Theoret. chim. Acta (Berl.) 28, 223—233 (1973)

The Electronic Structure of Bicyclo [2.1.1] hexane

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Received July 3, 1972

Non empirical SCF-LCAO-MO calculations have been performed on bicyclo [2.1.1] hexane using a molecule optimized minimal basis set of gaussian functions. The electronic structure, the nature of the molecular orbitals and of the bonds are analyzed. The most notable results lie in the strong interaction between the two bridgehead sites and between two of the CH bonds of the methylene bridges. Interactions between fragment orbitals are considered. The relations with the molecular properties are discussed, especially with respect to molecular strain.

Nichtempirische SCF-LCAO-MO-Rechnungen wurden für das Bicyclo [2.1.1]-Hexan durchgeführt, wobei ein minimaler am Äthylen optimierter Basissatz von Gaußfunktionen verwendet wurde. Die Elektronenstruktur sowie die Art der Molekülorbitale und der Bindungen wird untersucht. Als bemerkenswerte Resultate erscheinen die starke Wechselwirkung zwischen den beiden Brückenkopf-Gruppen sowie zwischen den beiden CH-Bindungen der Methylenbrücken. Die Wechselwirkungen zwischen den Orbitalen von Molekülbruchstücken werden untersucht. Die Beziehungen zu den molekularen Eigenschaften werden diskutiert, insbesondere im Hinblick auf molekulare Ringspannung.

Une étude théorique *ab initio* SCF-LCAO-MO du bicyclo [2.1.1] hexane a été effectuée en utilisant une base minimale de fonctions gaussiennes optimisée sur une molécule. La structure électronique, la nature des orbitales moléculaires et des liaisons ont été analysées. Le résultat le plus marquant est l'existence d'une forte interaction entre les deux sites en tête de pont et aussi entre deux des liaisons C–H des ponts méthylène. Par ailleurs on peut mettre en évidence des interactions entre «orbitales de fragments». Les relations entre structure électronique et propriétés moléculaires (spécialement la tension de cycle) sont discutées.

1. Introduction

Strained polycyclic molecules may be expected to present special bonding relationships, in line with their specific molecular properties.

The electronic structure of bicyclo [1.1.0] butane [1–3] and of bicyclo [1.1.1] pentane [3–5] has been investigated recently by means of non-empirical SCF-LCAO-MO calculations. Several other saturated polycyclic systems have also been analyzed within the same theoretical framework (cubane, *syn*- and *anti*-tricyclooctanes, bicyclo [2.1.0] pentane, spiropentane, [3]). These calculations revealed many pecularities in the electronic structures of these systems.

Extending our studies of strained molecules aimed at providing a theoretical description of the concept of molecular "strain", we present here a non-empirical study of bicyclo [2.1.1] hexane, I, whose chemistry has been actively investigated over the last years [6].

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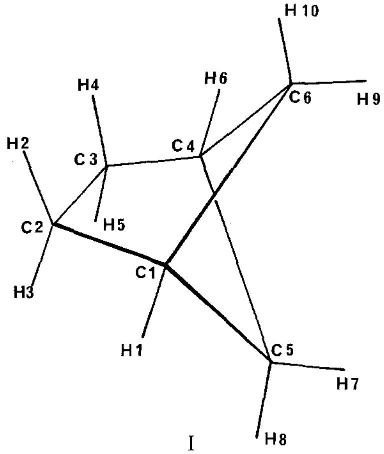
Two semi-empirical calculations of this system have also been performed recently [7], as well as a study of its thermal isomerization [8].



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2. Results

2.1. Method of Computation – Basis Set

The computations have been performed using the general program IBMOL [9].

The basis set employed was a molecule optimized minimal basis set of gaussian type functions (GTF's) containing 5*s* and 2*p* GTF's on carbon and 2*s* GTF's on hydrogen contracted into 2*s* and 1*p* on carbon and 1*s* on hydrogen: (5.2/2; 2.1/1) basis set.

