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# THE 9-BARBARALYL CATION, 1,4-BISHOMOTROPYLIUM ION AND SOME RELATED $C_9H_9^+$ CARBOCATIONS. ELECTRONIC STRUCTURES, STABILITY AND REACTIVITY

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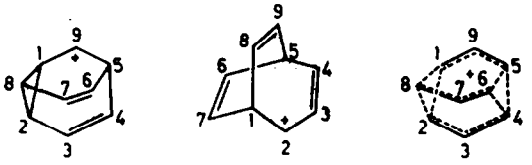
**Abstract**—The electronic structures of the 9-barbaralyl cation (1), the 1,4-bishomotropylium ion (5) and some related $C_9H_9^+$ isomers have been studied by *ab initio* STO-3G calculations. The stability of the cyclopropylcarbinyl cation 1 and the homoaromatic ion 5 as compared with their allylic counterparts is explained in terms of delocalization and MO interactions between molecular fragments. Both the symmetry of, and the distance between, molecular fragments are of importance for the electronic structure, and even symmetry-allowed interactions are negligible in the absence of favourable geometrical distortions. The non-classical ion 3 with $D_{3h}$ symmetry presents special problems where other factors, such as strain, are important for the total energy. A choice between proposed mechanisms for the degenerate rearrangements of 1 can now be made with confidence.

The $C_9H_9^+$ potential energy surface provides a multitude of closely related structures of theoretical interest, for example, totally degenerate ions, homoaromatic ions, bicycloaromatic ions and other proposed non-classical ions. Progress in experimental and theoretical methods has increasingly enabled distinction between proposed carbocation structures and rearrangement mechanisms.[1] However, a careful analysis of electronic structures can also provide answers to *why* certain structures and mechanisms are preferred.

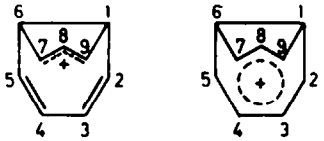
The 9-barbaralyl cation (tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dien-9-yl cation) 1, bicyclo[3.2.2]nona-3,6,8-trien-2-yl cation 2 and the $D_{3h}$ symmetrical ion 3 have all been proposed for the intermediate in solvolysis of 9-barbaralyl- and bicyclo[3.2.2]nonatrienyl substrates,[2,3] and for a totally degenerate ion obtained in superacid and studied by $^1$H NMR.[4] This controversy was recently resolved by $^{13}$C NMR, using $^{13}$C labelling[5] and isotopic perturbation with eight deuterium atoms to rule out ions 2 and 3.[6,7] This left the classical 9-barbaralyl cation 1 as the only possible structure.



1 2 3

The rapid sixfold degenerate rearrangement of 1 has a barrier ($\Delta G^{\ddagger}$) of approximately 3.8 kcal mol$^{-1}$. A divinylcyclopropylcarbinyl cationic rearrangement was preferred to a mechanism involving 3 as a transition state or intermediate (Scheme 1). The totally degenerate rearrangement of 1 ($\Delta G^{\ddagger}$ = 5.0 kcal mol$^{-1}$) has been proposed to proceed via opening of the cyclopropane ring to 2, with four different possibilities to return to 1 (Scheme 2).

At higher temperatures 1 rearranges to a 1,4-bishomotropylium ion 5, whose structure has been inferred from $^1$H and $^{13}$C NMR.[4,8,9] However, in solvolytical studies of the dihydroindenyl cation 4, homoconjugation seems to be absent.[8]



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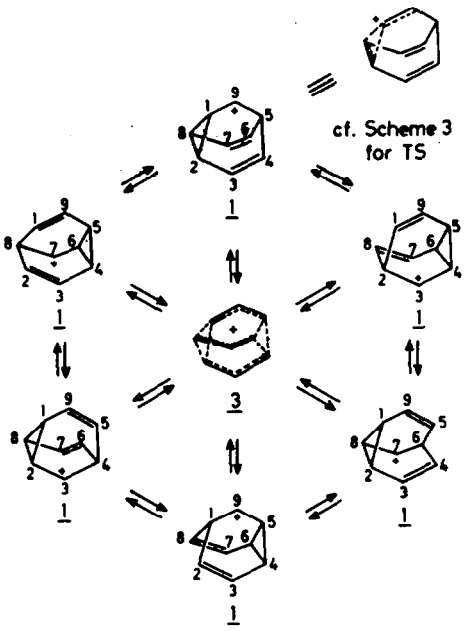



Scheme 1.

