

## *Ab-initio* Based $^{13}\text{C}$ NMR Shift Calculations as a Probe for Carbocation Structure. Homoaromaticity and Rearrangements of the $\text{C}_9\text{H}_9^+$ Ion<sup>†</sup>

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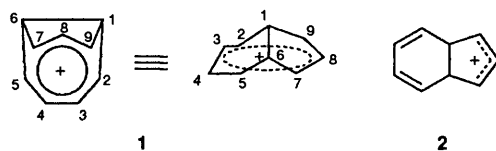
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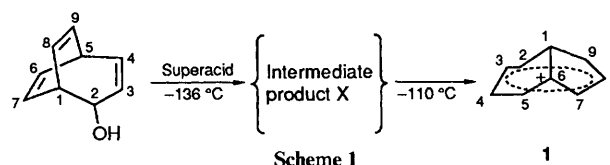
Geometries and energies of  $\text{C}_9\text{H}_9^+$  ions, in particular the 1,4-bishomotropylium cation (**1**) and the barbaralyl cation (**3**), have been calculated at the HF/6-31G(d) and MP2/6-31G(d)//HF/6-31G(d) level of theory. MP2 theory predicts, for **1**, a folded structure (folding angle  $93^\circ$ ) with distances  $r(2,9) = r(5,7)$  being *ca.* 2 Å. The corresponding parameters for the classic analogue of **1**, the dihydroindenyl cation (**2**), are  $114^\circ$  (folding angle) and 2.34 Å [distance  $r(2,9)$ ]. At MP2, **1** is 14 kcal mol<sup>-1</sup> more stable than **2**. However, a comparison of the relative energies of various  $\text{C}_9\text{H}_9^+$  structure reveals that MP2/6-31G(d)//HF/6-31G(d) is not sufficient to provide a reliable prediction of the relative stabilities of these ions. More useful are IGLO/6-31G(d) values of  $^{13}\text{C}$  chemical shifts which characterize **1** to be a bishomoaromatic ion. Also, they confirm that a precursor of **1** is the barbaralyl cation **3** and that **3** can undergo sixfold degenerate divinylcyclopropylcarbinyll rearrangements.

Homoaromaticity is still one of the most debated concepts in organic chemistry<sup>1</sup> and homoaromatic structures have been proposed for many organic species.<sup>1</sup> A variety of experimental and theoretical methods has been used to prove or disprove the existence of homoaromatic character. However, there are several cases where it is now generally accepted that homoaromaticity plays an important role with regard to structure and stability. One well known example is the monohomotropylium cation.<sup>2,3</sup> On the basis of its energetic, geometric, and magnetic properties, it has recently been characterized as the prototype of a monohomoaromatic system.<sup>4,5</sup>

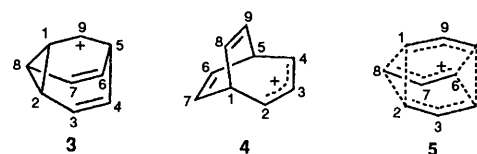
The first bishomotropylium cation to be prepared and experimentally investigated was the 1,4-bishomotropylium ion,  $\text{C}_9\text{H}_9^+$ , (**1**).<sup>6-8</sup> The observed properties of **1** in superacid media, in particular its  $^{13}\text{C}$  NMR chemical shifts<sup>7b</sup> and its  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants,<sup>9</sup> have indicated relatively strong through-space interactions not typical of a normal dihydroindenyl cation structure (**2**). These observations have been interpreted in terms of homoaromatic electron delocalization.<sup>7,9</sup> However, differing descriptions have been given on the basis of solvolytic measurements.<sup>10</sup> Also, semiempirical methods suggest comparable stability for structures **1** and **2**.<sup>11,12</sup>



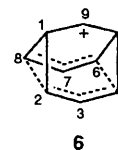
The  $\text{C}_9\text{H}_9^+$  ion is stable under superacid conditions and can be prepared from bicyclo[3.2.2]nona-3,6,8-trien-2-ol (Scheme 1).<sup>13</sup> At low temperatures ( $-135^\circ\text{C}$ ) an intermediate is formed characterized by a sharp singlet in the  $^1\text{H}$  NMR spectrum.<sup>13</sup> Symmetry arguments suggest that the NMR signal is due to a rapidly rearranging cation rather than an intermediate with a stable structure. On the basis of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy, isotopic perturbation studies, and quantum-chemical calculations (semiempirical and *ab initio* with minimal basis sets) Ahlberg and co-workers have assigned to the unknown



intermediate the structure of the 9-barbaralyl cation (**3**).<sup>14</sup> Other possible structures for the intermediate are the bicyclo[3.2.2]nona-3,6,8-trienyl cation (**4**) and the largely delocalized  $D_{3h}$  structure **5**.



If the intermediate cation is indeed **3**, then the question arises as to which way **3** rearranges to give just one signal in the  $^1\text{H}$  NMR spectrum. Cation **3** possesses the divinylcyclopropane entity, which, of course, can undergo fast Cope rearrangements. The corresponding transition state (TS) would be **6**. Hence, an investigation of the intermediate cation should also include calculation of a TS such as **6**.



Upon increasing the temperature the intermediate rearranges to give **1**. Bishomoaromatic character has been assigned to **1** on the basis of the measured  $^{13}\text{C}$  shifts and  $^1J_{\text{CC}}$  values.<sup>9</sup>

The key question in all these studies is the interpretation of the NMR data. The major problem is to know which change in the NMR shift values is indicative of special electronic effects such as homoaromaticity. A solution to this problem implies the definition of a suitable reference structure. Such a reference structure must possess all of the molecular properties of the

<sup>†</sup> Submitted to mark the 150th anniversary of the Chemical Society/Royal Society of Chemistry.

