The $C_9H_9^+$ Potential Energy Surface studied by MINDO/3, MNDO, and *ab initio*-SCF(STO-3G) Calculations

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Controversies about the $C_9H_9^+$ cations (1)—(5) and their reaction mechanisms have been resolved. The ions studied are barbaral-9-yl cation (1), bicyclo[3.2.2]nona-3,6,8-trienyl cation (2), a related ion having D_{3h} symmetry (3) and bicyclo[4.3.0]nonatrienyl cations with (5) and without (4) 1,4-bishomointeractions. All these ions are found to be represented by potential energy minima and the following energy ordering is obtained (STO-3G) (3) > (2) > (1) > (4) > (5). Since the controversial ion (3) is found to have too high an energy it is suggested not to participate significantly in the partial and totally degenerate rearrangements of (1). Most likely the totally degenerate rearrangement of (1) proceeds *via* ion (2). The computational results are in agreement with recent experimental results.

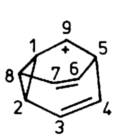
Controversy remains about the $C_9H_9^+$ potential energy surface. This surface hosts theoretically interesting structures like totally degenerate ions, homoaromatic and bicycloaromatic species, and other remarkable non-classical ions which are either stable ions or activated complexes. The complex energy surface has been partly uncovered through extensive experimental and some theoretical work.[1] To resolve the controversies about some $C_9H_9^+$ structures (1)—(5) and their reaction mechanisms the computational work presented here has been carried out.

The global-like and closely related structures barbaral-9-yl cation (1), bicyclo[3.2.2]nona-3,6,8-trienyl cation (2), and the two D_{3h} structures (3) and (3a) have been proposed as intermediates in the solvolysis of barbaral-9-yl and bicyclo[3.2.2]nona-3,6,8-trienyl substrates.[2,3] These ions have also been proposed as candidates for the ion generated from bicyclo[3.2.2]nona-3,6,8-trienol (6) in superacid at *ca.* −135 °C which is observed by ^1H n.m.r. as a sharp singlet.[4] Obviously, this $(CH)_9^+$ ion is a totally degenerate species.

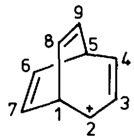
Recently we have been able to show, using ^{13}C n.m.r., ^{13}C labelling, and isotopic perturbation by eight deuteriums of the rapidly equilibrating cation generated from the substrate (7), that the totally degenerate ion observed has neither structure (2) nor (3).[5,6] Therefore the observed ion was assigned the barbaral-9-yl cation structure (1). Ion (1) is concluded to undergo a very fast six-fold degenerate rearrangement (Scheme 1), which does not involve Cope rearrangements (Scheme 2) but the mechanism shown in Scheme 3 (*cf.* ref. 4*b*). However this route and the mechanisms involving the transition states or intermediates (3) and (8) respectively (Schemes 1 and 3), are of interest because of this divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cation rearrangement. Ion (3) is suggested to be able to collapse to any one of six structures shown in Scheme 1. The barrier for the six-fold degenerate rearrangement has been estimated to be only *ca.* 4 kcal mol^{-1}.[5]

Furthermore the reaction which leads to the total degeneracy of ion (1) has been found to have a barrier of 5.5 kcal mol^{-1}.[5] It is proposed to take place *via* the bicyclic ion (2) (Scheme 4). In superacid at *ca.* −125 °C ion (1) rearranges rapidly to ion (5) which on the basis of ^1H and ^{13}C n.m.r. data has been concluded to have the 1,4-bishomotropylium ion structure rather than the bicyclo[4.3.0]nonatrienyl cation structure (4).[4a,7,8]

Ion (4) has been studied solvolytically. In contrast to the results obtained in superacid no indication of any presence of



(1)



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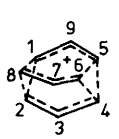

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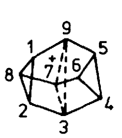
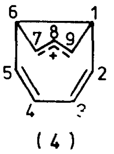
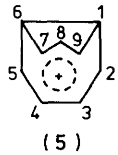


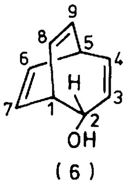
(3a)



