J. Phys. Chem. A **2003,** *107,* 1175−1180

Cope Rearrangement of 1,5-Hexadiene: Full Geometry Optimizations Using Analytic MR-CISD and MR-AQCC Gradient Methods

Elizete Ventura,*,† Silmar Andrade do Monte, Michal Dallos, and Hans Lischka*,‡

Institute for Theoretical Chemistry and Structural Biology, University of Vienna, Währingerstrasse 17, A-1090, Austria

Received: April 5, 2002; In Final Form: December 8, 2002

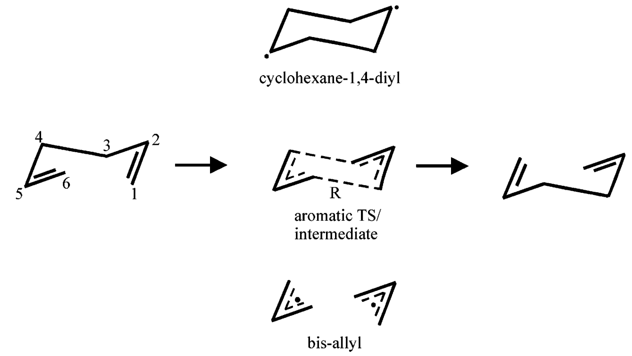
Full geometry optimizations within given molecular symmetries have been performed on the chair and boat forms involved in the Cope rearrangement of 1,5-hexadiene using highly correlated methods (MR-CISD and MR-AQCC) and extended basis sets. These optimizations are based on analytic gradient procedures developed within the COLUMBUS program system and are the first ones for the Cope rearrangement, which have been carried out at a multireference, post-CASSCF level. By comparison of MR-CISD and MR-AQCC results, the importance of size-extensivity corrections is clearly demonstrated. Computed energetic stabilities with respect to 1,5-hexadiene and bis-allyl are in good agreement with experimental data. Only a single saddle point for the chair form of C_{2h} symmetry is found in contrast to CASSCF results, but in agreement with CASPT2N and MRMP2 investigations. Thus, we confirm these previous results showing that the mechanism of the Cope rearrangement of 1,5-hexadiene is concerted via an aromatic transition state.

I. Introduction

The Cope rearrangement of 1,5-hexadiene is a very intensively investigated and debated reaction for which the nature of the reaction mechanism is still controversial. This reaction has been the subject of many experimental[1−5] and theoretical investigations involving semiempirical,[6−8] ab initio,[9−14] as well as density functional theory (DFT) calculations.[15,16] For recent reviews on theoretical results and further references see refs 17−20. As illustrated in Scheme 1, two possible chair-type alternatives for the reaction mechanism are being considered: (i) a concerted and synchronous mechanism allowed by Woodward and Hoffmann rules[21] involving an “aromatic” transition state and (ii) a nonsynchronous mechanism involving a biradicaloid cyclohexane-1,4-diyl as stable intermediate. Both structures have C_{2h} symmetry. The principal coordinate characterizing the interconversion of these two structures is the interallylic distance $R = R_{C1-C6} = R_{C3-C4}$ (see Scheme 1). A dissociative reaction path via bis-allyl also indicated in Scheme 1 has been ruled out on energetic grounds.[5] Nevertheless, bis-allyl is an important reference system. In addition to a chair structure in the Cope rearrangement, a higher energy transition state attributed to a boat structure has been observed also.[3]

Complete active space self-consistent field (CASSCF) (6 electrons/6 orbitals) calculations[11] show several stationary points on the potential energy surface (PES): a loose, “aromatic” transition state with R = 2.189 Å and a stable, “tight” intermediate at a significantly smaller R value of 1.641 Å (endo form), respectively, describing the diyl structure. Both structures have C_{2h} symmetry. Additionally, an unsymmetrical transition state connecting hexadiene and the stable intermediate was found. A maximum (two imaginary frequencies) connected the transition state and the stable intermediate. Complete active space perturbation theory to second order (CASPT2N)[12] and multireference Møller−Plesset perturbation theory calculations to second order (MRMP2)[13] showed that the accuracy of the CASSCF calculations was not sufficient and that dynamical electron correlation effects were very important. CASPT2N and MRMP2 potential energy curves along R in C_{2h} symmetry using CASSCF/6-31G* optimized geometries demonstrated that the two CASSCF minima collapsed into one at R values between 1.75 and 1.9 Å. On antisymmetric displacement of the two coordinates R_{C1-C6} and R_{C3-C4} at the C_{2h} structure the energy decreased indicating that this point was actually a saddle point. However, one should keep in mind that the geometries used were obtained from CASSCF calculations and only single-point calculations were performed at the post-CASSCF level because of the lack of analytic energy gradient programs for the latter methods.

SCHEME 1



The main effect of dynamical electron correlation on the electronic wave function is the reduction of the diradical character of the transition state.[13] Therefore, single-reference methods such as Møller−Plesset perturbation theory to the nth order (MPn), coupled cluster doubles (CCD), and quadratic configuration interaction with singles and doubles (QCISD) have been performed as well.[13,22] Analysis of results indicated[22] that triple excitations were very important in the CC and QCI

---

* To whom correspondence should be addressed.