**Table 1** HF/6-31G(d) geometries of the cations 1–5<sup>a</sup>

Parameter	1 (C <sub>s</sub> , 70)	1 (C <sub>s</sub> , 85)	1 (C <sub>s</sub> , 100)	2 (C <sub>s</sub> )
α	70	85	100	113.8
β	191.6	178.3	173.9	175.3
γ	185.2	175.1	172.0	176.7
r(2,9)	1.631	1.924	2.188	2.387
r(1,2)	1.474	1.502	1.518	1.519
r(2,3)	1.452	1.373	1.337	1.325
r(3,4)	1.331	1.394	1.445	1.466
r(1,6)	1.533	1.545	1.552	1.551
r(1,9)	1.534	1.499	1.492	1.492
r(7,8)	1.406	1.383	1.377	1.376
∠(2,1,9)	65.6	79.8	93.2	104.9
∠(2,1,6)	115.1	114.8	115.3	115.7
∠(6,1,9)	105.6	103.9	103.1	102.9
∠(1,2,3)	123.8	124.2	122.8	122.2
∠(2,3,4)	120.0	120.9	121.6	122.0
∠(1,9,8)	107.2	111.0	112.6	113.2
∠(7,8,9)	114.1	109.9	107.9	107.4

	3 (C <sub>s</sub> )	5 (D <sub>3h</sub> )		4 (C <sub>s</sub> )
r(1,2)	1.637	1.594	r(1,2)	1.497
r(1,9)	1.357	1.390	r(1,7)	1.540
r(2,3)	1.484		r(2,3)	1.380
r(2,8)	1.443		r(6,7)	1.309
r(3,4)	1.317		r(1,5)	2.716
r(4,5)	1.535			
r(4,6)	2.422			
r(5,9)	1.495			
r(1,5)	2.462	2.390		
r(3,7)	3.047	2.823		
∠(2,1,9)	112.4	116.2	∠(2,1,8)	108.7
∠(2,1,8)	52.3		∠(7,1,8)	108.0
∠(1,2,3)	114.9		∠(1,2,3)	125.3
∠(1,2,8)	63.8		∠(2,3,4)	121.3
∠(3,2,8)	122.7		∠(1,7,6)	117.2
∠(2,3,4)	120.6			
∠(3,4,5)	118.5			
∠(4,5,6)	104.2			
∠(4,5,9)	108.1			
∠(1,9,5)	119.3	118.4		
∠(1,2,3,4)	22.8	33.9	∠(2,1,5,6)	114.6
∠(2,3,4,5)	0.1		∠(1,7,6,5)	0
∠(9,1,2,3)	-14.2	0	∠(3,2,1,7)	58.7
∠(2,1,9,5)	-28.5			
∠(1,9,5,4)	56.4			
∠(3,4,5,9)	-40.6			

<sup>a</sup> Distances in Å, angles in deg. Only the geometry of the C framework is given.

target molecule with the exception of the electronic features to be investigated. This, of course, is almost impossible and, therefore, leads to the use of problematic reference structures and all kinds of assumptions. Because of this there have been controversies over how to interpret observed NMR data of potentially homoaromatic compounds.

Theory provides a tool for solving a problem such as this. On the basis of *ab initio* calculations, NMR chemical shifts can be predicted for the target molecule as well as for any suitable (stable or unstable) reference system that helps to analyse experimental shift data. In this way the *ab initio* calculation of NMR data becomes an extremely useful tool for the elucidation of electronic features such as homoaromaticity.

We present here the first part of an extensive investigation of the potential-energy surface of the C<sub>9</sub>H<sub>9</sub><sup>+</sup> ion including all the structures mentioned above, possible transition states and rearrangement paths connecting the minima on the surface. In this and future work, the following questions will be considered.

(1) What is the structure of the intermediate ion formed in superacid media at temperatures below -110 °C? Is it 3, 4, 5 or some other structure? (2) Which of the structures investigated

**Table 2** Absolute and relative energies of structures 1–5<sup>a</sup>

Structure	HF/STO-3G	HF/6-31G(d)	MP2/6-31G(d)
3	-341.607 28	-345.725 83	-346.904 74
1	-5.5	<sup>b</sup>	
1 (100) <sup>c</sup>		-14.3	18.3
1 (85) <sup>c</sup>		-5.5	11.9
1 (70) <sup>c</sup>		1.8	24.3
2	-6.3	-16.7	26.6
4	4.1	-0.1	8.5
5	12.4	20.7	-9.9

<sup>a</sup> Absolute energies of 3 in hartree; relative energies are given with regard to that of 3 in kcal mol<sup>-1</sup>. <sup>b</sup> No minimum found in the optimization. <sup>c</sup> The folding angle α of 1 is fixed to the value given in parentheses.

corresponds to the global minimum on the C<sub>9</sub>H<sub>9</sub><sup>+</sup> potential-energy surface? (3) Is the stability of 1 due to bishomoaromatic interactions and, if so, to what extent?

Apart from these more specific questions, the more general problem will be considered of whether the available theoretical methods are sufficient to describe potential bishomoaromatic molecules.

### Computational Methods

The geometries of 1–6 were optimized at the Hartree–Fock (HF) level of theory using the standard STO-3G and 6-31G(d) basis sets.<sup>15</sup> For each structure investigated the force constants were calculated analytically in order to characterize the type of the stationary point found by the optimization. For selected structures, second-order Møller–Plesset (MP2) perturbation calculations<sup>16</sup> utilizing HF/6-31G(d) geometries [MP2/6-31G(d)//HF/6-31G(d)] have been carried out to obtain a better description of the energetics of the C<sub>9</sub>H<sub>9</sub><sup>+</sup> cation and its potential-energy surface.

