **1988**, *39*, 213. (b) Dewar, M. J. S.; Jie, C. *Acc. Chem. Res.* **1992**, *25*, 537. Although the latter review fails to mention the former, it compensates by attributing to the first author of the former review some calculations on the Diels–Alder reaction that he did not perform. This error has been acknowledged (*Acc. Chem. Res.* **1993**, *26*, 226), but the correct reference for the alleged calculations was not provided and remains a mystery.

(2) Experimental studies through 1980 are reviewed in Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; 166–176.

(3) (a) Apparently first considered by Grob et al. (Grob, C. A.; Link, H.; Schiess, P. W. *Helv. Chim. Acta.* **1963**, *46*, 483) and given credibility by the later thermochemical analysis of Doering.[4] (b) First proposed by Foster, E. G.; Cope, A. C.; Daniels, F. G. *J. Am. Chem. Soc.* **1947**, *69*, 1893.

(4) (a) Doering, W. v. E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299. (b) Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.

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provided correlation for the six active electrons by allowing all possible occupancies of the six active orbitals.[14]

The aromatic transition state in this CASSCF study was found to have a bond distance, R, between the two allylic moieties of 2.086 Å. A C_{2h} diradical intermediate, 22.0 kcal/mol higher in energy, with R = 1.611 Å was also located. However, we have subsequently found the latter to be an artifact, resulting from an inadvertent change in the symmetries of the six orbitals used in the active space. When the correct set of orbitals is used, this diradical geometry is only 4.8 kcal/mol above the C_{2h} transition-state geometry, to which the diradical collapses on geometry optimization. Therefore, the only C_{2h} stationary point on the CASSCF/3-21G energy surface for the chair Cope rearrangement appears to be **2**.

RHF, MP2, MP3, and MP4 calculations by Dewar and Healy all showed that the energy difference between the aromatic, C_{2h} geometry with R = 1.92 Å and a higher energy diradical of C_{2h} geometry with R = 1.61 Å decreases on going from 3-21G to 6-31G*.[15] Subsequent CASSCF calculations with the 6-31G* basis set actually found C_{2h} stationary points for both an aromatic transition state (**2**) with R = 2.189 Å and a diradical intermediate (**1**) with R = 1.641 Å.[16] Diradical **1** is 1.9 kcal/mol lower in energy than **2**, but the C_2 transition state leading to **1** is only 0.6 kcal/mol below **2**.

The C_{2h} stationary points for **1** and **2** are connected by a third stationary point, which is a mountain top on the global potential energy surface and is about 3 kcal/mol above **1**. Thus, passage from the diradical to the aromatic transition-state geometry, which changes R by 0.548 Å, results in a net energy change of only 1.9 kcal/mol and encounters a barrier of only about 1 kcal/mol more. Obviously, the CASSCF/6-31G* potential surface along a cut that preserves C_{2h} symmetry is very flat with respect to changes in R.

Although a six-electron, six-orbital CASSCF wave function provides correlation for the electrons that are "active" in the Cope rearrangement, it provides no correlation between these electrons and the 28 other "inactive" valence electrons. This so-called "dynamic" electron correlation is likely to be of some importance, since the CASSCF/6-31G* enthalpy of activation for passage of 1,5-hexadiene over either the transition state leading to **1** or transition state **2**[16] is more than 12 kcal/mol higher than the experimental value of 33.5 kcal/mol.[4a] Providing dynamic electron correlation would be expected to stabilize selectively the weak bonds in the aromatic transition state[17a] and, thus, to lower its energy with respect to both the diradicaloid intermediate and to 1,5-hexadiene.[17b,c]

Ab initio calculations on a reaction, such as the Cope rearrangement, have an advantage over semiempirical methods in that *ab initio* calculations can be systematically improved by increasing the amount of electron correlation that is included and by expanding the size of the basis set. In this paper we report the results of calculations on the Cope rearrangement that include dynamic electron correlation between the active and the inactive electrons, as well as correlation among the inactive electrons. We find that calculations of this type, not only with the 6-31G* basis set but also with much larger basis sets, all give a potential surface with only a single C_{2h} stationary point. This stationary point is not a diradical intermediate (**1**) but the transition state (**2**) for a concerted Cope rearrangement, in which bond making and bond breaking are synchronous.

