[2+2+2]-Cycloreversion reactions: a theoretical elucidation of thermodynamic and through-bond coupling effects on activation energies †‡

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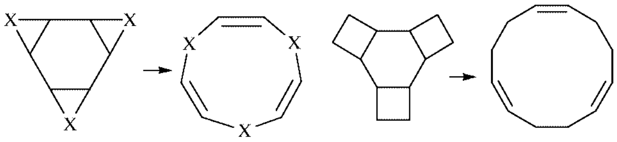
[2+2+2]-Cycloreversion reactions of cyclohexane and ten fused cyclohexanes were studied computationally with B3LYP/6-31G* and CASSCF methods. Reactions involving cleavage of bonds in three- and five-membered rings show distinctly lower barriers to cycloreversion than cleavage of four-membered rings. The lower activation energies for the cleavage of odd-membered rings arise from interactions of the sigma framework of the odd-membered ring with the orbitals of the breaking bond. NICS values were calculated to determine the aromaticity of the different rings involved in bond cleavage. In addition to concerted mechanisms, the stepwise diradical pathways for the [2+2+2]-cycloreversions of cyclohexane and *cis*-tris-cyclopropacyclohexane were studied.

Introduction

[2+2+2]-Cycloreversions are thermally allowed pericyclic reactions[1] that are expected to feature cyclic delocalization of six electrons in the transition state, resulting in significant aromatic character and transition state stabilization.[2] While the reaction of cyclohexane is not known, many polycyclic systems undergo the reaction with ease. For example, derivatives of the all-*cis*-tris-cyclopropacyclohexane, **1a**,§ have activation energies of only 22–28 kcal mol^{-1}.[3] By contrast, the *cis*-tris-cyclobutacyclohexane, **3**,¶ has an activation energy of about 50 kcal mol^{-1} and the reaction occurs only above 400 °C.[4] The origin of this high barrier for **3** relative to **1a** cannot be attributed to strain energy differences, because cyclopropane and cyclobutane have similar strain energies of 27.6 kcal mol^{-1} and 26.2 kcal mol^{-1} respectively.[5]



1a X = CH_2
1b X = O
1c X = NCH_3

2

3

4

Many cycloreversion reactions of cyclopropane fused cyclohexane derivatives have been studied experimentally.[6] Among the heterocyclic analogs of **1a**, the *cis*-tris-oxirane, **1b**,|| has the highest activation energy, 38.0 kcal mol^{-1}.[6a] The *cis*-tris-aziridine, **1c**, has the lowest activation energy of the heterocyclic series, 25.6 kcal mol^{-1}, resembling the hydrocarbon, **1a**.[6c] The pentacyclic hydrocarbons, diademane** and homodiademane, also undergo these reactions with low activation energies (31.6 and 28.3 kcal mol^{-1}).[7] Cycloreversion of the *trans*-substituted derivatives of **1a** has been studied experimentally, and activation barriers for the concerted cycloreversion are 21 kcal mol^{-1} higher than the *cis*-substituted derivatives of **1a**.[8] The cycloreversion of only a few cyclobutane substituted cyclohexanes, **3**, has been studied experimentally.[4,9] We are currently investigating cycloreversions of many *trans*-substituted derivatives of **1a** and heterocyclic derivatives of **1b** and **1c** computationally.

We have explored retro [2+2+2]-cycloadditions to characterize the nature of the transition states and to explore the origin of the large effect of ring fusion on the rates of these reactions. Most previous theoretical studies of the [2+2+2]-cycloaddition have focused on the origin of the very large barrier of the Woodward–Hoffmann allowed reaction. The trimerization of acetylene is a highly exothermic reaction ($\Delta H_{\text{rxn}} = -143$ kcal mol^{-1}),[10] but has a very high energy of activation. Houk *et al.* traced the origin of these high activation barriers to the energy required to distort the molecules and to overcome closed-shell repulsions between the π orbitals.[10] Bach concluded that no π-aromatic stabilization occurs at the transition state.[11] Ioffe and Shaik studied the [2+2+2]-cycloaddition of three ethylenes at the RHF/3-21G level (and up to the MP4/6-31G*//RHF/3-21G level) and compared this reaction to the Diels–Alder reaction of ethylene and butadiene.[12] The Diels-Alder reaction was found to have a much lower activation barrier than the [2+2+2]-cycloaddition of three ethylenes, even though the Diels–Alder reaction is less exothermic. Schleyer has also studied the trimerization of acetylene and used nucleus-independent chemical shift (NICS) values to determine the aromaticity of reactants, transition states, and products.[13] Schleyer's results indicate that aromatic stabilization energy at the transition state comes from the in-plane contribution of the σ orbitals rather than the out-of-plane contributions of the π orbitals. The [2+2+2]-cycloreversion of diademane was also studied by Schleyer at the B3LYP/6-311+G* level.[14] A MINDO/3 study compared activation energies for the [2+2+2]-cycloreversion of diademane and the [2+2+2]-cycloreversion of *cis*-tris-cyclopropacyclohexane, **1a**.[15]

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† Figs. 12–17 containing the geometries for the mono and bis fused cyclohexanes are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/2349, otherwise available from BLDSC (SUPPL. NO. 57644, pp. 7) or the RSC Library. See Instructions for Authors available *via* the RSC web page.

