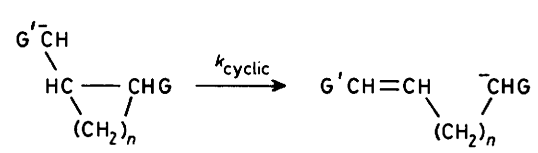
An *Ab initio* Theoretical Study of the Eliminative Ring Fission in Cyclopropylmethanide and Cyclobutylmethanide

Glauco Tonachini *
Istituto di Chimica Organica della Universita' di Torino, via Pietro Giuria 7, 10125 Torino, Italy
Fernando Bernardi
Istituto di Chimica Organica della Universita' di Bologna, via Selmi 2, 40126 Bologna, Italy
H. Bernhard Schlegel †
Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.
Charles J. M. Stirling
Department of Chemistry, University of North Wales, Bangor, Gwynnedd LL57 2UW

Ab initio computations of the eliminative ring fission of cyclobutylmethanide and cyclopropylmethanide have been performed by completely optimizing the stable geometrical structures of the cyclic and open-chain minima as well as the transition structures for ring opening. These results show that the transition state for the four-membered ring opening occurs later (in a geometrical sense) along the reaction path than for the three-membered ring opening, and that the difference in activation energy is negligibly small. The strain energy of cyclobutylmethanide is nearly equal to cyclopropylmethanide, but is released more gradually during the opening of the four-membered ring. The acceleration of ring fission due to ring strain is substantial and of comparable magnitude in the two ring openings, corresponding to a release of about three fourths of the initial strain energy in the transition states.

Recently the reactivity of substituted cyclopropanes and cyclobutanes in eliminative ring-opening reactions (Scheme 1) has been studied experimentally.[1–3]



G = CN, SO_2Ph ; G′ = SO_2Ph

$n = 1, 2$

Scheme 1.

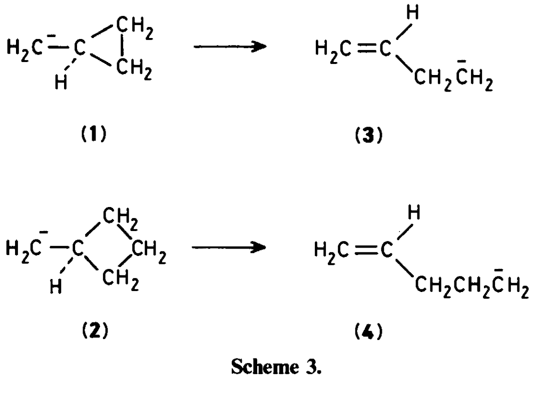
The compounds studied were substituted by electron-withdrawing groups on the carbon atoms bearing a negative charge. Comparison with acyclic analogues (Scheme 2) has allowed us to estimate the contribution of ring strain to the acceleration of the ring-fission process.

$$G'^{-}CH-CH_2-CH_2G \xrightarrow{k_{\text{acyclic}}} G'CH{=}CH_2 + {}^{-}CH_2G$$

Scheme 2.

In all cases a rate enhancement (k_{cyclic} *vs.* k_{acyclic}) has been observed relative to elimination in open-chain analogues. For example, when the electron-withdrawing substituent G on the leaving carbon atom is SO_2Ph, the measured ratio $k_{\text{cyclic}}/k_{\text{acyclic}}$ is 10^9 for cyclopropane ($n = 1$), and 10^5 for cyclobutane ($n = 2$). The result that ring fission is (a) substantially accelerated in strained cyclic compounds and (b) appreciably slower in cyclobutanes than in cyclopropanes has been rationalized in terms of the strain energy released during the ring opening.[1] Comparison with the open-chain analogues suggests that about 46% of the strain energy is released at the transition state for the three-membered ring compound and about 26% for the four-membered ring compound [1b] (the initial strain energies are very similar). These values are assumed to correspond at the transition state to a bond elongation of *ca.* 0.32 Å for the three-membered ring and of *ca.* 0.25 Å for the four-membered ring,[1b] suggesting that a similar degree of bond extension would be accompanied by a smaller release of strain energy in the four-membered ring, in agreement with the experimental activation enthalpies.[1] For other substituents the degree of ring cleavage at the transition state changes and consequently the fraction of ring strain released is different.[3]

In order to obtain a better understanding of these reactions a theoretical study of the gas-phase ring-fission reaction of unsubstituted (G = G′ = H) three- and four-membered rings has been performed. The molecules studied, shown in Scheme 3, are the cyclopropylmethanide (**1**) and the cyclobutylmethanide (**2**).