This basis set has been obtained by starting with the atomic (5.2) set derived for carbon by Whitman and Hornback [10], keeping the same exponents and contraction coefficients for the four inner *s* functions on carbon and optimizing the exponent of the outer *s* function and the exponents and contraction coefficients of the *p* functions. The exponents and the contraction coefficients of the hydrogen *s* functions have been taken from the work of Huzinaga [11], but the scaling factor of these *s* functions has been optimized. The optimization has been performed by minimizing the total energy of the ethylene molecule at the experimental geometry [3]. The exponents, contraction coefficients and scaling factor obtained in this way form the basis set employed in the present as well as in previous calculations [3, 5, 12].

The results are:

Exponents (contraction coefficients):

Carbon

s 381.0(0.0236); 59.18(0.1521); 13.79(0.4654); 3.833(0.4953); 0.3816(1.0),

p 1.413(1.0); 0.3058(1.9241).

Hydrogen (scaling factor = 1.35)

s 1.83216(0.27441); 0.2771(0.82123).

The total energies of methane, D_{3d} ethane and ethylene obtained with the atomic and the optimized basis sets are respectively: -39.9176 and -39.9468 a.u. for methane, -78.7136 and -78.7704 for ethane, -77.5017 and -77.5482 for ethylene. C–C bond length optimization in ethane [3] and cyclooctatetraene [12] yields slightly larger values (by three hundredth of an angström or less) than the experimental length.

2.2. Results

The geometry of the bicyclo [2.1.1] hexane molecule has been taken from the most recent electron diffraction study [13]. These geometrical parameters differ from those obtained in an earlier investigation [14]. However it is very unlikely that the changes involved would after significantly the electronic structure of the molecule.

The total energy calculated for bicyclo [2.1.1] hexane is equal to -270.5968 a.u., with $V_{nn}=329.0299$, $V_{ee}=416.5634$, $T=232.3466$ and $V_{ne}=-1248.5367$ a.u. The orbital energies and the overlap populations are given in Table 1. The first six molecular orbitals (MO's) are 1*s* MO's of energy -11.263 ($1A_1$ and $1B_2$ at C_5 and C_6), -11.262 ($2A_1$ and $1B_1$, at C_2 and C_3), -11.261 a.u. ($3A_1$ and $2B_1$ at C_1 and C_4).

Fig. 1 represents MO diagrams drawn approximatively to scale; it includes the lowest unoccupied MO.

The calculated ionization potential and dipole moment are respectively 8.56 eV and 0.167 D (along the *z* axis with the positive end at *z* positive).

3. Discussion

3.1. Electronic Structure of Bicyclo [2.1.1] *Hexane*

The population analyses given in Table 1 and the MO diagrams of Fig. 1 provide a detailed description of the electronic structure of bicyclo [2.1.1.] hexane.

The present discussion will therefore bear primilary on the special features present in this system (characteristic MO's; interaction patterns, nature of the bonds) and on their possible significance with respect to the molecular properties.

Nature of the Molecular Orbitals

The first six MO's are of C 1*s* type and will not be further discussed. It is noteworth that the seventeen remaining MO's may be grouped in two ways[1]:

a) one may distinguish C–C and C–H MO's; it is found that except for the highest occupied MO (HOMO), which is of C–H type, the C–H MO's are sandwiched between a group of low lying and a group of high lying C–C MO's;

b) one may also group together the MO's describing primarily the C–CH_2–CH_2–C fragment and those contributing mainly to the cyclobutane fragment; they may be either of C–C or of C–H type within each set. Some MO's are delocalized over the whole system; some also may be clearly recognized as

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[1] It should be stressed that none of the MO's is exclusively of a given type. They are more or less delocalized and this classification refers to the principal character of a given MO.

