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The Electronic Structure of Bicyclo [2.2.1] Heptane and of Bicyclo [2.2.2] Octane

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An *ab initio* SCF-LCAO-MO study of bicyclo[2.2.1]heptane(I) and of bicyclo[2.2.2]octane(II) has been performed. The electronic structure and the nature of the molecular orbitals and of the bonds have been analyzed. Interactions between fragment orbitals may be recognized. The bridgehead C–H bonds interact dominantly "through-space" in I and "through-bond" in II. Some relations between electronic structure and molecular properties are discussed.

Key words: Bicyclo[2.2.1]heptane – Bicyclo[2.2.2]octane

1. Introduction

Recent non-empirical SCF-LCAO-MO calculations have provided a detailed description of the electronic structure of bicyclo[1.1.1]pentane [1, 2] and of bicyclo[2.1.1]hexane [3].

The construction of the MO's of these strained molecules has been analyzed, and a number of special features have been found, especially characteristic "through space" interactions of C–H bonds.

It was of interest to pursue this work in order to complete the picture of MO structure and of specific interactions along a series of molecules from highly strained to comparatively strain free systems. We present here a non-empirical study of the electronic structure of bicyclo[2.2.1]heptane(I) and of bicyclo[2.2.2]-octane(II). Semi-empirical computations on these molecules and on their bridgehead cations have been reported earlier [4].

2. Results

2.1. Computations

SCF-LCAO-MO calculations have been performed using the same method and the same basis set of gaussian functions as previously used for bicyclo[1.1.1]-pentane(III) [2] and for bicyclo[2.1.1]hexane(IV) [3]. The geometries of I and II have been taken from an electron diffraction study [5] and from an X-ray diffraction study [6] respectively. For bicyclo[2.2.2]octane a geometry with D_{3h} symmetry has been used; a conformation of D_3 symmetry (with a small torsion of about 3° around the C_3 axis) could be energetically very slightly preferred [6, 7]. Using a D_{3h} conformation should thus not affect the results significantly.

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2.2. Results

The calculated total energies are as follows:
bicyclo[2.2.1]heptane:
$E_{tot} = -270.5968$ a.u., with
$V_{nn} = 329.0299$, $V_{ee} = 416.5634$, $T = 270.8749$ and $V_{ne} = -1287.0650$ a.u.;

bicyclo[2.2.2]octane:
$E_{tot} = -309.4193$ a.u., with $V_{nn} = 411.0126$,
$V_{ee} = 510.9925$, $T = 309.5298$ and $V_{ne} = -1540.9542$ a.u.

Figures 1 and 2 give schematic drawings[1] of valence MO symmetry, composition and energy for bicyclo[2.2.1]heptane(I) and bicyclo[2.2.2]octane(II) respectively.

We shall denote the carbon atoms in the bridges and at the bridgeheads by C_B and C_{BH} respectively. Overlap populations will be abbreviated by OP. The internal MO's of I comprise the four combinations of the $1s$ functions on the four equivalent CH_2 carbons (at -11.269 a.u.), the two $1s$ C_{BH} combinations (at -11.265 a.u.) and the $1s\,C_7$ orbital (at -11.257 a.u.). In II, one finds successively the two $1s\,C_{BH}$ MO's (at -11.280 a.u.) and the six $1s\,C_B$ combinations (at -11.268 a.u.).

In the following paragraphs we analyze the structure of the valence MO's of I and II, stressing, when suitable, their construction from group orbitals (CH_2, CH group orbitals [3, 9]) and from fragment orbitals (CH_2CH_2, cyclohexane fragments, etc.) [3].

3. Discussion

3.1. Electronic Structure of Bicyclo[2.2.1]Heptane (I)

Figure 1 shows that the seven lowest valence MO's ($4A_1$, $2B_2$, $3B_1$, $5A_1$, $2A_2$, $6A_1$, $4B_1$) are constructed mainly from C $2s$ functions; the first four are mainly C–C bonding, the three remaining one's are combinations of $s\sigma$ type CH_2 group orbitals and are C–H bonding.