In the second step of the investigation, NMR chemical shifts were calculated with the IGLO (individual gauge for localized orbitals) method developed by Kutzelnigg and Schindler.<sup>17</sup> It has recently been shown that satisfactory accuracy of calculated <sup>13</sup>C shift values can be obtained just by using a standard basis set of split valence quality that is augmented by polarization functions.<sup>5,18</sup> Calculations were performed on a Cray XMP-48 computer using the COLOGNE90<sup>19</sup> program package, which includes an implementation of the IGLO method of Kutzelnigg and Schindler.<sup>20</sup>

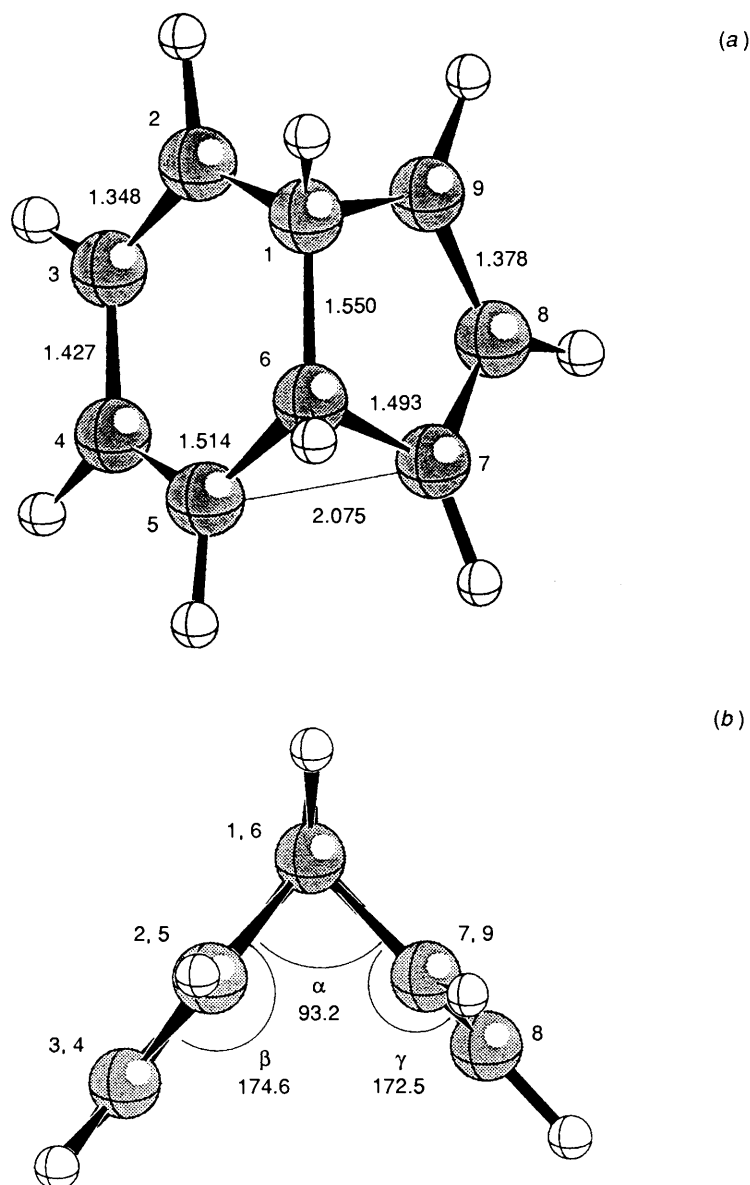
### Results and Discussion

**Energies and Geometries.**—HF/6-31G(d) optimized geometries for 1–5 are given in Table 1. Actually, a stationary point corresponding to 1 could not be found on the HF/6-31G(d) potential-energy surface and, therefore, the following approach was adopted. Starting from the bicyclo[4.3.0]nonatrienyl cation (2), structures, which should resemble 1, were generated by fixing the folding angle α (see Fig. 1) to 100, 85 and 70°. The remaining geometrical parameters were then optimized at HF/6-31G(d). These geometries, which are also shown in Table 1, were used for carrying out MP2 calculations.

Calculated *ab initio* energies of 1–5 are presented in Table 2. Transition state 6 is not included in either Table 1 or 2 since HF/STO-3G calculations indicate that its relative energy is too high to be of any concern. Also, it has two negative eigenvalues and, therefore, represents a second-order TS.

HF/6-31G(d) gives the following order of stabilities: 2 is the most stable cation, 3 and 4 are both about 17 kcal mol<sup>-1</sup>.\*

\* 1 cal = 4.184 J.

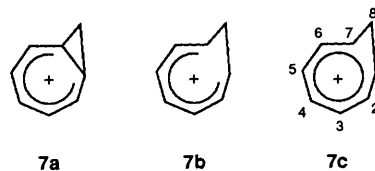


**Fig. 1** (a) and (b) HF/6-31G(d) geometry of the 1,4-bishomotropylium cation **1** obtained for a folding angle  $\alpha = 93.2^\circ$  (see the text). Definitions of the folding angle  $\alpha$ ,  $\beta$  and  $\gamma$  are given in (b).

higher in energy, **5** is highest in energy and **1** does not possess a stable structure at all. HF/STO-3G leads to a similar ordering but with one exception: **1** becomes a local minimum comparable in stability to **2**. The folding angle  $\alpha$  is  $69^\circ$  leading to an  $r(2,9)$  distance of just  $1.624 \text{ \AA}$ .

HF theory is known to underestimate the stability of non-classical carbocation structures. A typical example is the homotropylium ion (**7**) for which HF/6-31G(d) predicts **7b** to be more stable than **7a**, with **7c** not being a minimum on the potential-energy surface at all.<sup>3-5</sup> HF/STO-3G, on the other hand, predicts **7a** to be more stable than **7b**. Both predictions reflect the inability of HF to describe (non-classical) structures with elongated or dissolved C-C bonds [ $1.7 < R(\text{CC}) < 2.2 \text{ \AA}$ ] such as **7c** correctly.<sup>5</sup> Accordingly, one can predict that the stability of **1** and **5** will be underestimated, while that of **2**, **3** and **4** will be overestimated at the HF level of theory.