† E-mail: elizete.do-monte@univie.ac.at.

‡ E-mail: hans.lischka@univie.ac.at.

10.1021/jp0259014 CCC: $25.00 © 2003 American Chemical Society
Published on Web 01/30/2003

calculations and that the MPn series showed no sign of convergence. Moreover, single-reference methods are not well suited to compute the entire cut along the coordinate *R*. DFT calculations face the problem of adequately treating biradical character. Spin-restricted and spin-unrestricted calculations have been performed using a variety of density functionals.[15,16] The actual choice of the density functional significantly affects the shape of the PES.[19] There seem to be also spurious, additional intermediates in unrestricted calculations using the Becke three-parameter (B3) hybrid methods.

From this discussion it is clear that MR methods are necessary for a well-balanced assessment of the importance of the biradical character. The CASPT2N and MRMP2 methods are in principle capable to provide the required information. However, as has been already emphasized above, complete geometry optimizations are not possible for molecules of the size of hexadiene because of the lack of an analytic gradient procedure. Moreover, it would also be desirable for benchmarking purposes to use nonperturbative methods in order to evaluate the effect of truncation effects.

The aim of this work is to perform high-level correlated calculations with full geometry optimizations using analytic gradient procedures. The multireference configuration interaction with singles and doubles (MR-CISD) and the multireference averaged quadratic coupled cluster (MR-AQCC)[23,24] methods are used for that purpose. The MR-AQCC method has been chosen in order to compensate for the size-extensivity errors of truncated CI. With this method reliable estimates of size-extensivity effects can be obtained (see, e.g., ref 25). For both methods, efficient analytic gradient methods as implemented into the COLUMBUS program system[25−27] are available.[28−30]

II. Computational Details

In the first step CASSCF(6,6) calculations on structures of C_{2h} symmetry have been performed using the $7a_g$, $7b_u$, $5a_u$, $5b_g$, $8a_g$, and $8b_u$ orbitals for the definition of the active orbital space in analogy to previous CASSCF calculations by Dupuis et al.[11] For the symmetry classification of orbitals see also ref 19. Two reference spaces for the MR-CISD and MR-AQCC calculations have been selected. The first one (denoted CAS(6,6)) consists of the same CAS(6,6) as used in the CASSCF calculations. The second one (denoted CAS(4,4)) includes the $7b_u$, $5a_u$, $5b_g$, and $8a_g$ orbitals, which describe the most important configurations. As compared to the CAS(6,6) reference space, the $7a_g$ orbital has been moved to the doubly occupied reference orbitals and the $8b_u$ orbital has been shifted to the virtual space. The MR-CISD and MR-AQCC calculations were performed within the space of configuration state functions (CSFs) constructed by applying single and double excitations from all valence orbitals to all virtual orbitals for all reference CSFs. The interacting space restriction[31] and the reference symmetry equal to the symmetry of the electronic state was used mostly. Only in case of the final calculations on activation and stabilization energies and for the antisymmetric displacement of the C_{2h} structure all reference symmetries (*ars*) were used also. These cases will be explicitly noted in the text. The $1-2a_g$, $1-2b_u$, $1a_u$, and $1b_g$ core orbitals were kept frozen. Since the CSF expansion space is uniquely defined by the specification of the reference space, we use the latter in order to label the MR-CISD/MR-AQCC calculations. In addition to the MR-AQCC calculations, the extended Davidson correction (MR-CISD+Q)[32,33] has been used in single-point calculations. In case of the boat form, the CAS(6,6) for the CASSCF calculations and for the CAS(6,6) reference space consisted of the $7a_1$, $8a_1$, $5b_1$, $7b_2$, $5a_2$, and $8b_2$ orbitals. The CAS(4,4) reference space included the $8a_1$, $5b_1$, $7b_2$, and $5a_2$ orbitals. The $1-2a_1$, $1b_1$, $1-2b_2$, and $1a_2$ orbitals were frozen in the MR-CISD/AQCC calculations.

The calculations on 1,5-hexadiene and the allyl molecules proceeded in an analogous way. For 1,5-hexadiene the two conformations of C_i and C_{2h} symmetry were considered. The C_i structure has a gauche, anti, gauche conformation and corresponds to structure E in the recent systematic analysis by Rocque et al.[34] It was chosen for consistency reasons with the work Staroverov and Davidson.[19] The C_{2h} structure with a planar s-cis, anti, s-cis conformation (structure K in ref 34) was chosen for reasons of computational efficiency (see below). The active space for the CASSCF(6,6) calculation consisted of the $10a_g$, $2-3a_u$, $2-3b_g$, and $10b_u$ orbitals for the C_{2h} structure and $11-13a_g$ and $11-13a_u$ for the C_i structure. Again, two sets of reference wave functions were constructed. The CAS(6,6) reference space was identical to the just-described CAS(6,6) used in the CASSCF calculations. The CAS(4,4) reference space consisted only of the π and π^* part of the original CAS(6,6) space. In case of the allyl molecule, the CASSCF calculations were performed using a CAS(3,3) space in the $1b_1$, $1a_2$, and $2b_1$ π orbitals. The $1-2a_1$ and $1b_2$ orbitals were kept frozen.