Table 1. Bicyclo [2.1.1] hexane: Overlap populations

Molecular orbitals			Centers									
N°	Symmetry	Energy	C_1C_2	C_2C_3	C_1C_5	C_1H_1	C_2H_2	C_5H_7	C_5H_8	C_1C_4	C_5C_6	Total[a]
7	$4A_1$	−1.190	0.071	0.060	0.108	0.017	0.014	0.014	0.029	0.042	0.057	0.909
8	$5A_1$	−0.973	0.024	0.216	0.045	0.0	0.080	0.025	0.010	0.010	0.033	0.877
9	$3B_1$	−0.922	0.138	−0.002	0.043	0.099	0.042	0.0	0.0	−0.018	0.006	0.800
10	$2B_2$	−0.883	0.007	0.002	0.056	0.0	0.002	0.118	0.159	0.005	−0.016	0.791
11	$4B_1$	−0.718	0.011	0.002	0.042	0.072	0.123	0.0	0.0	−0.006	0.008	0.830
12	$6A_1$	−0.710	0.050	0.043	0.007	0.123	0.008	0.139	0.054	−0.003	0.0	0.832
13	$7A_1$	−0.652	0.027	0.022	0.032	0.188	0.010	0.090	0.009	0.042	0.024	0.884
14	$3B_2$	−0.615	0.010	0.084	0.0	0.0	0.119	0.100	−0.001	0.0	−0.007	0.771
15	$8A_1$	−0.582	0.031	0.034	0.055	0.0	0.025	0.0	0.164	0.010	0.095	0.849
16	$1A_2$	−0.507	0.059	−0.083	0.053	0.0	0.134	0.0	0.0	−0.012	−0.015	0.756
17	$4B_2$	−0.480	−0.019	0.030	0.030	0.0	0.054	0.176	0.085	0.004	−0.057	0.797
18	$5B_1$	−0.465	0.028	−0.008	0.070	0.215	0.0	0.0	0.0	−0.183	0.024	0.599
19	$9A_1$	−0.451	−0.016	0.394	0.006	0.016	0.040	0.050	0.051	0.003	0.018	0.801
20	$10A_1$	−0.400	0.141	0.132	−0.046	0.047	0.003	0.062	0.079	0.026	0.017	0.659
21	$2A_2$	−0.397	−0.058	−0.046	0.118	0.0	0.091	0.0	0.0	−0.021	−0.042	0.611
22	$6B_1$	−0.396	0.261	−0.119	0.023	0.004	0.039	0.0	0.0	−0.033	0.009	0.635
23	$5B_2$	−0.313	0.004	0.001	0.070	0.0	0.0	0.0	0.125	0.027	−0.338	0.228
24	$11A_1$	+0.427	−0.507	0.206	0.114	0.0	−0.036	−0.154	−0.410	0.107	0.089	−1.428
Total (MO 1 to 23)			0.768	0.759	0.715	0.781	0.784	0.774	0.763	−0.106	−0.184	

[a] Including overlap populations between non-bonded centers.