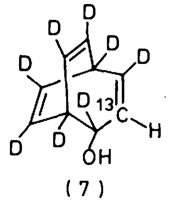
(4)



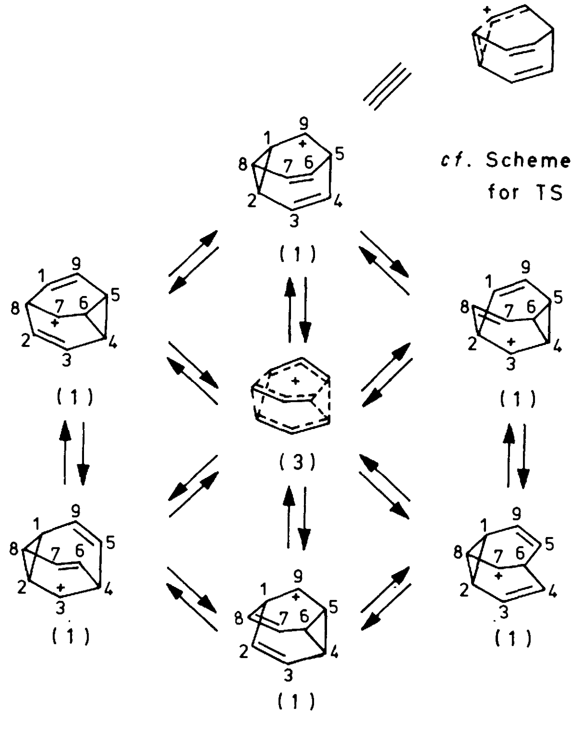
(5)



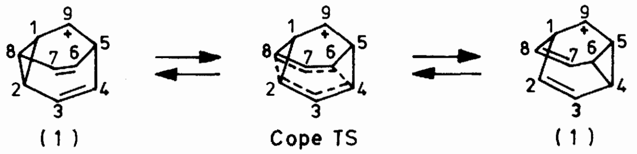
(6)



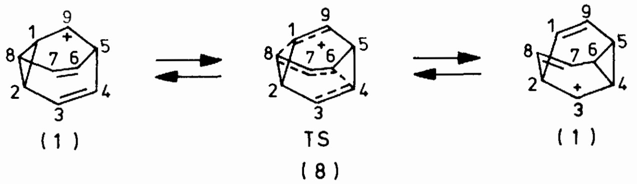
(7)



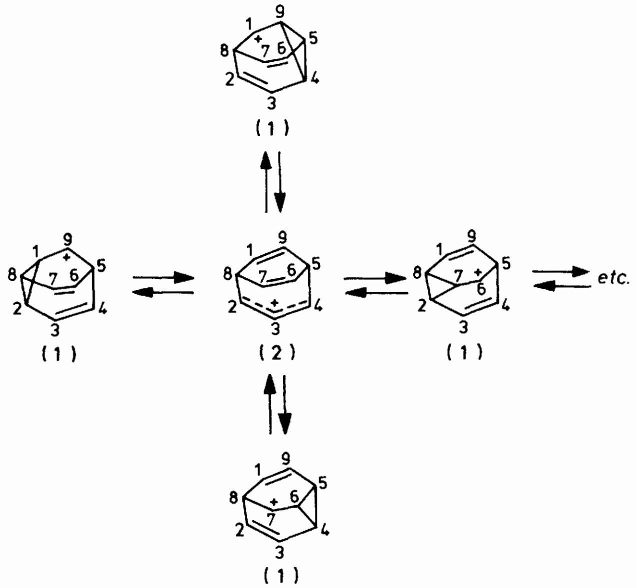
Scheme 1



Scheme 2



Scheme 3



Scheme 4

homointeractions between C-2 and -9 and between C-5 and -7 was found.[8]

Semiempirical calculations using the CNDO/2 method have been performed by Yoneda *et al.* for most of the above $C_9H_9^+$ ions.[9] Due to the low symmetry of the ions and limited computing resources energy optimizations could not be carried through except for ions (2) and (3). Both these ions were found to be represented by energy minima with (3) being much more stable than (2) and ion (5) was found to have somewhat higher energy than (3). An energy minimum for (1) was never reached. Obviously these results are also far from consistent with our recently reported results.