Table 1. Energies (hartrees) Calculated at the CASSCF/6-31G* Optimized C_{2h} Geometries for the Chair Diradical (R = 1.641 Å) and the Chair Transition State (R = 2.189 Å) and a Midpoint Geometry with an Interallylic Distance (R = 1.915 Å) Halfway between These Two

	R (Å)		
calculation	1.641	1.915	2.189
CASSCF/6-31G*	–232.9802	–232.9762	–232.9771
CASPT2N/6-31G*	–233.7311	–233.7301	–233.7234
CASSCF/6-311G**	–233.0348	–233.0322	–233.0345
CASPT2N/6-311G**	–233.9879	–233.9882	–233.9818
CASSCF/6-311G(2d,2p)	–233.0471	–233.0451	–233.0476
CASPT2N/6-311G(2d,2p)	–234.0544	–234.0585	–234.0541

Computational Methodology

Geometries were optimized with six-electron, six-orbital CASSCF calculations, using the 6-31G* basis set.[18] Geometry optimizations were performed using the Gaussian 92 suite of *ab initio* programs.[19]

For single-point calculations at these geometries, two larger basis sets, 6-311G**[20] and 6-311G(2d,2p),[21] were also employed. The former differs from 6-31G* by including a third, independent Gaussian function for each valence orbital and polarization functions on the hydrogens. The latter includes, in addition, a second set of polarization functions, d for carbon and p for hydrogen.

Single-point calculations were performed at both the CASSCF and CASPT2N levels. CASPT2N uses second-order perturbation theory to obtain the correlation energy for all the electrons in a molecule, starting from a CASSCF reference wave function.[22] CASPT2N is the multi-configurational equivalent of MP2,[23] to which it reduces for a reference wave function consisting of a single, closed-shell configuration. The CASSCF and CASPT2N calculations were performed with the MOLCAS suite of *ab initio* programs.[24]

Results

Table 1 gives both the CASSCF and CASPT2N energies with each of the three basis sets at three different C_{2h} geometries—the CASSCF/6-31G* stationary points for **1** and **2**[16] and a geometry that was optimized with a value of R = 1.915 Å, midway between the values of R at these two stationary points. Table 1 shows that with all three basis sets the CASSCF energy of the midpoint geometry is higher than that of the two endpoints. Consequently, with each basis set a barrier separates two C_{2h} stationary points on the CASSCF energy surface.

In contrast, at the CASPT2N level the midpoint geometry is computed to be lower in energy than one or both of the two endpoints with all three basis sets. This result suggests that with each basis set there is only a single C_{2h} stationary point, located somewhere near the midpoint geometry, on the CASPT2N energy surface.

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Table 2. Calculated Interallylic Bond Lengths, *R* (Å), and Energies and Enthalpies (kcal/mol), Relative to 1,5-Hexadiene, of the Transition States for the Chair and Boat Cope Rearrangements and of Two Allyl Radicals

	chair TS			boat TS			2 $H_2CCHCH_2^{\bullet}$	
calculation	*R*	Δ*E*	Δ*H*	*R*	Δ*E*	Δ*H*	Δ*E*	Δ*H*
CASSCF/3-21G[a]	2.086	40.7	37.7	2.316	47.3	43.6	54.2	
CASPT2N/3-21G	1.890	29.4[b]		2.316[c]	41.2[b]		61.1[b]	
CASSCF/6-31G* [d]	2.189	47.7	45.8	2.615	52.3	49.0	54.0	48.1
CASPT2N/6-31G*	1.745	31.2[e]	30.8[f]	2.139	44.0[e]	42.2[f]	61.6[e]	55.7[f]
CASPT2N/6-311G**	1.775	32.9[g]	32.3[f]	2.139	42.8[g]	41.0[f]	61.5[g]	55.6[f]
CASPT2N/6-311G(2d,2p)	1.885	33.1[h]	32.2[f]	2.204	43.3[h]	41.2[f]	66.0[h]	60.1[f]
experiment			33.5 ± 0.5[i]			44.7 ± 2.0[j]		59.6 ± 0.7[k]

[a] Reference 14. [b] Relative to −232.2456 hartrees. [c] Not reoptimized with CASPT2N. [d] Reference 16. [e] Relative to −233.7819 hartrees. [f] Vibrational corrections interpolated from CASSCF/6-31G* results in ref 16. [g] Relative to −234.0384 hartrees. [h] Relative to −234.1096 hartrees. [i] Reference 4a. [j] Reference 27. [k] Reference 28.