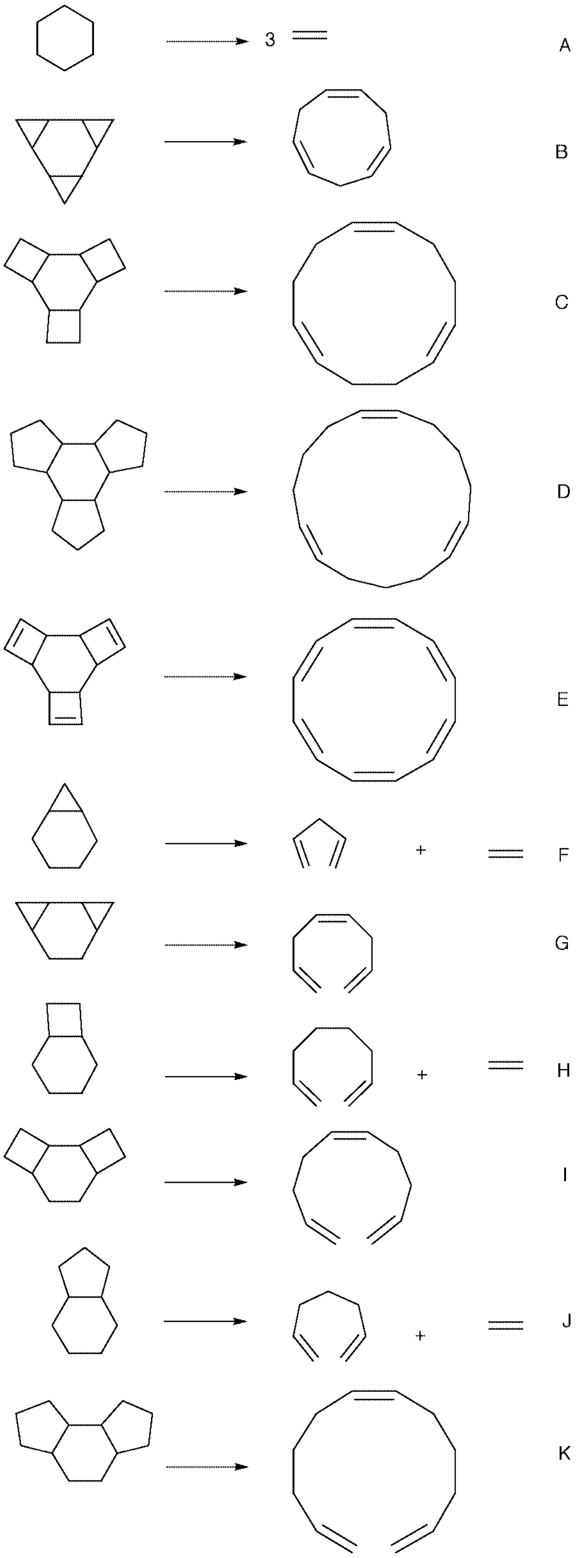
‡ This paper is dedicated to the memory of Robert Squires for his friendship and scientific inspiration.

§ The IUPAC name for **1a** is tetracyclo[6.1.0^{2,4}.0^{5,7}]nonane.

¶ The IUPAC name for **3a** is tetrahydro[8.2.0^{2,5}.0^{6,9}]dodecane.

|| The IUPAC name for **1b** is 3,6,9-trioxatetracyclo[6.1.0.0^{2,4}.0^{5,7}]-nonane.

** Diademane is hexacyclo[4.4.0.0^{2,4}.0^{3,9}.0^{5,7}.0^{8,10}]decane.



Scheme 1

We have studied the concerted cycloreversion reactions of cyclohexane and ten fused cyclohexanes, shown in Scheme 1. A preliminary communication of some of these results has appeared.[16] The stepwise diradical cleavage of cyclohexane and *cis*-tris-cyclopropacyclohexane was also investigated.

Computational procedure

The reactants, transition structures, and products for the reactions shown in Scheme 1 were fully optimized at the B3LYP/6-31G* level using GAUSSIAN94.[17] Reactions A–C were also optimized using CASSCF/6-31G* with a six-electron, six-orbital active space. Transition structures and intermediates for the stepwise diradical mechanism of cyclohexane and *cis*-tris-cyclopropacyclohexane cycloreversion were optimized using UB3LYP/6-31G* and UHF/6-31G* methods. Frequency calculations were performed on all structures (except the CASSCF structures for reaction C due to computational constraints). NICS values at the geometrical centers of interest were calculated with GIAO-SCF/6-31G* on B3LYP/6-31G* geometries using the GAUSSIAN94 program.