The early theoretical studies of these $C_9H_9^+$ ions included CNDO/2 calculations for 2 and 3,[10] electronic structure analysis of 3[11] and a permutation group theoretical study of the degenerate rearrangements of 1,[12] but the results were partly at variance with one other and with experimental results. Recent *ab initio* STO-3G calculations using geometries optimized with MINDO/3 or MNDO gave the reasonable energy ordering 3 > 2 > 1 > 4 > 5.[13] Ion 2 is ~4 kcal mol$^{-1}$ less stable than 1, in agreement with its intermediacy in the totally degenerate rearrangement of 1 (Scheme 2). The faster sixfold degenerate rearrangement of 1 is unlikely to involve 3, which is ~11 kcal mol$^{-1}$ less stable than 1.

An analysis of the electronic structures of ions 1–5 with respect to their structures, stabilities and rearrangements is reported in this paper.

*Methods of calculation*

Geometries were optimized with MINDO/3[14] (and for the highly symmetric 3 also with *ab initio* STO-3G[15]), and were reported previously.[13] *Ab initio* STO-3G calculations using MINDO/3 geometries gave the electronic structures, C–H group charges and C–C overlap populations. The localized molecular orbitals (LMOs) were generated using the procedure of Foster and Boys,[16] and some auxiliary *ab initio* calculations for fragments were performed.

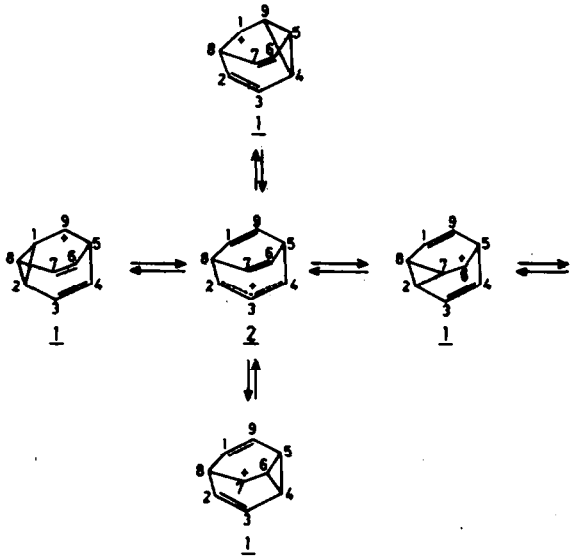
The MONSTERGAUSS[17] program and its internal STO-3G basis set were used in the calculations performed on a CDC CYBER 170.

## RESULTS AND DISCUSSION

*Bicyclo*[3.2.2]*nona*-3,6,8-*trien*-2-*yl cation* 2

The STO-3G C–H group charges and overlap populations for the carbon frameworks of ions 1–5 are given in Fig. 1. Ion 2 (with $C_{2v}$ symmetry) has the positive charge concentrated in the allylic bridge with almost 60% at only two C–H groups. The overlap populations 0.604 on C6–C7, 0.374 on C1–C2 and 0.352 on C1–C7 indicate that the first is a double bond and the latter are two single bonds.[18] The intermediate value 0.498 on C2–C3 is expected for a partial double bond. Small negative overlap populations are normal between nonbonded positions, e.g. C2–C7.

Of the 31 LMOs generated, 18 involve 1s orbitals on carbon and the C–H bonds. The remaining 13 LMOs provide information about the C–C bonds.[19] Two two-centred LMOs on each of the C6–C7 and C8–C9 bonds, one two-centred LMO on each of all the other bonds and a three-centred LMO on C2–C3–C4 are found, supporting the electronic structure 2.



