The C$_9$H$_9^-$ Potential Energy Surface studied by MINDO/3, MNDO, and *ab initio*-SCF(STO-3G) Calculations

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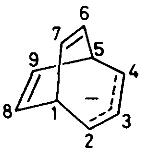
Parts of the C$_9$H$_9^-$ potential energy surface have been studied by MINDO/3, MNDO, and *ab initio*-SCF(STO-3G) methods. The following structures are found to correspond to energy minima: bicyclo[3.2.2]nona-3,6,8-trienyl anion (**1**), barbaral-9-yl (tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl) anion (**2**), and the two structures (**5**) and (**6**) which both have C_{2v} symmetry. As expected the D_{3h} structure (**3**) is presumably an energy maximum. Due to Jahn–Teller distortions it assumes structures (**5**) and (**6**). The following energy ordering (MNDO) was obtained (**1**) < (**2**) < (**5**) < (**6**). That ion (**1**) is more stable than (**2**) is in agreement with experimental results. However, ions (**5**) and (**6**) which both could be intermediates in the Cope rearrangement of (**2**), are found to have much higher energy than (**2**). This indicates a very slow Cope rearrangement of (**2**) contrary to earlier predictions. Comparison with results from experimental and theoretical studies of the C$_9$H$_9^+$ potential energy surface is also presented.

The C$_9$H$_9^-$ potential energy surface, like its cationic counterpart, contains several theoretically interesting structures. Carbanions showing complete degeneracy, homoaromaticity, and bicycloaromaticity are still controversial species,[1–4] and the effects of charge on Cope rearrangement rates, as well as challenging non-classical structures, inspired us to investigate these (CH)$_9^-$ ions further by using MO calculations.

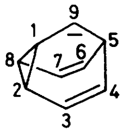
The C$_9$H$_9^-$ carbanions we have studied are the following: bicyclo[3.2.2]nona-3,6,8-trienyl anion (**1**), barbaral-9-yl (tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl) anion (**2**), the D_{3h} symmetrical ion (**3**), cyclononatetraenyl anion (**4**) (D_{9h}), and two tetracyclic ions with C_{2v} symmetry (**5**) and (**6**) considered as the products of Jahn–Teller distortions of (**3**). Both (**5**) and (**6**) may serve as intermediates in the potential Cope rearrangement of (**2**).[5] C$_9$H$_9^-$ ions have been studied in the search for longicyclic stabilization, a concept introduced by Goldstein[6] as an extension of Winstein's theory of homoaromaticity.[7] Experimental investigations of (**1**) gave some support for the bicycloaromatic structure (**7**) under stable ion conditions.[5,8,9]

Ion (**1**) was found to undergo a totally degenerate rearrangement with an activation energy of 22.5 kcal mol^{-1}, and it was proposed to use (**2**) as an intermediate.[5,10,11]

Yoneda and Yoshida performed semiempirical calculations, including partial geometry optimizations, for (**1**) and (**3**) using INDO.[12] To compare relative stabilities they assumed that (**2**) was close in energy to (**3**) and therefore much less stable than (**1**). Grutzner and Jorgensen analysed the electronic structure of (**1**) by using SCF-MO-LCAO STO-3G wave functions on a MINDO/3 optimized geometry, concluding that bicycloaromatic interactions through space were insignificant in favour of structure (**1**) rather than (**7**).[1] Recently (**4**) has been investigated by Owamerali using MNDO.[13]



(1)



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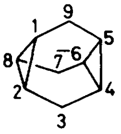
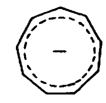
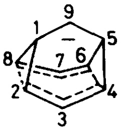


(3)



(4)



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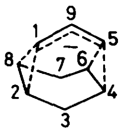

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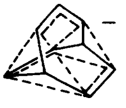


(7)

We present a comparatively systematic study of the C$_9$H$_9^-$ potential energy surface including geometry optimizations for (**1**), (**2**), and (**4**)—(**6**) using semiempirical MINDO/3 and MNDO calculations. For comparison the energy ordering was also determined with *ab initio*-SCF (STO-3G) calculations. Ions (**1**), (**2**), and (**4**)—(**6**) were found to be represented by energy minima but (**3**) is associated with an energy maximum. The energy ordering found is (**1**) < (**2**) < (**5**) < (**6**) (MNDO). This is in agreement with experimental results [*i.e.* that (**1**) is the most stable of the ions] and supports (**2**) as an intermediate in the degenerate rearrangement of (**1**). Contrary to predictions by simple theory[14] the negative charge seems to retard the Cope rearrangement of (**2**), since ions (**5**) and (**6**) are found to have much higher energy than (**1**) and (**2**). All three methods used in this work result in this conclusion.