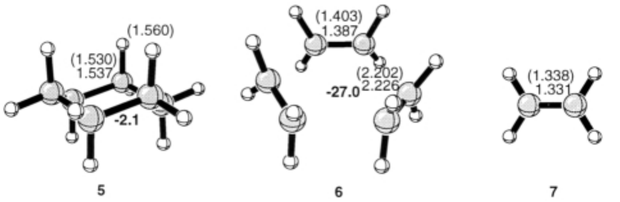


Fig. 1 CASSCF/6-31G* and B3LYP/6-31G* geometries of cyclohexane, concerted [2+2+2] transition structure, and ethylene.

Results and discussion

The transition structure for the concerted cycloreversion of cyclohexane, **6**, has a long bond breaking distance of 2.226 Å (Fig. 1), indicative of a late transition state, and is a highly endothermic reaction, $\Delta H_{\mathrm{rxn}} = 63.1$ kcal mol^{-1}. The calculated B3LYP/6-31G* closely matches the experimental $\Delta H_{\mathrm{rxn}} = 67.0$ kcal mol^{-1} from experimental heats of formation.[18] The activation energy, $\Delta E_{\mathrm{a}}^{\ddagger}$, for the cycloreversion of cyclohexane calculated at the B3LYP/6-31G* level is very high, 112.8 kcal mol^{-1}. The CASSCF method using the 6-31G* basis set reproduces an activation energy similar to the B3LYP results, $\Delta E_{\mathrm{a}}^{\ddagger} = 115.6$ kcal mol^{-1}. Since the energy required to break a C–C bond between two secondary carbons is only about 90 kcal mol^{-1}, this reaction undoubtedly would follow a stepwise pathway as described later. The six carbons in the transition state have a slight chair-like geometry with alternating dihedral angles of 16° and −18°. The NICS value for the center point of the six carbons in the transition state is −27.0, typical of an aromatic transition state.[19] NICS values for other aromatic transition states are similar; the NICS at the center of the central six carbon atoms at the transition structure for the cycloreversion of diademane to triquinacene[††] was calculated to be −26.8 by Schleyer.[14] The NICS value at the transition state for the trimerization of three acetylenes to form benzene is −24.1 and the NICS value at the transition structure for the hydrogen exchange of three hydrogen molecules is −24.0 as calculated by Schleyer.[13]

The reaction of the *cis*-tris-cyclopropacyclohexane, **1a**, is exothermic, $\Delta E_{\mathrm{rxn}} = -20.8$ kcal mol^{-1}. The computed activation energy, $\Delta E_{\mathrm{a}}^{\ddagger} = 22.0$ kcal mol^{-1}, closely matches the activation energy, $\Delta E_{\mathrm{a}}^{\ddagger} = 21.9$–$24.3$ kcal mol^{-1}, estimated from experimental gas phase activation energies for two structurally related compounds, diademane and homodiademane.[3] The CASSCF activation energies again closely match the energies obtained using the B3LYP method, $\Delta E_{\mathrm{a}}^{\ddagger} = 26.1$ kcal mol^{-1}. Schleyer *et al.* studied the cycloreversion of the structurally similar diademane; they computed an activation energy of 25.5 kcal mol^{-1} at the B3LYP/6-311+G* level for this cycloreversion.[14] A MINDO/3 study compared the cycloreversion of **1** to the [2+2+2]-cycloreversion of diademane and found that the activation energy for the cycloreversion of **1** is lower than for the diademane cycloreversion. This is confirmed by our and Schleyer's results.

[††] The IUPAC name for triquinarene is dodecahydro-1*H*-phenalene.

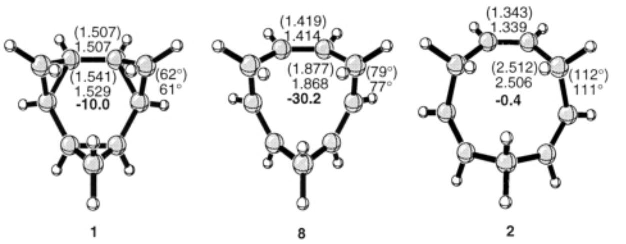


Fig. 2 CASSCF/6-31G* and B3LYP/6-31G* geometries of *cis*-tris-cyclopropacyclohexane, concerted transition structure, and cyclonona-1,4,7-triene.

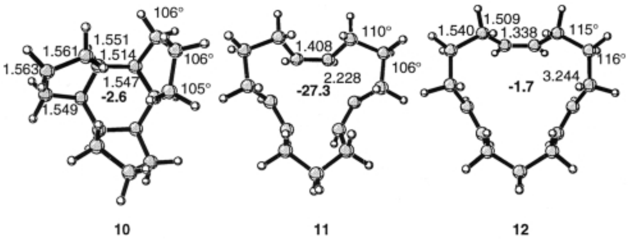


Fig. 4 B3LYP/6-31G* geometries of *cis*-tris-cyclopentacyclohexane, concerted transition [2+2+2] structure, and cyclopentadeca-1,6,11-triene.

