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Cycloreversion Reactions for Five to Seven Membered Rings

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The cycloreversion of the following ring systems was studied: (1) Cyclopentyl anion → allyl anion + ethylene, (2) Cyclohexene → butadiene + ethylene, (3) Cyclohept-4-enyl cation → butadiene + allyl cation. The potential energy surfaces of these reactions were investigated by the semiempirical MO method SINDO1 under inclusion of a 4×4 CI. All internal coordinates were varied. We found major differences in the nature and geometry of transition states and intermediates of these reactions. Diradical character is involved only in the fragmentation of the six membered ring.

Key words: Cycloreversion of rings.

1. Introduction

The Diels–Alder reaction of butadiene with ethylene to form cyclohexene has been the subject of many theoretical investigations. Dewar et al. [1] found a highly asymmetrical diradicaloid transition state with MINDO/3. Later *ab initio* calculations by Salem et al. [2] and Leroy et al. [3] claimed a symmetrical transition state without a diradical nature. Our own investigations [4] with the SINDO method seemed to support the non diradical nature of the transition state, but with an asymmetric geometry. Dewar et al. [5] had in the meantime repeated the calculations focussing on the cycloreversion. They found two asymmetric transition states and an intermediate. They classified the symmetric transition as a higher saddle point on the energy hypersurface. In view of the uncertainty of the previous results, we decided to study this reaction with the newly developed, more

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accurate semiempirical method SINDO1 [6]. To complement the study we included the cycloreversion of two ionic reactions: cyclopentyl anion → allyl anion + ethylene and cyclohept-4-enyl cation → butadiene + allyl cation. The cycloaddition of the latter reaction had been studied experimentally by Hoffmann [7]. He distinguished between a compact boat-like and an extended chair-like transition state. Our goal was to calculate the transition states and possible intermediates and to compare their geometry and activation energy. The following sections contain these results.

2. The Five Membered Ring

We optimized the geometry of reactant ring $C_5H_9^-$ and product fragments $C_3H_5^-$ and C_2H_4. The energy of the products was found to be 28.9 kcal/mol higher than that of the ring. For the study of the reaction the SINDO1 method was extended to include a 4×4 CI with the SCF ground state configuration and the LUMO singly and doubly excited configurations. The results for transition states and intermediates are shown in Fig. 1. We found that breaking of one bond through

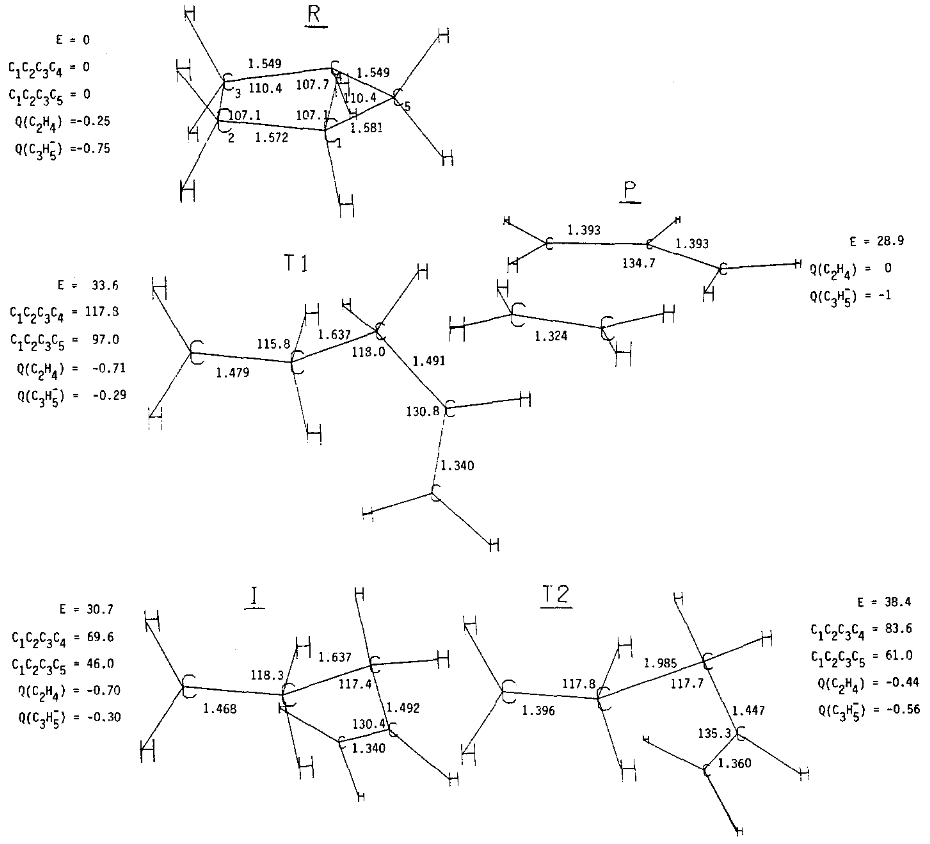

Fig. 1. Geometry (Å, degrees), relative energy E (kcal/mol) and net charge Q for $C_5H_9^-$ cycloreversion