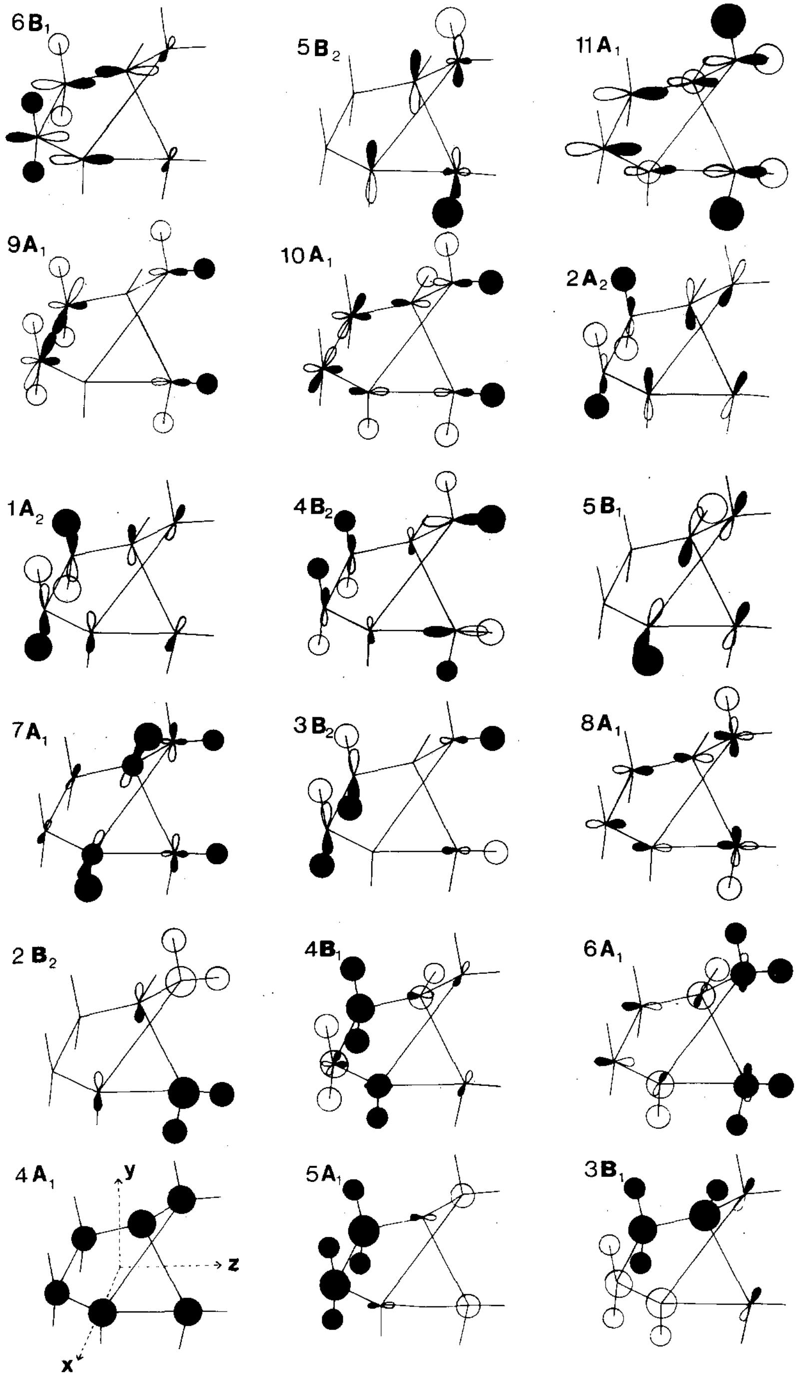

Fig. 1. Schematic representation of the molecular orbitals of bicyclo [2.1.1] hexane (see energies in Table 1)

combinations of fragment orbitals (FO's) resulting from the interaction between the orbitals of the ethylene and cyclobutane fragments.

We shall discuss in turn the C–C MO's, the C–H MO's and the interactions between fragment MO's.

1) C–C Type Molecular Orbitals

There are alltogether seven MO's of dominant C–C type. Three of them ($4A_1$, $5A_1$, $3B_1$, 7–9) form a group of low lying MO's containing mainly C 2*s* atomic orbitals (AO's). The four others ($9A_1$, $10A_1$, $2A_2$, $6B_1$, 19–22) are high lying MO's using exclusively C 2*p* AO's to complete the description of the C–C framework. Two low lying ($5A_1$, $3B_1$) and two high lying ($9A_1$, $6B_1$) MO's describe primarily the central ($5A_1$, $9A_1$) and lateral ($3B_1$, $6B_1$) C–C bonds of the ethylene fragment. $10A_1$ is delocalized over the whole molecule and contributes to all three C–C bonds of the ethylene bridge. The two remaining MO's, $4A_1$ and $2A_2$, lie predominantly on the C–C bonds of the cyclobutane moiety. In particular, $2A_2$ is reminiscent of the b_{1g} external Walsh orbital of cyclobutane [16, 17].

