

A New MINDO/3 Study of Rearrangements in Barbaralyl Cations

J. Bella and J. M. Poblet*

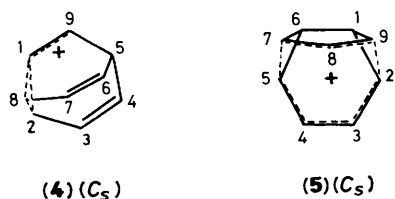
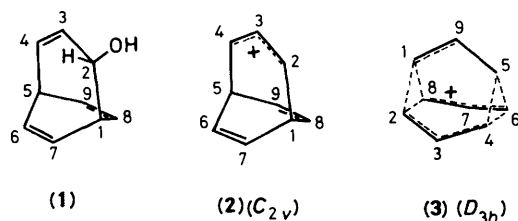
Department de Química, Universitat de Barcelona, Pz. Imperial Tarraco, Tarragona 43005, Spain

A. Demoulliens and F. Volatron

Departament de Chimie Théorique, Université de Paris Sud Bat-490, Orsay, France

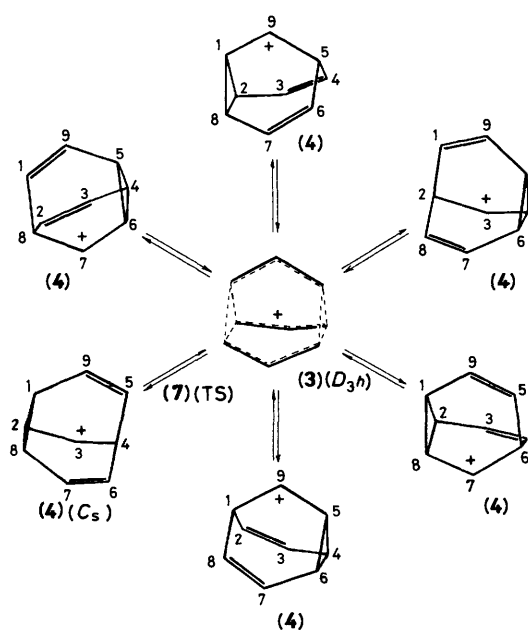
The MINDO/3 potential surface of some barbaralyl cations ($R-C_9H_8^+$; $R = H, CH_3, OH, C_6H_5$, etc.) has been studied. Some MNDO and STO-3G calculations have also been performed. The results of the present work strongly suggest that cations with $R = H, CH_3, Ph$, and $p-CH_3OC_6H_4$ rearrange *via* intermediates but they do not undergo a direct process as previously proposed. Protonated barbaralone rearranges by a Cope mechanism. Activation energies calculated by MINDO/3 are in good agreement with experimental data.

The barbaralyl cations $R-C_9H_8^+$ form an intriguing family of compounds that undergo rapid degenerate rearrangements at very low temperatures.¹ The simplest barbaralyl cation $C_9H_9^+$ ($R = H$) is obtained by reaction of the bicyclic alcohol (1) with superacid, and produce a sharp singlet in the 1H n.m.r. spectrum at $-135^\circ C$.² Since the nine hydrogens cannot be equivalent, the observed singlet suggests rapid equilibration between them. Recently Ahlberg *et al.*³ have shown that the $C_9H_9^+$ cation has neither structure (2) nor (3) and the observed ion was assigned to the barbaral-9-yl cation structure (4). Two kinds of rearrangements are possible for (4): a very fast six-fold degenerate rearrangement, the barrier of which has been estimated to be 4 kcal mol^{-1} ,⁴ and a totally degenerate rearrangement with a barrier of $5.5 \text{ kcal mol}^{-1}$.⁴ In superacid at *ca.* $-125^\circ C$ ion (4) rearranges rapidly and irreversibly to a 1,4-bishomotropylum ion with a 1,4-bishomoaromatic structure (5).

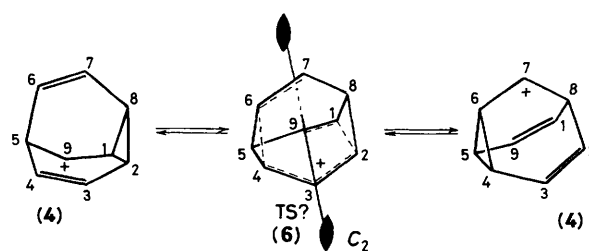


The six-fold degenerate rearrangement has been proposed to proceed *via* the divinylcyclopropylcarbinyl-divinylcyclopropylcarbinyl cationic rearrangement, shown in Scheme 1, where the D_{3h} structure can be an intermediate. The direct process (4) \rightarrow (4) would occur involving the transition state (6) of Scheme 2. The rearrangement which leads to the total degeneracy of ion (4) is shown in Scheme 3.