twisting the dihedral angle $C_1C_2C_3C_5$ between the ethylenic and allylic parts of the ring to an orthogonal form is necessary to achieve fragmentation. An alternative attempt to lengthen the bond C_1C_5 in a planar $C_1C_2C_3C_5$ carbon framework and bending the allylic part through the dihedral angle $C_1C_5C_4C_3$ led over a saddle point at 44.6 kcal/mol with subsequent rearrangement of the ring through formation of the C_1C_5 bond at the expense of the C_2C_3 bond. The twisted intermediate T_1 has a barrier of 33.6 kcal/mol with respect to the ring and a dihedral angle $C_1C_2C_3C_5 = 97°$. The twisted form can then stabilize to an intermediate I with a dihedral angle $C_1C_2C_3C_5$ at 46°. The energy of I is only 2.9 kcal/mol below that of T_1. From the intermediate a small barrier of 7.7 kcal/mol has to be overcome to fracture the second C_2C_3 bond and dissociate I into the products. The second transition state T_2 is described by a bond length $C_2C_3 = 1.985$ Å and a dihedral angle $C_1C_2C_3C_5 = 61°$.

In the three cases T_1, I, T_2 there is little correlation energy involved during the reaction. This means there is no diradical important for the reaction since the triplet lies high above the singlet. If we partition the negative unit charge of the anion into portions Q belonging to the ethylenic part and the allylic part of the molecule, we find in the ethylenic part of the ring 25% of the net charge whereas this number drops to zero in the fragments. However, in T_1 the ethylenic part contains 71% of the charge, in I 70% and in T_2 44%.

3. The Six Membered Ring

This is the well investigated Diels-Alder reaction of butadiene and ethylene to cyclohexene. We found the half-chair form of the ring to be 9.4 kcal/mol more stable than the half-boat form, which is somewhat higher than the 5.1 kcal/mol calculated by Townshend et al. [2]. The ring is 46.4 kcal/mol lower in energy than the fragments. The calculated value is referring to minima of the potential surface and means the difference of heats of formation and zero point energies of vibration. Since the zero point energy of vibration for cyclohexene is experimentally unknown at present, we cannot directly compare our result with experiment. We can only quote the experimental difference of 39.6 kcal/mol in heats of formation. As in the five membered system a subsequent 4×4 CI calculation was performed for the reaction. On the singlet CI surface two transition states T_1, T_2 and one intermediate I were found. The results are shown in Fig. 2. The first transition state T_1 occurs after twisting the ethylenic part of the ring about the bond C_4C_5 connecting ethylene and butadiene and breaking the bond C_1C_6. The dihedral angle $C_2C_3C_4C_5$ is 120° and the energy 81.6 kcal/mol above the energy of the ring. The experimental activation energy is in the range of 55.1–72.7 kcal/mol [8]. Dewar et al. [5] quote a value of 64 kcal/mol as the best experimental value. So our calculated value is about 17 kcal/mol too high, but the discrepancy is much less than the 30 kcal/mol obtained with MINDO/3. In agreement with the cycloreversion study of Dewar, our transition state T_1 is diradicaloid in nature with the singlet lying lower than the triplet by less than 0.1 kcal/mol. Further twisting leads to an intermediate which is lower by