The bridgehead C_{BH}–H bonds are principally described by the two MO's $7A_1$ and $6B_1$ which contribute respectively 0.160 and 0.167 OP to these bonds. These two orbitals may be considered respectively as the symmetric and antisymmetric combinations of the C_{BH}–H bonds. The splitting of 5.6 eV between these MO's is comparable to that found in bicyclo[2.1.1]hexane(IV) (5.1 eV) [3], although the distance between the bridgeheads is larger in I (2.26 Å) than in IV (2.10 Å). This is not too surprising since none of the MO's are pure C_{BH}–H combinations, so that none of them corresponds to pure through space interactions between the bridgeheads.

The CH_2 group in the methylene bridge (at C_7) is mainly of π type (B_2 symmetry). Indeed, the B_2 MO's contribute 0.386 OP to these C–H bonds, whereas the $p\sigma$ orbitals (in MO's 8–$10A_1$) contribute only 0.064 OP to the total OP

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[1] We wish to thank E. Haselbach and A. Schmelzer [8] for providing a copy of their program which we adapted for minimal basis sets of gaussian functions.

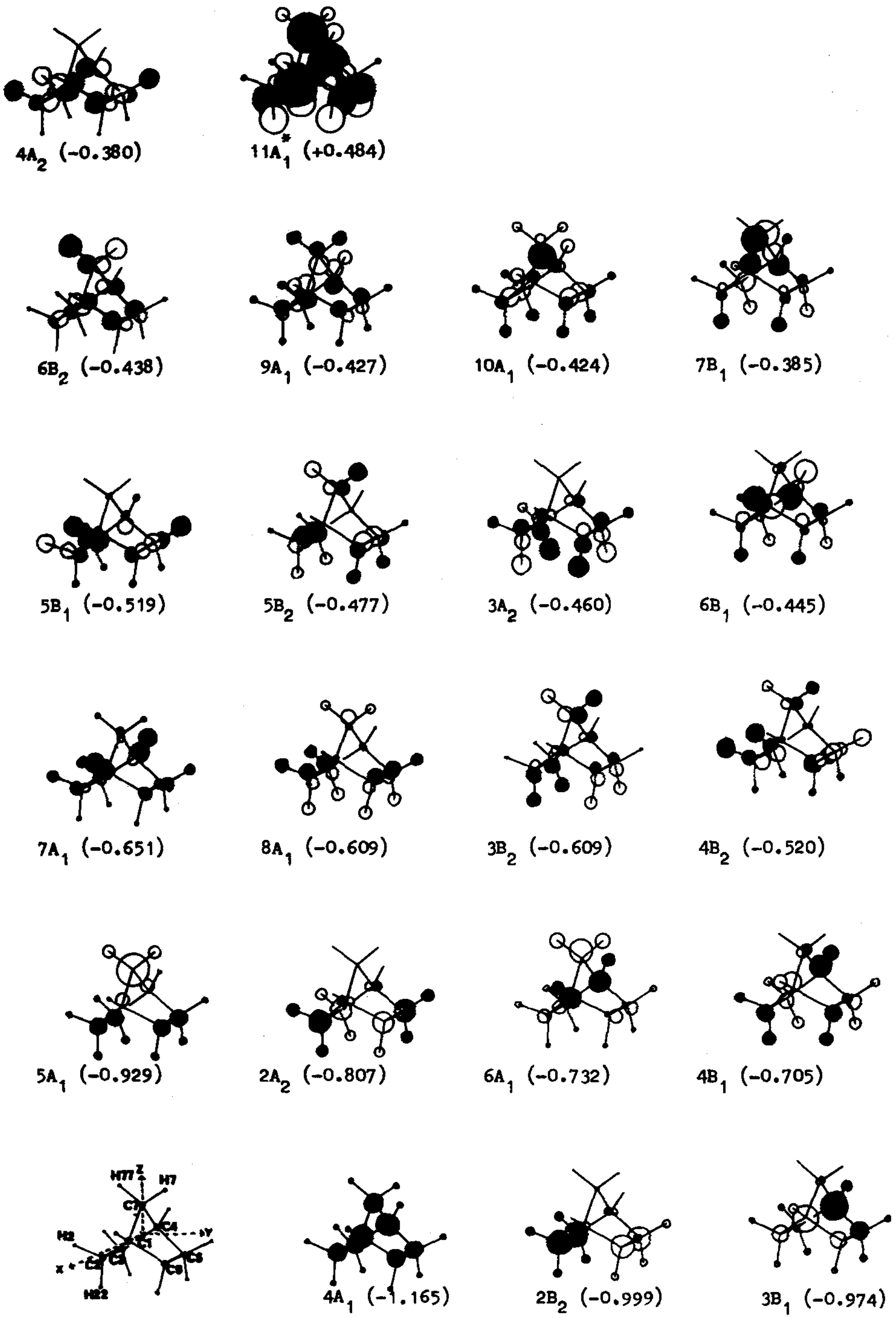


Fig. 1. Energies and schematic representation of the molecular orbitals of bicyclo[2.2.1]heptane(I)