In a paper by Hoffmann *et al.*, accompanying that of Yoneda *et al.*, a qualitative orbital interaction study of the barbaral-9-yl cation was presented.[10] They found that ion (1) assumes a structure with three-fold symmetry (3) and point at the interesting orbital pattern caused by strong conjugative interaction of the central *p*-orbitals on C-3, -7, and -9 with the cyclopropane rings. Ion (3) was suggested to be identical with the transition state for the Cope rearrangement of the barbaral-9-yl cation. This conclusion is in contradiction with extrapolated experimental results. Furthermore, Hoffmann *et al.* pointed out that structure (3a) is an inappropriate representation of an ion assigned the D_{3h} structure.

Bouman and Trindle have later applied permutation group theory to the degenerate rearrangement of (1).[11] Permutation symmetry constraints, imposed by the Pauli principle applied to interchange of spin $\frac{1}{2}$ nuclei, led to the exclusion of ion (3) either as a transition state or intermediate in the degenerate rearrangements of (1). However, these arguments cannot be directly applied in the present context since the authors did not consider the consequences of isotopic substitution. Application of McIver's rules also excludes (3) as a transition state in the rearrangements of (1) but *not* as an intermediate.[12]

The calculations presented in this paper were initiated with the aim of resolving these controversies about the structures and reaction mechanism of the $C_9H_9^+$ ions. The results of our studies of ions (1)—(5) by the MINDO/3 [13] and MNDO [14] semiempirical methods as well as *ab initio*-SCF(STO-3G) [15] are presented below. Energy minimizations were carried out for *all* the ions within the MINDO/3 and MNDO approximations and *all* ions were found to be represented by potential energy minima. The two semiempirical methods yield optimized geometries which differ only slightly for the ions. However, the energy ordering produced by the two methods was to our surprise very different. The order obtained with MINDO/3 was (2) > (3) > (1) > (5) > (4). MNDO on the other hand gave (3) > (5) > (1) > (2) > (4). This inconsistency forced us to use the usually more reliable but expensive *ab initio*-SCF(STO-3G) method. With this method and the MINDO/3 or MNDO optimized geometries the following order was obtained: (3) > (2) > (1) > (4) > (5). It was only possible to minimize the energy of ion (3) within the STO-3G approximation. The structures of the other ions, which have lower symmetry, were not optimized due to our limited computing resources. Upon STO-3G optimization the energy of ion (3) decreased somewhat but *remained* the least stable of all the ions studied. Thus the results that emerge from these STO-3G calculations appear to be in close agreement with those obtained experimentally for these shallow parts of the $C_9H_9^+$ potential energy surface.

Calculations.—Three different quantum chemical methods have been employed, MINDO/3, MNDO, and *ab initio*-SCF(STO-3G). Their sophistication and cost increase in the order given.

MINDO/3 (modified INDO) [13] uses a reparametrized version of the INDO SCF method. It is parametrized to reproduce experimental heats of formation rather than to mimic the results of *ab initio* calculations (which the original INDO method did). The actual SCF INDO part of MINDO/3 is only a small portion of the whole program. It is used as a subroutine by a Davidon–Fletcher–Powell direct minimization algorithm.[16]

The MNDO (modified neglect of diatomic overlap) program [14] uses the same DFP direct minimization algorithm as MINDO/3 and is also parametrized to reproduce experimental heats of formation. The main difference between MNDO and MINDO/3 is that in MNDO more two-electron integrals are included.

The *ab initio*-SCF calculations employed the MONSTERGAUSS 80 *ab initio* program [17] with a STO-3G basis set, *i.e.* each Slater-type orbital (1*s*, 2*s*, and 2*p*) is approximated by a linear combination of three Gaussian functions. No integral approximations nor correlation effects are included in these calculations.