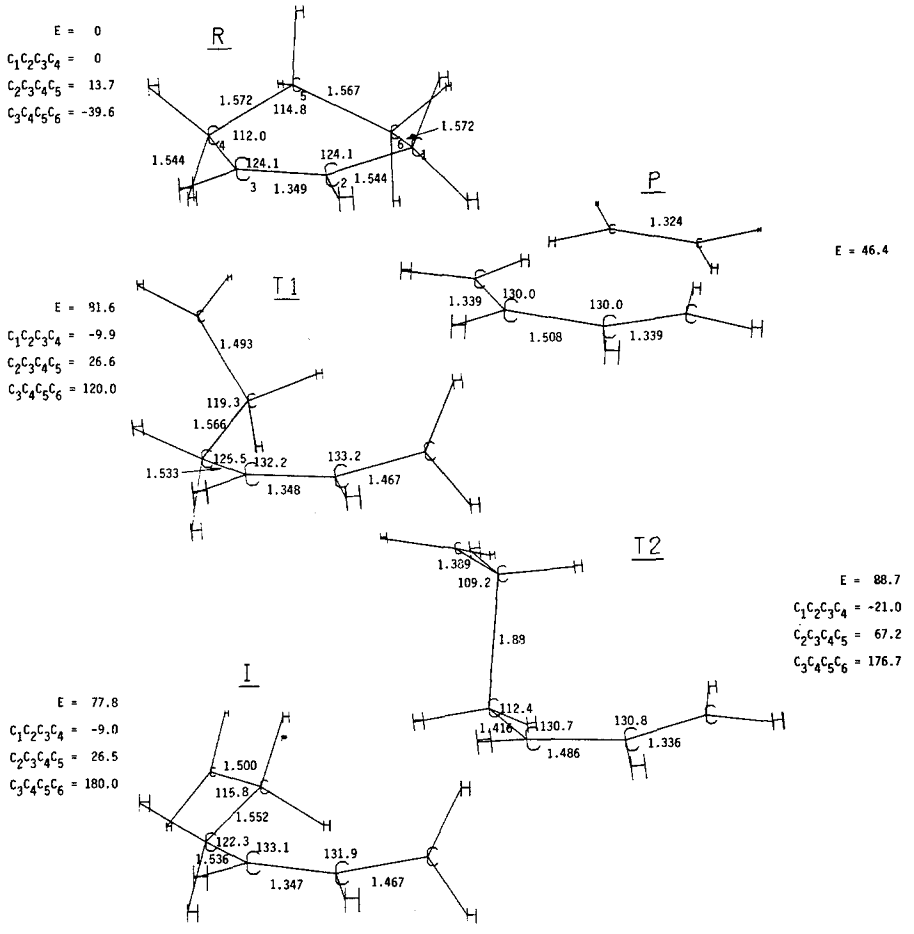

Fig. 2. Geometry (Å, degrees) and relative energy E (kcal/mol) for C_6H_{10} cycloreversion

3.8 kcal/mol than T_1. The dihedral angle $C_2C_3C_4C_5$ is about 180°. This *trans* intermediate is also a diradicaloid. Here the triplet is lower than the singlet by less than 0.1 kcal/mol. Finally the bond C_4C_5 is broken. The transition state T_2 appears at $C_4C_5 = 1.88$ Å with a barrier of 10.9 kcal/mol to the intermediate *I*. This transition state is not diradicaloid since the singlet is lower than the triplet by 37.9 kcal/mol.

4. The Seven Membered Ring

Here the cycloreversion of the cyclohept-4-enyl cation to butadiene and allyl cation is considered. We were motivated to study the seven membered ring by the work of Hoffmann [7] on syntheses of seven and five membered rings from allyl cations. The calculated geometry of the ring *R* is shown in Fig. 3 and the energy of *R* is set at 0 kcal/mol. The energy of the fragments is 73.8 kcal/mol