The basis sets 6-31G*,[35] 6-31G**,[35] 6-311G**,[36] and 6-311G(2d,1p)[37] have been used in this work. The calculations have been performed using the COLUMBUS program system[25−27] with analytical MR-CISD and MR-AQCC gradient methods.[28−30] The atomic orbital (AO) integrals and AO gradient integrals have been computed with program modules taken from DALTON.[38] Full geometry optimizations were performed within given molecular symmetries in natural internal coordinates[39] using the GDIIS method.[40] The largest calculations (e.g., C_{2h} saddle point structure, CAS(6,6) reference, all reference symmetries, 6-311G(2d,1p) basis) required CSF expansion spaces of about 368 million. These calculations were carried with the newly developed parallel CI program[41] based on a previous parallel version developed by Dachsel et al.[42] One Davidson iteration took about 3000 s wallclock time on 32 nodes each one equipped with Athlon XP 1700+ processors.

III. Results and Discussion

A. Methodological Tests. At the beginning methodological aspects referring to the choice of the reference space and to size-extensivity errors were investigated. The CAS(6,6) reference space introduced in the previous section should contain sufficient flexibility to allow a balanced description in the MR-CISD/MR-AQCC calculations. This reference space has also been used in previous CASPT2N[12] and MRMP2[13] calculations. For reasons of computational economy it is, of course, of interest to reduce the size of the reference space. Therefore, we investigated also a CAS(4,4) reference space (see section II), containing all major configurations. In a first test the size-extensivity error for the bis-allyl system (two allyl molecules treated as super molecule at infinite separation) in comparison to two individual allyl molecules was computed. In Table 1 the energy difference E(bis-allyl)−2·E(allyl) is given for the MR-CISD, MR-CISD+Q, and MR-AQCC methods using the CAS(4,4) and CAS(6,6) reference spaces and the 6-31G* basis set. First of all, one can see that the CI method severely violates size-extensivity. The MR-CISD+Q method improves the situation, but still gives bad results. On the other hand, the MR-AQCC results for the CAS(6,6) reference space are very good. The error of 0.65 kcal/mol is very much acceptable when compared to activation and stabilization energies (see below) of the order of 30−50 kcal/mol. Even the 4.8 kcal/mol obtained

TABLE 1: Energy Differences E(Bis-Allyl)−2·E(Allyl)[a−d]

	reference space	
	CAS(4,4)	CAS(6,6)
MR-CISD	55.5	37.3
MR-CISD+Q	31.3	20.2
MR-AQCC	4.8	0.65

[a] Energies in kcal/mol. [b]The 6-31G* basis set was used. [c] For allyl the CAS(3,3) reference space has been used always. [d] Total energies (au): bis-allyl (energy +233) MR-CISD/CAS(4,4) −0.55642, MR-CISD/CAS(6,6) −0.58536, MR-CISD+Q/CAS(4,4) −0.66656, MR-CISD+Q/CAS(6,6) −0.68426, MR-AQCC/CAS(4,4) −0.70420, MR-AQCC/CAS(6,6) −0.71087. Allyl (energy + 116) MR-CISD/CAS(3,3) −0.82240, MR-CISD+Q/CAS(3,3) −0.85819, MR-AQCC/CAS(3,3) −0.85595

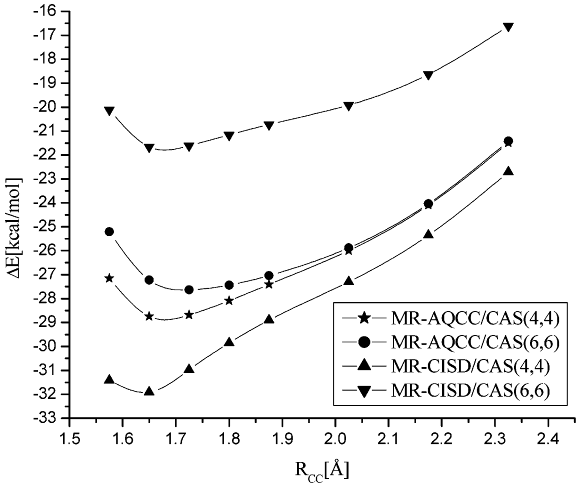


Figure 1. MR-CISD and MR-AQCC potential energy curves along the R_{C1C6} ($\equiv R_{C3C4}$) coordinate computed with the 6-31G* basis.

for the CAS(4,4) reference space represents a drastic improvement as compared to MR-CISD and MR-CISD+Q. The good performance of MR-AQCC for the CAS(4,4) reference case is quite remarkable since in this case different numbers of active orbitals (four for bis-allyl and 2 × 3 for the two allyl molecules) were used (the allyl calculations were performed with the CAS-(3,3) reference space always).