Calculations using the CNDO/2 method performed by Yoneda *et al.*⁵ and orbital correlation by Hoffmann *et al.*⁶ have suggested the D_{3h} structure as an intermediate for the six-fold rearrangement (Scheme 1). Later Bouman and Trindle⁷ used permutation group theory for the exclusion of the D_{3h} ion as a

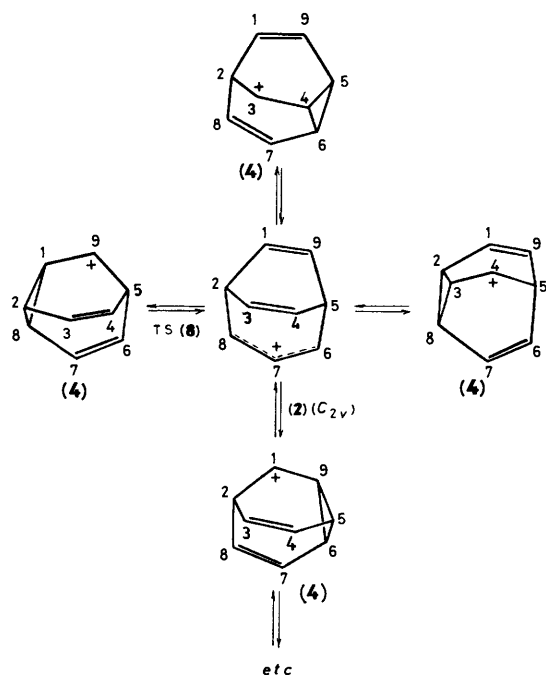


Scheme 1.



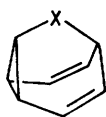
Scheme 2.

transition state and as an intermediate in this rearrangement, but as Ahlberg *et al.*⁸ have pointed out, these results cannot be directly applied in this case. These authors have performed a theoretical study of the $C_9H_9^+$ potential energy surface. From the energy minima, they have proposed a possible relationship between the degenerate rearrangement routes of Schemes 1–3. For these authors, the mechanism in Scheme 2 is most favourable.⁸



Scheme 3.

On the other hand, much effort has been expended on explaining the influence of positive charge on the rate of Cope or Cope-like rearrangements in barbaralyl systems. For neutral species such as barbaralane (9) and barbaralone (10), the Cope mechanism has not been discussed.⁹⁻¹² Positive charge seems to yield an increase in the activation energy.¹² The energy barrier for protonated barbaralone (11) (13.4 kcal mol⁻¹) is 3.2 kcal mol⁻¹ higher than the estimated energy for barbaralone.¹² In the barbaralyl cations (4) and (12)–(14) the activation energy increases with a decrease of positive charge on the barbaralyl framework.¹² From this fact, Jonsäll and Ahlberg have proposed that for some barbaralyl cations, *e.g.* (11) and (14), both Cope and divinylcyclopropylcarbinyl cation mechanisms could operate in parallel.

(9) X = CH₂

(10) X = C=O

(11) X = C=OH⁺

(4) R = H

(12) R = CH₃(13) R = C₆H₅(14) R = *p*-CH₃OC₆H₄

Previous theoretical studies are not conclusive because extensive analysis of the potential surface has not been performed. As no transition-state structures and energies for the different rearrangements are presented by Ahlberg *et al.*⁸ some of their conclusions are not entirely reliable. We present here a MINDO/3¹³ study of the potential surface of some R-C₉H₈⁺ cations (R = H, CH₃, OH, OCH₃, C₆H₅, and *p*-CH₃OC₆H₄). Our aim is to show the potential surface topology of the cation rearrangements. All stationary points have been checked by calculating and diagonalizing a constant matrix.¹⁴

Results and Discussion

Potential Surface of C₉H₉⁺ Cation.—Structures (2) (C_{2v}), (3) (D_{3h}), and (4) (C_s) were recalculated by the MINDO/3 method. They correspond to minima of the potential surface. The main parameters are given in Table 1 and the energies are in Table 2. According to MINDO/3 isomer (4) of C_s symmetry is the most stable in agreement with previous STO-3G calculations.⁸ As MINDO/3 minimum structures of the C₉H₉⁺ potential surface have been described previously,⁸ we begin our exposition with the analysis of the isomerization steps.