The MP2 method includes correlation effects due to consideration of doubly excited configurations in the calculation.<sup>16</sup> These are needed to describe stretched or dissolved C-C bonds.

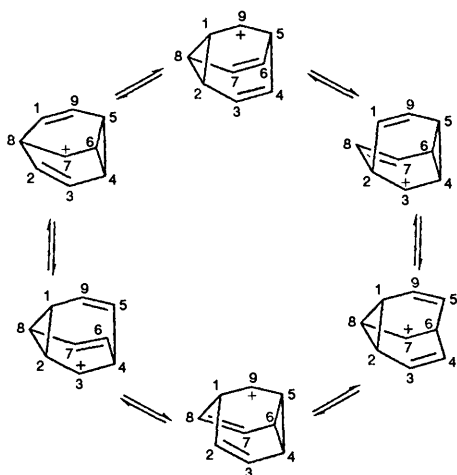


Therefore, MP2 gives a better account of the stability of non-classical structures such as **7c**.<sup>4,5</sup> This is also reflected by the energies in Table 2. At the MP2/6-31G(d) level, the non-classical structure **5** becomes lowest in energy while the classical structure **2** is highest in energy. Also, the cation **1** becomes a minimum on the potential-energy surface. This is predicted by MP2 calculations for the non-planar geometries **1** ( $\alpha = 100^\circ$ ), **1** ( $\alpha = 85^\circ$ ) and **1** ( $\alpha = 70^\circ$ ) (see Tables 1 and 2). The optimal folding angle at MP2 is  $87.6^\circ$  corresponding to a distance  $r(2,9) = 1.972 \text{ \AA}$ . This is almost exactly the distance, which has been calculated in the case of **7c** at the MP2/6-31G(d) level of theory and which has been found to support homoaromatic through-space interactions.<sup>5</sup> Hence, we note that **1** is described as a bishomoaromatic cation by MP2 theory.

**Table 3**  $^{13}\text{C}$  NMR chemical shifts of **3**, **4** and **5**<sup>a</sup>

Centre	<b>3</b>		<b>4</b>	<b>5</b>
	IGLO	Expt. <sup>b</sup>	IGLO	IGLO
C1	78.5	91.3	54.2	181.9
C2	86.7	114.1	236.9	181.6
C3	123.0	116.2	134.4	107.0
C4	137.4	130.2	236.9	181.9
C5	49.4	54.6	54.2	181.9
C6	137.4	130.2	143.4	181.9
C7	123.0	116.2	143.4	107.0
C8	86.7	114.1	143.4	181.9
C9	262.0	225.1	143.4	107.0

<sup>a</sup> IGLO/6-31G(d)//HF/6-31G(d) chemical shifts in ppm relative to  $(\text{CH}_3)_4\text{Si}$ . <sup>b</sup> Values taken from the 9-methylbarbaryl cation and corrected for the methyl-group effect. See ref. 14.

**Fig. 2** Sixfold degenerate divinylcyclopropylcarbinyl rearrangement of the barbaryl cation **3**

Unfortunately, MP2 exaggerates the stability of non-classical structures somewhat<sup>21</sup> and, therefore, the energy calculations presented here provide no ultimate proof of the relative energies of **1**–**6**. As was shown recently, reliable energies can only be expected at an *ab initio* level that contains infinite-order correlation effects with regard to all single or double excitations or, if such a method turns out to be too costly, at a level, where correlation effects due to double excitations are coupled to single and quadruple excitations, thereby correcting the deficiencies of MP2.<sup>5</sup> MP4(SDQ) is such a method, but the size of the cations considered and the available computer resources make MP4(SDQ) calculations unfeasible at the moment.

We conclude that the calculations presented here strongly indicate that **1** is a stable structure on the potential-energy surface of  $\text{C}_9\text{H}_9^+$  and possesses a bishomoaromatic electronic structure with delocalization of  $6\pi$  electrons. However, the methods used do not provide evidence for the correct ordering of the stabilities of **1**–**6**. For example, it is very well known that the  $D_{3h}$  structure **5** is not the intermediate cation observed at  $-135^\circ\text{C}$  in the experiment<sup>14</sup> and, therefore, it is highly unlikely that **5** is more stable than **3** as predicted at the MP2 level. In order to obtain answers to the questions posed in the introduction of this article we now describe a different approach to the problem.

**NMR Chemical-shift Calculations.**—Calculated  $^{13}\text{C}$  chemical shifts depend critically on the geometry employed.<sup>22,23</sup> Therefore, an agreement between calculated and experimental  $^{13}\text{C}$  chemical shifts provides strong indication that the geometry

**Table 4** Time-averaged  $^{13}\text{C}$  chemical shifts of cations **3**, **4** and **5**<sup>a</sup>

Structure	Centres	$\delta$	Centres	$\delta$
<b>3</b> (Expt.) <sup>b</sup>	3,7,9	153	1,2,8,4,5,6	106
<b>3</b> , IGLO		169		96
<b>4</b> , IGLO	2,3,4	203	1,5,6,7,8,9	114
<b>4</b> , IGLO	1,3,5	81	2,4,6,7,8,9	175
<b>5</b> , IGLO	3,7,9	107	1,2,8,4,5,6	182
Expt. <sup>c</sup>		152		101

<sup>a</sup> Averaged values in ppm. <sup>b</sup> Values taken from the 9-methylbarbaryl cation and corrected for the methyl group effect. See ref. 14. <sup>c</sup> Ref. 25.

used in the calculations reflects the true equilibrium geometry of the molecule under investigation. For example, in the case of the homotropylium cation it was possible to identify structure **7c** and to exclude **7a** and **7b** just on the basis of IGLO  $^{13}\text{C}$  chemical-shift calculations employing HF/6-31G(d) geometries.<sup>5</sup> In the following we use the same approach (a) to identify the intermediate product X of Scheme 1 and (b) to confirm the bishomoaromatic character of **1**.