In further calculations on energy differences between various structures, the results obtained with CAS(4,4) and CAS(6,6) reference spaces are even much closer. Thus, the CAS(4,4) reference case seems to be promising also. This is of importance in view of the considerable savings in CSF expansion sizes (MR-AQCC CSF expansion sizes: CAS(4,4)/6-311G(2d,1p) ~ 9.3 million, CAS(6,6)/6-311G(2d,1p) ~ 60.0 million). Nevertheless, we used the CAS(6,6) reference space for the largest calculations in order to obtain as accurate results as possible.

Next, potential energy curves along the characteristic coordinate $R = R_{C1-C6} = R_{C3-C4}$ are discussed. In Figure 1 MR-CISD and MR-AQCC curves for CAS(4,4) and CAS(6,6) reference cases are shown. Δ*E* is computed with respect to the energy of the bis-allyl super molecule for the respective method. In these calculations the bond distance *R* was kept fixed and all remaining coordinates were fully optimized under C_{2h} symmetry restriction at the respective MR-CISD or MR-AQCC level. The MR-CISD curves for the CAS(4,4) and CAS(6,6) reference space calculations differ significantly from each other (by ≈10 kcal/mol near the energy minimum). These discrepancies are not surprising in view of the severe failure of CI in case of size extensivity. In strong contrast thereto, the MR-AQCC curves differ only by ≈1.5 kcal/mol near the energy minimum. The minimum of the MR-AQCC/CAS(6,6) curves is shifted somewhat to larger *R* values and to smaller Δ*E* (in absolute value) in comparison to the CAS(4,4) reference case. Because of the serious inadequacies of the MR-CISD method, in the following only MR-AQCC calculations were performed.

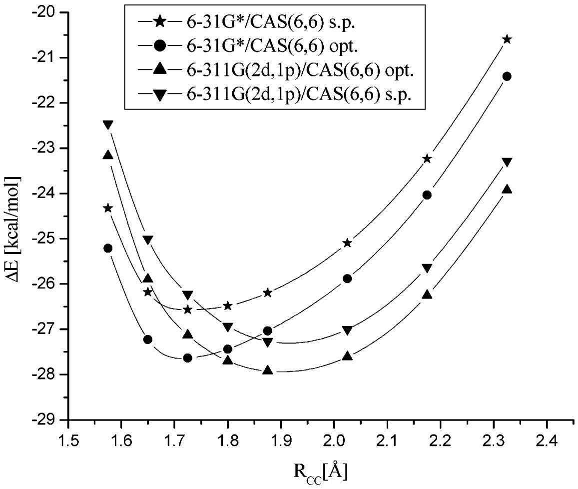


Figure 2. Potential energy curves along the R_{C1C6} ($\equiv R_{C3C4}$) coordinate for MR-AQCC geometry optimized structures (opt.) and single point (s.p.) calculations using the 6-31G* and 6-311G(2d,1p) basis sets.

In Figure 2 the effect of geometry optimization at the MR-AQCC level is displayed. Potential energy curves obtained from complete geometry optimization at a given bond distance R and from single-point MR-AQCC calculations based on CASSCF optimized geometries are compared using the 6-31G* and 6-311G(2d,1p) basis sets. The latter (single-point) procedure is the standard way in CASPT2 calculations. The shapes of the curves for the 6-31G* and 6-311G(2d,1p) basis differ quite significantly because of the large shift in the minimum value of R_{CC}. The effect of the MR-AQCC optimization is to reduce the location of the minimum by a few hundredths of an Å. The minimum of the fully optimized curve is about 1.0 kcal/mol below than of the single-point curve for the 6-31G* basis and a little less than 1.0 kcal/mol below for the 6-311G(2d,1p). This difference is not dramatic, but nonneglible.

B. 1,5-Hexadiene. As has already been stated above, the C_i structure had been chosen for consistency reason with the work Staroverov and Davidson.[19] As one can see from the work of Rocque et al.,[34] this structure is not quite the global minimum, however the principal conclusion in this work was that the 10 conformers of 1,5-hexadiene investigated were essentially degenerate. For our purposes the C_i structure is sufficiently close to the lowest-energy structures within about 0.1 kcal/mol. In MR-AQCC/6-31G* calculations the C_i, structure is more stable than the C_{2h} conformation by 1.17 (CAS(4,4) reference) and 1.41 (CAS(6,6) reference) kcal/mol, respectively. Using the 6-31G** basis set and the CAS(4,4) reference space the MR-AQCC energy difference between the C_i and C_{2h} conformations changes very little to 1.14 kcal/mol. This result suggests that this energy difference is not very sensitive to basis set effects. Therefore, in calculations with larger basis sets activation energies of transition states are computed with respect to the C_{2h} structure of 1,5-hexadiene, since this is computationally more efficient because of the higher symmetry of the C_{2h} structure. All-reference-symmetry (ars) calculations have been carried out for the energy difference between the C_i and C_{2h} conformations as well. The energy difference is 1.47 kcal/mol. To compare with the C_i structure of 1,5-hexadiene, activation energies are corrected by adding the energy difference of 1.41 and 1.47 kcal/mol, respectively, between C_{2h} and C_i structures