In the (4) → (3) isomerization (Scheme 1) conservation of the symmetry plane occurs and therefore the transition state (7) belongs to the C_s point group. Transition state (7) has an average geometry between those of (3) and (4). The major change is in the C(4)–C(6) distance: this shortens from 2.438 Å in (4) to 1.890 Å in the transition state to 1.587 Å in (3). As a result of this intermediate geometry for the transition state structure, (7) has incipient charge delocalization. In (4) the positive charge on C(9) is 0.23 e, in the isomer of D_{3h} symmetry this charge is only 0.02 e. At the saddle point the corresponding charge has an intermediate value, 0.12 e. The (4) → (2) rearrangement occurs by breaking of the C(1)–C(2) bond (see Scheme 3). In the transition state (8) this parameter has an average value between the corresponding distances in the isomers. In (4) r_{C(1)–C(8)} is 1.618 Å, whereas in (2) the same distance is 2.471 Å; in the transition state its value is 2.089 Å. For the six-fold degenerate rearrangement a barrier of 7.43 kcal mol⁻¹ has been obtained very close to the activation energy of 7.13 kcal mol⁻¹ found for rearrangement *via* a C_{2v} intermediate. The experimental energies are only slightly lower than calculated ones. They have been estimated to be 4 and 5.5 kcal mol⁻¹ respectively.⁴

Let us now analyse the proposed direct rearrangement (Scheme 2). Because of symmetry it can be seen that structure (6) should belong to the C₂ point group. In this symmetry, after an exhaustive search, only a stationary point has been found, with two imaginary modes but no saddle point. This structure corresponds to a concerted process with a shortening of the C(4)–C(6) distance and a lengthening of the C(1)–C(2) bond. In (6) these two parameters have the same value (1.945 Å by MINDO/3). A modification of structure (6) taking into account each imaginary mode leads to (4) (C_s) or, alternatively to (2) (C_{2v}) or (3) (D_{3h}). The symmetry of these modes according to the McIver Rules¹⁵ is respectively B and A. The associated frequencies are 471 and 304 cm⁻¹. A break in the C₂ symmetry in (6) does not lead to a transition state for the rearrangement in Scheme 2. The energy found for structure (6) is *ca.* 4 kcal mol⁻¹ higher than the isomerization energies *via* C_{2v} and D_{3h} intermediates. The activation energies for C₉H₉⁺ rearrangements are in Table 2 and mainly geometric parameters of transition states are in Table 1.

Figure 1a shows schematically the MINDO/3 potential energy surface for C₉H₉⁺ rearrangements. An intensive search has been made in order to find the situation shown in Figure 1b, where the negative curvature associated with the imaginary mode A is converted into positive curvature. It has not been found. Structure (6) has been recalculated by using the STO-3G basis set.¹⁶ The STO-3G geometry* is very similar to the MINDO/3 one. The most significant differences are in the C(1)–C(2) and C(3)–C(4) distances. The respective values are 1.989 and 1.389 Å, not far from 1.945 and 1.411 Å obtained by the MINDO/3 method. In the STO-3G basis set (6) is a stationary point with two positive curvatures. As pointed out previously MINDO¹⁸ energies are less realistic for barbaralyl

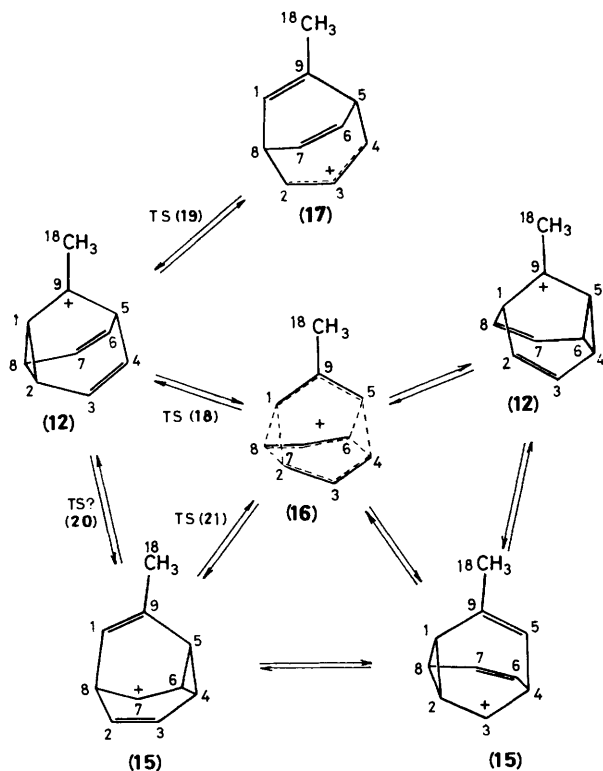
* The MONSTERGAUSS program package¹⁷ was used to calculate STO-3G geometry for (6).