It has long been evident that calibration of semiempirical methods by *ab initio* calculations is necessary in order to get an

Table 1. Energies (kcal mol^{-1}) of ions (1)—(5) obtained by MINDO/3, MNDO, and *ab initio*-SCF(STO-3G) calculations

	Structure				
	(1)	(2)	(3)	(4)	(5)
MINDO/3 optimized energy values *	0 [a]	4.43	3.65	−8.80	−1.48
MNDO optimized energy values	0 [b]	−9.32	16.21	−17.84	3.33
STO-3G energies for MINDO/3 optimized geometries	0 [c]	4.84	10.68	−2.91	−6.05
STO-3G energies for MNDO optimized geometries	0 [d]	3.67	10.85	−6.28	−6.30
STO-3G optimized energy value			6.82 [c]		

[a] The energy value −1 263.9361 eV of ion (1) is set as reference. [b] The energy value −1 267.5005 eV of ion (1) is set as reference. [c] The energy value −341.598 281 a.u. of ion (1) is set as reference. [d] The energy value −341.597 906 a.u. of ion (1) is set as reference.

* We thank Professor P. v. R. Schleyer for communicating MINDO/3 results for ions (1)—(4). The energies obtained were similar to ours, *i.e.* 0, 4.4, 3.6, and −8.5 kcal mol^{-1}, respectively.

unbiased picture of reactants, products, and transition states. Recent work on homoaromatic ions by Haddon [18] compares MINDO/3 with *ab initio* calculations. Geometries appear to be well reproduced by MINDO/3 but energy differences are described less satisfactorily. The need of an unbiased treatment of a given system is demonstrated in a recent evaluation of MINDO/3 for carbocations in which the relative stabilities of various ions are compared. Large errors can occur for systems, with different types of bonding.[19]

The MINDO-3 and MNDO calculations have been carried out with an IBM 155 and the *ab initio*-SCF(STO-3G) computations on a CDC CYBER 170.

Using the MINDO/3 program the geometries of structures (1)—(5) have been optimized assuming that they have C_s, C_{2v}, D_{3h}, C_s, and C_s symmetries respectively. Unrestricted optimizations starting from optimized structures (obtained under the above given symmetry restrictions) with slightly perturbed geometry yielded the same geometries and energies respectively as the restricted optimizations.

The transition state in the transformation of structure (4) into (5) was traced assuming C_s symmetry and r_{12} being constant (1.51 Å). The angle φ_2 was used as reaction co-ordinate (Table 2). The structures and energies of the transition states in the other reactions considered have not been calculated because of convergence problems and lack of computing resources.

Since the MINDO/3 results (Table 1) were at variance with our experiments the somewhat more sophisticated MNDO method was employed. Also with this method geometry optimizations were performed under the above given symmetry restrictions. Closely similar geometries to those obtained with MINDO/3 were obtained (Table 2). However the energy ordering was different (Table 1) and also these results were at variance with our experimental results and therefore the presumably more reliable *ab initio*-SCF(STO-3G) calculations were executed. For this purpose the MINDO/3 and MNDO optimized geometries for structures (1)—(5) and the transition state of the transformation of (4) into (5), which are very similar, respectively, were used. The two sets of geometries produced very similar energies (Table 1). Within the STO-3G approximation it was only possible to perform geometry optimization of the ion having the highest symmetry, *i.e.* ion (3) (which has D_{3h} symmetry). This ion has only six independent geometry parameters (including CH bond parameters). Ion (2) on the other hand has 15 independent geometry parameters and the other structures [(1), (4), and (5)] have more than 20. The optimization of (3) demanded *ca.* 9 computing hours (CDC CYBER 170) and remained the ion with highest energy (Table 1).

Discussion

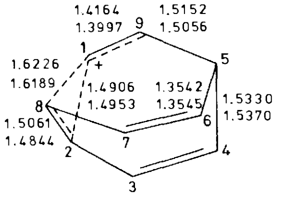
First the energy results will be discussed in the context of the experimental results and proposed reaction mechanisms for the degenerate rearrangements. The calculated geometries will be compared with those qualitatively suggested by simple theory and n.m.r. chemical shifts. Since the STO-3G energies obtained for the ions are considered to be more reliable than those calculated with the other methods mainly the STO-3G results are used in the discussion of the potential energy surface (Table 1). The calculated energies refer to a vacuum and to 0 K. No corrections for differences in zero-point energies of the ions have been made. However, the same ordering of the energies of the investigated ions are expected in superacid solutions and in vacuum since only small differential solvation is predicted in these low nucleophilic media.