Scheme 3.

The purpose here is to obtain information about the activation energies of the two model reactions, the geometrical features of the transition states, and the release of strain energy during the ring opening.

The strain energy of the reactants and transition structures for ring opening is evaluated by studying (Scheme 4) an acyclic analogue to the process of Scheme 3.

In this model reaction CH_3^- is eliminated from a molecule

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† Camille and Henry Dreyfus Teacher-Scholar.

$$H_2\bar{C}-CH_2-CH_3 \longrightarrow H_2C{=}CH_2 + \bar{C}H_3$$

(5)

Scheme 4.

'without strain' (**5**), where the $-(CH_2)_n-$ part of (**1**) and (**2**) is replaced by two hydrogens.

Method

The geometries of the minima and transition structures for the processes shown in Schemes 3 and 4 were optimized by gradient methods at the Restricted Hartree–Fock (RHF) level of theory using the 3-21G split-valence shell basis set.[4a] For anionic species, diffuse *s* and *p* functions on non-hydrogen atoms are essential for a correct description of the energetics.[4d,5] Furthermore *d*-type polarization functions are crucial for estimating isomerization energies of cyclic and open-chain compounds.[6] Hence the RHF energies were recomputed using the 3-21G geometries and the following basis sets: (a) split-valence shell 6-31G;[4b] (b) 6-31G*,[4c] containing *d* functions on carbon atoms; (c) 6-31+G,[4d] containing diffuse functions on the carbon atoms; (d) 6-31+G*,[4d] containing both diffuse and polarization functions. Second-order Møller–Plesset perturbation theory (MP2) was used to evaluate the electron correlation correction,[7] in conjunction with the basis sets (a)—(c). These data provided an estimate of the MP2 correction for the best basis set (d). At the RHF level the effects of diffuse and polarization functions are almost additive; an estimate based on additivity overestimates the actual overall energy difference by only 0.3—0.7 kcal mol^{-1}.* If a similar degree of additivity is assumed for the correlation corrections (E2), the MP2/6-31+G* energies can be estimated from the MP2 data computed with the 6-31G, 6-31G*, and 6-31+G basis sets using equations (1) and (2):

$$\text{Est.E2}(6\text{-}31+G^*) = \text{E2}(6\text{-}31G^*) + \text{E2}(6\text{-}31+G) - \text{E2}(6\text{-}31G) \quad (1)$$

$$\text{Est.E(MP2}/6\text{-}31+G^*) = \text{E(RHF}/6\text{-}31+G^*) + \text{Est.E2}(6\text{-}31+G^*) \quad (2)$$

In the next section the RHF results obtained with the basis set (d), including both diffuse and polarization functions, will be discussed together with the related MP2 values, estimated as in (2).

The computations have been performed using the GAUSSIAN80 and GAUSSIAN82 series of programs[8] on an OH-5560 computer at CSI-Piemonte (Torino, Italy), on a VAX-11/780 at Facolta' di Chimica Industriale (Bologna, Italy), and on a VAX-11/780 at Wayne State University (Detroit, U.S.A.).

Results and Discussion

The eliminative ring-opening processes shown in Scheme 3 have been studied by determining the relevant stable structures and transition structures. The optimized geometries of the cyclic minima (**1**) and (**2**), open-chain minima (**3**) and (**4**), and of the transition structures for ring fission are shown in Figures 1 and 2; only the internal co-ordinates relevant to the carbon atoms are reported.† The relative energies of these critical points are reported in Table 1.

Table 1. Relatives energies[a]

Level of theory	RHF	MP2[b]
3-Membered ring		
(**1**)	0.00	0.00
Transition structure	10.44	7.68
(**3**)	−8.01	−1.30
4-Membered ring		
(**2**)	0.00	0.00
Transition structure	11.22	7.06
(**4**)	−7.83	−1.11
Unstrained model		
(**5**)	0.00	0.00
Transition structure	29.51	28.92
Complex	17.82	24.51
Dissociation limit	19.47	26.76

[a] kcal mol^{-1}; 6-31+G*//3-21G computations. [b] From estimated energies [see equations (1) and (2)].