Results

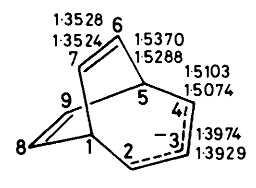
The choice of MINDO/3[15] and MNDO[16] as methods of calculation stems from the possibility of optimizing the geometry of molecular systems of the present size within reasonable efforts. These methods usually predict geometries for neutral hydrocarbons and carbocations in good agreement with experimental and/or sophisticated *ab initio* calculations.[17] For carbanions there is less information available but there are indications that MINDO/3 and MNDO also fare well for this class of ions.[1,2]

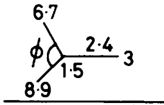
The optimized geometry of ion (**1**), which is given in Table 1, was obtained without any imposed symmetry restriction. However, C_{2v} symmetry was imposed on the initial structure being optimized. But removal of this restriction did not change the symmetry of the fully optimized molecule from C_{2v}. The geometry of (**1**) is similar to its cationic counterpart, *i.e.* bicyclo[3.2.2]nona-3,6,8-trienyl cation but (**1**) has longer r_{24} [*i.e.* larger C(2)–C(3)–C(4) angle].[18,19]

Structure (**2**), which also corresponds to an energy minimum, was difficult to locate on the potential energy surface. A similar problem was met in our studies of the C$_9$H$_9^+$ potential energy surface when searching for the barbaral-9-yl cation structure. As

Table 1. Bond distances (r) and bond angles (Φ) for energy optimized structures are shown. The numbers attached to bonds in the structures are bond distances. The upper ones are MINDO/3 values and the lower ones are MNDO values

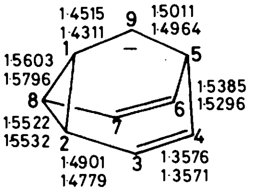
(1) C_{2v}





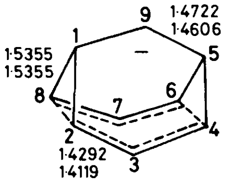
	ϕ	r_{15}	r_{24}
MINDO/3	127·0	2·7682	2·5026
MNDO	130·0	2·7645	2·4869

(2) C_s



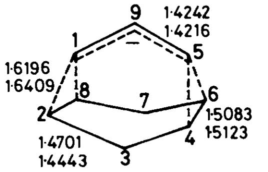
	r_{46}	r_{79}	r_{37}
MINDO/3	2·4738	2·8585	3·1523
MNDO	2·4709	2·8341	3·1340

(5) C_{2v}



	r_{46}	r_{79}	r_{37}
MINDO/3	1·7336	2·9150	2·9537
MNDO	1·8605	2·8902	2·9247

(6) C_{2v}



	r_{79}	r_{37}
MINDO/3	2·9561	2·9516
MNDO	2·8608	2·9345

Table 2. Energies[a] of structures (**1**), (**2**), and (**4**)—(**6**) obtained by MINDO 3, MNDO, and *ab initio*-SCF (STO-3G) calculations

Structures	(**4**)	(**1**)	(**2**)	(**5**)	(**6**)
MINDO/3					
Optimized energy values	−51.5	0[b]	11.4	32.4	27.8
MNDO					
Optimized energy values	−10.5	0[c]	16.7	52.9	54.8
STO-3G					
Energies for MINDO/3 optimized geometries	−8.4	0[d]	16.8	64.3	52.2

[a] Energy values in kcal mol^{-1}. [b] The energy value −1 271.1735 eV of ion (**1**) is set as reference. [c] The energy value −1 276.4110 eV of ion (**1**) is set as reference. [d] The energy value −341.581 941 a.u. of ion (**1**) is set as reference.

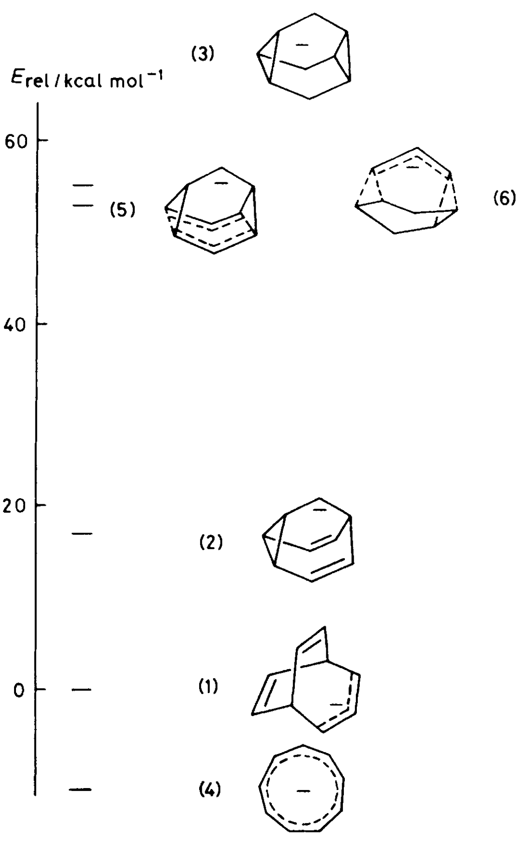


Figure 1. Relative energies (kcal mol^{-1}) of the $C_9H_9^-$ ions (**1**)—(**6**) obtained by MNDO calculations. An energy minimum has not been obtained for structure (**3**) and therefore its relative energy is uncertain