The $C_9H_9^+$ *Potential Energy Surface.*—As mentioned above we were recently able to show (by isotopic perturbation) that ion (1) is the most stable of the three ions (1)—(3).[6] The STO-3G calculations produce similar result for this C_s ion using either MINDO/3 or MNDO optimized geometries. The STO-3G energy optimized D_{3h} structure (3) on the other hand is found to be 7 kcal mol^{-1} higher in energy than (1) and this energy difference might increase significantly when the energy of ion (1) is also optimized (which is presently too expensive). Since also ion (3) is found to be represented by an energy minimum the barrier of the transformation of ion (1) to (3) has to be even larger (Figure). Therefore the results suggest that structure (3), due to its high energy, is not used to any significant extent as an intermediate or transition state in the observed degenerate rearrangements of ion (1). This conclusion is consistent with our prediction that the barrier for the Cope rearrangement in Scheme 2 is substantially larger than, *e.g.* for barbaral-9-one. Our results contradict the conclusions reached by Hoffmann *et al.* and by Yoneda *et al.* The recognition of a symmetry-allowed process does of course not prove that the rearrangement makes use of such a route.

An energy difference of *ca.* 4 kcal mol^{-1} between ions (2) and (1) is obtained in the STO-3G calculations with MINDO/3

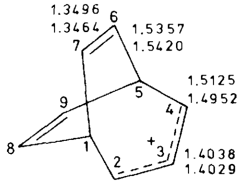
Table 2. Bond distances (r/Å) and bond angles (φ/°) for energy optimized structures are shown. The numbers connected to bonds in displayed structures are bond distances (upper values obtained by MNDO; lower values by MINDO/3)

(1) C_s

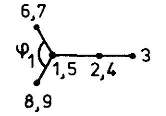


	r_{46}	r_{79}	r_{37}
MINDO/3	2.436	2.831	3.113
MNDO	2.444	2.839	3.105

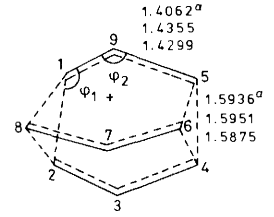
(2) C_{2v}



	φ_1	r_{15}	r_{24}
MINDO/3	129.4	2.784	2.454
MNDO	130.6	2.773	2.459

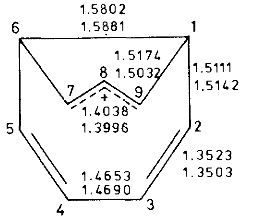


(3) D_{3h}

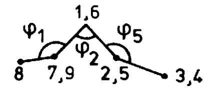


	φ_1	φ_2	r_{97}
MINDO/3	116.6	117.6	2.870
MNDO	116.5	118.0	2.876
STO-3G	116.3	118.4	2.841

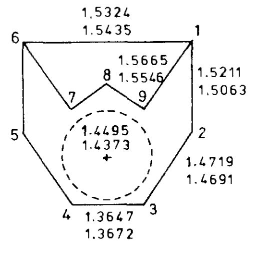
(4) C_s



	φ_1	φ_2	φ_3	r_{57}	r_{79}	r_{25}
MINDO/3	179.5	132.6	178.3	2.613	2.512	2.894
MNDO	179.4	124.1	178.0	2.525	2.296	2.882



(5) C_s



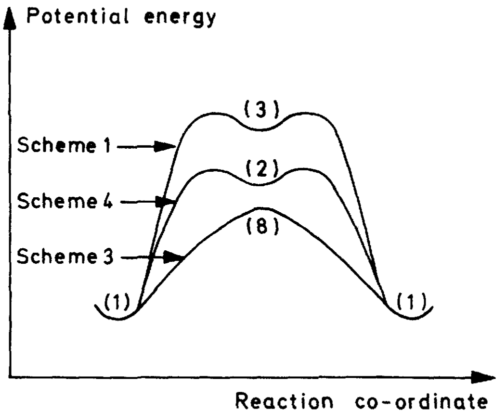
	φ_1	φ_2	φ_3	r_{57}	r_{79}	r_{25}
MINDO/3	169.7	68.5	165.6	1.623	2.402	2.868
MNDO	174.1	68.1	166.6	1.628	2.401	2.881

