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A Molecular-Orbital Study of the Thermal Walk Rearrangement of Bicyclo[2.1.0]pent-2-ene

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Ab initio molecular orbital studies with geometry optimizations indicate that in the walk rearrangement of bicyclo-[2.1.0]pent-2--ene the reaction path that goes *via* inversion of the migrating center is slightly preferred. The transition state is however found to have a diradical nature and thus is not stabilized by positive orbital interaction between the migrating center and the ring.

INTRODUCTION

The walk rearrangement is certainly one of the most fascinating unimolecular processes in chemistry. It has been observed in thermal[1] as well as in photochemical processes[1], and experimental results relating to both pure hydrocarbons and heteroatomic analogues are available[3].

Moreover, this type of reaction, that may be defined as one in which a divalent group, such as —O—, —NR—, and —CH$_2$—, moves along the surface of a cyclic π-system[3], turns out to be of central importance in the discussion of the predictive power of the symmetry rules of Woodward and Hoffman[1].

If we consider the circumambulation of a >CH$_2$-group in consecutive (1, n) sigmatropic shifts the Woodward-Hoffmann rules predict that the (1, 3) shift goes via inversion for suprafacial processes whereas the (1, 5) shift goes via retention. In contrast to this the Berson-Salem rules[5], based on the assumption of subjacent orbital control, predict retention for the (1,3) shift and inversion for the (1, 5) shift.

The present paper is the first report of a study aiming at an exploration of the possibility of describing gross features of these processes within the single-configuration approximation.

As prototype for the process studied in the present paper we have chosen the thermal (1, 3) sigmatropic rearrangement of bicyclo[2.1.0]pent-2-ene. Our study was prompted by an extensive experimental investigation[6] of several derivatives of the bicyclopentene system.

A systematic choice of substituent groups on the parent compound made possible an unequivocal conclusion regarding the path of the walk process. It was found that the walk rearrangement was highly stereospecific and proceeded with inversion at the migrating center in accordance with the Woodward-Hoffmann symmetry rules. Furthermore it was claimed that the low activation barrier found (between 21.7 and 24.8 kcal/mol for different

substituents) could in part be explained by the high ground state enthalpy of the bicyclopentene system.

In the experimental work the energetics of the competing electrocyclic ring opening was also studied.

A semi-empirical molecular orbital study[7] of the (1, 3) rearrangement in the unsubstituted bicyclopentene predicts a slight preference for migration with retention. This result is thus at variance with the experimental findings for the substituted species. The molecular orbital study did not encompass a discussion of different electronic states of the »walking« system.

COMPUTATIONAL METHODS AND RESULTS

In Figure 1a is given the reference molecule bicyclo[2.1.0]pent-2-ene. For reasons of symmetry the species depicted in Figure 1b and 1c represent either minima or maxima along the curve on the potential surface described by the reaction coordinate for the walk-rearrangement. In the first case they are meta-stable states, and in the second case they are transition states. All the species are assumed to belong to the symmetry group C_s. The two reaction schemes considered are depicted in Figure 2.
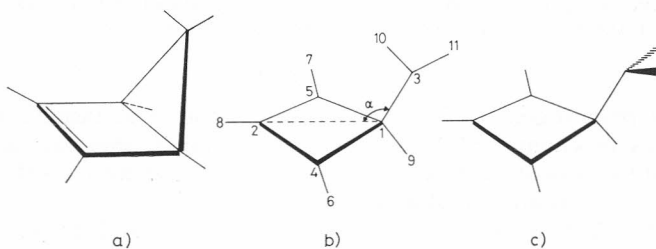

Figure 1. A sketch of the parent molecule bicyclo[2.1.0]pent-2-ene a), the transient species in inversion process b), and in retention process c). Labelling of atoms given in b).
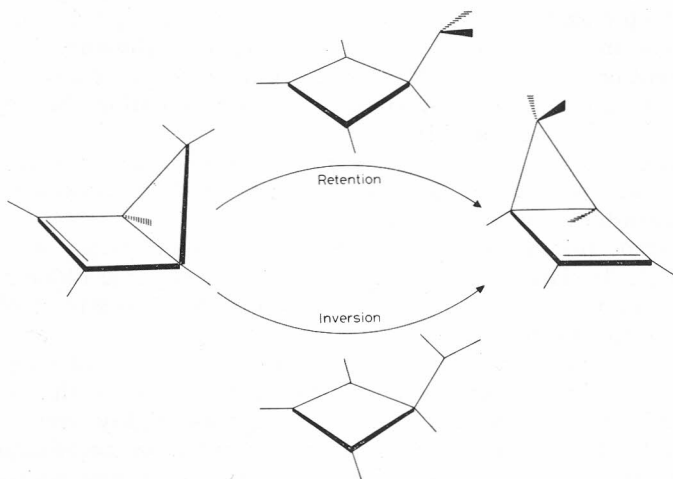

Figure 2. A picture of the two reaction schemes considered.