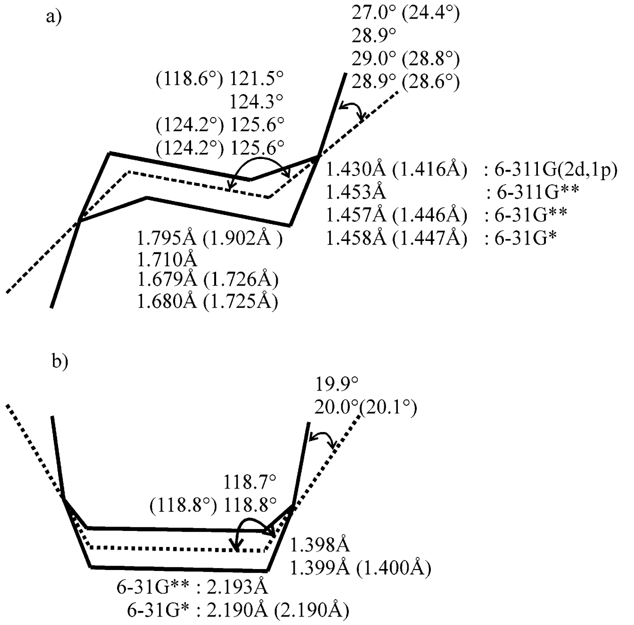


Figure 3. Basis set dependence of selected geometry parameters obtained from full geometry optimizations for (a) the chair and (b) the boat form at the MR-AQCC level using the CAS(4,4) reference space (CAS(6,6) values in parentheses).

in case of standard or *ars* calculations. Hrovat et al.[12] have used a similar procedure concerning the utilization of higher symmetry.

From standard enthalpies of formation $\Delta H^0_{f,298}$ for 1,5-hexadiene and the allyl radical and computed vibrational frequencies an "experimental" energy difference E(hexadiene)−2E(allyl) of −65.1 kcal/mol is computed (see Table 1 of ref 19 for details). Computed MR-AQCC 6-31G* values (using the C_i structure of 1,5-hexadiene) are CAS(4,4), −67.5 kcal/mol; CAS(6,6), −64.9 kcal/mol. These differences are rather insensitive to further basis set changes. Our largest basis set (6-311G(2d,1p)) together with the CAS(4,4) and CAS(6,6) references gives MR-AQCC energy differences of −68.1 kcal/mol and −64.6 kcal/mol. This last value, obtained with the most extended calculation, compares very well with the above-mentioned "experimental" value of −65.1 kcal/mol.

C. Geometry and Stability of Chair and Boat Structures. Boat and chair structures as described in the CASCF investigations by Dupuis et al.[11] have been fully optimized under C_{2h} and C_{2v} symmetry restrictions, respectively, at the MR-AQCC level using various basis sets and reference spaces. In Figure 3 the most important geometry parameters are shown. Complete Cartesian geometries are available as Supporting Information . As one could see already from the potential energy curves shown in Figures 1 and 2, only one minimum for the chair structure and not two (a loose and a tight chair) as in the CASSCF case is obtained. Thus, we confirm the previous findings of CASPT2N[12] and MRMP2[13] calculations that the two structures found at the CASSCF level coalesce to one. The chair structure shows an "endo" arrangement with respect to the C_2H and C_5H bonds. No minimum was found for a corresponding "exo" structure. The most important geometry parameter is the interallylic distance R. For the CAS(4,4) and CAS(6,6) reference spaces using the 6-31G* basis R values of 1.680 and 1.725 Å, respectively, are obtained (see Figure 3a). These bond distances are somewhat smaller than the CASPT2N[12] (1.745 Å) and MRMP2[13] (1.85 Å) values. Increasing the basis set leads to a substantial increase of R (1.795 Å for CAS(4,4)-ref/6-311G(2d,1p) and 1.902 Å for CAS(6,6)-ref/6-311G(2d,1p)). This relatively large difference of ≈0.1 Å in the latter case as compared to the smaller basis sets is due to the fact that the potential energy curve becomes significantly shallower for the 6-311G(2d,1p) basis set (see also Figure 2). Our best value of 1.902 Å is somewhat larger than the 1.885 Å obtained in the CASPT2N calculations[12] for the 6-311G(2d,2p) basis. In the boat form (see Figure 3b) R is substantially reduced from 2.615 Å (CASSCF/6-31G*[11]) to 2.190 Å (MR-AQCC/6-31G*). This agrees well with the CASPT2N results.[12]

TABLE 2: Activation[a] and Stabilization[b] Energies Calculated for Chair and Boat Forms Using the 6-31G* Basis Set[c,d]

	reference space			
	activation		stabilization	
	CAS(4,4)	CAS(6,6)	CAS(4,4)	CAS(6,6)
	Chair (C_{2h})			
MR-CISD	44.8	40.5	−32.0	−21.7
MR-CISD+Q	41.5	38.4	−31.5	−25.7
MR-AQCC	38.7	37.3	−28.8	−27.6
	Boat (C_{2v})			
MR-CISD	59.1	50.9	−17.6	−11.4
MR-CISD+Q	54.7	49.5	−18.3	−14.6
MR-AQCC	51.0	48.5	−16.5	−16.4