2) C–H Type Molecular Orbitals

It may be noted at the start that some C–H MO's may be clearly recognized as combinations of semi-localized methylene group orbitals of either σ or π type [15] (Fig. 2).

a) Among the ten C–H MO's, four are primarily localized on the CH_2 groups. $2B_2$ and $4B_1$ are antisymmetric combinations of σ type CH_2 group orbitals; $2B_2$ combines the two methylene groups of the one carbone bridges and $4B_1$ mixes those of the ethylene bridge. They both contain mainly *s* type AO's at the CH_2 sites. $3B_2$ and $1A_2$ are respectively the symmetric (*S*) and antisymmetric (*A*) combinations of the π type CH_2 orbitals of the methylene groups in the ethylene fragment.

b) MO $6A_1$ describes both the bridgehead and the *exo* C_5–H_7, C_6–H_9 C–H bonds. $4B_2$ is mainly localized on these last bonds but contributes also to the C–H bonds in the ethylene bridges. $6A_1$ and $4B_2$ contain respectively the *S* and *A* combinations of the C_5–H_7 and C_6–H_9 bonds.

c) Among the remaining four MO's, $7A_1$ and $5B_1$ describe mainly the bridgehead C–H bonds. They are respectively the *S* and *A* combinations of these two bonds. The large splitting of these two levels (ca. 5.1 eV) is due to the relatively short $C_1 \ldots C_4$ distance (2.10 Å) which leads to a marked interaction between the two bridgeheads. An even larger splitting (6.7 eV) has been found between the corresponding bridgehead levels in bicyclo [1.1.1] pentane where the distance between the bridgeheads is even shorter [5].

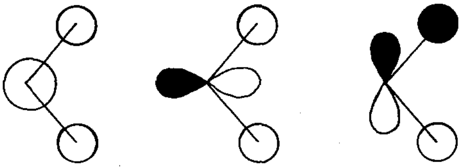

Fig. 2. Methylene group orbitals

d) The two remaining MO's $8A_1$ and $5B_2$ may be considered respectively as the S and A combinations of the two *endo* C–H bonds, C_5–H_8 and C_6–H_{10}. The splitting of these two levels amounts to 7.6 eV, i.e. it is even larger than the splitting of the bridgehead levels in bicyclo [1.1.1] pentane although the $C_5 \ldots C_6$ distance is larger (2.06 Å) than the bridgehead distance is the latter molecule (1.845 Å). $5B_2$ also contributes to the cyclobutane C–C bonds in a manner analogous to the e_u type external Walsh orbital of cyclobutane [15–17] (see also below).

Figs. 3 and 4 show some selected MO electron density diagrams.

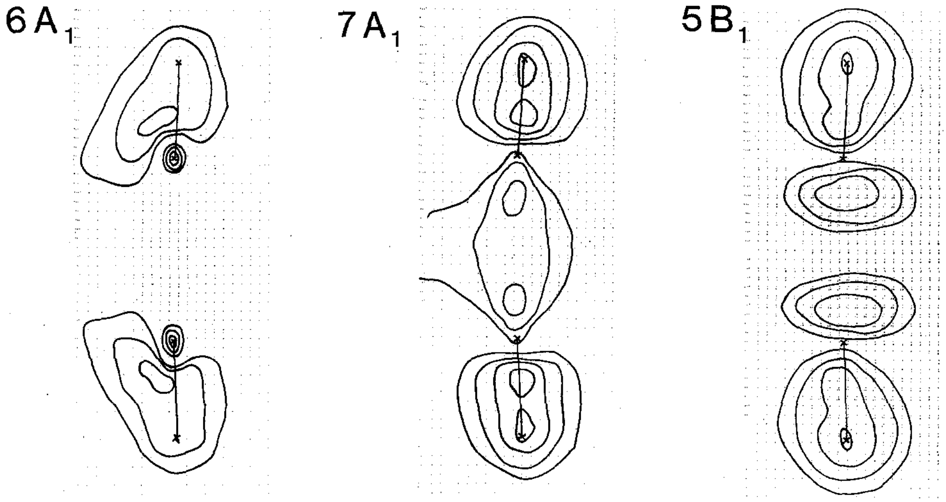

Fig. 3. Electron density diagrams of the three MO's describing the bridgehead C–H bonds of bicyclo [2.1.1] hexane