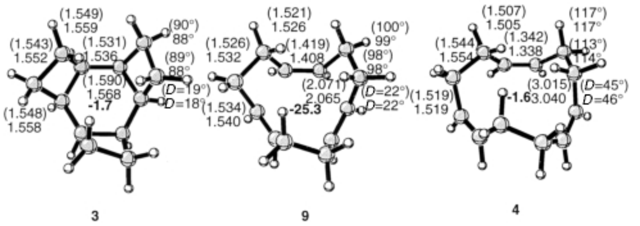


Fig. 3 CASSCF/6-31G* and B3LYP/6-31G* geometries of *cis*-tris-cyclobutacyclohexane, concerted transition [2+2+2] structure, and cyclododeca-1,5,9-triene.

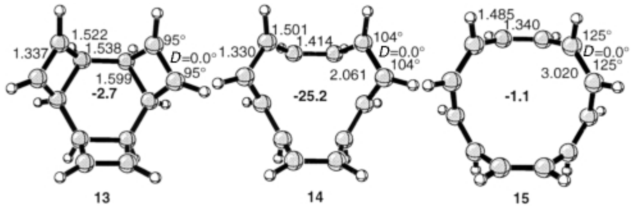


Fig. 5 B3LYP/6-31G* geometries of *cis*-tris-cyclobutenacyclohexane, concerted transition [2+2+2] structure, and dodecahex-1,3,5,7,9,11-ene.

The length of the breaking C–C bond is an unusually short 1.87 Å in the transition structure, **8** (Fig. 2) suggesting an early transition state. The reactant, transition structure, and product are all C_{3v} symmetric. The six central carbon atoms of the transition structure, reactants, and products are completely planar; the dihedral angles of the central six carbon atoms are all zero. The NICS value at the center of the six carbon atoms is largest in this system, −30.2. The planarity of this system along with the large negative NICS value at the center of the six carbon atoms implies a highly delocalized aromatic transition state.

The cycloreversion of the *cis*-tris-cyclobutacyclohexane, **3**, to form all-*cis* cycloundeca-1,5,9-triene, **4**, is an exothermic reaction, $\Delta E_{rxn} = -13.9$ kcal mol^{-1}. The activation energy is 50.4 kcal mol^{-1}. The experimental activation enthalpy for this reaction is 50–52 kcal mol^{-1}.[4] The activation energy for cycloreversion of the *cis*-tris-cyclobutacyclohexane is 28.4 kcal mol^{-1} higher than the similarly exothermic cycloreversion of **1**, CASSCF also predicts high activation energies for this process, $\Delta E_a^{\ddagger} = 59.2$ kcal mol^{-1}. This is the non-zero point corrected activation energy because the frequency calculation for the CASSCF transition structure could not be done due to the lack of computer memory needed for this large system. The transition structure, **9**, is a later transition structure than in the cycloreversion of the *cis*-tris-cyclopropacyclohexane, with a bond breaking distance of 2.07 Å (Fig. 3). The reactant, transition structure, and product are all C_3 symmetric. The central six carbon atoms have a slight chair-like geometry as in the cyclohexane transition structure, **6**; dihedral angles among the central six carbon atoms alternate between −17° and 19° in the transition structure. This chair-like geometry also prevails in the reactant and product. The NICS value at the center of the central six carbons is −25.3 in the transition state indicative of an aromatic transition state. The NICS value at the center of the opened cyclobutane rings in the transition structure is small and positive, 2.5, suggesting slight antiaromatic character. In the reactant, **3**, the NICS value in the center of the cyclobutane rings is −1.4 typical of non-aromatic systems. In cyclobutane itself, the NICS value in the center of the four carbon atoms is −0.3.

Cycloreversion of the *cis*-tris-cyclopentacyclohexane, **10**,‡‡ occurs with a computed activation energy of 78.0 kcal mol^{-1}. This reaction is endothermic, $\Delta E_{rxn} = 29.7$ kcal mol^{-1}, and has a late transition structure with a breaking bond distance of 2.23 Å (Fig. 4). The reactant is C_3 symmetric, and the transition structure and product are C_{3v} symmetric. The central six carbon atoms in the transition structure and product are planar; dihedral angles are zero among the central six carbon atoms. The reactant has a chair-like geometry at the central six carbon atoms; the dihedral angles alternate between 45.8° and −45.8°. The NICS value at the center of the central six carbon atoms is −27.4 which is slightly more aromatic than the *cis*-tris-cyclobutacyclohexane and slightly less aromatic than the *cis*-tris-cyclopropacyclohexane.

The activation energy for the reaction of *cis*-tris-cyclobutenacyclohexane, **13**,§§ is 37.3 kcal mol^{-1} and the reaction is exothermic, $\Delta E_{rxn} = -32.8$ kcal mol^{-1}. The bond breaking distance in the transition structure, **14**, is 2.06 Å (Fig. 5). This is a high activation energy compared to the less exothermic reaction of *cis*-tris-cyclopropacyclohexane ($\Delta E_{rxn} = -20.8$ kcal mol^{-1}). The NICS value at the center of the central six carbon atoms is −25.2.