Scheme 2.

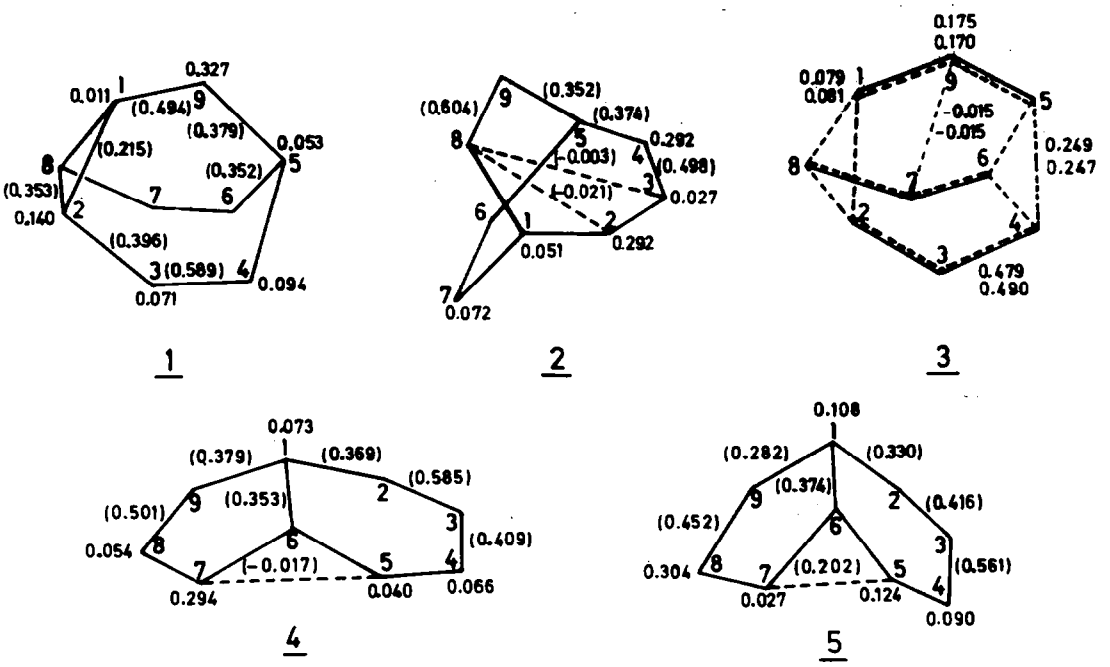



Fig. 1. The STO-3G C–H group charges and overlap populations (numbers within parentheses) of ions 1–5. For ion 3, the upper numbers refer to the MINDO/3 geometry and the lower numbers to the STO-3G optimized geometry.[13]

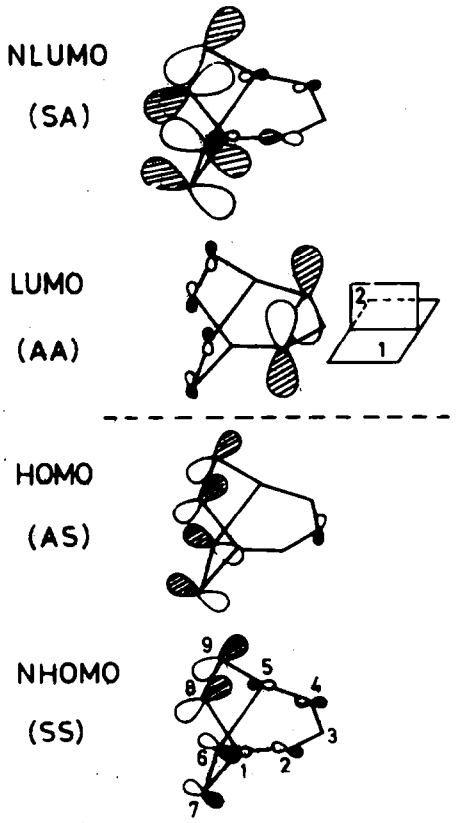



Fig. 2. The STO-3G frontier MOs of bicyclo[3.2.2]nona-3,6,8-trien-2-yl cation 2. The atomic orbital sizes represent approximately the magnitude of the relevant coefficients. Orbitals below the dashed line are occupied. S and A denote symmetry or antisymmetry with respect to the molecular planes 1 and 2.

