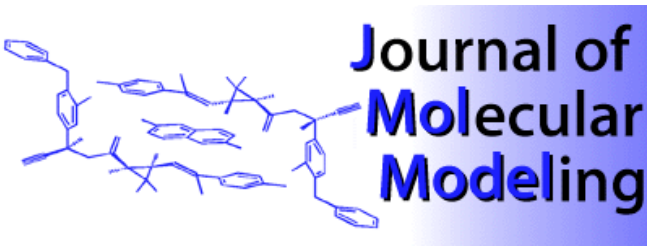
J. Mol. Model. **2000**, *6*, 158 – 165



FULL PAPER

Aromaticity and Antiaromaticity in Small Ring Transition States, Assessed by NICS Values and Energetics

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Abstract Nucleus Independent Chemical Shift (NICS) values, pioneered by Schleyer, provide detailed insights into electronic structures of transition states. These show that the [2+2+2]-cycloaddition transition states, studied early by Schleyer and by us, have aromatic transition structures and that fused cyclopropanes are aromatic in the transition structure, while fused four-membered rings are antiaromatic. The nucleophilic ring-opening of 1- and 2- cyanobicyclo[1.1.0]butanes, studied earlier by Hoz, and ring openings of cyanocyclopropane, cyanocyclobutane, and 2-cyanobicyclo[2.2.0]hexane by hydroxide were investigated at the B3LYP/6-31+G* level. Orbital interactions through bonds explain relative facilities of ring opening.

Keywords NICS, Aromaticity, Molecular orbital theory

Introduction

The remarkable differences between the activation barriers of [2+2+2] cycloreversions of cyclopropane and cyclobutane fused cyclohexanes shown in Scheme 1, **1** and **3**, have been explained as a result of orbital interactions through bonds (OITB).[1] Verhoeven had suggested that OITB could influence the rate of bond formation in bifunctional carbon chains, intramolecular hydrogen and hydride transfer, and radical-olefin cyclizations.[2] We noted the aromaticity of transition states involving 3-membered ring cleavage and antiaromaticity of 4-membered rings in these cases, and proposed OITB should be a general phenomenon. An alternative hypothesis for the facility of 3-membered ring-opening in several nucleophilic reactions was proposed by Hoz et al., based upon frontier MOs of reactants.[3]

In this paper we report the results of an examination of the transition states of the nucleophilic ring opening reactions by hydroxide of cyanocyclopropane, **5**, and cyanocyclobutane, **6**, the systems studied by Hoz, **7** and **8,** and 2-cyanobicyclo[2.2.0]hexane, **9**, shown in Scheme 2. Nucleus Independent Chemical Shift (NICS) values, a probe of aromaticity created by Schleyer,[4] were used to test the hypothesis that aromatic stabilization of the transition state is responsible for the faster ring opening of 1-cyanobicyclobutane vs. 2-cyanobicyclobutane and cyanocyclopropane vs. cyanocyclobutane.

Three-membered rings open much faster than four-membered rings, in spite of the fact that both ring openings are similarly exothermic.[5] In our earlier study of [2+2+2]

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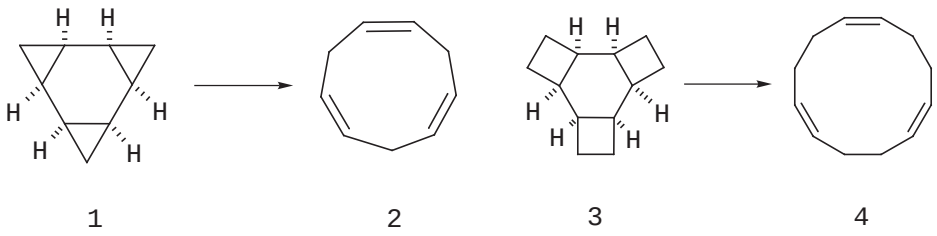
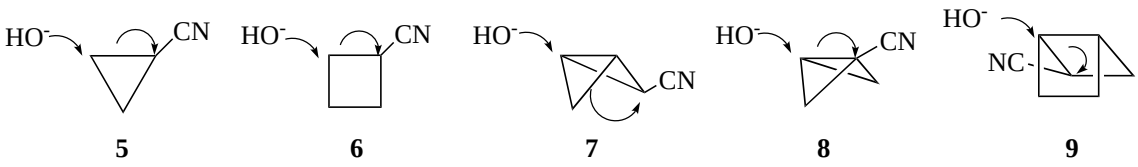
Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