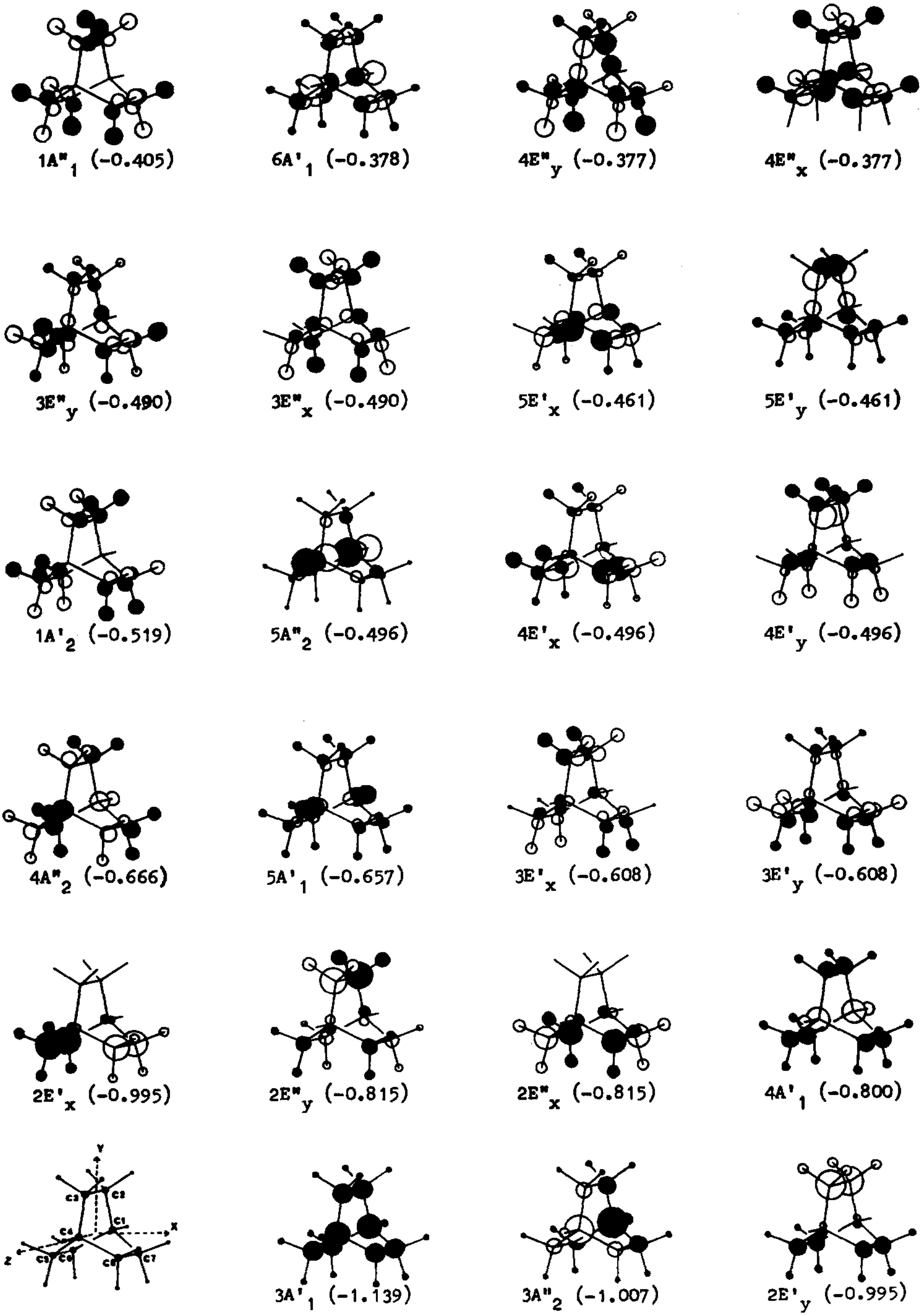


Fig. 2. Energies and schematic representation of the molecular orbitals of bicyclo[2.2.2]octane(I). (In the case of E'' type MO's the subscripts x and y are used only to differentiate the two degenerate MO's)

(0.782). Symmetric ($3B_2, 4B_2$) and antisymmetric ($6B_2$) combinations with p_y orbitals at C_{BH} are observed.

The *endo* and *exo* CH bonds in the ethylene bridges (C_2–C_3, C_5–C_6), being not symmetry equivalent, are differentiated in most MO's (except $8A_1$); they lead to π bonding and π^* antibonding interactions along the C_2–C_3 and C_5–C_6 bonds. The corresponding MO's may be classified as follows:

C–H *exo* bonds: $\pi_{23}+\pi_{56}(8A_1)$; $\pi_{23}-\pi_{56}(4B_2)$; $\pi^*_{23}+\pi^*_{56}(5B_1)$;
$\pi^*_{23}-\pi^*_{56}(4A_2)$;

C–H *endo* bonds: $\pi_{23}+\pi_{56}(8A_1)$; $\pi_{23}-\pi_{56}(3B_2)$; $\pi^*_{23}-\pi^*_{56}(3A_2)$;
$\pi^*_{23}+\pi^*_{56}(6B_1;\ 7B_1)$.

Both types of bonds have the same OP (0.786).

The MO's $9A_1$ and $7B_1$ describe the C–C bonds in the methylene bridge, whereas $5B_2$ and $10A_1$ contribute to the C_2–C_3 and C_5–C_6 bonds respectively; the destabilization of the symmetric combination $10A_1$ $[(C_2–C_3)+(C_5–C_6)]$ with respect to the antisymmetric one $5B_2$ $[(C_2–C_3)-(C_5–C_6)]$ may be ascribed to the negative overlap (-0.052) with the bridgehead carbons in the latter case.

The four symmetry equivalent bonds of type C_1–C_2 are spread over most MO's, $6B_2$ and $4A_2$ giving the largest OP contributions (0.096 and 0.098).

One may also to some extent recognize in the MO's of bicyclo[2.2.1]heptane combinations of the fragment MO's of a cyclohexane moiety [21] in the boat conformation with those of a bridging CH_2 group. The interactions between these two fragments may be of σ type (A_1 and B_1 MO's, for instance $7A_1$ or $7B_1$) or of π type (B_2 MO's, for instance $6B_2$). The boat cyclohexane fragment has an antibonding C_1, C_4 interaction in the HOMO $4A_2$, while this interaction is bonding in $6B_2$ and $10A_1$.