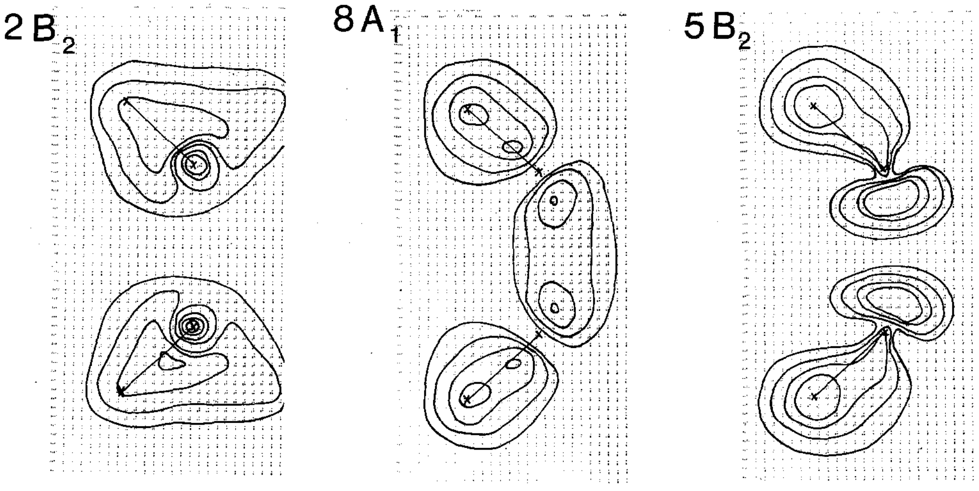

Fig. 4. Electron density diagrams of the three MO's describing the *endo* C_5–H_8 and C_6–H_{10} bonds of bicyclo [2.1.1] hexane

3) Interactions between Fragment Orbitals

Among the MO's of bicyclo [2.1.1] hexane, some result more clearly than others from the interaction between FO's localized on the ethylene and cyclobutane fragments of the molecule. We shall now analyze how some MO's are constructed. The *A* combination of the π type group orbitals belonging to two methylene groups in the ethylene bridge lead to a FO: $[\pi(CH_2)_a - \pi(CH_2)_b]$ which may interact with the b_{1g} type Walsh FO of cyclobutane. Since the CH_2 orbitals are expected to be lower in energy than the cyclobutane Walsh orbital (by analogy with the respective energies of C–H MO's and C–C MO's in cyclobutane itself), the lower lying CH_2–CH_2 FO will mix in the Walsh FO in a bonding manner and the higher lying Walsh FO will mix in the CH_2–CH_2 FO in an antibonding manner [18]. The resulting MO's correspond to $1A_2$ and $2A_2$ respectively. The interaction pattern is illustrated in Fig. 5. An additional slight admixture of the unoccupied a_{2g} Walsh orbital of cyclobutane [15–17] is also observed.

Another example is found in MO's $3B_2$ and $4B_2$ which contain respectively the *S* and *A* combinations of the π FO's built on the CH_2–CH_2 bridge on one side and on the two methylene bridges on the other side. The resulting MO's are of the type:

$$3B_2\colon\ [\pi(CH_2)_a + \pi(CH_2)_b] + [C_5H_7 - C_6H_9]\,,$$

$$4B_2\colon\ [\pi(CH_2)_a + \pi(CH_2)_b] - [C_5H_7 - C_6H_9]\,.$$

However in the one carbon bridges the C_5–H_7 and C_6–H_9 bonds contribute to these MO's much more than the C_5–H_8 and C_6–H_{10} bonds. It may be noted that in these two MO's the CH_2–CH_2 group enters by its FO built on the *S* combination of the individual $\pi(CH_2)$ group orbitals.

One also notices that $3B_1$ and $4B_1$ are respectively the *S* and *A* combinations of the two *A* FO's built from the ethylene groups CH_2 on one side and from the bridgehead CH bonds on the other side.

Nature of the Bonds

A general study of various strained molecules has shown that the characteristic features of strained bonds are, in terms of electronic structures: low C–C overlap population (OP), high *p* character, "bent bond" electron distribution; in addition the MO's describing strained bonds have generally relative high energies and form the top occupied MO's of the system.