Scheme 1 *[2+2+2]-Cycloreversion of cyclopropane and cyclobutane fused cyclohexanes*





Scheme 2 *Nucleophilic ring opening of cyanocyclopropane **5**, cyanocyclobutane **6**, 2-cyanobicyclobutane **7**, 1-cyanobicyclobutane **8**, and 2-cyanobicyclohexane **9***

cycloreversions of fused cyclohexanes, we showed the origin of the 25 kcal·mol^{-1} lower activation barrier to cycloreversion of derivatives of **1** relative to **3**.[1,5] In a cleaving cyclopropane, σ bonds' interactions with the breaking bond stabilize the transition state. For the cyclobutane, the transition state is destabilized by these interactions. The reaction of **3** is less exothermic than that of **1** by only 7 kcal·mol^{-1}, but the activation barrier to cycloreversion of **3** is more than four times the change in heat of reaction. The lower barrier of cyclopropane-fused cyclohexanes relative to cyclobutane fused cyclohexanes cannot be explained by ring strain, since cyclopropane and cyclobutane have only slightly different strain energies of 27.6 kcal·mol^{-1} and 26.2 kcal·mol^{-1}, respectively.[6]

Sella, Basch, and Hoz found another example where there is no relationship between reaction exothermicity and activation energy.[3] They studied the nucleophilic ring openings of 1- and 2-cyanobicyclo[1.1.0]butane. Ring opening of 1-cyanobicyclobutane involves cleavage of the central bond shared by the two trimethylene fragments. In the ring opening of 2-cyanobicyclobutane, a side bond of bicyclobutane is cleaved, leaving one cyclopropane ring intact. At the RHF/6-31+G* level, these two reactions differ in exothermicity by only 4 kcal·mol^{-1}. However, the activation barrier for cleavage of the central bond is 26 kcal·mol^{-1} lower than cleavage of the side bond. Strain relief does not explain the different activation barriers for these cleavages. The proposed explanation involves frontier MO's of the central or side bond. The σ* orbital of the cleaving bond interacts with the HOMO of the nucleophile. The LUMO of the central bond is lower in energy than the LUMO of the side bond and will thus interact more readily with the HOMO of hydroxide in the transition state of the reaction.

Is it possible that the through-bond effects which explain the [2+2+2] rates could also explain these results? We have studied the nucleophilic opening of cyanocycloalkanes by hydroxide and compared these with the [2+2+2] reactions using orbital interactions through bonds. The Schleyer NICS values were analyzed to examine the aromaticity or antiaromaticity in the center of the ring undergoing bond cleavage.

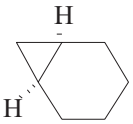
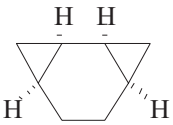
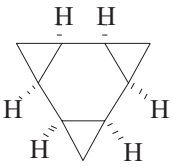
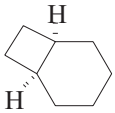
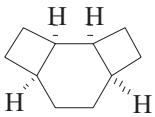
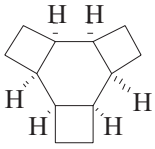
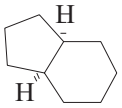
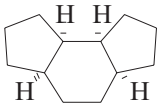
Computational methods

Reactants, transition structures, and products for systems **5-7** and **9** were fully optimized using the B3LYP/6-31+G* method. Complexes for systems **5** and **8** were also fully optimized with B3LYP/6-31+G*. The transition structure for system **8** could not be located with DFT, so a B3LYP/6-31+G* single point calculation on the RHF/6-31+G* geometry was performed. Computations were carried out using GAUSSIAN94[7] and GAUSSIAN98.[8] To assess the aromatic properties of the transition states, NICS values were calculated with GIAO-SCF/6-31+G* on B3LYP/6-31+G* geometries.[4]