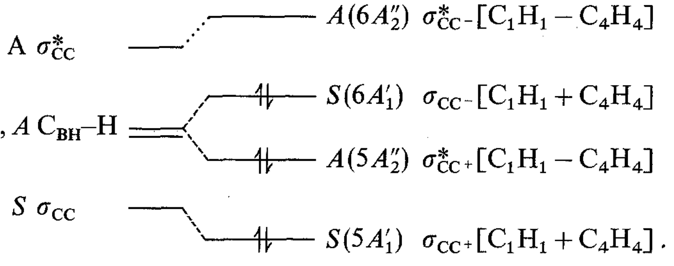
3.2. *Electronic Structure of Bicyclo[2.2.2]Octane* (II)

The MO's of II may be either symmetric S or antisymmetric A with respect to the XOY plane, a given S MO being in general more stable than the corresponding A MO except in the presence of through-bond interactions.

The eight lowest valence MO's are built on C 2*s* and H 1*s* functions. $3A'_1$ and $3A''_2$ are respectively the S and A combinations of ($2s\,C_{BH}+2s\,C_B$); $4A'_1$ and $4A''_2$ are the corresponding S and A ($2s\,C_{BH}-2s\,C_B$) combinations. $2E''$ and $4A''_2$ are C–H MO's; the other five describe the C–C bonds. The fifteen remaining MO's contain only C 2*p* and H 1*s* functions.

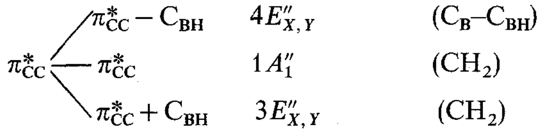
The most remarkable feature concerns the bridgehead C–H bonds. They are described by the MO's $5A'_1$, $5A''_2$, and $6A'_1$ (OP's: 0.130; 0.215; 0.147; total OP: 0.784). It is clearly seen that the antisymmetric C_{BH}–C combination $5A''_2$ is *below* the symmetric one $6A'_1$, which lies very close in energy to the HOMO. The corresponding splitting amounts to 3.22 eV ($C_1 \ldots C_4$ distance $= 2.60$ Å).

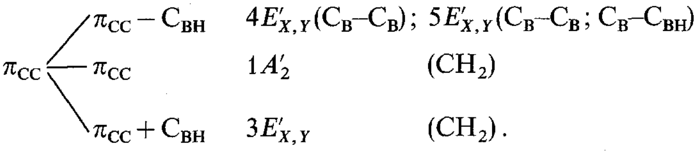
This ordering may be considered to result from through-bond interaction [11, 12] of the two C_{BH}–H bonds via the three interposed C–C bonds of the CH_2–CH_2 bridges. With the relative energies $\sigma^*_{CC} > C_{BH}\text{–}H > \sigma_{CC}$, the interaction diagram becomes:



The signs of the $C_1 \ldots C_2$ OP's agree with this scheme: +0.04 for $5A'_1$, +0.07 for $5A''_2$ and −0.03 for $6A'_1$.

The remaining twelve MO's may be classified by considering the p functions on the carbon atoms in the ethylene bridges. The $S(\pi_{CC})$ combinations lies below the $A(\pi^*_{CC})$ one, and each is split by interaction with the p orbitals on C_{BH}, according to the following scheme:





Again some orbitals may be considered as resulting from the interaction between a boat form cyclohexane fragment and a bridging ethylene fragment. For instance the following combinations may be recognized:

$4E''_{X,Y}$	$[A(CH_2–CH_2) - A$(cyclohexane)]
$3E''_{X,Y}$	$[A(CH_2–CH_2) + A$(cyclohexane)]
$4E'_{X,Y}$	$[S(CH_2–CH_2) - S$(cyclohexane)]
$3E'_{X,Y}$	$[S(CH_2–CH_2) + S$(cyclohexane)].