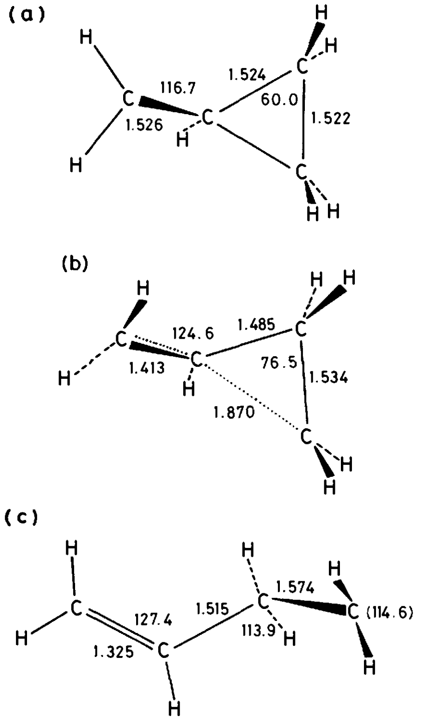

Figure 1. (a) The cyclopropylmethanide, (b) the transition structure for the three-membered ring opening, and (c) the open-chain product (fully optimized at the RHF/3-21G level). Bond lengths in (Å) and bond angles in (°)

It is found that in both reactions the open forms are more stable than the cycles (Table 1). However, the reactions are less exothermic at the MP2 level than at the RHF level (the correlation correction is more effective in lowering the energy of the cyclic structures than that of the open-chain structures ‡

At the RHF level the barriers to ring opening are 10.4 kcal mol^{-1} for the three-membered ring and 11.2 kcal mol^{-1} for the four-membered ring. The estimated MP2 values of the barriers

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* 1 kcal = 4.814 kJ.

† The complete set of optimized geometrical parameters and related total energies is available on request to the authors.

‡ The finding that correlation preferentially stabilizes the 'more crowded' situations is not limited to the present case. Compare J. S. Binkley and J. A. Pople, *Chem. Phys. Lett.*, 1977, **45**, 197 and F. Bernardi, M. A. Robb, and G. Tonachini, *Chem. Phys. Lett.*, 1979, **66**, 195.

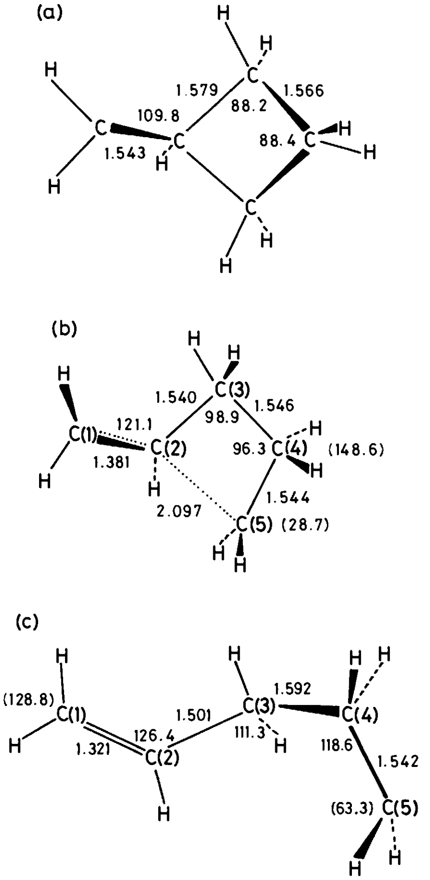

Figure 2. (a) The cyclobutylmethanide, (b) the transition-state structure for the four-membered ring opening, and (c) the open-chain product (fully optimized at the RHF/3-21G level). Bond lengths in (Å) and bond angles in (°)