Table 1. Main MINDO/3 parameters for $C_9H_9^+$ cation^{a,b}

Bond	Cation					
	(2)	(3)	(4)	(6)	(7)	(8)
C(1)-C(2)	1.541	1.587	1.618	1.945	1.609	1.555
C(1)-C(8)	2.471	1.587	1.618	1.548	1.609	2.089
C(2)-C(8)	1.495	1.587	1.484	1.500	1.523	1.474
C(2)-C(3)	1.541	1.429	1.495	1.411	1.460	1.519
C(3)-C(4)	1.346	1.429	1.354	1.411	1.387	1.351
C(4)-C(5)	1.541	1.587	1.536	1.500	1.538	1.540
C(4)-C(6)	2.471	1.587	2.438	1.945	1.890	2.409
C(5)-C(6)	1.495	1.587	1.536	1.548	1.538	1.512
C(6)-C(7)	1.402	1.429	1.354	1.374	1.387	1.378
C(7)-C(8)	1.402	1.429	1.495	1.492	1.460	1.434
C(9)-C(5)	1.541	1.429	1.505	1.492	1.465	1.526
C(9)-C(1)	1.346	1.429	1.400	1.374	1.465	1.359

^a Bond lengths in Å. ^b For numbering see Scheme 1.**Table 2.** Relative MINDO/3 energies (in kcal mol⁻¹) of stationary points of $C_9H_9^+$ potential surface

Minima		No minima	
Structure	Energy	Structure	Energy ^a
(2)	4.44	(6)	11.24
(3)	3.66	(7) TS (3) → (4)	7.43 (4.0)
(4)	0.00	(8) TS (2) → (4)	7.13 (5.5)

^a Estimated experimental energies in parentheses.**Scheme 4.**

cations,⁸ but it is interesting to observe that by this method (6) has an equivalent topology to that found by the MINDO/3 and STO-3G methods. In fact, although qualitatively, the MNDO method reproduces Figure 1a.

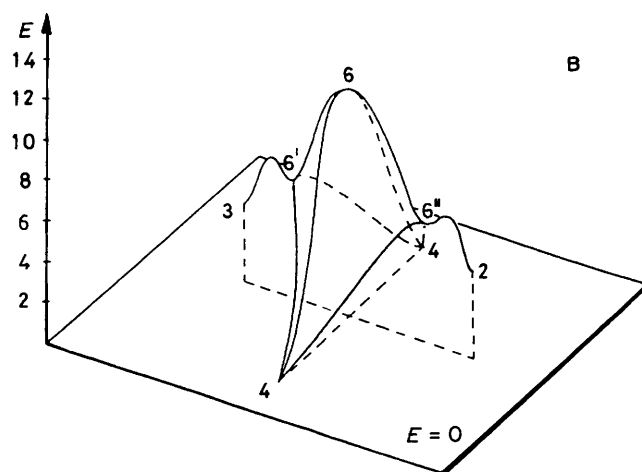
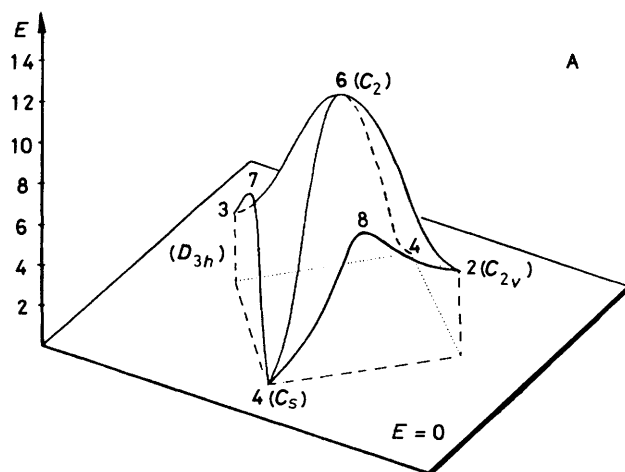


Figure 1. A, Schematic representation of MINDO/3 potential surface of $C_9H_9^+$ cation rearrangement. B, Hypothetical potential surface where there is a saddle point associated with the (4) → (4) rearrangement (see text)