[a] Energies relative to 1,5-hexadiene in the C_i conformation. [b] Energies relative to the bis-allyl super molecule. [c] Energies in kcal/mol. [d] Total energies + 233 (au): 1,5-hexadiene (C_{2h}) MR-CISD/CAS(4,4) −0.67655, MR-CISD/CAS(6,6) −0.68241, MR-CISD+Q/CAS(4,4) −0.78063, MR-CISD+Q/CAS(6,6) −0.784153, MR-AQCC/CAS(4,4) −0.80952, MR-AQCC/CAS(6,6) −0.81204; for total energies of bis-allyl see Table 1.

In Table 2 the activation and stabilization energies for chair and boat forms are compared for CAS(4,4) and CAS(6,6) reference spaces at MR-CISD, MR-CISD+Q and MR-AQCC levels (6-31G* basis). The activation energy is computed relative to the C_i conformation of 1,5-hexadiene and the stabilization energy is given relative to bis-allyl computed as super molecule. Large differences up to 10 kcal/mol between CAS(4,4) and CAS(6,6) reference cases are observed at the MR-CISD level. The Davidson correction reduces these discrepancies significantly, but they are still quite large (up to ≈6 kcal/mol). The situation is much more satisfactory at the MR-AQCC level. Here, the largest difference between results obtained for the two reference space cases is 2.3 kcal/mol. The chair form is more stable than the boat form by 11.2 kcal/mol at the CAS(6,6)/MR-AQCC level. This value is significantly larger than the CASSCF(6,6) energy difference between loose chair and loose boat forms of 4.6 kcal/mol,[11] but is in good agreement with CASPT2N results[12] (12.8 kcal/mol for the 6-31G* basis set). To convert our ΔE of 11.2 kcal/mol to an enthalpy difference we use the corrections given in Table 2 of ref 12 and arrive at ≈9.8 kcal/mol: a value in good agreement with the experimental activation enthalpy difference of 11.2 kcal/mol[3] between chair and boat form. In the following more extended calculations only the chair form was investigated further.

In Table 3 the MR-AQCC activation and stabilization energies based on fully optimized structures within a given symmetry are shown for increasing size of basis set. In case of the MR-AQCC-ars approach only single point calculations have been performed. The dependence on basis set is not very pronounced and amounts to ≈1.3 kcal/mol in the maximum. The largest difference between CAS(4,4) and CAS(6,6) reference cases amount to 2.9 kcal/mol. The most interesting effect is observed in a comparison of calculations using the standard approach of interacting space restriction and one reference symmetry with the all-reference-symmetry (ars) version. The effect is larger

TABLE 3: Basis Set Dependence of the Activation[a] and Stabilization[b] Energies for the Chair Form Calculated at the MR-AQCC Level[c,d]

	reference space			
	activation		stabilization	
	CAS (4,4)	CAS (6,6)	CAS (4,4)	CAS (6,6)
MR-AQCC/6-31G*	38.7	37.3	−28.8	−27.6
MR-AQCC-ars/6-31G*		35.0		−28.1
MR-AQCC/6-31G**	38.7	37.2	−29.1	−27.7
MR-AQCC/6-311G**	38.4		−29.7	
MR-AQCC/6-311G(2d,1p)	39.7	36.8	−28.5	−27.8
MR-AQCC-ars/6-311G(2d,1p)		33.4	-	−29.7
CASPT2N/6-311G(2d,2p)[e]		33.1		−32.9
B3LYP/6-31G*[f]	34.4		−22.7	
‘Experiment’[g]	35.0		−30.1	

[a] Energies relative to 1,5-hexadiene in the C_i conformation. [b] Energies relative to the bis-allyl super molecule. [c] Energies in kcal/mol. [d] Total MR-AQCC energies + 233 (au): 1,5-hexadiene (C_{2h}) CAS(4,4)/6-31G* −0.80952, CAS(6,6)/6-31G* −0.81204, CAS(4,4)/6-31G** −0.89086, CAS(6,6)/6-31G** −0.89342, CAS(4,4)/6-311G** −0.97482, CAS(4,4)/6-311G(2d,1p) −1.01464, CAS(6,6)/6-311G(2d,1p) −1.01755; CAS(6,6)-*ars*/6-311G(2d,1p) −1.02576 bisallyl CAS(4,4)/6-31G* −0.70420, CAS(6,6)/6-31G* −0.71087, CAS(4,4)/6-31G** −0.78502, CAS(6,6)/6-31G** −0.79220, CAS(4,4)/6-311G** −0.86864, CAS(4,4)/6-311G(2d,1p) −0.90828, CAS(6,6)/6-311G(2d,1p) −0.91643 CAS(6,6)-ars/6-311G(2d,1p) −0.92752. [e] Reference 12, 6-311G(2d,2p) basis. [f] Reference 19. [g] See reference 19, Table 1 for details.

for the activation energy than for the stabilization energy. In the first case it amounts to 2.3 kcal/mol for the CAS(6,6)/6-31G* calculations and to 3.4 kcal/mol for the CAS(6,6)/6-311G-(2d,1p) calculations. Corresponding numbers for the stabilization energy are 0.5 and 1.9 kcal/mol, respectively. Experimental values for activation and stabilization energies (for details of evaluation see ref 19) are given in Table 3 also. Our most extended result (CAS(6,6)-*ars* reference, 6-311G(2d,1p) basis set) approaches the experimental one for the stabilization energy very closely within 0.4 kcal/mol.