The mono and bis fused[20] analogs of **1**, **3**, and **10** exhibit similar trends in activation energies; the cyclopropa-fused cyclohexanes have the lowest activation energies for a given heat of reaction while the cyclobuta-fused cyclohexanes have the highest activation energies. The cyclopenta-fused cyclohexanes have intermediate activation energies. Table 1 summarizes available experimental and theoretical energies for the concerted cycloreversions of systems A–K. NICS values are given in Table 2. Geometries for systems F–K are also provided as supplementary data. For **1** and **3**, the theoretical values can be compared to experimental values estimated by de Meijere[3] and obtained by Prinzbach *et al.*[4] In both systems, computed activation energies using the B3LYP/6-31G* method are comparable to experimental values. The activation energy for the tris-cyclobuta-fused system is almost 30 kcal mol^{-1} higher than the tris-cyclopropa-fused system, even though ring strain energies for cyclopropanes and cyclobutanes are comparable. The ring strain in cyclopropane is 27.6 kcal mol^{-1}, and the ring strain energy in cyclobutane is 26.2 kcal mol^{-1}.[5]

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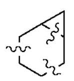
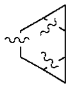
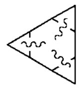
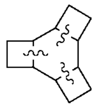
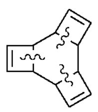
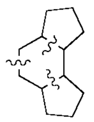
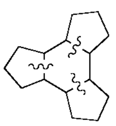
‡‡ The IUPAC name for **10** is tetradecahydro-1*H*-cyclopenta[*e*]*as*-indacene.

§§ The IUPAC name for **13** is tetracyclo[8.2.0.0^{2,5}.0^{6,9}]dodeca-3,7,11-triene.

Table 1 B3LYP/6-31G* Zero point corrected activation energies and energies of reaction for [2+2+2]-cycloreversion reactions of bridged and unbridged cyclohexanes. CASSCF values are given in parentheses

System	$\Delta E^‡$/kcal mol^{-1}	ΔE_{rxn}/kcal mol^{-1}
	112.8 (115.6)	63.1 (33.6)
	71.7	30.8
	49.1	1.95
	22.0 (26.1)	−20.8 (−44.2)
	90.1	34.0
	70.9	5.04
	50.4 (59.2)[a]	−13.9 (−32.4)[a]
	37.3	−32.8
	97.1	46.6
	90.4	37.0
	78.0	29.7

[a] Not zero-point energy corrected.

The B3LYP activation energies ($\Delta E^‡ = E_{ts} - E_{reactant}$) for eleven cycloreversion reactions are plotted against the corresponding energies of reaction ($\Delta E_{rxn} = E_{product} - E_{reactant}$) in Fig. 6.[21] The least squares fit for all the systems is shown. The solid line represents a Brønsted plot for the systems where the activation energy is related to the energy of reaction by $\Delta E^‡ = 0.86\Delta E_{rxn} + 55.8$. A strict Brønsted relationship between energy of reaction and activation energy would predict that all points for the cycloreversion reactions should lie along a single line. However, the data presented here show that only cyclohexane and the cyclopentane fused systems fall on the line. Thus, the cyclopropane fused cyclohexanes have anomalously low activation energies relative to cyclohexane and the cyclopentane fused cyclohexanes. The cyclobutane fused cyclohexanes have activation energies that are much higher than would be predicted from a simple Brønsted relationship.

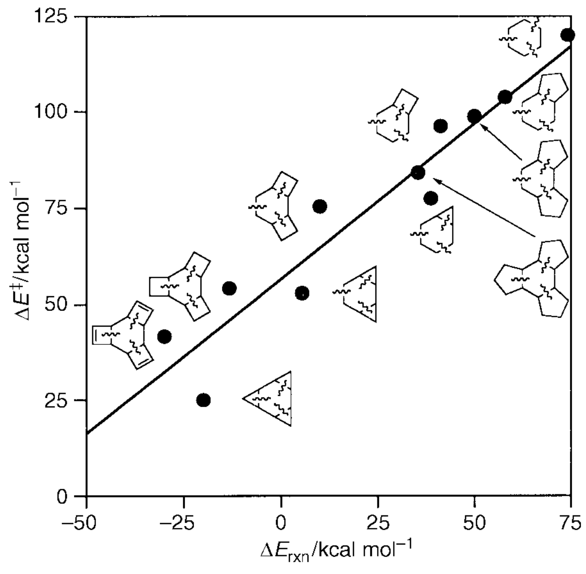


Fig. 6 Graph of energy of reaction ΔE_{rxn} *versus* activation energy $E_a^‡$.

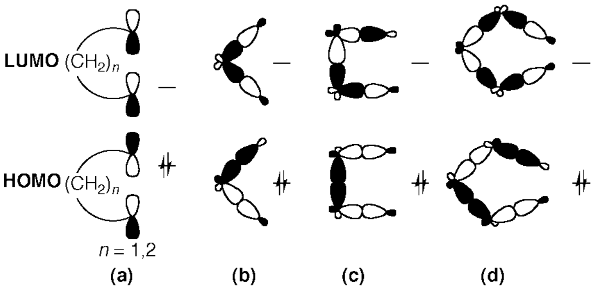


Fig. 7 Schematic representation of HOMO and LUMO of (a) a cleaving σ bond in the transition state, (b) trimethylene, (c) tetramethylene, and (d) pentamethylene groups.