$C_9H_8CH_3^+$ Surface.—An equivalent study has been made of the 9-methylbarbaral-9-yl cation rearrangements. The high symmetry of the ions is broken by the introduction of a methyl group. The potential surface of $C_9H_8CH_3^+$ cation is very similar to that of barbaralyl cation; however in this case the number of stationary points is higher because the substitution of hydrogen by a methyl group yields several isomers. We have limited the study to the structures in Scheme 4, where (12) is the reference structure. The geometry of (12) compares very well with that of (4). In fact, the introduction of a CH_3 group produce a very small change in the barbaralyl framework. MINDO/3 calculations give structure (12) as the lowest in energy. If in structure (4) methyl substitution is performed at C(3), (15) is the corresponding structure in Scheme 4; its energy is only 4.48 kcal mol⁻¹ higher than that of (12).

When methyl substitution is made in structure (3), there is a descent from D_{3h} point group to C_s symmetry; nevertheless the change in the framework is minor. For instance, in the D_{3h} structure of $C_9H_9^+$ cation the two rings formed by atoms 1, 2, and 8, and 5, 4, and 6 have a common distance of 1.587 Å. From Table 3 we can see that for (16) C(1)-C(2) and C(1)-C(8) are the shortest distances at 1.580 Å. 1.594 Å is the greatest value of the C(2)-C(8) bond length. The average value of the six distances is 1.580 Å. There are also small changes when a hydrogen of isomer (2) is substituted by a methyl group, leading to structure

Table 3. Main MINDO/3 distances for $C_9H_8CH_3^+$ cation

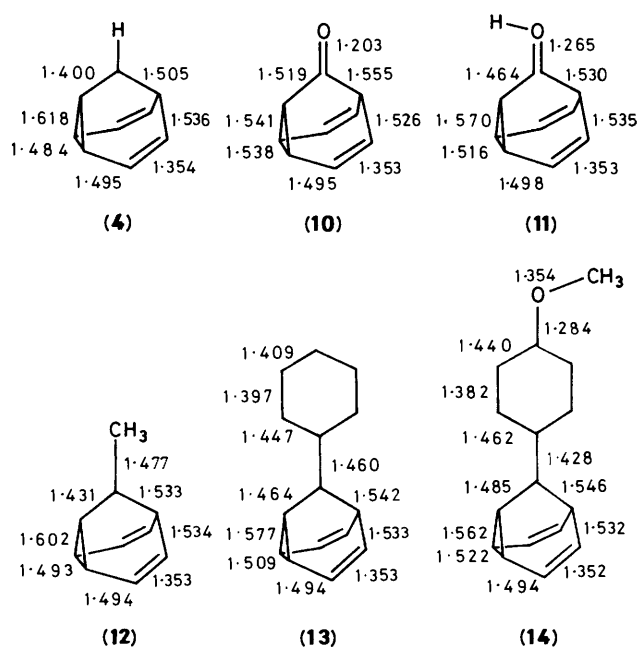
	Cation							
	(12)	(15)	(16)	(17)	(18)	(19)	(20)	(21)
C(1)–C(2)	1.602	2.438	1.580	2.465	1.597	2.132	1.983	1.916
C(1)–C(8)	1.602	1.535	1.580	1.540	1.597	1.551	1.543	1.536
C(2)–C(8)	1.493	1.535	1.594	1.494	1.532	1.475	1.500	1.535
C(2)–C(3)	1.494	1.354	1.428	1.401	1.457	1.429	1.406	1.384
C(3)–C(4)	1.354	1.494	1.428	1.402	1.389	1.381	1.414	1.461
C(4)–C(5)	1.534	1.484	1.582	1.495	1.537	1.508	1.496	1.518
C(4)–C(6)	2.446	1.620	1.591	2.473	1.859	2.415	1.939	1.614
C(5)–C(6)	1.534	1.611	1.582	1.536	1.537	1.538	1.546	1.601
C(6)–C(7)	1.353	1.399	1.428	1.346	1.389	1.349	1.373	1.410
C(7)–C(8)	1.494	1.501	1.428	1.537	1.457	1.519	1.492	1.465
C(9)–C(5)	1.533	1.522	1.452	1.575	1.487	1.557	1.520	1.486
C(9)–C(1)	1.431	1.369	1.453	1.362	1.437	1.373	1.389	1.401
C(9)–C(18)	1.477	1.492	1.485	1.488	1.482	1.486	1.487	1.489

^a Bond lengths in Å. ^b For numbering see Scheme 4.