Because of the current unavailability of analytical energy derivatives for CASPT2N wave functions, it was not feasible to optimize fully at the CASPT2N level the geometry of the C_{2h} stationary point. However, single-point CASPT2N calculations were performed at additional, CASSCF/6-31G* optimized, C_{2h} geometries with different fixed values of *R*. These calculations allowed the value of *R* at the C_{2h} stationary point to be located at the CASPT2N level with each basis set.

Table 2 gives the CASPT2N value of *R* at the C_{2h} stationary point with all three basis sets. Both the large values of *R* and the dominance of one configuration, rather than two, in the wave functions show that these C_{2h} stationary points are much better described by delocalized structure **2** than by structure **1** for cyclohexane-1,4-diyl.

A CASPT2N/6-31G* calculation was performed at a C_2 geometry in which one interallylic C–C bond was shortened by 0.04 Å from the CASPT2N/6-31G* value of R = 1.745 Å for the C_{2h} stationary point, the other bond was lengthened by the same amount, and the rest of the geometry was reoptimized at the CASSCF/6-31G* level. The energy was found to go down by 0.06 mhartrees from that of the C_{2h} stationary point. This result indicates that the C_{2h} stationary point is a transition state on the CASPT2N/6-31G* energy surface.

A similar result was obtained in a CASPT2N/6-311G** calculation at a C_2 geometry in which the interallylic bond lengths were fixed at R = 1.775 ± 0.04 Å. By inference, the C_{2h} stationary point with R = 1.885 Å is the CASPT2N/6-311G(2d,2p) transition state for a concerted chair Cope rearrangement.

As in the case of the C_{2h} chair calculations, a single stationary point of C_{2v} symmetry for the boat Cope rearrangement was located by CASPT2N calculations with each basis set. As shown in Table 2, the CASPT2N value of *R* for each boat stationary point was longer than that of the corresponding C_{2h} chair transition state, but considerably shorter than the CASSCF/6-31G* value of R = 2.615 Å for the boat transition state. A CASPT2N/6-31G* calculation at a C_s geometry verified that the C_{2v} geometry with R = 2.139 Å is the transition state for a concerted boat Cope rearrangement.

The CASPT2N energies of the boat and chair transition states are given in Table 2. Also shown are the CASPT2N//CASSCF/6-31G* energies of two allyl radicals.[25] All the CASPT2N energies are given relative to that of 1,5-hexadiene at its CASSCF/6-31G* optimized geometry. The diene prefers a nonplanar C_2 to a planar C_{2h} geometry by 4.1 kcal/mol at the CASPT2N level with the 6-31G* basis set and by 4.5 kcal/mol with 6-311G**.[26]

CASPT2N calculations on 1,5-hexadiene in C_2 symmetry with the 6-311G(2d,2p) basis set proved too large to be performed. Comparison of the 6-31G* and 6-311G** results suggests that the energy difference between the C_2 and C_{2h} conformations of 1,5-hexadiene is unlikely to be significantly affected by further improvements in the basis set. Therefore, the CASPT2N energy of C_2 1,5-hexadiene with the 6-311G(2d,2p) basis set was estimated by subtracting from the CASPT2N energy at the optimized C_{2h} geometry the 4.5 kcal/mol difference between the CASPT2N/6-311G** energies at the optimized C_{2h} and C_2 geometries.[26]

In order to compare with experiment, the CASPT2N energies in Table 2 must be converted to enthalpies by correcting for the effects of differences in zero-point energies and heat capacities. The results of the CASSCF/6-31G* vibrational analyses[16] were used to obtain these contributions to the enthalpy difference between two allyl radicals and 1,5-hexadiene. The differences in zero-point energies and heat capacities between hexadiene and two allyl radicals cause the difference between their enthalpies at 500 K to be 5.9 kcal/mol smaller than the difference between their electronic energies.