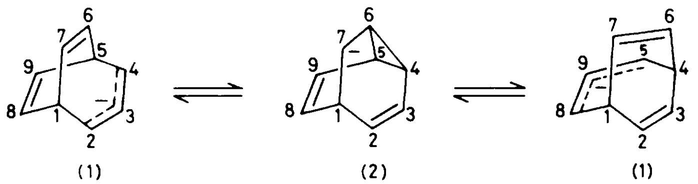
expected the cyclopropylcarbinyl anion part of (**2**) shows quite different geometry from its cationic counterpart. Some negative charge is delocalized into the cyclopropane ring of the anion which is enlarged. This may be understood by assuming that the charge that is delocalized to the ring is populating the Walsh LUMO having antibonding interactions between each pair of the three carbon atoms. In the barbaral-9-yl cation on the other hand delocalization of the positive charge shortens the C(2)–C(8) bond and elongate the C(1)–C(2) and C(1)–C(8) bonds of the cyclopropane ring.[18] The double bonds of the anion like those of the cation appear to be essentially unperturbed.

In our search for an energy minimum for a structure with D_{3h} symmetry, *i.e.* (**3**), no SCF convergence was obtained. This was also the result when the D_{3h} geometry proposed by Yoneda and Yoshida was used as starting structure.[12] The electronically degenerate state leads to convergence problems associated with the MO energy degeneracy.

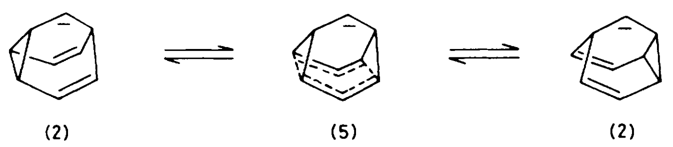
When the D_{3h} symmetry restriction was removed, two new structures (**5**) and (**6**) represented by energy minima were obtained. Structures (**5**) and (**6**) both show C_{2v} symmetry and are products of Jahn–Teller distortions of (**3**).[20] Ions (**5**) and (**6**) are possible intermediates in Cope rearrangements of (**2**). In (**5**) long bonds are found between C(2)–C(8) and C(4)–C(6). In (**6**), on the other hand, long bonds are found between C(1)–C(2), C(4)–C(5), C(5)–C(6), and C(1)–C(8).

Table 1 shows the MINDO/3 optimized geometries of (**1**), (**2**), (**5**), and (**6**) which all are represented by energy minima. Also shown in Table 1 are MNDO optimized geometries obtained by using MINDO/3 optimized geometries as starting geometries. The MINDO/3 and MNDO geometries show only minor differences.

Table 2 shows the energies of the energy minima corresponding to ions (**1**), (**2**), and (**4**)—(**6**). The energy ordering of the structures obtained by MINDO/3 and MNDO [(**4**) < (**1**) < (**2**) < (**5**) ~ (**6**)] are practically the same. However, big energy differences are noticed. Table 2 also shows energies obtained with *ab initio*-SCF(STO-3G)[21] calculations using MINDO/3 optimized geometries and the program MONSTERGAUSS 80.[22] It is interesting to note that similar relative energies are produced by this method as with MNDO



Scheme 1.



Scheme 2.

though minimal basis set *ab initio* calculations of anions are not considered reliable.

It should be noted that in the calculations presented in this paper no explicit account of electron correlation has been made.

Discussion

The general results of our calculations are summarized in Figure 1 which shows energy orderings of the ions. Detailed geometries and energies are found in Tables 1 and 2, respectively. As expected we found the aromatic ion (**4**), introduced as a reference point, to be the most stable of the structures investigated. The allylic ion (**1**) is more stable, by *ca.* 17 kcal mol $^{-1}$ (MNDO and STO-3G), than its barbaralyl isomer (**2**), in agreement with the known rearrangement of (**2**) into (**1**),[11] and the experimentally observed degenerate rearrangement of (**1**), proposed to use (**2**) as an intermediate, with E_a 22.5 kcal mol $^{-1}$ (Scheme 1).[5]

The results in this work and on $C_9H_9^+$ [18] reproduce qualitatively and quantitatively the proposed charge control of the bicyclo[3.2.2]nonatrienyl $\rightleftharpoons$ barbaral-9-yl equilibrium.[11] Positive charge favours the barbaralyl cation and negative charge favours ion (**1**), indicating the relative abilities of a cyclopropane ring and a double bond to participate in cationic or anionic conjugation.