IGLO/6-31G(d)//HF/6-31G(d) values of the  $^{13}\text{C}$  NMR chemical shifts for structures **3**, **4** and **5** are given in Table 3 together with experimentally based estimates of  $^{13}\text{C}$  chemical shifts for **3**. The latter have been derived from the NMR spectrum of the 9-methyl-9-barbaryl cation using appropriate shift corrections for the methyl group.<sup>14</sup> Calculated and estimated  $^{13}\text{C}$  chemical shift values are in reasonably good agreement. The mean deviation between these two sets of shift values is 15.3 ppm but improves to 7.6 ppm if shift values for C2 (C8) and C9 are excluded from the comparison. These, however, are exactly those C atoms that, in the cyclopropylcarbinyl unit of **3**, are strongly influenced by the methyl substituent. The empty  $2p\pi$  orbital at C9 overlaps with the antibonding C2C8 Walsh orbital, thereby reducing its destabilizing character.<sup>24</sup> Any substituent that changes the electron acceptor ability of the  $2p\pi$  orbital at C9 will have a major impact on the  $^{13}\text{C}$  shifts at C9, and C2(C8). These changes are difficult to mimic by normal substituent effects in saturated hydrocarbons. Therefore, the calculated  $^{13}\text{C}$  chemical shifts of **3** probably give a better account of the magnetic properties of the barbaryl cation than estimates derived from experimental shift values of 9-methyl substituted **3**.

At  $-150^\circ\text{C}$  the  $^{13}\text{C}$  NMR spectrum of the intermediate cation shows two peaks with the intensity ratio 6:3.<sup>25</sup> To explain both the  $^{13}\text{C}$  spectrum and the sharp singlet in the  $^1\text{H}$  NMR spectrum at  $-135^\circ\text{C}$  it has been suggested that **3** undergoes rapid degenerate divinylcyclopropylcarbinyl cationic rearrangements as shown in Fig. 2.<sup>13</sup> Fig. 2 reveals that in such a process atoms C3, C7 and C9 (formally carrying the positive charge) and atoms C1, C2, C4, C5, C6, C8 give rise to similar chemical shifts thus leading to the observed intensity ratio. The time averaged structure would give a spectrum with a symmetry corresponding to that of **5** and, therefore, one might consider the possibility that the NMR spectra actually are due to an intermediate form identical with the  $D_{3h}$  cation **5** that could be a transient point of the process shown in Fig. 2 at these temperatures.

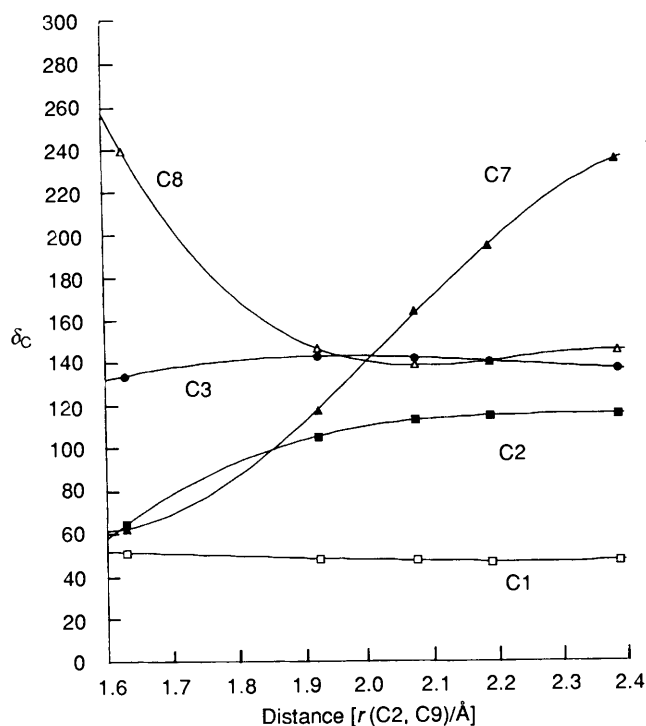
In principle, it could also be possible to generate the observed intensity ratio for structure **4** by some kind of dynamic process in which any of the centres 2, 3 and 4 are exchanging with each other with the rest of the centres exchanging amongst themselves, or in which there is an exchange between centres 1, 3 and 5 on one side and centres 2, 4, 6, 7, 8 and 9 on the other.

We tested all possibilities by comparing appropriate average values of calculated  $^{13}\text{C}$  chemical shifts with the experimental shifts (Table 4). There is agreement between experimental and theoretical values for **3**, but not for **4** and **5**, i.e. the averaged  $^{13}\text{C}$  chemical shift values  $C_{3,7,9}$  and  $C_{1,2,8,4,5,6}$  calculated at IGLO/6-

**Table 5** Comparison of the magnetic properties of **1**, **2**, **8** and **9**<sup>a</sup>

Centre	C1	C2	C3	C7	C8	$\Delta$	$\chi$
<b>1</b> , Expt.	52.6	117.2	140.2	155.5	144.0	—	
<b>2</b>	46.6	114.9	136.0	234.0	144.6	18.4	81.2
<b>1</b> (100)	46.4	114.1	139.7	193.4	139.7	10.4	92.3
<b>1</b> (93.2) <sup>b</sup>	47.0	112.4	141.4	163.5	138.3	5.1	99.0
<b>1</b> (85)	48.0	104.8	142.4	117.2	146.2	12.0	107.2
<b>1</b> (70)	50.9	64.2	133.6	62.1	239.2	50.0	95.8
<b>8</b> , Expt.				234.7	145.7		
<b>9</b> , Expt.		126.0	124.3				