Results

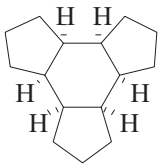
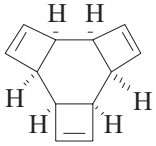
The [2+2+2]-cycloreversion of the all-*cis* tris-cyclopropacyclohexane, **1**, and the mono and bis analogs were studied previously at the B3LYP/6-31G* level.[1] Cycloreversions of the *cis* mono-, bis-, and tris-cyclobutacyclohexane, **3**, were also studied and were found to have activation barriers which are 18-28 kcal·mol^{-1} higher than the corresponding cyclopropacyclohexanes even though the reactions of the cyclobuta fused systems were only 3-7 kcal·mol^{-1} less exothermic. *Cis* mono-, bis-, and tris-cyclopentacyclohexanes were examined and found to have activation barriers that were lower than the cyclobuta-fused compounds based on their heats of reaction. In order to understand this oscillating trend of activation barrier with increasing ring size, NICS values were calculated at the center of cyclohexane rings and also in the center of the cyclopropane, cyclobutane and

Table 1 (continues next page) *NICS values for concerted cycloreversion systems*

Reactant	TS Center [a]	TS Small Ring [b]	Reactant Center [a]	Reactant Small Ring [b]	Product [a]
	-27.0		-2.1		
	-25.2	-29.4	-4.6	-43.7	
	-28.0	-36.1	-6.4	-43.7	
	-30.2	-39.4	-10.0	-44.3	-0.4
	-25.5	2.2	-1.9	-2.6	
	-25.3	1.3/2.6[c]	-1.9	1.2/-0.1[c]	
	-25.3	2.5	-1.7	-1.4	-1.6
	-26.5	-6.0	-2.7	-5.6	
	-26.2	-4.5/-6.6[d]	-2.9	-5.4	-0.5

[a] NICS value at the center of the 6 carbon atoms of the cyclohexane ring
[b] NICS value at the center of the cyclopropane, cyclobutane, or cyclopentane, or cyclobutene ring
[c] Two NICS values are given, one for the center of each cyclobutane ring
[d] Two NICS values are given, one for the center of each cyclopentane ring

Table 1 (continued) *NICS values for concerted cycloreversion systems*

Reactant	TS Center [a]	TS Small Ring [b]	Reactant Center [a]	Reactant Small Ring [b]	Product [a]
	-27.3	-4.4	-2.6	-5.2	-1.7
	-25.2	0.4	-2.7	-0.5	-1.1
			-42.9 [b]		
			-0.3 [b]		
			-5.6 [b]		

[a] NICS value at the center of the 6 carbon atoms of the cyclohexane ring
[b] NICS value at the center of the cyclopropane, cyclobutane, or cyclopentane, or cyclobutene ring
[c] Two NICS values are given, one for the center of each cyclobutane ring
[d] Two NICS values are given, one for the center of each cyclopentane ring

cyclopentane fused rings in reactants, transition structures, and products.

Table 1 shows the NICS values from our previous work for **1** and **3** and also their mono- and bis- substituted analogs, in addition to the mono-, bis-, and tris- substituted cyclopentane, and tris- substituted cyclobutene. The NICS values for cyclopropane, cyclobutane, and cyclopentane are also given. The NICS values reveal that cyclohexanes fused with cyclopropane and cyclopentane are the most aromatic, i.e. have the highest negative NICS values. This trend goes across reactants, transition states, and products. In the center of the tetramethylene fragment of the cyclobutane-fused cyclohexanes and the tris-cyclobutenacyclohexane transition structures, the NICS value is positive. Schleyer has noted that the NICS value in a cyclopropane ring may be inflated due to the close proximity of the σ bonds, however the qualitative trends should still be valid.[4c] That is the three- and five- membered rings are aromatic and the cyclobutanes are antiaromatic. The cyclopropane rings have large negative NICS values which are still quite large in the transition state. While the through-bond coupling increases in the transition state because of the narrowing HOMO-LUMO gap itself as well as the increasing size of the ring, the increase in ring size causes the absolute value of the NICS to decrease along the reaction coordinate. Nevertheless, comparisons of the cyclopropane-, cyclobutane-, and cyclopentane-fused systems provide a clear pattern reflecting aromatic, antiaromatic, and non-aromatic contributions from the fused rings.