Investigation of the Cope rearrangement of (**2**), which could be expected from simple theory to have a barrier lower than that of barbaralane ($\Delta G^{\ddagger}$ 8.6 kcal mol $^{-1}$),[14,23] turned out to be more complex than previously anticipated. Optimization of an assumed transition state geometry gave (**5**) as one energy minimum. It's geometry was reasonable for a Cope rearrangement intermediate[23] but its energy, *ca.* 36 kcal mol $^{-1}$ less stable than (**2**) (MNDO), indicates a very high barrier (Scheme 2).

Our efforts to optimize the D_{3h} symmetrical anion (**3**) gave only two different structures of lower symmetry (C_{2v}), one of which was (**5**). As indicated in Figure 2 addition of two more electrons to the D_{3h} symmetrical $C_9H_9^+$ *carbocation* gives a *carbanion* which is subject to Jahn–Teller distortions of the molecular structure (Figure 3).[20] The breakdown of the adiabatic approximation leads to vibronic coupling and a mixing of degenerate surfaces. The D_{3h} anion structure is excluded as a stable structure by the computational results as well as by theoretical analysis and must be associated with a high energy maximum. Therefore it will not participate in the rearrangement of (**2**) into (**1**) which was suggested by Yoneda and Yoshida.[12] Actually both (**5**) and (**6**) can be considered as intermediates in the Cope rearrangement of (**2**). The intermediates (**5**) and (**6**) are both related, *via* Jahn–Teller distortions, to the unstable D_{3h} anion (**3**), indicating a high barrier to the Cope rearrangement of (**2**).

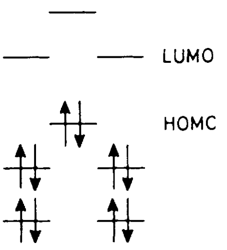


Figure 2. The highest occupied and lowest unoccupied MOs of the D_{3h} symmetrical $C_9H_9^+$ carbocation[24]

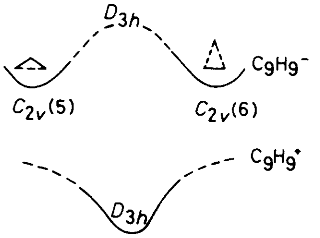
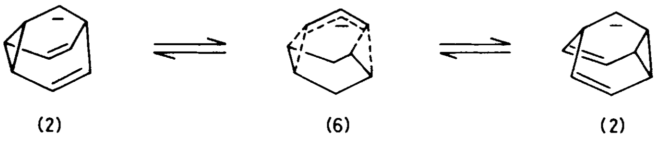


Figure 3. Potential energy surface for the C_9H_9 anion and cation in the vicinity of D_{3h} symmetry



Scheme 3.

Again a comparison with the $C_9H_9^+$ potential energy surface can be illuminating since the Cope rearrangement has also been proposed for the barbaralyl cation. The use of (**5**) and (**6**) as starting geometries for MINDO/3 calculations on $C_9H_9^+$ gave only the D_{3h} optimized structure, supporting its proposed identity with a Cope rearrangement intermediate transition state.[24,25] However, even the stabilized D_{3h} *cation* has too high an energy to contribute significantly to the fast degenerate rearrangements of the barbaralyl cation.[18]

The semiempirical methods used, MINDO/3 and MNDO, have both been claimed to give reasonable geometries also for carbanions, but less reliable energies.[1,2] At least MNDO gives satisfying proton affinities for anions.[26] STO-3G, like other minimal basis sets, is known to behave less satisfactorily for anions,[26] but is still widely used for larger systems.[1–3] Our STO-3G calculations gave positive energies to the HOMOs of all the structures, but the MINDO/3 and MNDO methods still gave negative energies to HOMOs.

The similarity of the results of the different methods indicate that the energy ordering (**4**) < (**1**) < (**2**) < (**5**) ~ (**6**) will probably not change in *ab initio* calculations with larger basis sets or when election correlation energy is included since the energy differences are large. The calculated energy difference between (**1**) and (**2**) (17 kcal mol $^{-1}$) is close to the experimental value for the rearrangement barrier E_a 22.5 kcal mol $^{-1}$, and all the methods used indicate a high barrier for the Cope rearrangement of (**2**).

Improved *ab initio* calculations using extended basis sets (*e.g.* Schleyer's 4 − 31 + G)[26] and including electron correlation energy remain a challenge for large carbanions. The effects of counterions and solvent ought to be evaluated to compare theory with experimental results for carbanions where ion pairing is important which is probably the case for the present ions.

Acknowledgements

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