Relative to 1,5-hexadiene, the corrections for differences in zero-point energies and heat capacities to the enthalpies of the CASSCF/6-31G* C_{2h} and C_{2v} stationary points are −0.1, −1.9, and −3.3 kcal/mol for, respectively, the chair diradical (R = 1.641 Å), the chair transition state (R = 2.189 Å), and the boat transition state (R = 2.615 Å) geometries.[16] Since these corrections are, to a good approximation, a linear function of *R*, the corrections to the enthalpies of the CASPT2N transition-state geometries were obtained by linear interpolations between the corrections at these three values of *R*. The resulting enthalpies are given in Table 2.

Dicussion

The calculated enthalpy differences in Table 2 may be compared with the experimental values of 33.5 ± 0.5 kcal/mol for the chair Cope rearrangement,[4a] 44.7 ± 2.0 kcal/mol for the boat,[27] and 59.6 kcal/mol for cleavage of 1,5-hexadiene to two allyl radicals.[28] The CASPT2N values are obviously in far better agreement with experiment than are the CASSCF/6-31G* values,[16] which are also given in Table 2.

Comparison of the CASSCF and CASPT2N results with the 6-31G* basis set shows that the additional correlation provided by CASPT2N lowers the energy, relative to that of 1,5-hexadiene, by 16.5 kcal/mol for the chair and by 8.3 kcal/mol for the boat transition state. At the same time the energy required to dissociate 1,5-hexadiene to two allyl radicals is increased by 7.6 kcal/mol, so that the CASPT2N enthalpy of the boat transition state is now 13.5 kcal/mol lower than that of two allyl radicals and that of the chair 11.4 kcal/mol lower still.

CASPT2N/3-21G calculations, performed at the CASSCF/3-21G optimized geometries,[14] give changes from the CASSCF/

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(25) The CASPT2N energies of two allyl radicals were the same to within 0.2 mhartree, whether they were calculated at R = 10 Å or taken to be twice the CASPT2N energy of two allyl radicals. Thus, as they should be, the CASPT2N calculations are size-consistent.

(26) The CASSCF/6-31G* C_2 *gauche* geometry was employed, since the results of a vibrational analysis at this geometry have been published.[16] CASSCF and CASPT2N energies at the CASSCF/6-31G* optimized C_2 *anti* and C_i geometries were lower than at the C_2 *gauche* geometry, but by less than 0.5 kcal/mol.

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3-21G energies, similar to, but of a smaller magnitude than, those found with the 6-31G* basis set. Relative to the energy of 1,5-hexadiene, the CASPT2N/3-21G energies for the chair and boat transition states are, respectively, 9.6 and 6.1 kcal/mol lower than at the CASSCF/3-21G level; the dissociation energy to two allyl radicals increases by 6.9 kcal/mol. As shown in Table 2, reoptimization of R for the chair transition state by single-point CASPT2N/3-21G calculations at CASSCF/3-21G optimized C_{2h} geometries gives R = 1.890 Å and lowers the CASPT2N/3-21G energy of the transition state by an additional 1.7 kcal/mol to 29.4 kcal/mol above that of 1,5-hexadiene.

Comparison of the 3-21G and 6-31G* results in Table 2 reveals that although the CASSCF results with the two basis sets are quite different, the CASPT2N results are rather similar. Table 2 also shows that the CASPT2N results are not much affected on going from 6-31G* to the larger 6-311G** and 6-311G(2d,2p) basis sets. The largest effect of basis set expansion is to increase the CASPT2N/6-31G* BDE of 1,5-hexadiene by 4.4 kcal/mol with the 6-311G(2d,2p) basis set and thus to bring it into excellent agreement with the experimental value. At the CASPT2N/6-311G(2d,2p) level the calculated enthalpies of activation of both the boat and the chair Cope rearrangements are lower than the experimental values by about 1 and 3 kcal/mol, respectively.[26] The experimental difference between the enthalpies of the two transition states[27] thus also appears to be slightly underestimated by our calculations.