<sup>a</sup> IGLO/6-31G(d)//HF/6-31G(d) chemical shifts in ppm relative to (CH<sub>3</sub>)<sub>4</sub>Si; mean deviation  $\Delta$  between experimental and IGLO chemical shifts in ppm; magnetic susceptibility  $-\chi$  in 10<sup>-6</sup> cm<sup>3</sup> mol<sup>-1</sup>. Experimental values from ref 7(b). <sup>b</sup> Folding angle leading to the best agreement between IGLO and experimental values. Relative HF/6-31G(d) Energy: -11.0 kcal mol<sup>-1</sup> (compare with Table 2). For geometry see Fig. 1.

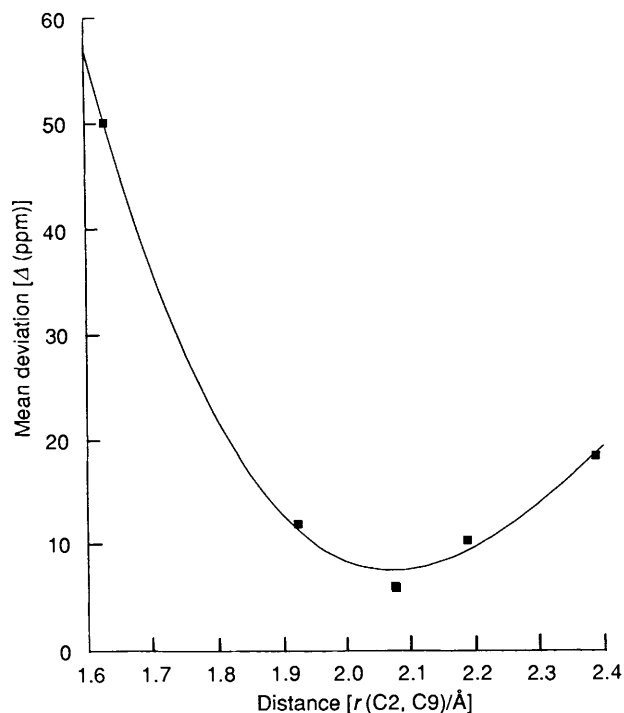


**Fig. 3** IGLO/6-31G(d) <sup>13</sup>C chemical shifts ( $\delta_C$ ) given as a function of the distance  $r(2,9) = r(5,7)$  (for the corresponding  $\alpha$  values, see Table 1)

31G(d) agree, to within 15 ppm, with the corresponding experimental values. Again, this provides convincing proof that **3** is the structure present in superacid media and confirms conclusions drawn from isotopic perturbation studies carried out by Ahlberg and co-workers.<sup>9</sup> Structures **4** and **5** can clearly be excluded as being responsible for the observed NMR spectra.

We note that even in the case where HF and MP2 energy calculations do not provide sufficient information on the relative stabilities of the cations considered, the use of calculated NMR chemical shift calculations is sufficient to identify the intermediate of the process shown in Scheme 1. Hence, IGLO NMR chemical-shift calculations represent a very useful tool for characterizing the structure of short-lived species.

In Table 5 and Fig. 3, calculated <sup>13</sup>C chemical shifts for **1** ( $\alpha = 100^\circ$ ), **1** (85), **1** (70), and **2** are compared with the corresponding experimental values for **1**. Obviously, the chemical shifts of C1 and C3 do not depend on the folding angle  $\alpha$  or the distance  $r(2,9)$ . However, there are strong variations in the shift values of C2, C7 and C8. Of these, the values for C2 and C8 seem to converge to a limiting value with increasing  $\alpha$  or  $r(2,9)$ . Only the



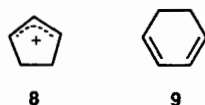
**Fig. 4** Mean deviation of IGLO/6-31G(d) <sup>13</sup>C chemical shifts from experimental values of **1** given as a function of the distance  $r(2,9) = r(5,7)$  (for the corresponding  $\alpha$  values, see Table 1)

<sup>13</sup>C chemical shift of C7 is sensitive to geometrical changes over the whole range of possible  $r(2,9)$  values (see below).

The mean deviation  $\Delta$  between experimental and calculated <sup>13</sup>C shift values is plotted in Fig. 4 as a function of the distance  $r(2,9)$ . Assuming that, for the correct geometry of **1**, the mean deviation between experimental and calculated shift values has to adopt a minimum, the optimal folding angle  $\alpha$  should be 93.2°. Utilizing this  $\alpha$  value and reoptimizing the geometry at the HF/6-31G(d) level, the geometry given in Fig. 1 was obtained. It is characterized by a distance  $r(2,9) = r(5,7) = 2.07$  Å. The IGLO <sup>13</sup>C chemical shifts calculated for this geometry (see Table 5 and Fig. 3) lead to the best agreement between theory and experiment ( $\Delta = 5.1$  ppm). We conclude that **1** possesses a geometry similar to that shown in Fig. 1 with a folding angle close to 90° and  $r(2,9)$  value close to 2 Å. The (homoaromatic) interaction distance is almost identical with that recently found for  $r(1,7)$  in the homotropylium cation **7c**.<sup>5</sup>