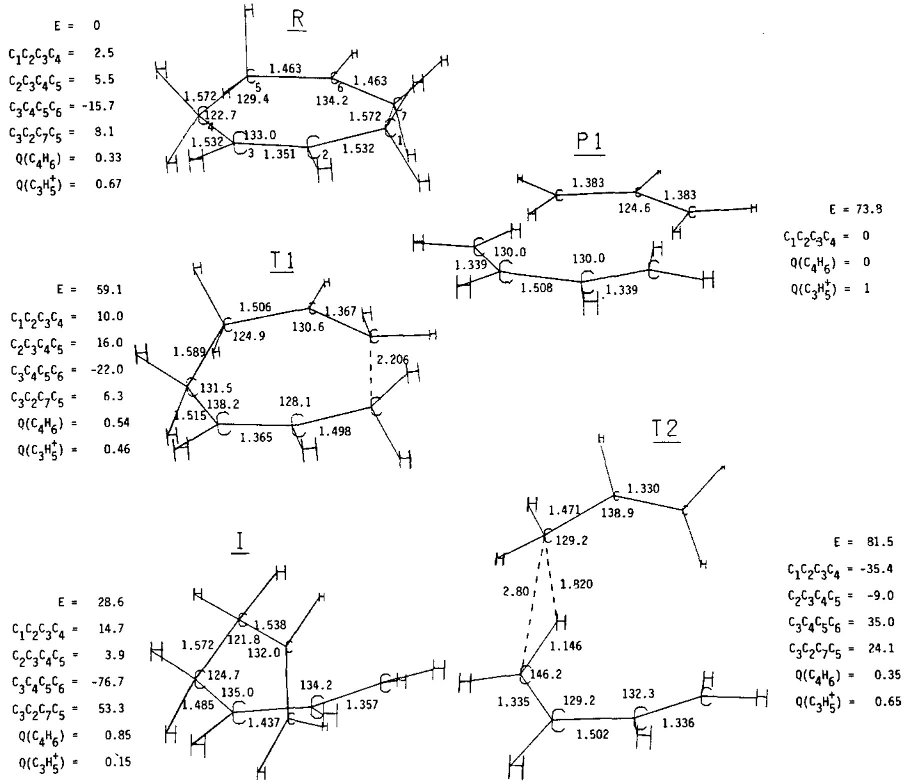

Fig. 3. Geometry (Å, degrees), relative energy E (kcal/mol) and net charge Q for $C_7H_{11}^+$ cycloreversion

above the energy of the ring, relatively higher than in the five and six membered ring[1]. Study of the reaction revealed that the correlation energy involved in the 4×4 CI calculation was negligible and the triplet energy was always much higher than the singlet energy. Again two transition states T_1 and T_2 and an intermediate I were found. Some numbers are given in Fig. 3. In this case T_1 is characterized by a small twisting angle $C_3C_4C_5C_6 = 22°$ of the butadiene and allyl cation part of the ring. The energy of T_1 is 59.1 kcal/mol above the ring energy. Further twisting of $C_3C_4C_5C_6$ to 76.7° allows the decrease of the bond length C_4C_5 and the adjacent bond angles $C_3C_4C_5$ and $C_4C_5C_6$.

But more important is that the breaking of bond C_1C_7 allows the bonds C_1C_2 and C_6C_7 to contract. All important bond angles change. These geometrical changes are accompanied by a shift of the unit charge from the allyl moiety to butadiene. The net effect is a stabilization of about 30 kcal/mol with respect to T_1. Whereas in the ring one third of the net charge Q is contained in the butadiene part, this

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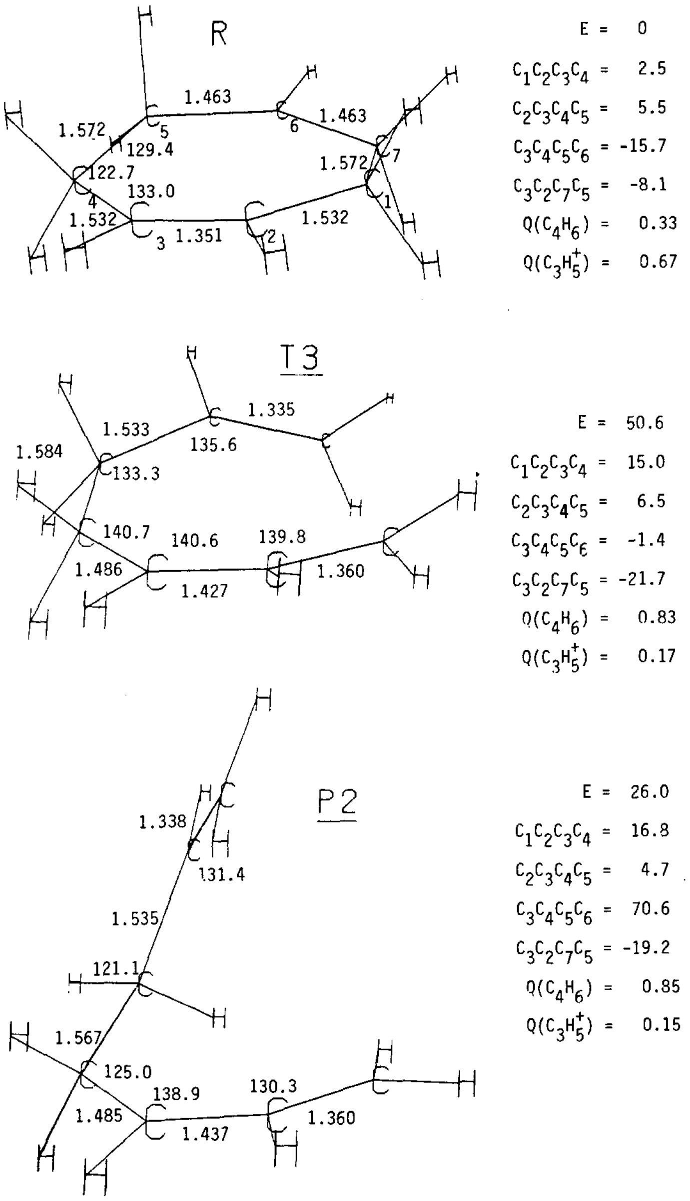
[1] Upon suggestion of the referee we repeated this calculation with MINDO/3 and found 68.5 kcal/mol as heat of reaction for this case on the basis of MINDO/3 optimized geometries.