The nucleophilic ring opening of cyanocyclopropane, **5**, by the hydroxide ion was studied. Geometries for reactant, complex, transition structure, and product are shown in Figure 1. The transition structure is early with a O-C bond forming distance of 2.20 Å and a short C-C bond cleavage distance of 1.85 Å. The relative energies of the complex, transition state, and product are shown in Table 2. The complex is 17.7 kcal·mol^{-1} lower than the isolated reactants, due to the anion-dipole attraction. Although the activation energy for this ring-opening reaction is negative compared to the energy of isolated reactants, 11.0 kcal·mol^{-1} is required to reach the transition structure from the reactant complex. The transition structure lies 6.7 kcal·mol^{-1} lower than the isolated reactants, and the energy of reaction is -37.1 kcal·mol^{-1}.

Reactant, transition structure, and product for the nucleophilic ring opening of cyanocyclobutane, **6**, by the hydroxide ion are shown in Figure 2. A reactant complex for this system was not found. The transition structure is 0.9 kcal·mol^{-1} higher than the isolated reactants. The transition state is later than for the cyanocyclopropane ring opening; for cyano-

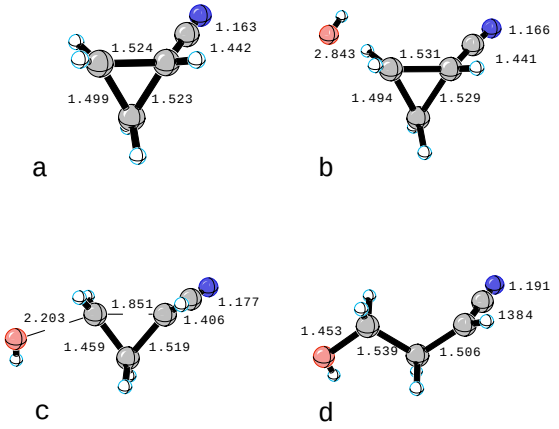


Figure 1 *B3LYP/6-31+G* optimized geometries of (a) cyanocyclopropane, (b) hydroxide anion-cyanocyclopropane complex, (c) transition structure, (d) 1-cyano-3-hydroxypropyl anion*

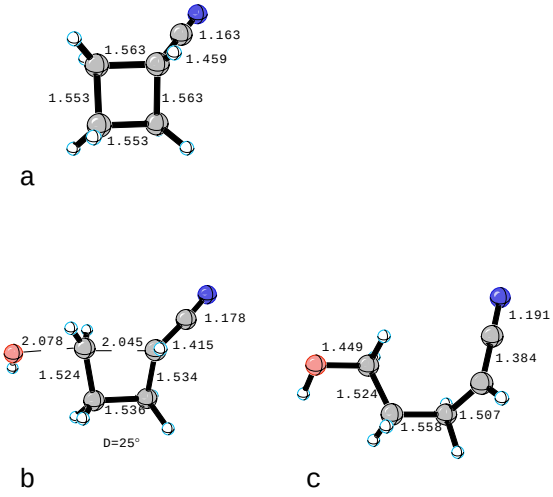


Figure 2 *B3LYP/6-31+G* optimized geometries of (a) cyanocyclobutane, (b) transition structure, (c) 1-cyano-4-hydroxybutyl anion*

cyclobutane the C-C cleaving bond distance is 2.04 Å. The reaction is exothermic with an energy of reaction of -33.9 kcal·mol^{-1}. The activation barrier for the cyclobutane ring-opening relative to isolated reactants is 7.6 kcal·mol^{-1} higher than for the cyclopropane ring-opening. These data are in agreement with our results in the [2+2+2] cycloreversion of cyclopropa- and cyclobuta- cyclohexanes. The cyanocyclopropane has a 7.6 kcal·mol^{-1} lower activation energy for bond breaking, but is more exothermic overall by 3.2 kcal·mol^{-1}.

The cleavage of the side bond in 2-cyanobicyclobutane, **7**, is exothermic, ΔH_{rxn} = -48.9 kcal·mol^{-1}. The reactant, transition structure and product for this ring opening are shown in Figure 3. The transition structure is early, with an O-C bond forming distance of 2.20 Å. The C-C bond breaking distance is 1.90 Å. The transition structure lies 2.2 kcal·mol^{-1} below the reactants.