The two highest occupied molecular orbitals (HOMO and NHOMO) and the two lowest unoccupied MOs (LUMO and NLUMO) of 2 are presented in Fig. 2. An orbital interaction diagram (Fig. 3) was constructed considering the allylic MOs $\chi_1$, $\chi_2^*$ and $\chi_3^*$[20] and the symmetry combinations of ethylenic $\pi$ orbitals $\pi_+$, $\pi_-$, $\pi_+^*$ and $\pi_-^*$ as in norbornadiene,[20] classified as symmetric (S) or antisymmetric (A) with respect to the symmetry planes in 2.

The destabilizing interactions between $\pi$ and $\chi$ orbitals predicted by simple theory[21] cannot be identified, and we may write NHOMO = $\pi_+$, HOMO = $\pi_-$, LUMO = $\chi_2^*$ and NLUMO = $\pi_+^*$. The splitting between NHOMO and HOMO is 0.85 eV, in agreement with the experimental value for norbornadiene (0.85).[22] The only significant interactions occur between filled $\pi$ orbitals and $\sigma$ bonds, but the resulting four-electron repulsion only contributes a net destabilization of ion 2.

In calculations for the bicyclo[3.2.2]nonatrienyl *anion*, the expected stabilizing HOMO–LUMO interactions, predicted by simple theory, could not be observed. Only destabilizing interactions be-

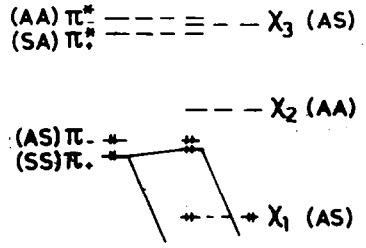



Fig. 3. MO interaction diagram for the bicyclo[3.2.2]nona-3,6,8-trien-2-yl cation 2.

tween filled $\pi$ and $\chi$ orbitals were found, and other explanations for the stability of this anion were sought.[23] For *cation* **2** ($C_{2v}$), HOMO–LUMO interactions are ruled out by symmetry, leaving the destabilizing $\pi$–$\sigma$ interactions and inductive effects to determine stability.

*9-Barbaralyl cation* **1**

The C–H group charges in Fig. 1 show most charge to be in the cyclopropylcarbinyl cationic part of **1**, with approx. 60% at the C9, C2 and C8 groups. Overlap populations show a considerable weakening of the C1–C2 and C1–C8 bonds (0.215), while the C2–C8 bond is strong compared with those of an unsubstituted cyclopropane ring.[18] The C1–C9 bond is a partial double bond, comparable to an allylic bond, all in agreement with the properties of a cyclopropylcarbinyl cation.[24,25] Involvement of the double bonds in conjugation with the cyclopropylcarbinyl cationic fragment is also indicated, strengthening the single bonds (C2–C3, C7–C8) and weakening the double bonds as in a 1,3-diene, e.g. **4**. The 13 LMOs of the carbon framework are all two-centred, two on each of the C3–C4 and C6–C7 bonds and one for each of the other bonds.