The lower activation energy for cleavage of three- and five-membered rings relative to four-membered rings can be explained by examining the interactions between the orbitals of the breaking bonds and the sigma frameworks of the small rings. Fig. 7 shows the HOMO and LUMO of a breaking sigma bond (a), along with the simple C-approximation[22] σ orbitals of trimethylene (b), tetramethylene (c), and pentamethylene (d) chains. The highest occupied sigma molecular orbital (HO-σ-MO) of the breaking four-membered ring is symmetric, and therefore mixes with the σ orbital of the breaking bond. These orbitals are both doubly occupied, resulting in a destabilizing interaction which raises the activation energy. In contrast, the HO-σ-MOs of the trimethylene and pentamethylene are antisymmetric, and therefore of the wrong symmetry to mix with the σ orbital of the breaking bond which results in an absence of destabilizing interactions. The HO-σ-MO of trimethylene and pentamethylene can mix with the σ* orbital of breaking bond and this will be a stabilizing two-electron interaction. The LU-σ-MO of trimethylene and pentamethylene can also mix with the HO-σ-MO of the breaking bond resulting in another two-electron stabilizing interaction. The inability of cyclobutane to participate in homoaromatic conjugation has been commented on by Haddon.[23]

Hoffmann used through bond interactions to explain sigma delocalization which accounts for the transmission of electronic effects between functional groups *via* many saturated atoms.[24] In 1980, Verhoeven discussed how OITB (orbital interactions through bonds) can be used to explain reactivity patterns in reactions containing bifunctional carbon chains, in hydrogen and hydride transfer reactions, and as an alternative to Baldwin's rules in radical olefin cyclizations.[25] Spectroscopic evidence for OITB has been found in the non-degeneracy of ionization potentials in large symmetric unsaturated cyclic systems.[26] Aside from the heterolytic Grob fragmentation,[27] the Birch reductions of Paddon-Row and Hartcher,[28] and the carbanion cyclizations of Stirling,[29] until now, experimental

Table 2 NICS values for concerted cycloreversion systems A–K

Bridge type	TS	TS Small ring	Reactant	Reactant small ring	Product
none	−27.0		−2.1		
1 cyclopropane	−25.2	−29.4	−4.6	−43.7	
2 cyclopropane	−28.0	−36.1	−6.4	−43.7	
3 cyclopropane	−30.2	−39.4	−10.0	−44.3	−0.4
1 cyclobutane	−25.5	2.2	−1.9	−2.6	
2 cyclobutane	−25.3	1.3/2.6	−1.9	1.2/−0.1	
3 cyclobutane	−25.3	2.5	−1.7	−1.4	−1.6
1 cyclopentane	−26.5	−6.0	−2.7	−5.6	
2 cyclopentane	−26.2	−4.5/6.6	−2.9	−5.4	−0.5
3 cyclopentane	−27.3	−4.4	−2.6	−5.2	−1.7
3 cyclobutene	−25.2	0.4	−2.7	−0.5	−1.1
cyclopropane			−42.9		
cyclobutane			−0.3		
cyclopentane			−5.6		

evidence for OITB has been rare. We have found that OITB can explain the large rate enhancement in three-membered rings relative to four-membered rings in concerted cycloreversions.

The NICS values complement our OITB rationale for the increased activation energies in the cyclobutacyclohexane systems. NICS values are an effective probe of aromaticity in transition states of pericyclic reactions.[13,19] Aromatic molecules such as benzene have large negative NICS values (−11.5), and aromatic transition states have NICS values of around −25.[13,19] Antiaromatic molecules such as cyclobutadiene have positive NICS values (28.8) and nonaromatic molecules have NICS values close to zero.[13,19] Table 2 shows the NICS values in the center of the cyclohexane rings of the transition state, reactant, and product and in the center of the fused rings of the reactant and transition state. The NICS value at the center of the central six carbon atoms is the least negative in the transition states for the cyclobutacyclohexane systems. More strikingly, however, the NICS value at the center of each cyclobutane ring in these systems is small but positive (+2.5) in the transition state and suggests an anti-aromatic system. These positive NICS values are evidence of the repulsive interactions we suggest are responsible for the high activation energies in the cyclobutacyclohexane systems. The negative NICS values in the three-membered or five-membered rings in the transitions states in the cyclopropa (−39.4) and cyclopentacyclohexane (−4.4) systems indicate an aromatic system which may result from the stabilizing interactions of the LUMO of the rings with the HOMO of the breaking bond.

The experimental activation energy for cleavage of a cyclopropane bond is 64–65 kcal mol^{-1}, while the experimental activation energy for breaking cyclobutane is 62.5 kcal mol^{-1}.[30] By contrast to the fused systems, these activation energies are virtually identical. This is because the transition states for the cleavage of the simple cycloalkanes are essentially identical to the product diradicals, and these are equally stable. The lowered activation barriers observed in the [2+2+2] cycloreversions of cyclopropane fused cyclohexanes is a result of homoaromatic conjugation of the trimethylene fragment with the breaking σ bond. The anomalous activation energies in the cycloreversions are strictly transition state effects.