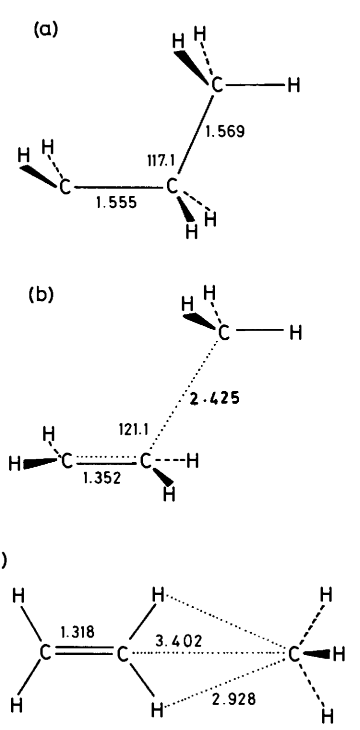

Figure 3. 'Unstrained' model: (a) propan-l-ide, (b) the transition-state structure and (c) the complex (fully optimized at the RHF/3-21G level). Bond lengths in (Å) and bond angles (°)

are substantially lower *ca.* 7.7 and 7.1 kcal mol^{-1} respectively. Therefore both levels of theory indicate that the two processes occur with very similar activation energies; at the RHF level the three-membered ring opening is favoured by 0.8 kcal mol^{-1}, while at the MP2 level the four-membered ring opening is favoured by 0.6 kcal mol^{-1}. The effect of electron correlation, introduced at the MP2 level, results in a pronounced stabilization of the transition structures relative to the minima, *i.e.* in an overall flattening of the energy profile for the process of ring opening.

The release of strain energy plays a central role in the rate enhancement of the ring-opening process.[1] In order to estimate the strain energy for the two cyclic compounds and to assess how much of the strain energy is released in the transition states, the acyclic analogue to the ring-opening process of Scheme 3 has been studied (Scheme 4). In addition to the linear chain minimum (**5**), the transition structures for dissociation and the dissociation limit geometries, another minimum on the energy hypersurface, corresponding to a complex, has been found (Figure 3).* The relative energies of the critical points for this model reaction are also reported in Table 1.

The strain energy (ΔE_s) can be estimated by comparing the heat of reaction for the ring openings of Scheme 3 to the energy differences in the dissociation process shown in Scheme 4. The heat of reaction for the reference acyclic model (ΔE_{model}) can be computed in two ways; (A) by choosing the dissociation limit as product, or (B) by choosing the complex as product. If the dissociation limit is used, there are no interactions between the anionic centre (CH_3^-) and the remaining parts of the system, while these interactions are present in the products of the ring-opening reaction, (**3**) and (**4**). In contrast, if the complex is selected as the product of the reference acyclic reaction, there is a strong electrostatic interaction of CH_3^- with two hydrogens of C_2H_4, not present in (**3**) and (**4**). Thus, both references are somewhat arbitrary and the related strain-energy values, ΔE_s^A and ΔE_s^B, could be considered as two extreme values. They can be estimated by the following formulae:

$$\Delta E_s^A = \Delta E_{model}^A - \Delta E_{cyclic} \qquad (3)$$

$$\Delta E_s^B = \Delta E_{model}^B - \Delta E_{cyclic} \qquad (4)$$

The strain energies released in the transition structures can be approximated in a similar manner:

$$\Delta E_s^{\ddagger} = \Delta E_{model}^{\ddagger} - \Delta E_{cyclic}^{\ddagger} \qquad (5)$$

where the $\Delta E^{\ddagger}$s are the energy differences between transition structures and reactants. The strain energies and the percent of strain energy released in the transition structures, $\Delta E_s^{\ddagger}/\Delta E_s^A \times 100$ or $\Delta E_s^{\ddagger}/\Delta E_s^B \times 100$, are given in Table 2. Strain energies computed using equation (4) (reference B) are less sensitive to the level of theory. The strain energies computed for the cyclic compounds are in reasonable agreement with the experimental data on cyclopropane and cyclobutane.[9,10] The calculated percent of strain energy released at the transition state appear to be rather large, ranging from *ca.* 70% at the RHF level to *ca.* 80% at the MP2 level.

The information provided by Table 2 is qualitatively the same whichever the choice (A or B) for the reference, as will be presently discussed in connection with the different position of the two transition structures on the reaction path.