Hoz et al. examined this reaction at the RHF/6-31+G* level.[3] Relative to a reactant complex, the activation barrier was 30.6 kcal·mol^{-1} and the heat of reaction was -34.0

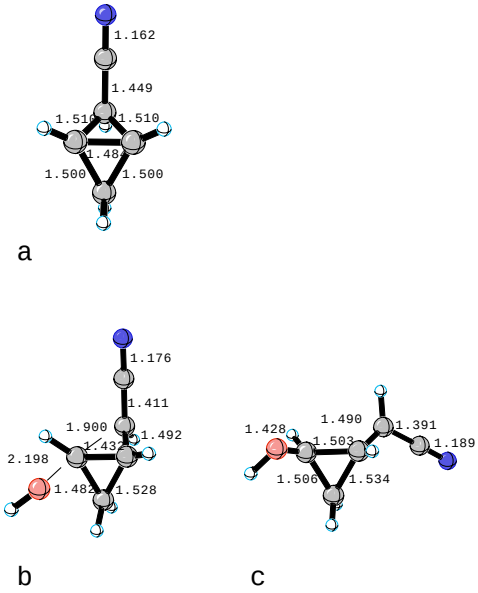


Figure 3 *B3LYP/6-31+G* optimized geometries of (a) 2-cyanobicyclobutane, (b) transition structure, (c) 2-hydroxycyclopropylcyanomethyl anion*

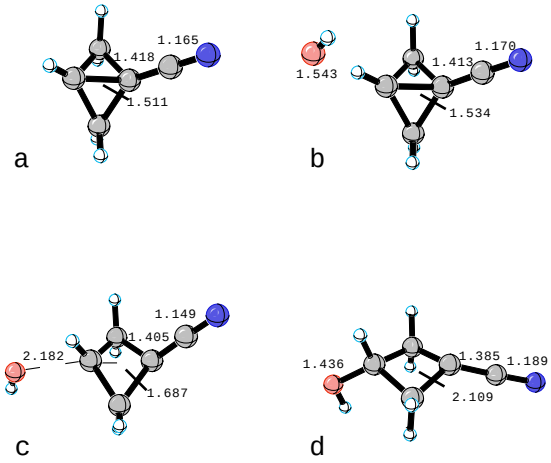


Figure 4 *B3LYP/6-31+G* optimized geometries of (a) 1-cyanobicyclobutane, (b) complex, (c) RHF/6-31+G* transition structure, (d) B3LYP/6-31+G* 3-cyanohydroxylcyclobutanyl anion*

Table 2 *B3LYP/6-31+G* Zero Point Corrected Activation Energies and Energies of Reaction for Nucleophilic Ring Opening Reactions (kcal·mol^{-1})*

System[a]	Reactant	Complex	TS	Product
5	0.0	-17.7	-6.7	-37.1
6	0.0		0.9	-33.9
7	0.0		-2.2	-48.9
8	0.0	-25.4	-17.3[b]	-49.4
9	0.0		2.0	-41.5

[a] Numbers refer to the respective compound in Scheme 2
[b] B3LYP/6-31+G//RHF/6-31+G**

kcal·mol^{-1}. At this level of theory, the activation barrier relative to the isolated reactants is 12.0 kcal·mol^{-1} and the heat of reaction is -52.6 kcal·mol^{-1}.

Reactant, complex, transition structure, and product of central bond cleavage in 1-cyanobicyclobutane, **8,** are shown in Figure 4. The activation energy is based on the B3LYP/6-31+G* single point calculation on the RHF/6-31+G* geometry and will therefore be underestimated. Even in spite of this approximation, the activation energy for cleavage of the central bond in **8** is 15.1 kcal·mol^{-1} lower than the energy for cleavage of the side bond in **7**. The heat of reaction for **8** is -49.4 kcal·mol^{-1}, which is similar to **7**.

This system was also studied by Hoz et al. at the RHF/6-31+G* level.[3] The activation barrier relative to a reactant complex is 4.4 kcal·mol^{-1}, and the heat of reaction is -38.3 kcal·mol^{-1}. When isolated reactants are used to compute the activation barrier, it is -9.5 kcal·mol^{-1}. The heat of reaction computed using isolated reactants is -52.2 kcal·mol^{-1}. The difference in activation barrier for cleavage of the side and central bond at the RHF/6-31+G* level relative to isolated reactants is 21.4 kcal·mol^{-1}. This is in close agreement to the $\Delta\Delta E^{\ddagger}$ at the B3LYP/6-31+G*, 19.5 kcal·mol^{-1}. The difference in product energy of the side and central bond, relative to isolated reactants, is 0.4 kcal·mol^{-1} at the RHF/6-31+G* level. This is nearly identical to the $\Delta\Delta E_{rxn}$ using B3LYP/6-31+G*, 0.5 kcal·mol^{-1}.