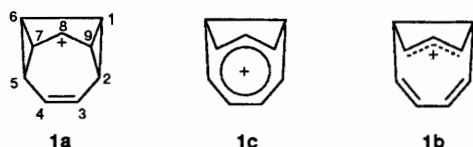
*Bishomoaromaticity—Fact or Fiction?*—As pointed out above, the concept of homoaromaticity can only be quantified by selecting an appropriate reference state. In the case of the homotropylium cation **7** its planar form has been chosen<sup>5</sup> since in this form  $\pi, \pi$  interactions between centres C1 and C7 are not significant. A similar choice in the case of **1** is not possible since planar **2** possesses two inverted C atoms (C1, C6) which lead to an unrealistically high strain energy and electronic effects that make any comparison with **1** difficult. On the other hand, the HF/6-31G(d) equilibrium geometry of **2** possesses a folding angle of 113.8° which corresponds to  $r(2,9) = 2.34$  Å (Table 1). As a consequence the  $p\pi$  orbitals at C2, C9, C5, C7 point towards each other and overlap to some extent. Even though overlap is rather small, through-space interactions and electronic interactions similar to those in **1** cannot be fully excluded. To test this we compared the <sup>13</sup>C chemical shifts of **2** with those of **8** and **9** (Table 5)<sup>7b</sup> which contain structural units of **2**, namely the allyl cation and the diene unit.

The shift values of the allyl unit of **8** compare well with the corresponding values of **2**, but there is a 12 ppm difference



between the  $^{13}\text{C}$  shift values of the diene units in **9** and **2**. This difference may already indicate through-space interactions between the diene and the allyl entities in **2** [ $r(2,9) = 2.34 \text{ \AA}$ , see Table 1]. Compared with the  $^{13}\text{C}$  shifts of **9**,  $\delta(\text{C}3)$  of **2** is shifted to low field by *ca.* 10 ppm while  $\delta(\text{C}2)$  is shifted to high field by the same amount. Hence, C3 (C4) are somewhat more deshielded than C2 (C5), which would be the case if structure **1c** contributed to the electronic wavefunction of **2**. Obviously, **2** possesses electronic features that make its use as a reference system for **1** problematic.

In Table 5 and Fig. 3, calculated  $^{13}\text{C}$  chemical shifts of **1** and **2** are given as a function of the folding angle  $\alpha$  or the distance  $r(2,9)$ . For a folding angle of  $70^\circ$  [ $r(2,9) = 1.63 \text{ \AA}$ ], **1** is similar to structure **1a**, for a folding angle of  $100^\circ$  [ $r(2,9) = 2.19 \text{ \AA}$ ], **1** is close to **1b** (or **2**).



On going from **1a** to **1b** [increasing  $\alpha$  and  $r(2,9)$ ] some typical changes in the electronic structure of **1** take place which are reflected to some extent by the changes in the gross atomic charges of the CH groups (Fig. 5) and the  $^{13}\text{C}$  chemical shift values (Fig. 3). These changes can be described in the following way.

C1,C6: the electronic characteristics of these C atoms change little upon increasing  $\alpha$  or  $r(2,9)$ . According to the observations made for **7**, the C atoms should be hybridized in a similar way for **1a**, **1b** and **1c**. Gross atomic charges as well as  $^{13}\text{C}$  chemical shift values depend only slightly on the distance  $r(2,9)$  or the folding angle  $\alpha$  (see Figs. 3 and 5).

C2,C5: the C atoms of three-membered rings such as cyclopropane are known to possess similar electronic characteristics as the C atoms of ethene.<sup>26</sup> Accordingly, there is no significant change in the electronic nature of C2 and C5 on going from **1a** to **1b**. There is reflected by both calculated gross atomic charges and  $^{13}\text{C}$  chemical shifts (see Figs. 3 and 5).

C3,C4: for all possible distances  $r(2,9)$  or folding angles  $\alpha$ , these C atoms are  $\text{sp}^2$  hybridized. Hence, gross atomic charges and  $^{13}\text{C}$  shift values are only weakly dependent on changes in  $\alpha$  or  $r(2,9)$  (see Figs. 3 and 5).

C7,C9: in **1a**, these C atoms are (formally) electronically neutral. In **1c**, they become more and more positive with increasing  $r(2,9)$ . However positive charge is delocalized over seven C atoms thus giving each C atom only a fraction of the total positive charge. In **1b**, the positive charge is (formally) constrained to the allyl entity C7C8C9 and, therefore, C7 and C9 take a larger share of the positive charge than in either **1a** or **1c**. On going from **1a** to **1b** the gross atomic charge of C7 and C9 steadily increases, showing a characteristic dependence on the folding angle  $\alpha$  and the distance  $r(2,9)$  (Fig. 5). Similarly, the calculated  $^{13}\text{C}$  chemical shifts increase in the range  $r(2,9) = 1.6$  to  $r(2,9) = 2.4 \text{ \AA}$  from 60 to 240 ppm (Table 3 and Fig. 3).

C8: for **1a**, the positive charge is (formally) located at C8. The more C7–C8–C9 changes to become an allyl entity for large values of  $r(2,9)$ , the more C8 adopts the electronic nature of the central C atom of the allyl cation. Accordingly, the gross atomic charge at C8 first rapidly decreases, but then asymptotically