[a] Value obtained using STO-3G.

or MNDO optimized geometries. This value might change somewhat upon STO-3G optimization of the energies of the two ions. However, we do not expect that the energy order between the two compounds is going to change. The findings obtained so far agree nicely with the proposition (based upon the experimental results) that ion (2) is used as an intermediate in the totally degenerate rearrangement of (1). The barrier for this reaction must of course be larger than the energy difference between ions (1) and (2) but is not expected to be much larger. Thus the observed 5.5 kcal mol^{-1} barrier for the totally degenerate rearrangement is well matched by the one estimated by the calculations.[5]

The six-fold degenerate process (Scheme 1) must proceed by a mechanism which does not involve ion (2). Experimentally it has been found that the transition state for this process is *ca.* 1.5 kcal mol^{-1} more stable than that of the process in Scheme 4.[5] Of the mechanistic proposals only the divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cation rearrangement shown in Scheme 3 remains.

Ion (1) rapidly and irreversibly rearranges at -125 °C to a 1,4-bishomotropylium ion which on basis of ^{1}H and ^{13}C n.m.r. chemical shifts is concluded to have the 1,4-bishomoaromatic structure (5). Results (rates) from solvolytic experiments with bicyclo[4.3.0]nonatrienyl derivatives on the other hand indicate that under these conditions little or no homoaromatic interactions are present in the solvolysis transition state. In the light of these results it is interesting to note that both MINDO/3 and MNDO predict ions (4) (with no homointeraction) and (5) to be stable species, *i.e.* they are represented by energy minima and that they have about the same STO-3G energy (Table 1). Furthermore an energy barrier of 7.4 kcal mol^{-1} (STO-3G) between the ions (5) and (4) is obtained using MINDO/3 geometries. Ion (4) has the structure which has been proposed for the solvolysis inter-



Possible relationships between the degenerate rearrangement routes shown in Schemes 1, 3, and 4

mediate. However our isotopic perturbation studies in super-acid indicate that ion (4) is not present to any significant extent in equilibrium with ion (5).

The $C_9H_9^+$ *Geometries.*—The present calculations (Table 2) confirm the structural conclusions about the observable ions (1) and (5) which were based upon ^1H and ^{13}C n.m.r. chemical shifts and simple resonance theory.

The C_s symmetric ion (1) is found to be composed of the structural elements, cyclopropylcarbinyl cation and two ethylene moieties. Essentially no positive charge is delocalized into the ethylene groups. Due to the electron delocalization in the cyclopropylcarbinyl cation the bond distances r_{19} and r_{28} are considerably shorter and r_{12} (and r_{18}) considerably longer than normal single bonds.

The C_{2v} symmetric ion (2), which has not been observed but has been proposed as an intermediate or transition state in the reactions leading to complete degeneracy, appears through the calculations to be composed of two ethylene moieties and an allyl cation structural element. The charge is mainly confined to the allylic system and no evidence for the presence of any antibicycloaromaticity is found.

The D_{3h} symmetric ion (3), is another ion which has been proposed as an intermediate or transition state in the degenerate rearrangements of (1). This remarkable structure is composed of two cyclopropane rings which are strongly interacting with each other through three sp^2 hybridized CH groups. The positive charge is delocalized all over the molecule with some preference for the cyclopropane rings.

The C_s symmetric rearrangement products (4) and (5) of ion (1) differ considerably in structure but they have similar energy and are separated by only a small calculated barrier (*ca.* 7.4 kcal mol^{-1}). The bicyclic ion (4) is calculated to be composed of through space non-interacting allyl cation and butadiene system. The r_{16} distance is found to be unusually long possibly because of strain.

In ion (5) on the other hand there is strong interaction (through space) between the allyl cation and the butadiene system and it is therefore adequately represented by the 1,4-bishomoaromatic structure (5).

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