The difference to the experimental activation energy is +1.8 kcal/mol for the standard CAS(6,6)/6-311G(2d.1p) calculation and −1.6 kcal/mol for the respective ars calculation. It is interesting to note that the CASPT2N results[12] for the activation energy are close to the just-mentioned ars data, even though the theoretical approaches are quite different (only the interacting space is considered in the CASPT2N method). Both calculations predict the energy barrier to be smaller than the experimental one by 1.6 and 1.9 kcal/mol, respectively. One should not forget at this point that in the evaluation of the energy barrier from the measured activation enthalpy approximations, such as harmonic vibrational frequencies, enter. However, it is difficult to speculate about the effect of these approximations. Nevertheless, both sets of results are, in our opinion, within good limits with respect to the experimental activation energy considering the size and the complexity of the problem. In case of the stabilization energy our best result is significantly closer to the experimental one than the CASPT2N value (AQCC deviation 0.4 kcal/mol, CASPT2 deviation 2.8 kcal/mol). The B3LYP/6-31G* fails severely for the stabilization energy.

After having performed the MR-AQCC geometry optimizations under C_{2h} restriction, the question concerning the character of the stationary point still remained open. Calculation of the entire force constant matrix at the MR-AQCC level would be too expensive since we do not have an analytic method for second derivatives available. Therefore, we adopted the procedure of Hrovat et al.[12] and Kozlowski et al.[13] by considering only a displacement along the antisymmetric combination $R_{C1-C6}-R_{C3-C4}$ of the two interallylic distances. This antisymmetric stretch leads to a symmetry reduction to C_2. To perform consistent calculations at C_{2h} and C_2 symmetry, the interacting space restriction was not used and all reference symmetries were allowed. The 6-31G* and 6-311G(2d,1p) basis sets and the CAS(4,4) reference space were considered: Displacements of 0.02 and 0.04 Å from the equilibrium distance were performed. The energy increased (minimum) in the 6-31G* calculation and decreased (saddle point) in the 6-311G(2d,1p) calculation. In the first case the value of 1.680 Å for R is relatively close to the CASSCF value of 1.641 Å for the tight chair intermediate.[11] For the larger 6-311G(2d,1p) basis, which gives a significantly longer bond distance R of 1.795 Å, we find a decrease in energy with antisymmetric displacement. Since the CAS(6,6)-ref/6-311G(2d,1p) calculations give an even larger value for R, we expect that also in this case a saddle point would be found. Therefore, we conclude that the chair form is a saddle point in agreement with the findings by Hrovat et al.[12] and Kozlowski et al.[13]

IV. Conclusions

Extended MR-CISD and MR-AQCC calculations including full geometry optimization have been performed on the chair and boat structures of the Cope rearrangement. Energetic stabilities with respect to 1,5-hexadiene and the bis-allyl system have been computed. As has already been discussed and documented in the literature before (see ref 19 and references therein), a proper theoretical treatment is quite involved and requires both an adequate choice for the reference space and inclusion of dynamical electron correlation. The main problem so far was that geometry optimizations could not be performed at that combined level because of lack of analytic gradient procedures in multireference cases (e.g., CASPT2). It has been shown in this work that full geometry optimizations at the required extended *multireference* level (MR-CISD and MR-AQCC) are possible using the analytic gradient techniques developed within the framework of the COLUMBUS program system. The MR-CISD calculations on bis-allyl and on potential energy curves for the interallylic distance performed with CAS-(4,4) and CAS(6,6) reference spaces are far from being satisfactory, demonstrating in this way the crucial importance of size-extensivity effects. Correcting for size-extensivity by means of the Davidson correction (MR-CISD+Q) shows insufficient improvements, whereas the MR-AQCC method gives very consistent results.

In agreement with previous CASPT2N[12] and MRMP2[13] calculations we find only one stationary point for a chair-type structure of C_{2h} symmetry. The interallylic bond distance is found to be sensitive to basis set effects and increases with basis set size. At the largest basis set used (6-311G(2d,1p)) the chair structure is found to be a saddle point and not a stable intermediate. This result is obtained at a completely consistent computational level including a multireference approach, non-dynamic electron correlation and complete geometry optimization. Thus we confirm the previous CASPT2N[12] and MRMP2[13] results showing that the mechanism of the Cope rearrangement of 1,5-hexadiene is concerted via an aromatic transition state.