The frontier MOs of **1** are given in Fig. 4. An orbital interaction diagram was constructed (Fig. 5) from a cyclopropylcarbinyl cationic fragment, optimized in STO-3G calculations, and the $\pi$ and $\pi^*$ combinations of a 1,4-pentadiene fragment in line with an analysis of the semibullvalene electronic structure.[26] The geometry of the cyclopropylcarbinyl cation is close to the relevant part of the MINDO/3 optimized geometry of **1**, and its HOMO is antisymmetric ($A_1$), as found in calculations with larger basis sets.[25]

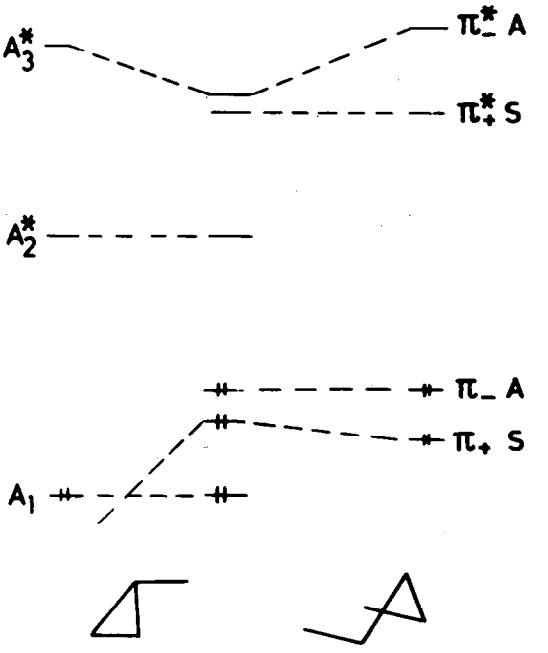



Fig. 5. MO interaction diagram for the 9-barbaralyl cation **1**.

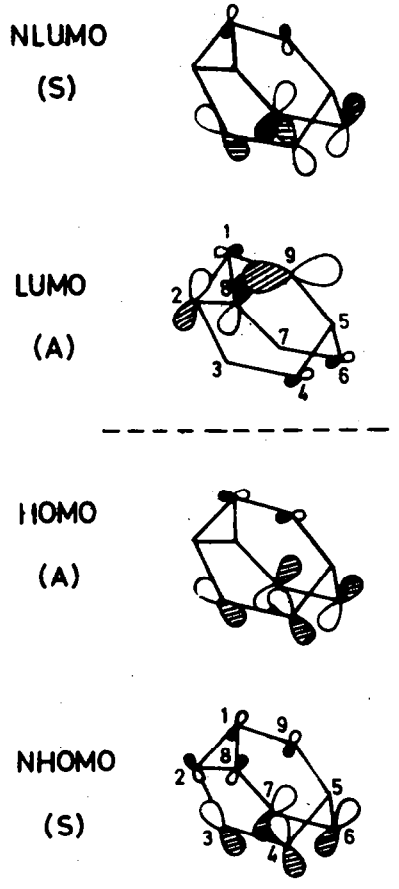



Fig. 4. The STO-3G frontier MOs of the 9-barbaralyl cation **1**.

Several of the frontier MOs of **1** show mixing of cyclopropylcarbinyl cationic and $\pi$ orbitals, but stabilizing HOMO–LUMO interactions seem to be of minor importance. In HOMO, $\pi_-$ interacts with A orbitals but does not bond in the important C2–C3 (C7–C8) region and contributes little to stability. NHOMO show interaction between $\pi_+$ and a symmetric fragment orbital below $A_1$, but LUMO and NLUMO can be approximated with $A_2^*$ and $\pi_+^*$, respectively.

Experimentally and theoretically, **1** is found to be more stable than **2**,[7,13] even though cyclopropylcarbinyl cations usually rearrange to allylic isomers.[24] However, the electronic structure of **1**, in contrast to **2**, involves an interaction of the double-bond $\pi$ orbitals with the fragment bearing the positive charge.

*The $D_{3h}$ symmetrical ion* **3**

The highly symmetric ion **3** has its charge delocalized all over the molecule with some preference for the central C–H groups (>50% on these three positions). Overlap populations indicate partial double bonds connecting the central carbons with the three-membered rings, and rather weak bonds within the cyclopropane rings. Our results differ from those of earlier CNDO/2 calculations, which predicted shorter and stronger bonds in the cyclopropane rings leading to a very stable structure.[10]

The 13 LMOs of the carbon framework are un-

symmetrically located with 6 two-centred LMOs on the left part, one for each bond. To the right, two two-centred LMOs on each of the C3–C4, C5–C9 and C6–C7 bonds are supplemented with a three-centred LMO on C4–C5–C6. Of course, molecular symmetry also permits 7 LMOs on the left and 6 LMOs on the right part of the molecule. These two resonance forms support an electronic structure with three allylic fragments interacting symmetrically to form two weakened cyclopropane rings.