portion is increased to 54% in T_1 and finally to 85% in I. We reach the second transition state T_2 by a barrier of about 53 kcal/mol from the intermediate. T_2 has a decreased dihedral angle $C_3C_4C_5C_6 = 35°$ but a substantially lengthened bond $C_4C_5 = 2.80$ Å. Only 25% of the unit charge are left in the butadiene. Upon fragmentation, the whole charge will go into the allyl moiety to form the cation.



E = 0
$C_1C_2C_3C_4$ = 2.5
$C_2C_3C_4C_5$ = 5.5
$C_3C_4C_5C_6$ = -15.7
$C_3C_2C_7C_5$ = -8.1
$Q(C_4H_6)$ = 0.33
$Q(C_3H_5^+)$ = 0.67

E = 50.6
$C_1C_2C_3C_4$ = 15.0
$C_2C_3C_4C_5$ = 6.5
$C_3C_4C_5C_6$ = -1.4
$C_3C_2C_7C_5$ = -21.7
$Q(C_4H_6)$ = 0.83
$Q(C_3H_5^+)$ = 0.17

E = 26.0
$C_1C_2C_3C_4$ = 16.8
$C_2C_3C_4C_5$ = 4.7
$C_3C_4C_5C_6$ = 70.6
$C_3C_2C_7C_5$ = -19.2
$Q(C_4H_6)$ = 0.85
$Q(C_3H_5^+)$ = 0.15

Fig. 4. Geometry (Å, degrees), relative energy E(kcal/mol) and net charge Q for $C_7H_{11}^+$ ring to open chain conversion

Actually this seven membered ring reaction is more complicated and the fragmentation of two bonds represents only a part of the possible processes. In principle the following competing process can occur (Fig. 4). One bond breaks with comparatively little twisting, $C_3C_4C_5C_6 = -1.4°$ but a substantial shift of charge (83%) into butadiene to form a transition state T_3. Further twisting to 70.6° with retention of the charge yields an open chain stable product P_2. This product can best be described as a substituted allyl with the center at C_2 and an asymmetry in the bond lengths C_1C_2 and C_2C_3 because of the "substitution" at C_3. 85% of the positive charge in P_2 is in butadiene and only 15% in allyl.

Our calculations were unfortunately flawed by an inaccuracy in the relative stability of the allyl and 2-propenyl cation. Whereas the calculated binding energy of the former should be correct within a few kcal/mol, the binding energy of the latter appears too low by 30 kcal/mol. Experimental enthalpies of formation favor allyl cation by about 10 kcal/mol [9]. In practice this means that during the reaction a migration of one hydrogen atom to form the respective substituted vinyl cation was favored. Nevertheless, we are confident that the mechanism of the reaction is qualitatively correct. This means we trust that the early model of compact and extended transition states [7] for the seven membered ring is merely a simplification of the reaction without a physical counterpart.

5. Conclusion

A comparison of three $[\pi^2 + \pi^4]$ cycloreversion reactions in five to seven membered rings involving anion, neutral molecule and cation, suggests the following conclusions: (1) The thermodynamic stability of the ring relative to the fragments increases with the number of ring atoms. (2) The fragmentation involves two steps namely breaking of the first bond involving a high barrier and breaking of the second bond involving an additional, but much lower barrier. (3) The stability of the intermediate increases with increasing ring size. (4) The initial step favors a twisting to an asymmetric geometry before the second bond is broken. (5) Only the neutral molecule reaction of the six membered ring involves a diradical during the reaction. (6) The shifting of the charge in ions can give rise to stabilization of open chain systems which may compete with the second C—C bond breaking.

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