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* See footnote * on p. 706.

Table 2. Strain energies[a]

Level of theory	RHF[b]	MP2[b,c]
3-Membered ring		
ΔE_s^A	27.48	28.06
ΔE_s^B	25.83	25.81
$\Delta E_s^{\ddagger}$	19.07	21.24
$\%\Delta E_s^A$(T.S.)	69	76
$\%\Delta E_s^B$(T.S.)	74	82
4-Membered ring		
ΔE_s^A	27.30	27.87
ΔE_s^B	25.65	25.62
$\Delta E_s^{\ddagger}$	18.29	21.86
$\%\Delta E_s^A$(T.S.)	67	78
$\%\Delta E_s^B$(T.S.)	71	85

[a] kcal mol^{-1}; the computed values can be compared with the experimental values for cyclopropane (27.6[9] or 27.4[10] kcal mol^{-1}) and for cyclobutane (26.2[9] or 26.0[10] kcal mol^{-1}). [b] 6-31+G*//3-21G computations. [c] From estimated energies [see equations (1) and (2)].

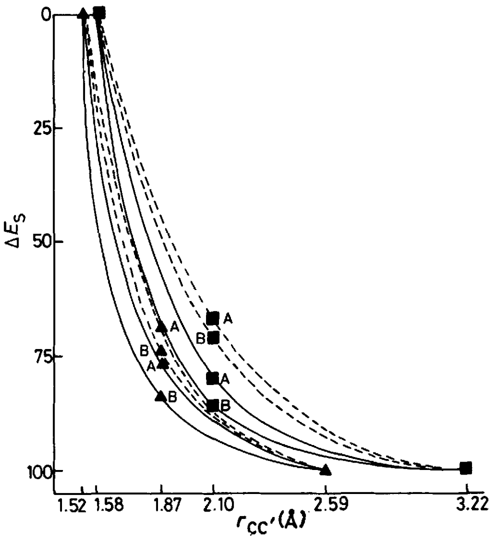

Figure 4. Percentage of strain energy released during ring opening plotted as a function of the distance between the two carbons atoms involved in the bond being broken [r(CC′)]. Triangles: 3-ring opening; squares: 4-ring opening. Solid lines: MP2/6-31+G* values; dashed lines: RHF/6-31+G* values. 'A-values': strain energies computed using equation (3); 'B-values': strain energies computed using equation (4)

Considering the MP2 estimated energies, a slightly larger percent of the initial strain energy (2.2—2.5%) is released at the four-membered ring-opening transition state, with respect to the three-membered ring, corresponding to a slightly easier opening of the four-membered ring ($\Delta\Delta E^{\ddagger}$ 0.62 kcal mol^{-1}). At the RHF level the percent of strain energy released at the transition state is again almost the same for (**1**) and (**2**), but the small difference (2.4—2.5%) goes now in the opposite direction, corresponding to a difference in activation energies $\Delta\Delta E^{\ddagger}$ 0.78 kcal mol^{-1} in favour of the three-membered ring opening.

These values should be considered in conjunction with the different position of the two transition states on the ring-opening reaction paths (Figures 1—3). It can be seen in Figures 1(b) and 2(b) that the two transition-state structures occur at different values of r(CC′) the distance for the carbon–carbon bond being broken;* the elongation from the value in the cyclic minima is +0.35 Å (+23% of the initial value) for the three-membered ring and +0.52 Å (+33% of the initial value) for the four-membered ring. Of course, the later occurrence (in a geometrical sense) of the four-membered ring transition structure is also reflected in the values assumed by other geometrical parameters; for instance the C^-–C bond in the cycle, evolving to a double bond in the product, has a bond length in the transition-state structure corresponding to 56% of the total shortening in the three-membered ring opening (Figure 1), but to 73% in the four-membered ring opening (Figure 2).†

For qualitative purposes the reaction co-ordinate can be roughly approximated by r(CC′). When the percentage of strain energy released in the ring opening is plotted *versus* r(CC′) (Figure 4), it is apparent that strain is relaxed more gradually in the four-membered ring opening. This is in agreement with an earlier interpretation[1a] of the effects of strain energy on ring fission. Although the release of strain energy for the four-membered rings is more gradual than in the three-membered ring, the strain energies released in the corresponding transition-state structures are very similar, because the four-membered ring transition-state structure occurs later (in a geometrical sense) on the reaction path.

