J. Am. Chem. Soc. **1986**, *108*, 3819-3824

One-Bond ^{13}C–^{13}C Coupling Constants as a Probe for Carbocation Structure. Doubly ^{13}C-Labeled 1,4-Bishomotropylium Ion

Göran Jonsäll*† and Per Ahlberg*‡

Contribution from the Department of Organic Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden, and Department of Organic Chemistry, University of Göteborg, S-412 96 Göteborg, Sweden. Received November 14, 1985

Abstract: One-bond ^{13}C–^{13}C coupling constants as probes for homoaromatic structures have been explored. Thus, it is supported that the rearrangement product of 9-barbaralyl cation (**7**) under conditions of long life, that is, in superacid, has the 1,4-bishomotropylium ion structure (**3a**) rather than the dihydroindenyl cation structure (**4**). The bridgehead carbons in **3a** are found to be considerably rehybridized, compared with those in **4**, and two partial three-membered rings have been formed by through-space interaction of the allyl cationic and butadiene part of the ion. These structural conclusions are based upon s-characters in C–C bonds in **3a**, which have been calculated from ^{13}C–^{13}C and ^{13}C–^{1}H coupling constants and comparison with reference compounds. All carbons in **3a** are found to be approximately sp^2-hybridized. The results provide strong support for earlier conclusions on homoaromaticity in ions **3a** and **3b** based upon ^1H and ^{13}C NMR chemical shifts in superacid. These latter results have been questioned in view of results obtained under solvolytic conditions, which favored the presence of the dihydroindenyl cation structure **4** rather than the homoaromatic structure **3a**. The preparation of the doubly ^{13}C-labeled ion precursor [2,3-$^{13}C_2$]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**5**) and its 2-methyl derivative (**6**) is also reported. It was possible to measure *all but two* of the $^1J_{CC}$'s in **3a** since in ion **7**, which is the first observed carbocation by reaction of **5** in superacid, the ^{13}C labels are evenly distributed among the nine carbon positions. The measured coupling constants were $^1J_{C1C2} = {}^1J_{C5C6} = 28.1$ Hz, $^1J_{C1C9} = {}^1J_{C6C7} = 28.7$ Hz, $^1J_{C2C3} = {}^1J_{C4C5} = 60.4$ Hz, and $^1J_{C7C8} = {}^1J_{C8C9} = 51.9$ Hz. Ion **3b** generated from **6** via **9** does not have a plane of symmetry like **3a**. Therefore, this ion enabled the important coupling constant $^1J_{C1C6} = 38.1$ Hz to be measured. An interesting degenerate rearrangement of **9** was revealed through the double ^{13}C labeling. The ^{13}C label in the C1 and C5 positions is found to be rearranged at the same rate to each of the six positions C2–C4 and C6–C8. The mechanism for this process is discussed.

Many organic species have been assigned homoaromatic structural features.[1] However, despite considerable experimental and theoretical efforts, the structure of most of these species remains controversial.[2] Homoaromatic structures have been proved beyond all doubt for only a limited number of carbocations, for example, the monohomotropylium ion (**1**).[3] Thus, for many other carbocations, carbanions, and neutral species, for example, the bicyclo[3.2.1]octadienyl anion (**2**),[4] controversy is the rule rather than the exception.

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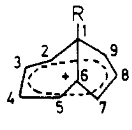
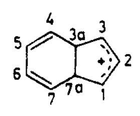
A major reason for the persistence of these controversies has been the lack of proper tools to enable conclusive statements about homoaromatic structural features to be made. In this paper we have explored the potential of ^{13}C–^{13}C coupling constants as a structural probe for homoaromaticity. The first reported bishomotropylium ion, the 1,4-bishomotropylium ion[5] (**3**), has been investigated with the aid of this novel tool.