The current lack of analytical derivatives for CASPT2N wave functions prevented us not only from optimizing fully at the CASPT2N level the transition-state geometries but also from performing CASPT2N vibrational analyses. Therefore, we were unable to calculate the entropies of the transition states at the CASPT2N level. However, on the basis of the CASSCF/6-31G* results,[16] the difference in calculated entropies between the two transition states is likely to be rather smaller than the experimental value of about 10 cal/mol·K.[27]

For example, the CASSCF/6-31G* C_{2h} chair transition state is computed to have an entropy that is only 3.0 cal/mol·K larger than the C_{2h} chair intermediate.[16] The value of R for the CASPT2N boat transition state is about the same as that of the CASSCF/6-31G* chair transition state, and the value of R for the CASPT2N chair transition state is slightly larger than that of the CASSCF/6-31G* chair intermediate. Therefore, the entropy difference between the boat and chair CASPT2N transition states might be expected to be slightly less than 3 cal/mol·K. This estimate is consistent with the entropy difference of 3.8 cal/mol·K that is actually calculated for the CASSCF/3-21G boat (R = 2.316 Å) and chair (R = 2.086 Å) transition states.[14]

As previously suggested,[14] it is possible that the computed enthalpy and entropy differences between the two transition states are both smaller than those that have been measured, because the transition states actually occur not at the C_{2h} and C_{2v} geometries that minimize the electronic energies but rather at the geometries that minimize the free energies.[29] Since for both C_{2h} and C_{2v} geometries, large changes in R result in rather small changes in electronic energy, at 500 K changes in the entropy along R can affect the location of the transition state, particularly for the boat.

For example, for the boat transition state, on going from the CASPT2N/6-311G(2d,2p) value of R = 2.244 Å to the CASSCF/6-31G* value of R = 2.615 Å, the CASPT2N/6-311G(2d,2p) energy increases by 3.7 kcal/mol. On the basis of the CASSCF/6-31G* entropies,[16] the increase of 0.37 Å in R would increase the entropy by about 6 cal/mol·K. Thus, in the free energy at 500 K this increase in entropy would offset nearly all of the increase in the enthalpy.

The chair potential energy surface is also quite flat with respect to changes in R along the C_{2h} cut of lowest energy. For example, on either increasing or decreasing R by 0.30 Å from the CASPT2N/6-311G(2d,2p) value of R = 1.885 Å at the chair transition state, the CASPT2N/6-311G(2d,2p) energy changes by less than 3 kcal/mol. Previous calculations have found that the flatness of the chair potential surface along this coordinate allows substituents to have a substantial effect on the value of R in the chair transition state.[9] This computational finding supports the inferences, drawn from the experiments of Gajewski and Conrad, who measured the effect of substituents on the isotope effects for bond making and bond breaking in the Cope rearrangement.[30]

Conclusions

In finding that for optimized C_{2h} geometries large changes in the interallylic distance, R, result in only small changes in the energy, our CASPT2N calculations are similar to the previous CASSCF/6-31G* study of the Cope rearrangement.[16] However, in contrast to the CASSCF/6-31G* results, CASPT2N calculations with four different basis sets find a single C_{2h} stationary point. This stationary point is the transition state (**2**) for a concerted chair Cope rearrangement in which bond making and bond breaking are synchronous. There is no evidence of the existence of a second stationary point, corresponding to a cyclohexane-1,4-diyl intermediate (**1**), which was found in the CASSCF/6-31G* calculations.

Unlike the CASSCF/6-31G* energetics, those obtained from CASPT2N calculations with 6-31G* and with two larger basis sets are in very good agreement with experiment. With the 6-311G(2d,2p) basis set, the calculated dissociation energy of 1,5-hexadiene to two allyl radicals is within the error limits of the experimental value.[28] With the same basis set the calculated values of $\Delta H^{\ddagger}$ for the chair[4a] and boat[27] Cope rearrangements are, respectively, about 1 and 3 kcal/mol too low. However, at least for the boat, part of the discrepancy between the results of the calculations and the experiments may be that the C_{2v} stationary point on the free energy surface occurs at a larger value of R and, hence, has both a higher enthalpy and entropy than the C_{2v} stationary point on the potential energy surface.