The results of the present theoretical study can now be compared with the relevant experimental data. The computed 'gas-phase' activation energies (7—11 kcal mol^{-1}) are smaller than the experimental activation enthalpies (18—25 kcal mol^{-1} for the three-membered ring opening and 29—31 kcal mol^{-1} for the four-membered ring opening).[1,3] The experimental values were obtained for cyclic compounds substituted with electron-withdrawing groups (G = CN, SO_2Ph) in ethanolic sodium ethoxide. A substituent G on the carbon atom bearing a formal negative charge in the open-chain products (C′) stabilizes the open-chain product carbanions and should also stabilize to some extent the transition state (which has a partial negative charge on C′) relative to the cyclic minimum (C′ uncharged); but this relative stabilization is not expected to occur if the carbon atom bearing the negative charge in the cyclic compound is substituted in the same way (Scheme 1). In this case the situation should not be very different from the unsubstituted case from the point of view of the activation energies. On the other hand the polar solvent preferentially stabilizes the carbanionic minima, where the charge is rather localized, with respect to the transition states, where the charge is more delocalized, thus raising the barrier. Comparing the present 'gas-phase' computational data on unsubstituted compounds with the experimental data, the solvent effect seems to be at the origin of the significantly higher experimental activation enthalpies.

The rate enhancement for the cyclic structures can be evaluated from the difference in the barrier heights of the cyclic and acyclic compounds, *i.e.* from the strain energy released in the transition structure. Without taking into account entropy, the values range for the three-membered ring from 10^{14} at the RHF level to 10^{15} at the MP2 level, and for the four-membered ring from 10^{13} at the RHF level to 10^{16} at the MP2 level. These figures compare with a factor of *ca.* 10^9 found experimentally for substituted compounds in EtOH–EtONa solution.[1b] The

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* The extent of ring fission in the transition state does not depend only on the ring structure; it is known from experimental data[3] to be sensitive to the nature of the stabilizing substituents on the leaving C′RR′ group. Thus, the strain energy is released in different amounts depending on the substituents on C′.

† It is interesting to note that in the model reaction of Scheme 4, where the elimination proceeds without release of ring strain, the transition-state structure occurs at an even longer C–C′ distance (Figure 3), corresponding to an elongation of 0.86 Å (+55% of the initial value); the $^-$C–C bond in (**5**) (Scheme 4) undergoes at the transition structure a shortening corresponding to 86% of the total.

calculated percent of strain energy released at the transition structure, *ca.* 70% (RHF) to *ca.* 80% (MP2), is considerably larger than the experimental estimates[1b,2] which range from 46% for cyclopropanes to 26% for cyclobutanes.

Conclusions

The purpose of the present theoretical study on the two model reactions shown in Scheme 3 is to obtain information about the activation energies, the release of strain energy during the process of ring opening and the geometrical features of the transition structures.

The release of strain energy as a function of the degree of ring opening is slower in the four-membered ring than in the three-membered ring, both in the experimental study[1] (where fission of molecules substituted with electron-withdrawing groups on the carbanionic centre takes place in ethanolic sodium ethoxide) and in the present theoretical 'gas-phase' study on unsubstituted rings (Figure 4).

Nonetheless the strain energy released in the two transition structures is almost the same. This happens because the four-membered-ring opening transition structure occurs later (in a geometrical sense) along the reaction path than the three-membered-ring opening transition structure, due to the more gradual release of strain energy.

For both the three-membered and the four-membered rings, the computed 'gas-phase' activation energies are significantly lower than the activation enthalpies reported for the reaction in solution (and the calculated values for strain energy released at the transition state are larger than the values estimated in the experimental study). The polar solvent is thought to play a role in raising the barrier to the ring-opening reaction, preferentially stabilizing the cyclic minima, where the charge is more localized, with respect to the transition states, where it is more delocalized.

The activation energies for the two ring openings differ negligibly, while in the experimental study the activation enthalpies for the four-membered ring opening are *ca.* 6 kcal mol^{-1} higher than for the three-membered ring opening.

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