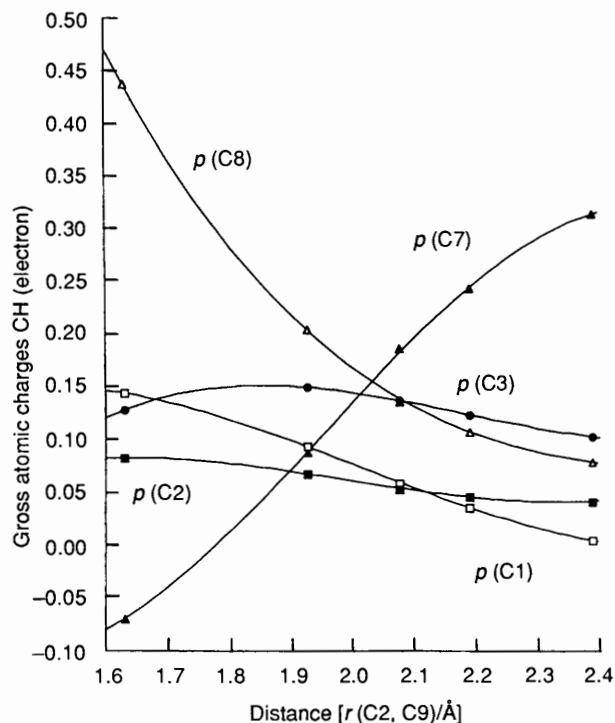


Fig. 5 Gross atomic charges of CH groups given as a function of the distance  $r(2,9) = r(5,7)$  (for the corresponding  $\alpha$  values, see Table 1)

approaches a limiting value when increasing  $\alpha$  [or  $r(2,9)$ ] from the value of **1a** to that of **1b**. The same is true for the dependence of the  $^{13}\text{C}$  chemical shift value on  $\alpha$  or  $r(2,9)$ .

Owing to the peculiar topology of **1**, only the atomic charge and the  $^{13}\text{C}$  chemical shift of atoms C7 and C9 are sensitive enough to distinguish between structures **1a**, **1b** and **1c** (or **2**) (Figs. 3 and 5). For example,  $\delta(\text{C}7)$  for **1** and **2** differ by 80 ppm (Table 5), but on the average the difference between the  $^{13}\text{C}$  shift values of the two structures is just 18 ppm. (The corresponding difference between **7** and its planar form is 40 ppm.<sup>5</sup>) This is different from the situation observed for **7** where all C atoms but C8 are sensitive to change from **7a** to **7c** and **7b**.<sup>5</sup> In the following we make use of the properties of C7 and C9 to determine whether or not **1** is bishomoaromatic.

For **7**, homoaromaticity establishes itself in the following way.<sup>5</sup> (1) The potential-energy surface of **7** possesses only one minimum at  $r(1,7) = 2 \text{ \AA}$  along the (homoaromatic) 1,7 coordinate. (2) At the potential-energy minimum, the positive charge of **7** is equally distributed in the C1–C7 ring. Also there is an equalization of bond lengths in the C1–C7 ring. (3)  $^{13}\text{C}$  chemical shifts of **7c** clearly reflect the equalization of the properties of C atoms in the C1–C7 ring. (4) The magnetic susceptibility of **7** adopts a maximum value for the equilibrium geometry **7c**.

Considering (1)–(4) as reasonable criteria of homoaromatic character<sup>5</sup> and applying these criteria to **1**, then the cation **1** must be considered as a bishomoaromatic system with a delocalized  $6\pi$  electron ensemble in the ring made up of atoms C2, C3, C4, C5, C7, C8 and C9.

(1) The potential-energy surface of **1** along the (homoaromatic)  $r(2,9) = r(5,7)$  coordinate possesses a single minimum at about  $2 \text{ \AA}$ . (2) At the equilibrium, there is an equalization of positive charge (Fig. 5), *i.e.* the gross atomic charges of C7 (C9) and C8 take values similar to those of the other C atoms. However, owing to the topology of **1**, charge equalization and, in particular, bond equalization is not as large as in **7c**. (3) The  $^{13}\text{C}$  chemical shift values of those atoms establishing the 7-membered ring approach each other as much as possible if  $r(2,9)$  adopts its equilibrium value (Fig. 3, Table 3). Again, this is due

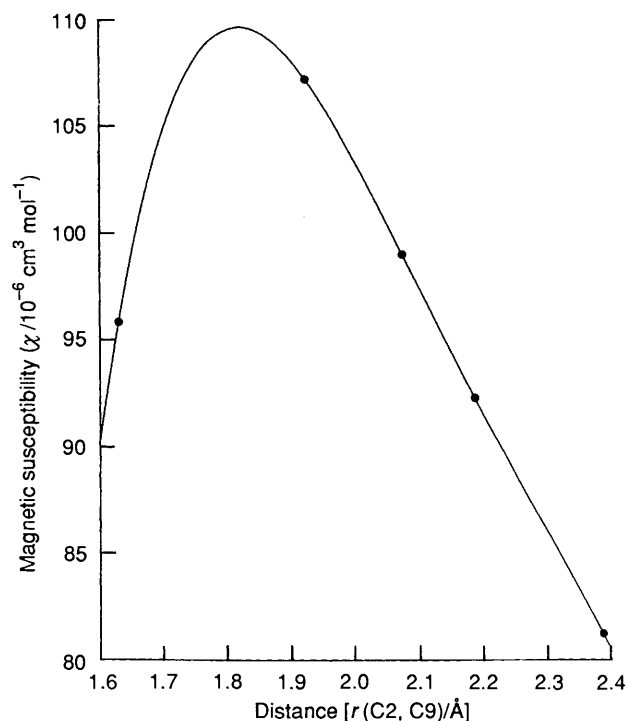


Fig. 6 IGLO/6-31G(d) values of the magnetic susceptibility given as a function of the distance  $r(2,9) = r(5,7)$  (for the corresponding  $\alpha$  values, see Table 1)

to the changes in the values for C7 (C9) and C8. (4) The magnetic susceptibility  $\chi$  (Fig. 6) takes maximum values in the vicinity of the equilibrium of **1**.

Hence, the electronic properties of **1** are best represented by **1c**. Through-space interactions involving C atoms C2, C9, C5 and C7 establish a delocalized  $6\pi$  electronic system that make **1** a true bishomoaromatic cation. We conclude that bishomoaromaticity is a molecular feature that may be observed not only for **1** but also for other cations.

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