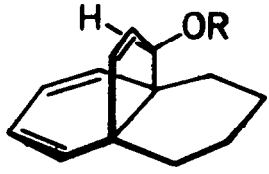
The *ab initio* STO-3G electronic structure of **3** provides the same frontier MOs and the same energy ordering as an earlier study based on an extended Hückel calculation.[11] The results—the details of which are not presented here—confirm the strong conjugation between the p orbitals on central carbons and Walsh orbitals on the cyclopropane carbons.

In CNDO/2 calculations **3** was found to be more stable than **2** and comparable with **5**.[10] Our results with STO-3G have reversed this and shown **3** to be the least stable of all the ions **1**–**5**.[13] Ion **3** is even too unstable to participate significantly as intermediate in the sixfold degenerate rearrangement of **1** (Scheme 1). The great extent of delocalization in **3** can probably not fully compensate the strain associated with the formation of a second weakly bound cyclopropane ring.

*Dihydroindenyl cation* **4**

The MINDO/3 optimized geometry ($C_s$) of **4** has the five- and six-membered rings almost planar with a large dihedral angle (132.6°) between them. This isolates the allylic and butadiene fragments from each other and the charge is located at the allylic carbons as in **2**, with a very small charge at other positions. Overlap populations and LMOs are in agreement with double bonds on C2–C3 and C4–C5, and partial double bonds on C7–C8–C9. All other bonds are single bonds. The overlap populations between the bridges on C5–C7 are small and negative, and no LMOs are found between these carbons.

The four frontier MOs shown in Fig. 6 and the orbital interaction diagram in Fig. 7, using the allylic $\chi$ orbitals and the butadiene $\pi_1$, $\pi_2$, $\pi_3^*$ and $\pi_4^*$ orbitals, confirm the absence of interaction between these two fragments. The frontier MOs can simply be designated NHOMO = $\pi_1$, HOMO = $\pi_2$, LUMO = $\chi_2^*$ and NLUMO = $\pi_3^*$. This lack of interaction has also been postulated in solvolysis of the dihydroindenyl system,[8] but recent results on the tricyclic system **6** are in favour of a bishomoaromatic transition state.[27] Some symmetry-like orbitals of the different fragments in **4** are very close in energy. Thus, in the absence of geometrical distortions towards **5**, the insignificant through-space interactions must be accounted for by the large distance (C5–C7 r = 2.613 Å).




**6**

1,4-*Bishomotropylium ion* **5**

In the MINDO/3 optimized geometry of **5** ($C_s$), the five- and six-membered rings are no longer planar and the dihedral angle between them has decreased to 68.5°, shortening the C5–C7 (C2–C9) distances to 1.6230 Å, in almost complete agreement with calculations[28] and X-ray data[29] for monohomotropylium ions. The positions of the hydrogens on the C2, C5, C7 and C9 positions also indicate substantial rehybridization. The electronic structure of **5** has changed accordingly, and the C–H group charges (Fig. 1) show that positive charge is extensively delocalized with least charge at the C7 (C9) positions.