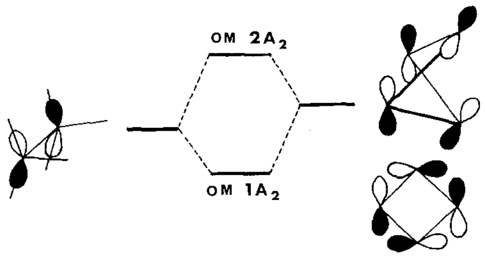

Fig. 5. Interaction diagram between the antisymmetric C–H type fragmant orbital of the ethylene bridge and the b_{1g} Walsh type fragment orbital of the cyclobutane moiety of bicyclo [2.1.1] hexane

Table 1 clearly shows that indeed, the cyclobutane C–C bonds which are expected to be more strained than the C–C bonds of the two carbon bridge also have lower OP. How quantitatively total overlap population may serve as a measure of "strain" in a bond remains to be seen. Nevertheless, there seems to be a noticeable correlation between these two terms in a variety of systems [3]. Computations performed with the same basis set yield the following C–C OP's [3]: 0.75 for ethane, 0.72 for cyclobutane, 0.71 for bicyclo [1.1.1] pentane, 0.65 for cyclopropane. In bicyclo [1.1.0] butane, the low OP of the central C–C bond has been noted by several authors [2–4]; indeed the OP's of the central and lateral bonds are respectively 0.48 and 0.68 [3], the former being even lower than in cyclopropane. It thus is seen that in bicyclo [2.1.1] hexane the ethylene bridge is unstrained and the C–C bonds in the cyclobutane fragment are comparable to those of cyclobutane itself.

Localization of the delocalized SCF MO's using the procedure of Foster and Boys [19] yield the following hybridizations of the carbon orbitals involved in the localized MO's:

$$sp^{2,50} - sp^{2,60} \text{ for } C_1\text{–}C_2,\ sp^{2,65} \text{ for } C_2\text{–}C_3,\ sp^{3,10} - sp^{2,05} \text{ for } C_1\text{–}C_5.$$

On the same basis one obtains $sp^{2,50}$, $sp^{2,80}$ and $sp^{3,90}$ for ethane, cyclobutane and cyclopropane respectively. Thus the carbon sites in the ethylene bridge are more strained than in ethane but less than in cyclobutane in agreement with the small C_1–C_2–C_3 angle of 102.1° [14] (C–C–C angle = 87.8° in cyclobutane [20]). The high p character in the C_1 orbitals used in the cyclobutane bonds is also in line with the very small C_5–C_1–C_6 angle of 78°2 [13]. But the low p character found for the C_5 center is rather surprising in view of a C_1–C_5–C_4 angle of 89.4° [13]; this result is difficult to rationalize at the present stage.

The above discussion seems to indicate that overlap population and orbital hybridization may be used for describing "*strain*" in C–C *bonds* and at C *centers* respectively. However it will be necessary to analyze in detail other strained systems [3] in order to test the generality of these results.

Finally, coming to the orbital energies of the C–C MO's, it is seen that they are indeed high lying; however, the HOMO is of C–H type.

This is due to the strong interaction between the C_5–H_8 and C_6–H_{10} bonds which leads to a large level splitting and places the A combination of these two bonds (HOMO, $5B_2$) well *above* the top C–C MO's[2].

The same feature was found for bicyclo [1.1.1] pentane, where the A combination of the bridgehead C–H bonds is the HOMO. In the present case, the interaction between the bridgeheads themselves is much weaker so that the corresponding MO's ($7A_1$ and $5B_1$) remain both below the top C–C MO's.

With respect to the non-bonded OP's between $C_1 \ldots C_4$ and $C_5 \ldots C_6$ it is seen that the antibonding character found arises from the A C–H combinations (MO's $5B_1$ and $5B_2$ respectively).

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[2] We have found that in tricyclo [3.3.0.0] octane the HOMO (symmetry $2B_1$; energy: -0.368 a.u.) describes the cyclobutane ring and is strongly antibonding for the other C–C bonds. The A combination of the C–H bonds is appreciably lower in energy.