The parent molecule has a closed-shell ground state described by the configuration ..... $(13a')^2 (5a'')^2$. For the transient species (inversion and retention) we have in addition to this configuration also considered the open-shell configuration ..... $(13a')^2 (5a'')^1 (6a'')^1$ with state symmetries $^1A'$ and $^3A'$. Test calculations at the 4-31G level showed this to be the preferred open-shell configuration. All states considered were geometry optimized using a 4-31G basis. The closed-shell configurations were optimized by means of the programme TEXAS written by Pulay[8], whereas the open-shell configurations were treated in the UHF approximation by the programme Gaussian 76.[9]

For the transient species in the inversion process the $^3A'$ state has the lowest energy. Its optimized geometry is given in Table I. Of particular interest

TABLE I

Optimized Geometries of Transient Species for Inversion (WI) and Retention (WR). Triplet Ground States. UHF-Calculations. 4-31G Basis. For Labelling of Atoms see Figure 1[a]

Parameter	WI	(RHF)	WR
C1—C3	1.488	1.454	1.506
C1—C4	1.557	1.541	1.548
C2—C4	1.407	1.391	1.408
C4—H6	1.068	1.080	1.069
C2—H8	1.071	1.071	1.069
C1—H9	1.079	1.090	1.089
C3—H10	1.073	1.090	1.079
C3—H11	1.078	1.090	
∠ α	127.2	133.6	127.8
∠ H9C1C3	108.9	110.1	110.0
∠ H10C3H11	117.7	117.2	149.1
∠ H10C3C1	121.2	121.8	116.4

[a] Bond distances are given in Å and bond angles in degrees.

regarding the geometry is the observation that the 4-membered ring is found to be planar. The H-atoms attached to the ring are however slightly tilted out of the ring plane. The interesting orbitals in the discussion of this state are $5a''$ and $6a''$ which both describe an interaction between the non-bonding quasi π-orbital of the allylic unit and the p-orbital of appropriate symmetry on the migrating carbon atom. The MO $5a''$ describes a bonding interaction and $6a''$ an antibonding interaction. A qualitative picture of these orbitals showing their gross features, is presented in Figure 3.
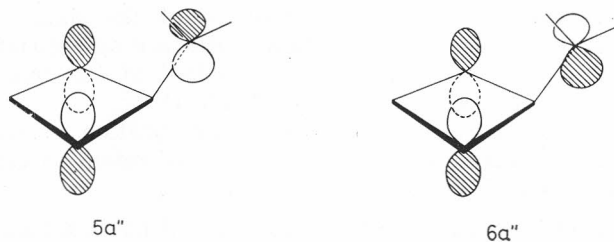

5a"   6a"

Figure 3. The molecular orbitals $5a''$ and $6a''$ of the transient species in the inversion process.

An orbital population analysis indicates that the $5a''$-electron is mainly localized on the migrating carbon whereas the $6a''$-electron is situated in the allylic non-bonding π-orbital. This is in accordance with the generally delocalized nature of triplet states, and thus indicates a diradical nature of this state. This is underlined by the data in Table II giving the atomic spin densities for the p-orbital of appropriate symmetry on the migrating carbon, $2p_y$ for WI and primarily $2p_z$ for WR. The spin densities found for the quasi-π orbital on the terminal carbon of the allylic unit support the picture of two well localized electrons. A population analysis both at the 4-31G and 6-31G level indicates a negative overlap between the migrating carbon and the terminal carbons of the allylic system, the values being —0.132 and —0.138 respectively. Thus this state does not display a species stabilized by a continuity of orbital overlap throughout the process. The optimized value of the angle between the link to the migrating CH_2-group and the ring plane (127°) is in harmony with a diradical state.

TABLE II

Relative Energies, Electron Populations and Atomic Spin Densities for Triplet and Open-Shell Singlet States, $^3A'$ and $^1A'$, for Inversion (WI) and Retention (WR). Open-Shell Configuration $(5a'')^1 (6a'')^1$. Basis 6-31G. For Labelling of Atoms see Figure 1

| | WI | | WR | |
	$^3A'$	$^3A'$	$^1A'$	$^1A'$
Overlap-population				
C3—C4	—0.138	—0.116	—0.120	—0.115
Atomic spin density				
$2p$ on C3	0.95	0.96	1.02	0.99
$2p\pi$ on C4	0.77	—0.76	0.78	—0.77
ΔE/kcal/mol	0.0	1.4	2.1	3.8

The results for the geometry of the transient species in the process maintaining retention, also shown in Table I, give a picture that is rather similar to the one for the inversion process discussed above. The lowest-energy state $^3A'$ has an electron distribution at the SCF level that is very close to the corresponding state in the alternative process, and the energy difference between the two states is only 2.1 kcal/mol the inverted configuration being the preferred one. See Table II.

The overlap populations and spin-densities for the singlet-coupled open shell configurations indicate that also these states are appropriately described as diradicals with one unpaired electron localized at the migrating carbon and the other in the allylic π-system. See Table II.

Energetically the singlet states of the configuration $\ldots (5a'')^1 (6a'')^1$ are slightly above the triplets both for the inversion and retention case, the energy differences being 1.4 and 1.7 kcal/mol respectively.

The closed shell configuration $\ldots (13a')^2 (5a'')^2$ has a substantially higher energy, *viz.* 46.3 and 47.8 kcal/mol above the triplet states for the inverted and retended case respectively. These differences have to be considered as

upper limits, however, due to the higher flexibility of the UHF functions, and to the inappropriateness of the single-configuration closed shell function. The last point is underlined by the lowering of the energy differences to 28.0 and 31.4 kcal/mol respectively by using a two-configuration MCSCF wave function including the configuration ..... $(13a')^2 (6a'')^2$.

At this stage of our calculations it seems appropriate to conclude that the ground states of the transient species studied probably are triplets, and that the open shell singlets displaying a pronounced diradical character represent the transition states for the walk processes considered.

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SAŽETAK

Teorijski MO studij preuređenja biciklo[2.1.0]pent-2-ena putem termičkog koraka

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Napravljeni su *ab initio* MO računi s optimizacijom geometrije za reakciju termičkog koraka bicyclo(2.1.0)pent-2-ena. Pokazano je da je reakcijski put preko inverzije migracijskog centra povoljniji. No, prijelazna struktura ima diradikalna svojstva. Zbog toga ne dolazi do stabilizacijske orbitalne interakcije između migracijskog centra i prstena.