To provide a comparison with a system having two cyclobutane moieties, Figure 5 shows the reactant, transition structure, and product for 2-cyanobicyclohexane, **9**. This nucleophilic ring opening involves cleavage of the side bond as in 2-cyanobicyclobutane, **7**. The transition structure for the ring opening of 2-cyanobicyclohexane by hydroxide lies 2.0 kcal·mol^{-1} above the isolated reactants. The reaction is exothermic by -41.5 kcal·mol^{-1}. A transition structure corresponding to cleavage of the central bond in cyanobicyclohexane was not located successfully.

NICS values for systems **5-8** are given in Table 3. The NICS values at the centers of the cyclopropane rings of reactants, transition structures, and products, are large and negative, typical of aromatic systems. In cyanocyclobutane, **6**, and 2-cyanobicyclohexane, **9**, the ring opening transition structure have NICS values that are close to zero, as in non-aromatic systems. The heightened aromaticity of transition structure of cyanocyclopropane may account for its more facile ring opening compared to cyanocyclobutane. The NICS values at the center of the rings in the transition structure of 1-cyanobicyclobutane, **7**, are slightly more negative than for the transition structure of 2-cyanobicyclobutane, **8**. The more negative NICS values of the 1-cyanobicyclobutane transition structure, reflect the doubly activated nature due to the two trimethylene fragments.

Discussion

The HOMO and LUMO of a breaking σ bond (a), and the Sandorfy-Daudel C-approximation [9] σ orbitals of trimethylene (b), and tetramethylene (c) chains are shown in Figure 6. The LUMO of the breaking σ bond is of the correct symmetry to overlap with the HOMO of the trimethylene frag-

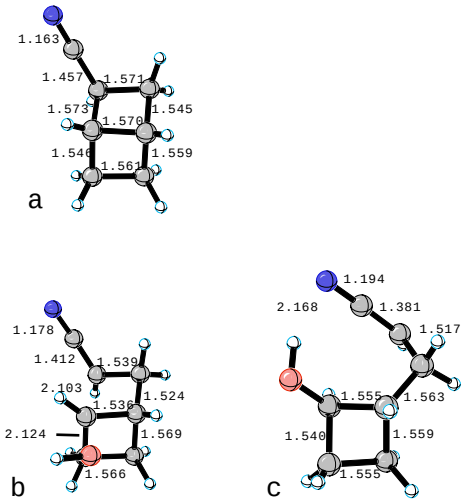


Figure 5 *B3LYP/6-31+G* optimized geometries of (a) 2-cyanobicyclohexane, (b) transition structure, (c) 2-hydroxycyclobutylcyanoethyl anion*

Table 3 *NICS values of at the centers of rings in nucleophilic ring-opening reactions*

System[a]	Reactant	Complex	TS	Product
5	-44	-44	-38	-26
6	-2.0		-3.9	-18
7 [b]	-49/-49		-38/-42	-41/-39
8 [b]	-50/-50	-50/-50	-42/-42[d]	-13/-23
9 [c]	1.4/2.2		2.2/-5.0	-12/-8.0

[a] Numbers refer to the respective compound in Scheme 2
[b] Two NICS values are given, one for the center of each cyclopropane ring
[c] Two NICS values are given, one for the center of each cyclobutane ring
[d] B3LYP/6-31+G//RHF/6-31+G**

ment. The HOMO of the breaking σ bond can likewise interact with the LUMO of the trimethylene fragment. These are stabilizing two-electron interactions. The HOMO of the tetramethylene fragment is symmetric; of the same symmetry as the HOMO of the breaking bond. This is a four-electron destabilizing interaction.