3.2. Electronic Structure and Properties

The most striking electronic features which might confer characteristic properties to the bicyclo [2.1.1] hexane molecule, lie in the interaction between the bridgeheads and, especially, in the stereospecific interaction between the C_5–H_8 and C_6–H_{10} bonds.

It is found that the bridgehead bromide of bicyclo [2.1.1] hexane solvolyses 10^7 times faster than 1-bromobicyclo [2.2.1] heptane, which is less strained [22]. Furthermore *endo*-5-bicyclo [2.1.1] hexyl tosylate (-OTs in the H_8 position) undergoes acetolysis at a rate 10^8 faster than its *exo* isomer, and at a rate 10^3 faster than cyclobutyl tosylate itself [23].

Although the exact nature of the transition state is not known, the striking rate accelerations observed may be connected with the stereospecific transannular interactions found here in the parent hydrocarbon; these interactions should stabilize the developping carbocation in the solvolysis process. Furthermore, one expects the cross-ring interaction to be stronger in *I* (C_5, C_6 interaction) than in cyclobutane itself, since *I* contains a much more puckered cyclobutane ring, thus enhancing the rate of solvolysis, in addition to other effects (like C–C participation) which may also operate.

Semi-empirical calculations have shown that a stereospecific cross-ring interaction exists in cyclobutane cations, which may explain the higher reactivity of an equatorial leaving group as compared to the axial isomer [24].

The high solvolytic reactivity of bridgehead derivatives of bicyclo [1.1.1] pentane is also in agreement with the strong bridgehead interaction present in the parent molecule [5]. In addition, it has been found that the overlap population between the bridgehead carbons goes from antibonding in bicyclo [1.1.1] pentane to non-bonding in its bridgehead cation [5]. It is probable that similar stabilization effects operate in the cationic species derived from leaving groups at C_1 and *endo* at C_5 in bicyclo [2.1.1] hexane.

It also appears that the rate of solvolysis of bicyclo [2.1.1] hexyl-2-tosylate is appreciably higher than one would expect on the basis of purely geometrical (small C_1–C_2–C_3 angle) considerations [25, 26]. Conjugation of the cyclobutane fragment Walsh orbital with the developping cation empty orbital at C_2 (bisected conformation of cyclobutylcarbinyl cation [17]) should indeed lead to a rate enhancement[3].

In view of the structural[4] and reactional[5] analogies between bicyclo [2.1.1] hexane and bicyclo [3.1.1] heptane, it is probable that the latter molecule presents electronic features similar to those of *I*, in particular its HOMO is probably also the antisymmetric combination of the two *endo* C–H bonds at C_5 and C_6.

The large *s* character of the bridgehead C–H bond ($sp^{2.20}$) as compared to ethane ($sp^{3.00}$) and cyclobutane ($sp^{2.85}$) C–H bonds also accounts for the decreased basicity and increased acidity of the bridgehead amine and carboxylic acid

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[3] Conjugation of the cyclobutane system with the π systems of bicyclo [2.1.1]-2-hexanone [27] and of bicyclo [2.1.1]-2-hexene [28, 29] may explain the unsual UV spectra of these molecules (see also [17]).

[4] The C_6, C_7 distance in bicyclo [3.1.1] heptane is 2.1 Å [30].

[5] The *endo*-6-bicyclo [3.1.1] heptyl tosylate undergoes acetolysis 10^6 times faster than its *exo* isomer [31].

respectively [22]. Furthermore, one would expect a large $^{13}C_1$–H_1 nuclear spin-spin coupling constant; no experimental value has yet been reported, but a correlation between *s* character and ^{13}C–H coupling constants [3] leads to a value of about 160–165 Hz for this coupling.

Finally, in analogy with the case of bicyclo [1.1.1] pentane [4, 5], the large long range coupling between the two *endo* hydrogens H_8 and H_{10} (7 Hz; [32]) may be related to the cross-ring interaction described above.

For the same reason the existence of a significant long range coupling between the bridgehead protons is also to be expected.

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