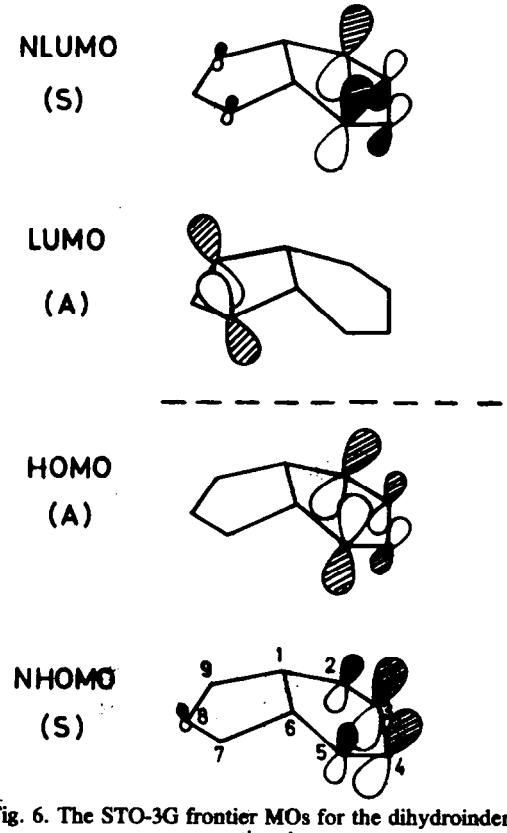



Fig. 6. The STO-3G frontier MOs for the dihydroindenyl cation **4**.

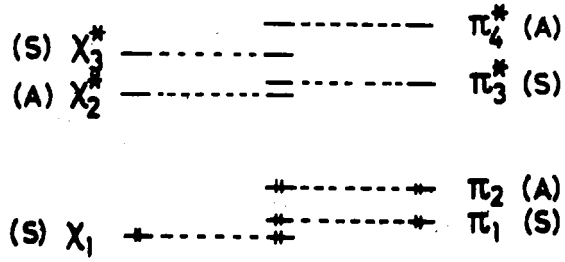



Fig. 7. MO interaction diagram for the dihydroindenyl cation **4**.

Overlap populations are in agreement with a large extent of bond delocalization in the bishomotropylium ring, with weak single bonds on C5–C7 (C2–C9), strong single bonds on C7–C8 (C8–C9) and C2–C3 (C4–C5) and a weak double bond on C3–C4. The 13 LMOs of the carbon framework are all two-centred, two on the C3–C4 and one each on all other bonds, including C5–C7 (C2–C9). This, again, is in agreement with the LMOs obtained for the monohomotropylium ion.[28] Superposition of two sets of LMOs from the monohomotropylium ion, in a 1,4-relative orientation, gives qualitatively the same result as our STO-3G LMOs for 5.

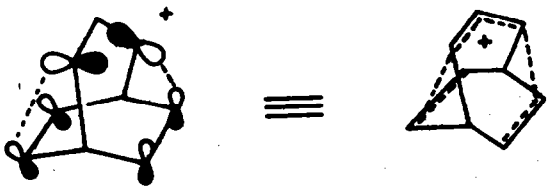
MONOHOMO-
TROPYLIUM ION[28]

The four frontier MOs in Fig. 8 confirm the fundamentally different electronic structure of 5, when compared with 4, making a separation into relevant fragment orbitals difficult. However, if ion 5 has significant homoaromatic character, some of the properties of the parent tropylium ion 7 should also be present in 5. Comparison with the Hückel MOs of 7 included in Fig. 9 shows that this is indeed the case.[30] The degenerate pair of HOMOs ($E_1''$) of 7 compares well with NHOMO and HOMO of 5, even if the small coefficients in 7 are attenuated even further in ion 5. LUMO and NLUMO of 5 show an even better agreement with the degenerate LUMO of 7 ($E_2''$). The degeneracies are removed in 5, thereby lowering the member of each pair (HOMO and LUMO of 7) involving bonding overlap on the homoconjugate bond (C5–C7 and C2–C9), relative to the members having antibonding interactions across these bonds.

This analysis reveals the true homoaromatic character of 5,[31] obvious in the delocalization of charge and bonds and in the shape and energy ordering of its frontier MOs.