3a R=H

3b R=CH$_3$



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Earlier evidence for the homoaromatic structure of this ion was based upon measured ^1H and ^{13}C NMR chemical shifts in superacid.[5,6] However, studies under conditions of short life, that is, solvolytic investigations, have raised questions about the conclusions based on measurements in superacid and have favored the dihydroindenyl cation structure **4** with no homoaromaticity.[5a] Recent semiempirical and ab initio (STO-3G) calculations have shown structures like **3a** and **4** to be represented by energy minima and to have similar energy.[7]

Apart from diffraction methods, one-bond ^{13}C–^{13}C coupling constants ($^1J_{CC}$) have the potential to provide information on bonding within the carbon framework of organic molecules.[8] The pioneering work of Olah and Westerman showed the general relationship between $^1J_{CC}$ and hybridization to be qualitatively valid also for carbocations.[9a] These experiences were later utilized in the study of the methylcyclobutyl cation where Kirchen and Sorensen measured $^{13}C^+$–$^{13}CH_3$ coupling constants of this ion and some related cycloalkyl cations. These results did not, however, lend support to the nonclassical structure proposed by other data, such as ^{13}C NMR chemical shifts.[10]

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† University of Uppsala.
‡ University of Göteborg.

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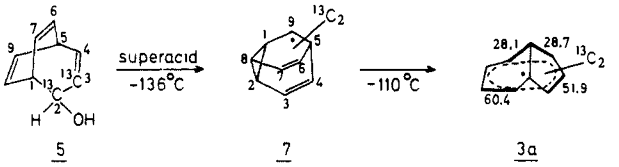
Scheme I



5 7 3a

Only recently, after the introduction of multiple quantum coherence techniques, have such measurements been possible on a more systematic basis, since the laborious labeling with ${}^{13}C$-enriched substrates was no longer necessary. Olah and co-workers have studied a wide range of stable carbocations, such as protonated benzaldehydes and acetophenones, where high concentrations of ions can be prepared.[9b] Their results have provided valuable reference data on the fundamentals of ${}^{1}J_{CC}$ in carbocationic species, especially substituent effects.

In parallel with experiments, important progress on the theoretical evaluation of J_{CC} has been contributed by Contreras and co-workers, using SCPT-INDO MO calculations to study the contribution of different transmission mechanisms to J_{CC}.[8d] The separation of π- and σ-transmitted components for the three types of interactions involved, Fermi contact interaction, spin–orbital interaction, and spin–dipolar interaction, showed σ-transmitted Fermi contact to dominate one-bond coupling for a single bond. For such bonds π-contributions are negligible in all three interactions, and the total contribution of spin–orbital and spin–dipolar interactions is small. In formal double bonds, on the other hand, π-contributions give an appreciable contribution to Fermi contact interaction and even dominate spin–orbital and spin–dipolar interactions, and only due to a cancellation of π-contributions for Fermi contact and spin–orbital terms is the net π-contribution brought down to a mere 5–7 Hz (ca. 10%). Thus ${}^{1}J_{CC}$ is expected to reflect s-electron densities at the coupled nuclei in a formal single bond, due to the dominant σ-transmitted Fermi contact interactions, while for multiple bonds great care should be taken in the evaluation of ${}^{1}J_{CC}$.

Since the highly reactive $C_9H_9^+$ ions can only be studied in relatively dilute solutions, we have now prepared the doubly ${}^{13}C$-labeled 1,4-bishomotropylium ions **3a** and **3b**, in order to measure carbon–carbon coupling constants. The preparation of their respective precursors **5** and **6** is also reported. The results obtained strongly support earlier conclusions that the ion observed under conditions of long life has the 1,4-bishomoaromatic structure.

An interesting degenerate rearrangement of the 9-methylbarbaralyl cation (**9**)[11] was revealed through the double ${}^{13}C$ labeling. The ${}^{13}C$ label in the C1 and C5 positions is found to be rearranged at the same rate to each of the six positions C2–C4 and C6–C8. The mechanism for this process is also discussed.

Results

The doubly ${}^{13}C$-labeled alcohols, [2,3-${}^{13}C_2$]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**5**) and 2-methyl[2,3-${}^{13}C_2$]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**6**), with 90% ${}^{13}C$ in each of the labeled positions, were prepared by the procedure used previously in the preparation of mono-${}^{13}C$-labeled and ${}^{13}C,{}^{2}H_8$-labeled alcohols,[12] using 90% enriched [1,2,3-${}^{13}C_3$]malonic acid. Ions were prepared by adding ca. 8 mg of alcohol **5** or **6** dissolved in $CHCl_2F$ to a mixture of FSO_3H–SO_2ClF–SO_2F_2–$CHCl_2F$ (2:7:7:2, v/v/v/v) at ca. −135 °C in an ion-generation apparatus.