Stepwise cleavage of cyclohexane and *cis*-tris-cyclopropacyclohexane

Since the predicted activation energy for the concerted cycloreversion of cyclohexane, 112.8 kcal mol^{-1} using B3LYP/6-31G*, is very high, the cleavage of one bond of cyclohexane, and subsequent bond cleavage to form three ethylenes, must be a more energetically favorable process. The lowest energy transition structure that was located for this first bond cleavage is a boat-like structure, **16b**, with a bond-breaking distance of 3.51 Å (Fig. 8). Dihedral angles among the carbons in this transition structure are all about 60°; therefore, this structure will be referred to as twist boat transition structure. Stretching the broken C–C bond in this transition structure leads to a twist boat diradical intermediate. The potential energy surface is very flat in this region and many diradicals with *gauche* or *anti* arrangements around the three internal C–C bonds have about the same energy (Fig. 9).

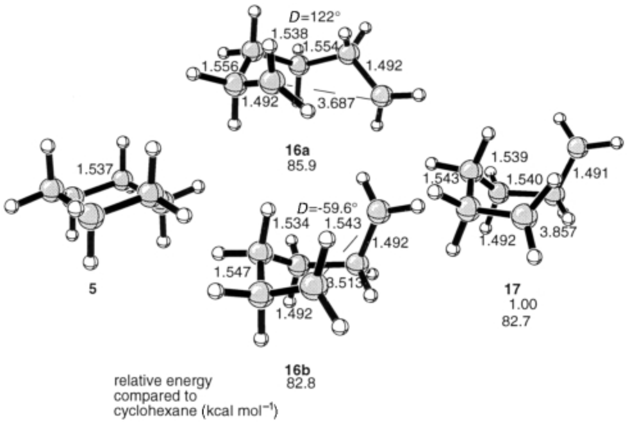


Fig. 8 B3LYP/6-31G* geometry of cyclohexane and UB3LYP/6-31G* geometries of cyclohexanediyl transition structure and hexanediyl biradical intermediate.

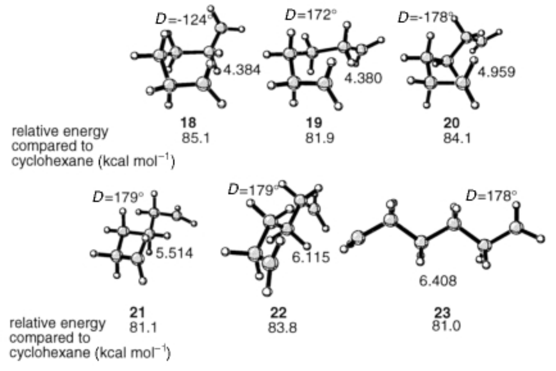


Fig. 9 Conformational processes in hexane-1,6-diyl.

There is spin contamination in the wavefunctions of biradicals **16**–**23** which are essentially 50:50 mixture of singlet and triplet states; $\langle S^2 \rangle$ values range from 0.92–1.02, except for **23a**, which is a second order saddle point, $\langle S^2 \rangle = 0.55$. The lowest energy intermediate of this series of diradical structures is the all-*anti* hexane-1,6-diyl biradical, **23**. This all-*anti* hexane-1,6-diyl biradical can cleave *via* a concerted pathway to yield three ethylenes, $\Delta E^{\ddagger} = 32.7$ kcal mol^{-1}. A second order saddle

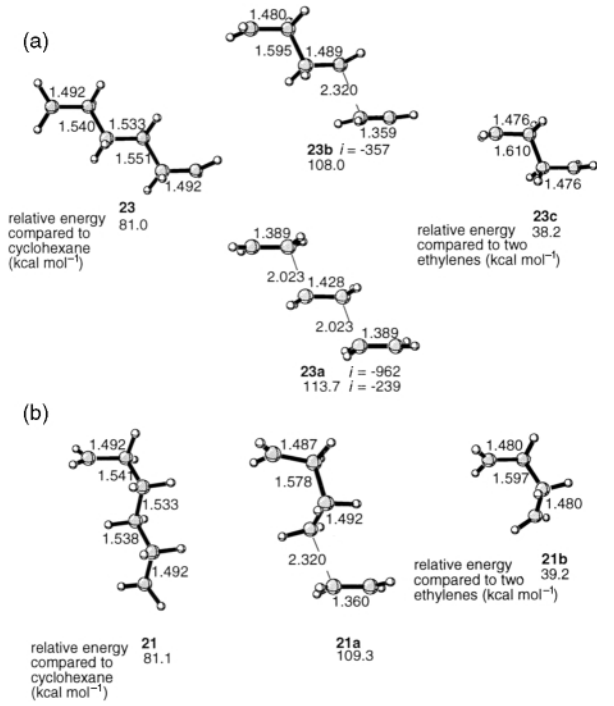


Fig. 10 (a) UB3LYP/6-31G* geometries of all-*anti* hexane-1,6-diyl biradical intermediate, hexane-1,6-diyl one bond breaking stepwise transition state, hexane-1,6-diyl two bond breaking second order saddle point, *anti* butane-1,4-diyl biradical intermediate. (b) UB3LYP/6-31G* geometries of *gauche anti anti* hexane-1,6-diyl biradical intermediate, *gauche* hexane-1,6-diyl one bond breaking stepwise transition state, *gauche* butane-1,4-diyl biradical intermediate.