Table 4. Relative MINDO/3 energies^a of stationary points of $C_9H_8CH_3^+$ potential surface^b

Minima		No minima	
Structure	Energy	Structure	Energy ^a
(12)	0.00	(18) TS (12) → (16)	8.89
(15)	4.48	(19) TS (12) → (17)	10.16
(16)	6.18	(20)	14.44
(17)	8.54	(21) TS (15) → (16)	11.10

^a Energies are in kcal mol⁻¹. ^b For numbering see Scheme 4. ^c Experimental energy of (12) → (12) rearrangement is estimated to be 7.63 kcal mol⁻¹ at –129 °C.²⁰

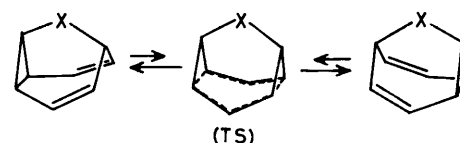
**Figure 2.** MINDO/3 bond lengths of lower-energy isomer of several barbaralyl systems. All structures have C_s symmetry

(17) in Scheme 4. Therefore, we will refer to structures (16) and (17) as pseudo- D_{3h} and pseudo- C_{2v} .

The relative MINDO/3 energies of pseudo- C_{2v} and pseudo- D_{3h} structures are 8.54 and 6.18 kcal mol⁻¹, respectively. For

$C_9H_9^+$ cation the corresponding relative energies are lower (see Table 2). The activation energies for the substituted cation are slightly higher. The relative energies of transition-state structures (18) [TS (12) → (16)] and (19) [TS (12) → (17)] are 8.89 and 10.16 kcal mol⁻¹, respectively. This result is in agreement with the experimental observation that the 3- and 7-H do not exchange rapidly with 2-, 8-, 4-, and 6-H.¹⁹ The experimental barrier for this rearrangement has been estimated to be 7.63 kcal mol⁻¹ at –129 °C.²⁰ As in barbaralyl cation a direct transition state between (12) and (15) has not been found; however, a stationary point (20) (pseudo- C_2) with two imaginary modes has also been obtained, with the highest energy (14.44 kcal mol⁻¹). The imaginary modes with associated frequencies of 475 and 288 cm⁻¹ and with pseudo-B and pseudo-A symmetries respectively, are equivalent to those found for structure (6). We have also studied the isomerization path between (15) and (16); its transition state (21) has an energy of 2.21 kcal mol⁻¹ higher than that of (18) [energy barrier between (12) and (16)]. So, MINDO/3 potential surface shows that the isomerization (12) → (12) occurs *via* an intermediate of pseudo- D_{3h} symmetry. All calculated energies for $C_9H_8CH_3^+$ cation are in Table 4.

Other Barbaralyl Systems.—In the analysis of barbaralyl rearrangements protonated barbaralone plays an important role since although it is a charged system the isomerization (11) → (11) seems to be a Cope rearrangement. Barbaralone isomerization was calculated several years ago by the MINDO/2 method. The calculations indicated a typical Cope rearrangement.¹⁰ The protonation of barbaralone produces a lengthening of the double bond C=C, from 1.203 in (10) to 1.265 Å in (11). The consequence being a noticeable shortening of the C(1)–C(9) and C(5)–C(9) bonds (see Figure 2). The total charge on cyclopropylcarbonyl fragment in barbaralone (10) is +0.56 e but this charge comes entirely from C(9) (0.55e). In (11) the situation is different; the total charge is 0.75 e, 0.57 e being the positive charge on C(9). Therefore, in protonated barbaralone there is an incipient delocalization of positive charge.



The difference of energy between (11) and (11') is negligible (<1 kcal mol⁻¹), their symmetry being of C_s type. During the isomerization the plane of symmetry is conserved, and therefore the transition state also belongs to the C_s point group. From Figure 3, it can be seen that the transition state of protonated barbaralone is quite different to that for neutral barbaralone, and it has some characteristics of structures (3) and (16). For instance, the C(1)–C(9) and C(5)–C(9) distances in barbaralone are typical for a single bond, 1.524 Å, which contrasts with the value of 1.429 Å in barbaralyl cation (3). The values of 1.461 and 1.475 Å for protonated barbaralone are not far from 1.453 Å, C(1)–C(9) distance in methylbarbaralyl cation (16) (Figure 3). In any case, the transition vector associated with the (11) → (11') isomerization indicates clearly that (24) is a saddle point of a Cope rearrangement. The imaginary frequency associated with the transition vector has a small value (167 cm⁻¹). From this small value we cannot conclude that (11) isomerizes with low activation energy. In fact, in agreement with