Acknowledgment. The authors acknowledge support by the Austrian Science fund within the framework of the Special Research Program F16 and Project P14442-CHE, and by the COST Chemisty/D9, Project D9/0006/98. The calculations were performed in part on the Schroedinger I Linux cluster of the Vienna University Computer Center.

Supporting Information Available: MR-AQCC energies and Cartesian geometries for chair and boat structures and for 1,5-hexadiene optimized at the MR-AQCC level using different basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Cope, A. C.; Hardy E. M. *J. Am. Chem. Soc*. **1940**, *62*, 441.

(2) Doering, W. E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

(3) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc*. **1972**, *4*, 7147.

(4) Shear, K. J.; Phillips, R. B. *J. Am. Chem. Soc*. **1980**, *102*, 3156.

(5) Doering, W. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279.

(6) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Wade, L. E. *J. Am. Chem. Soc*. **1977**, *99*, 5069.

(7) Dewar, M. J. S. *J. Am. Chem. Soc*. **1984**, *106*, 209.

(8) Dewar, M. J. S. *Acc. Chem. Res*. **1992**, *25*, 537.

(9) Osamura, Y.; Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc*. **1984**, *106*, 3362.

(10) Morokuma, K.; Borden, W. T.; Hrovat, D. A. *J. Am. Chem. Soc*. **1988**, *110*, 4474.

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

(12) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc*. **1994**, *116*, 1072.

(13) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc*. **1995**, *117*, 774.

(14) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc*. **2000**, *122*, 186.

(15) Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc*. **1994**, *116*, 10336.

(16) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc*. **2000**, *122*, 7377.

(17) Houk, K. N.; Gonzalez, J.; Li Y. *Acc. Chem. Res*. **1995**, *28*, 81.

(18) Wiest, O. In *Encyclopedia of Computational Chemistry*, Schleyer, P. v. R., Ed.; Wiley: Chichester, 1998; Vol. 5, p 3104.

(19) Staroverov, V. N.; Davidson, E. R. *J. Mol. Struct. (THEOCHEM)* **2001**, 573, 81.

(20) Borden, W. T. *Mol. Phys.* **2002**, *100*, 337.

(21) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc*. **1965**, *87*, *7*, 4389

(22) Davidson, E. R. *J. Phys. Chem.* **1996**, *100*, 6161.

(23) Szalay, P. G.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *214*, 481.

(24) Szalay, P. G.; Bartlett, R. J. *J. Chem. Phys.* **1995**, *103*, 3600.

(25) Lischka, H.; Shepard, R.; Pitzer, R. M.; Shavitt, I.; Dallos, M.; Müller, Th.; Szalay, P. G.; Seth, M.; Kedziora, G. S.; Yabushita, S.; Zhang, Z. *Phys. Chem. Chem. Phys.* **2001**, *3*, 664.

(26) Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J. *Int. J. Quantum Chem*. **1988**, *S22*, 149.

(27) Lischka, H.; Shepard, R.; Shavitt, I.; Pitzer, R. M.; Dallos, M.; Müller, Th.; Szalay, P. G.; Brown, F. B.; Ahlrichs, R.; Böhm, H. J.; Chang, A.; Comeau, D. C.; Gdanitz, R.; Dachsel, H.; Erhard, C.; Ernzerhof, M.; Höchtl, P.; Irle, S.; Kedziora, G.; Kovar, T.; Parasuk, V.; Pepper, M.; Scharf, P.; Schiffer, H.; Schindler, M.; Schüler, M.;. Zhao, J.-G. COLUMBUS, an ab initio electronic structure program, release 5.8; 2001.

(28) Shepard, R.; Lischka, H.; Szalay, P. G.; Kovar, T.; Ernzerhof, M. *J. Chem. Phys.* **1991**, *93*, 2085.

(29) Shepard, R. In *Modern Electronic Structure Theory, Part I*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 345.

(30) Lischka, H.; Dallos, M.; Shepard, R. *Mol. Phys*. **2002**, *100*, 1647.

(31) Bunge, A. *J. Chem. Phys*. **1970**, *53*, 20.

(32) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem*. **1974**, *8*, 61.

(33) Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys. Lett*. **1981**, *72*, 278.

(34) Rocque, B. G.; Gonzales, J. M.; Schaefer, H. F., IIII *Mol. Phys*. **2002**, *100*, 441.

(35) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(36) Krishanan, R.; Binkely, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(37) Frisch, M. P.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(38) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. DALTON, an ab initio electronic structure program, release 1.0; 1997.

(39) Fogarasi, G.; Zhou, X.; Taylor, P. W.; Pulay, P. *J. Am. Chem. Soc*. **1992**, *114*, 8191.

(40) Császár P.; Pulay, P. *J. Mol. Struct*. **1984**, *114*, 31.

(41) Müller, Th.; Lischka, H. Unpublished work.

(42) Dachsel H.; Lischka H.; Shepard R.; Nieplocha J.; Harrison R. J. *J. Comput. Chem.* **1997**, *18*, 430.