The HOMO of boat form cyclohexane corresponds to the cyclohexane fragment MO found for instance in $4A_2$ of I and in $4E''_X$ in II; the next highest MO of cyclohexane is found in the fragment MO's $10A_1$ in I and $6A'_1$ in II.

3.3. *Bridgehead-Bridgehead Interactions in Bicyclo[1.1.1], [2.1.1], [2.2.1], and [2.2.2] Systems*

Combining the present results on I and II with the earlier ones on III and IV, one notes the presence of an interaction between the bridgehead C–H bonds of the same type as but appreciably larger (by several eV's) than the lone pair-lone pair splittings found in the corresponding diaza-bicycloalcanes [11]. The S combination lies below the A one in the bicyclo[1.1.1], [2.1.1], and [2.2.1] systems; a reversal $S > A$ occurs in bicyclo[2.2.2]octane due to through bond interactions. In the case of the corresponding diaza systems, this reversal occurs already in 1,4-diaza-bicyclo[2.2.1]heptane [11].

3.4. *Nature of the Bonds and Molecular Properties*

In terms of a MO description, molecules containing strained C–C bonds display high lying C–C MO's, low C–C OP's, high p character at strained centres, "bent bond" electron distribution [3, 13].

The total OP's of the C–C bonds are:

C_1–$C_2 = 0.768$; C_2–$C_3 = 0.757$ (as in the ethylene bridge of III); C_1–$C_7 = 0.750$ in I; C_1–$C_2 = 0.763$; C_2–$C_3 = 0.748$ in II. These values lie between those found for cyclobutane (0.730) and for n-heptane (0.763) using the same basic set.

The Foster and Boys type [14] localized MO's yield the following hybridizations of the carbon atoms: $sp^{2.47} - sp^{2.63}$ for C_1–C_2; $sp^{2.44}$ for C_2–C_3; $sp^{2.94} - sp^{2.57}$ for C_1–C_7 in I; $sp^{2.52} - sp^{2.22}$ for C_1–C_2; $sp^{2.47}$ for C_2–C_3 in II.

The corresponding values are $sp^{2.70}$ in cyclobutane and $sp^{2.33}$ to $sp^{2.51}$ in n-heptane.

The localized C–H bonds give: $sp^{2.82}$ for C_{BH}–H; $sp^{2.83}$ for C_7–H; $sp^{3.09}$ and $sp^{3.12}$ for C_2–H *endo* and *exo* respectively in I; $sp^{3.19}$ for C_{BH}–H; $sp^{3.37}$ for C_B–H in II.

For the C–H bonds in cyclobutane and n-heptane one finds respectively $sp^{2.85}$ and $sp^{3.20-3.30}$.

Thus, whereas the C–C and C–H bonds of bicyclo[2.2.2]octane are very close to those of an unstrained alcane molecule, C_{BH} and C_7 in bicyclo[2.2.1]heptane display the electronic features of strained sites (especially along the C_{BH}–C_7 bond). A correlation between s character and ^{13}C–H coupling constants [13] leads to $^{13}C_{BH}$–H couplings of 142 and 128 Hz for I (experimental value 142 Hz [15]) and (II) respectively. The latter value should be close to that present in n-alcanes. No clear relation is found between the order of bridgehead solvolytic reactivities, III > IV ~ II > I, and the interaction between the bridgeheads, probably because of additional effects in the cation (for instance opening of a cyclobutane ring in III and IV).

It may be worth noting that in the D_{3h} bicyclo[1.1.1] and [2.2.2] molecules, one of the bridgehead combinations is among the HOMO's, whereas in the bicyclo[2.1.1] and [2.2.1] systems the bridgehead C–H MO's lie appreciably below the HOMO. Interestingly, radical chlorination of these systems goes almost exclusively to the ethylene bridges in the [2.1.1] and [2.2.1] systems [16, 17], while appreciable bridgehead chlorination takes also place in the [1.1.1] and [2.2.2] systems [18, 19].

The photoelectron spectra of I and II [20] display broad bands resulting from the proximity of the high lying MO's.

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