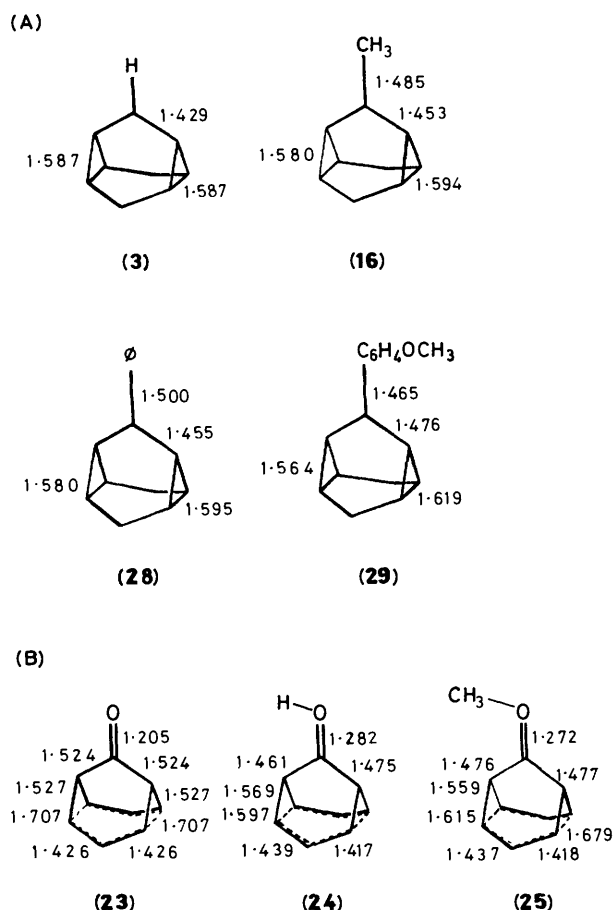


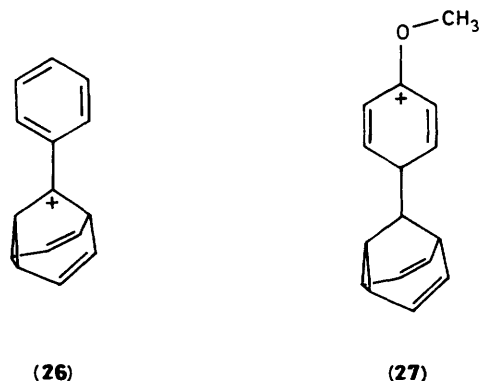
Figure 3. MINDO/3 parameters of calculated *pseudo-D_{3h}* intermediates (A) and Cope transition states (B)

experimental data, the calculated activation energy is higher than these for barbaralyl and methylbarbaralyl. The MINDO/3 relative energy is 16.23 kcal mol⁻¹, the experimental value being 13.4 kcal mol⁻¹.¹⁹⁻²¹

In order to verify the results for protonated barbaralone we have carried out calculations on the isomerization (22) → (22'). For this reaction structure (25) is also a saddle point with characteristics of a Cope transition state. Figure 3 gives the main bond distances for (25). They are not very different to those found for (24). The substitution of the hydroxylic hydrogen by a methyl does not imply any important change in the behaviour of the compound. The substitution produces a small decrease in the C(9)–O bond length and there is some approach to the barbaralone transition structure. Calculations for (11) and (12) confirm that for this kind of cation the isomerization occurs *via* a Cope mechanism.

Finally, we present the results obtained for *p*-anisyl- (14) and phenyl-barbaral-9-yl cation (13). For cation (14) both kinds of isomerization operate in parallel. The substitution in (4) of an hydrogen by a phenyl group (R = C₆H₅) or by an anisyl group (R = *p*-CH₃OC₆H₄) leads to two isomers. In both cases the *cis* isomer [C(1), C(9), C(5), and the carbons of the phenyl group are in the same plane] are lower in energy than the *trans* conformation. In the *trans* conformation the π interaction between the phenyl and barbaralyl groups is not possible, the delocalization of positive charge being small, +0.178 and +0.182 e, respectively. Another effect is the single-bond character between C(9) and R [bond C(9)–C(10)]. The bond distances are respectively 1.488 and 1.484 Å. In the *cis* conformation the π interaction is allowed and a considerable

delocalization of the positive charge occurs. For *p*-anisyl-barbaralyl this effect is stronger than in phenylbarbaralyl. The charge on the anisyl group is +0.43 e and on the phenyl group +0.30 e. The charge delocalization is due to the fact that the π -acceptor character of C(10) is activated by the presence of an OCH₃ group in the *para* position. The strong interaction between the anisyl and barbaralyl groups leads to C(9)–C(10) having double-bond character. This distance is 1.428 Å in the *cis* conformation. In the case of R = C₆H₅ the delocalization effect is minor and the C(9)–C(10) distance is 1.460 Å. Stabilization energy appears upon the delocalization of positive charge. This energy is very small in the case of R = Ph, only 1 kcal mol⁻¹. However, when R = *p*-CH₃OC₆H₄ the difference of energy between both conformations is 7.5 kcal mol⁻¹.