These orbital interactions influence the energetics of both [2+2+2]-cycloreversions of cyclopropane or cyclobutane fused cyclohexanes and the ring opening reactions studied here. In the [2+2+2]-cycloreversions these orbital effects are most dramatically illustrated in the 25 kcal·mol^{-1} stabilization in the transition state present in *cis*-tris-cyclopropane-fused cyclohexane derivatives, **1**, relative to *cis*-tris-cyclobutane fused cyclohexanes, **3**. The more facile ring opening of cyanocyclopropane relative to cyanocyclobutane can also be accounted for using this orbital explanation. In the case of side bond cleavage of 2-cyanobicyclobutane, **7**, there is a stabilizing effect due to the presence of the trimethylene fragment. A concurrent destabilizing effect occurs due to the tetramethylene fragment and a less facile ring opening relative to central bond cleavage results. Cleavage of the central bond of 1-cyanobicyclobutane, **8**, is doubly stabilized. In the transition structure of **8**, there are two trimethylene fragment HOMOs which have the correct symmetry so they can interact with the breaking σ LUMO. The LUMOs of the trimethylene fragment can also interact with the HOMO of the breaking σ bond. The net effect of this stabilization is a very facile ring-opening reaction with an activation energy of -17.3 kcal·mol^{-1}. Cleavage of the side bond of 2-cyanobicyclohexane, **9**, is even more unfavorable than side bond cleavage of 2-cyanobicyclobutane, **7**. In the transition state for ring-opening of 2-cyanobicyclohexane, a tetramethylene fragment is cleaved. The HOMO of the tetramethylene fragment and the HOMO of the breaking σ bond will interact in a destabilizing fashion, and this is reflected in the positive activation barrier for this reaction. Haddon used similar orbital interaction arguments to explain the preference of a cyclopropane unit over a cyclobutane unit as a homoaromatic linkage.[10]

Sella, Basch, and Hoz proposed an alternative analysis to explain the more facile ring opening of 1-cyanobicyclobutane.[3] The LUMO of the central bond in 1-cyanobicyclobutane is lower in energy than the LUMO of the side in 2-cyanobicyclobutane. The HOMO-LUMO gap between hydroxide and 1-cyanobicyclobutane will be smaller, and thus result in faster ring cleavage. The frontier molecular orbital arguments proposed by Hoz, while valid, are limited to only these particular nucleophilic reactions. In the case under consideration, there is a parallel between the LUMO energy of the reactant and the aromaticity of the transition state. This can be considered to be a result of the favorable distortion which results from aromaticity, results in bond stretching, and lowers the LUMO energy. Indeed, the two explanations may be parallel, but the transition state aromaticity appears to us to be the origin of the effect.

Considerations of orbital interactions through bonds provide a general approach that can be applied to the nucleophilic ring opening reactions of 1- or 2-cyanobicyclobutane studied here, [2+2+2]-cycloreversions of fused cyclohexanes,[1] radical ring cleavage reactions,[11] the intramolecular S_N2 reactions of Mandolini,[2c] the heterolytic Grob fragmentation,[12] the Birch reductions of Paddon-Row and Hartcher,[13] and the carbanion cyclizations of Stirling.[14]

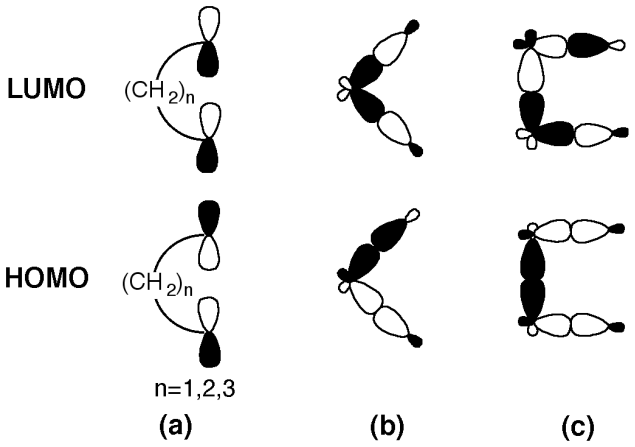


Figure 6 *Schematic representation of HOMO and LUMO of (a) a cleaving s bond in the transition state, (b) trimethylene, and (c) tetramethylene*

Conclusions

The general nature of orbital interactions through bonds has been extended to include nucleophilic ring opening reactions of cyano substituted small ring systems. OITB can explain the greater reactivity of central bond cleavage compared to side bond cleavage in 1- and 2- cyanobicyclobutane, respectively. This theory also accounts for the more facile ring opening of cyanocyclopropane vs. cyanocyclobutane. NICS values at the transition state centers are more negative in the systems which undergo facile ring cleavage, providing supporting evidence for OITB.

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Supplementary material Two supplementary figures contain the geometries of alternate product conformers of **5** and **6**. Gaussian archive records for molecules **1-5** and conformers of **5** and **6** are available as text files.

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