point, **23a**, was located corresponding to this concerted pathway (Fig. 10). The larger negative frequency for the second order saddle point corresponds to the simultaneous cleavage of two bonds of the all-*anti* hexane-1,6-diyl biradical to form three ethylenes. The smaller negative frequency corresponds to the lengthening of one bond of the hexane-1,6-diyl biradical and concomitant shortening of the bond, leading to the buta-1,4-diyl biradical, **23c**, and ethylene. A transition structure, **23b**, corresponding to the stepwise cleavage of the all-*anti* hexanediyl biradical, was located. This transition structure leads to the *trans*-buta-1,4-diyl biradical and ethylene, $\Delta E^{\ddagger} = 27.0$ kcal mol^{-1}. High level calculations of the cleavage of cyclobutane suggest that the potential energy surface for the fragmentation of the buta-1,4-diyl biradical, **23c**, is extremely flat and an enthalpic barrier to this process is unlikely.[31] Stepwise single bond cleavage of the higher energy conformers of the hexane-1,6-diyl biradical can also occur (Fig. 10b), but these will be at higher energy than the transition state for cleavage of the all-*anti* hexane-1,6-diyl biradical.

An all-*gauche* chair-like version of transition structure **16** was also located. However, the chair-like transition structure for the cleavage of one bond in cyclohexane lies 3.1 kcal mol^{-1} higher in energy than the corresponding twist boat transition structure. The $\langle S^2 \rangle$ value for the stepwise cleavage is nearly 1.0, indicating that the wavefunction is approximately 50 : 50 singlet and triplet, the usual situation for pure diradical species. The activation energy for the stepwise cleavage of one bond in cyclohexane producing the all-*gauche* boat-like transition structure is 82.8 kcal mol^{-1}, which is 30.0 kcal mol^{-1} lower in energy than the concerted cycloreversion for cyclohexane, making the stepwise pathway for cyclohexane cleavage much preferred over the concerted cycloreversion of cyclohexane.

We also examined the stepwise cleavage pathway for the *cis*-tris-cyclopropacyclohexane, **1**. Stretching one σ bond opens the cyclopropane ring and leads to a C_s symmetric transition structure, **24**, at the UHF/6-31G* level. This transition structure lies 26.8 kcal mol^{-1} higher than the reactant, **1**, located at the UHF/6-31G* level; there is spin contamination in the wavefunction, $\langle S^2 \rangle = 0.63$. Further lengthening of the former σ bond leads to a diradical intermediate, **25**, which is 2.3 kcal mol^{-1} lower in energy than the transition structure, **24** ($\langle S^2 \rangle = 0.92$). Lengthening a second bond in the diradical intermediate, **25**, leads to a second transition structure, **26**, which is 7.5 kcal mol^{-1} above the diradical intermediate, ($\langle S^2 \rangle = 1.1$). We could not locate a transition structure for the cleavage of the third bond and we infer that cleavage of this bond should be a spontaneous process leading to the product, **2**. Although we could not optimize the biradical transition structure for cleavage of the first bond, **24**, at the UB3LYP/6-31G* level, a UB3LYP/6-31G* single point calculation on the UHF/6-31G* transition structure geometry, reveals that the activation energy for the stepwise cleavage of one bond of *cis*-tris-cyclopropacyclohexane is 3.4 kcal mol^{-1} higher than the concerted cycloreversion. The concerted cycloreversion is therefore predicted to be favored over the stepwise cleavage of one bond in *cis*-tris-cyclopropacyclohexane.

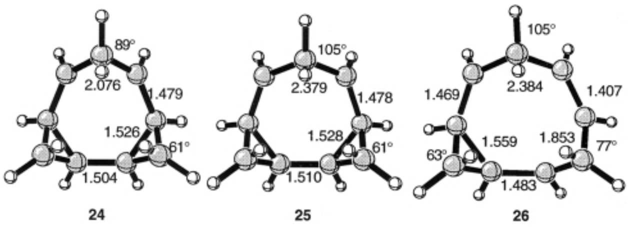


Fig. 11 UHF/6-31G* geometries of the *cis*-tris-cyclopropacyclohexane diradical transition structure, intermediate and second transition structure.

Conclusions

Experimental activation energies and heats of reaction for the concerted cycloreversions of fused cyclohexanes are reproduced well computationally using the B3LYP/6-31G* method. Concerted reactions of fused cyclohexanes are favored over stepwise processes. Cycloreversion of three-membered fused cyclohexanes is favored over four-membered fused cyclohexanes. We have explained this preference for cycloreversion of three-membered fused cyclohexanes by examining the orbital interactions through bonds (OITB).

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