The dramatic improvement in the computed energetics for the chair and boat Cope rearrangements on going from CASSCF/6-31G* to CASPT2N/6-31G* wave functions suggests that CASPT2N may prove a generally useful method for improving upon CASSCF in calculations on pericyclic reactions. The results of CASPT2N/6-31G* calculations on the conrotatory ring opening of cyclobutene to butadiene, a reaction that has previously served as a test of various computational methodologies,[31] support this conjecture.[32]

The excellent agreement between the CASPT2N and the experimental enthalpies of activation for the chair and boat Cope rearrangements lends support to the CASPT2N finding that both reactions are concerted and do not involve diradical intermediates. This CASPT2N result appears to be invariant to basis set expansion. Since CASPT2N provides correlation for *all* the electrons in 1,5-hexadiene, not just the six electrons that are "active" in the Cope rearrangement, we believe that the CASPT2N finding of a concerted mechanism for the Cope rearrangement,

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(29) Consequently, transition states should actually be located using variational transition-state theory: Truhlar, D. G.; Garrett, B. *Acc. Chem. Res.* **1980**, *13*, 440. Hase, W. L. *Acc. Chem. Res.* **1983**, *16*, 258.

(30) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693. Gajewski, J. J. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1987; Vol. 7, pp 115–175. Gajewski, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 4548.

(31) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412.

(32) In calculations performed at CASSCF/6-31G* optimized geometries, the CASSCF/6-31G* energy of −154.8581 hartrees for the transition state for conrotatory opening of cyclobutene is 54.9 kcal/mol higher than that of cyclobutene and 73.7 kcal/mol higher than that of 1,3-butadiene. At the CASPT2N/6-31G* level the transition-state energy of −155.4315 hartrees is only 36.8 kcal/mol above that of cyclobutene and 47.4 kcal/mol above that of 1,3-butadiene. The "experimental" values are 34.5 and 45.4 kcal/mol.[31]

involving synchronous bond making and bond breaking, is likely to survive future calculations at even higher levels of theory.[33]

Experimental evidence for a concerted mechanism comes from a study by Owens and Berson.[34] Their experiments show that a diradical intermediate, if formed, would have a lifetime of less than 10^{-13} s, a lifetime shorter than that allowed for an intermediate by transition-state theory. Recently, Houk and coworkers have found that the secondary isotope effects that are calculated for a concerted chair transition state (**2**) are in much better agreement with the experimental values[30] than the isotope effects that are calculated for formation of a diradicaloid intermediate (**1**).[35] Although it has been found experimentally that suitable substituents can force 1,5-hexadiene derivatives to react by mechanisms that involve the formation of diradical intermediates,[36,37] we are unaware of any experimental evidence that contradicts our computational finding of a concerted mechanism for the parent Cope rearrangement and for the rearrangement of relatively unperturbed 1,5-hexadienes.

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[33] MP4(SDTQ)/6-31G* calculations, which are based on a single reference configuration, give results that are similar to those obtained at the CASPT2N/6-31G* level. Using CASSCF/6-31G* optimized geometries, MP4(SDTQ)/6-31G* calculations give $R = 1.794$ Å and $E = -233.7855$ hartrees for the C_{2h} stationary point in the chair Cope rearrangement. Additional calculations show this geometry to be a transition state and to be 33.8 kcal/mol higher in energy than 1,5-hexadiene. One way of going beyond both the CASPT2N and the single-reference MP4(SDTQ) calculations would be to implement an equivalent of MP4 with a CASSCF reference wave function. Alternatively, variational SD-CI calculations might be performed with the CASSCF wave function as reference. However, the C_{2h} CI calculations would require finding the lowest eigenvalue of a matrix representing the interactions of nearly 85 000 000 spin-adapted configurations.

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[37] Suitable substituents also make dissociation to two allyl radicals competitive in rate with the boat Cope rearrangement at high temperatures: Gajewski, J. J.; Benner, C. W.; Hawkins, C. M. *J. Org. Chem.* **1987**, *52*, 5198.