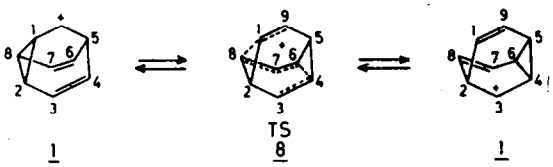
*Rearrangements*

In the rearrangements of 1, ion 2 has been proposed as the intermediate that provides complete degeneracy. A lower energy path leading to sixfold degeneracy has been demonstrated experimentally,[2,3,7] but the symmetrical ion 3 has been rejected as an intermediate in this process because of its high energy[13] (Scheme 1). The symmetry of 2 ($C_{2v}$) does not allow stabilizing interactions between the allyl part and the ethylenic bridges. However, a slight twisting of the allylic bridge will make a less symmetrical overlap between $\chi_2^*$ and $\pi_+$ possible.



8

This stabilized structure 8 ($C_2$) is identical with the transition state proposed for one step in the partially degenerate divinylcyclopropylcarbinyl cation rearrangement of 1 (Scheme 3). Orbital symmetry favours a rearrangement via 8, but it has not yet been possible to locate this structure in MO calculations.




1 8 1

Scheme 3.

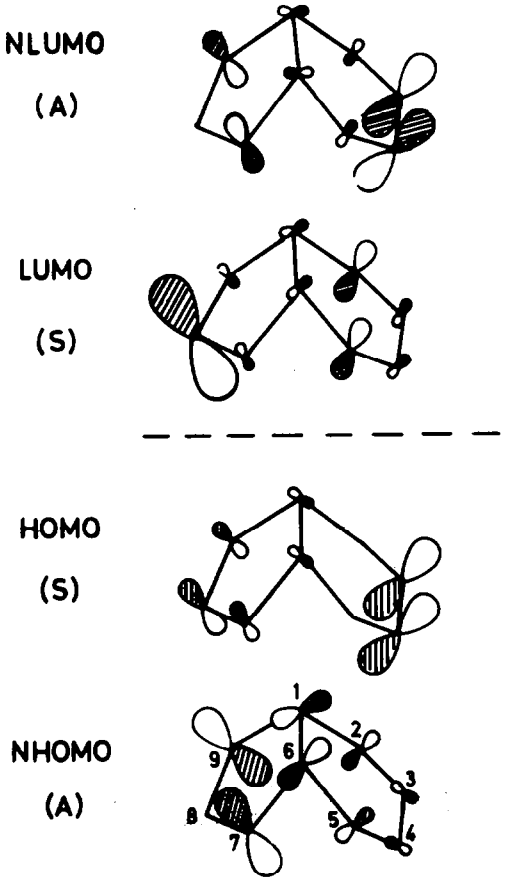
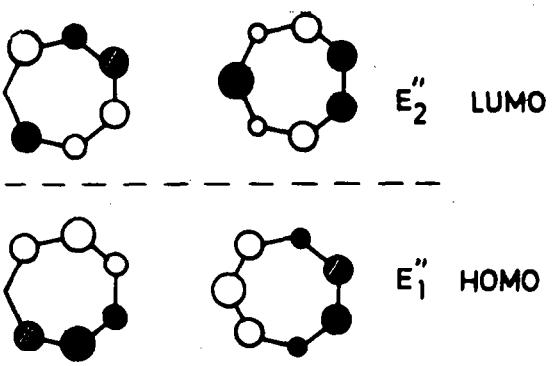



Fig. 8. The STO-3G frontier MOs of the 1,4-bishomotropylium ion 5.




7

Fig. 9. The frontier MOs of the tropylium ion 7 from Hückel MO calculations.[30]

## CONCLUSIONS

The allylic ions 2 and 4 are not the preferred isomers in super-acid solutions. Interactions with olefinic bridges, symmetric if allowed or unsymmetric, give more stable cyclopropylcarbinyl cationic counterparts favoured by extensive charge and bond delocalization. An analysis of electronic structures can rationalize the difference in stability between related isomers even if non-classical structures like 3 pose special problems. An increased understanding in how rearrangements choose their mechanism can also be provided.

*Acknowledgements*—We wish to thank Professors P. Ahlberg and O. Goscinski for their encouragement and helpful comments and the Swedish Natural Science Research Council for financial support to G.J.

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