Thus, from the above discussion and the data of Figure 2 the isomers of cations (13) and (14) can be represented by (26) and (27). From (27) and with Ahlberg and Jönsall we can conclude that *p*-anisylbarbaral-9-yl cation could be a candidate for Cope rearrangement. Nevertheless, MINDO/3 calculations show that for the potential surface associated with cation (14) there is a minimum with a *pseudo-D_{3h}* structure. The main distances are in Figure 3. From Figure 3 it can be seen that (29) is a *pseudo-D_{3h}* structure better suited for a Cope transition state than (24) or (25). So, in this cation the Cope rearrangement collapses to an isomerization mechanism *via* a *pseudo-D_{3h}* structure, and consequently (29) is an intermediate in the isomerization of (27). The MINDO/3 relative energy of (29) is 14.3 kcal mol⁻¹. The activation energy for the (27) → (29) rearrangement, a value which has not been calculated, will be higher than 14.3 kcal mol⁻¹.^{*} Thus, MINDO/3 method indicates that the rearrangement energy of *p*-anisylbarbaral-9-yl cation is in the range for Cope energies, as previously proposed.¹² It must be remarked that the delocalization of the positive charge on the substituent R is more important in *C_s* structures than in *pseudo-D_{3h}* ones. Therefore, the increase of the activation energy rather is due to a stabilization effect of *C_s* structures than an increase of transition-state energy. For phenylbarbaral-9-yl cation the *pseudo-D_{3h}* structure (28) has also been found; however in this case the energy of (28) is only 7.5 kcal mol⁻¹ higher than that of (26).

A question which has not been answered yet is why a cation of the R–C₉H₈⁺ type rearranges *via* an intermediate whereas a cation such as protonated barbaralone does not have intermediates in its rearrangements? It must be noted that during the rearrangement C(9) must lose an important part of its positive charge. In other words, the π electron density must increase

* Probably the MINDO/3 relative energy calculated for (29) is too high, therefore the estimated limit of activation energy for (27) → (29) rearrangement is overestimated.

during isomerization. For instance, in barbaralyl cation the p_z electron density on C(9) in (4) is 0.62 and in (3) 0.92 e. For (14) and (29) it is 0.63 and 0.77 e, respectively. In barbaralone (10) and protonated barbaralone (11), the p_z population is 0.60 and 0.51 e, respectively. In their Cope transition states the corresponding values are 0.61 and 0.66 e. Although, for protonated barbaralone there is a significant increase in π electron density, the electronegativity of the oxygen atom does not allow delocalization of the positive charge. Therefore, the participation of the fragment C(1)C(9)C(5) in the rearrangement is small, the result being a Cope rearrangement.

In summary, the semiempirical MINDO/3 method seems to give a good description of the rearrangements of barbaralyl cations. Contrary to what happens in neutral systems such as barbaralane and barbaralone, a Cope rearrangement does not occur in cations of the R-C₉H₈⁺ type (R = H, CH₃, Ph, etc.). The present results strongly suggest that they rearrange *via* intermediates, as shown in Schemes 1 and 3, but do not undergo a direct rearrangement as previously proposed⁸ (Scheme 2). The Cope rearrangement collapses in the mechanism shown in Scheme 1, where the intermediate is a structure with a D_{3h} or pseudo- D_{3h} symmetry. For protonated barbaralone, the rearrangement occurs *via* a Cope mechanism. For R-C₉H₈⁺ cations the ordering of MINDO/3 rearrangement energies is $E_{R=H} < E_{R=CH_3} < E_{R=C_6H_5} < E_{R=p-CH_3OC_6H_4}$. The process in Scheme 2, the divinylcyclopropylcarbinyl cationic rearrangement, has not been characterized. By using the MINDO/3 method (6) (R = H) and (12) (R = CH₃) are stationary points with two positive curvatures. In the STO-3G and MNDO potential surfaces, structure (6) has the same topology as in the MINDO/3 surface.

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