The secondary alcohol **5** gave the doubly labeled 9-barbaralyl cation (**7**), undergoing rapid totally degenerate rearrangements even at −135 °C. These rearrangements of **7** provided an even distribution of the ${}^{13}C$ labels among all positions. This scrambling was necessary for the further study of **3a**. ${}^{13}C$ NMR spectra of **7** obtained at −158 to −135 °C were practically identical with those of the mono-${}^{13}C$-labeled ion studied previously.[12] At −110 °C, **7** rearranged rapidly to the 1,4-bishomotropylium ion **3a**, identified by its ${}^{13}C$ NMR spectrum[5b] (Scheme I). All ${}^{13}C$ resonances were accompanied by ${}^{13}C$ satellites, with an intensity of ca. 10% relative to the central peaks, originating from isomers with adjacent labeled positions (Figure 1a). The couplings confirmed previous assignments and gave the following C–C coupling constants: ${}^{1}J_{C1C2} = 28.1$ Hz, ${}^{1}J_{C2C3} = 60.4$ Hz, ${}^{1}J_{C7C8} = 51.9$ Hz, and ${}^{1}J_{C1C9} = 28.7$ Hz. The C2–C9 coupling is not resolved in the central resonance of either C2 or C9, both broadened by long-range couplings, and must be less than 11 Hz. Two couplings, C1–C6 and C3–C4, disappear by symmetry, which evoked the preparation of **3b**.

To be able to estimate the contribution of s-orbitals in all C–C bonds, we also obtained the one-bond C–H coupling constants (${}^{1}J_{CH}$) for **3a** and, for comparison, also for the bicyclo[4.3.1]decatrienyl cation (**8**).[13] The couplings for **3a** were close to

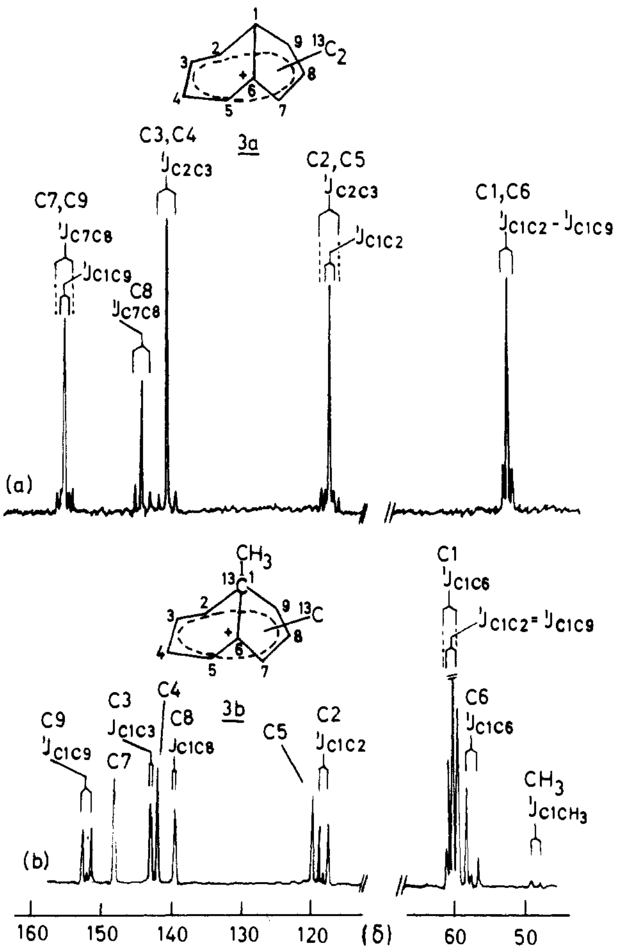
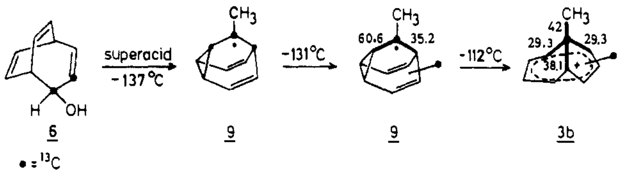
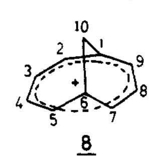


Figure 1. Proton-noise-decoupled ${}^{13}C$ NMR spectra for (a) 1,4-[${}^{13}C_2$]bishomotropylium ion (**3a**) and (b) 1-methyl-1,4-[${}^{13}C_2$]bishomotroplyium ion (**3b**). Spectra obtained in FSO_3H–SO_2ClF–SO_2F_2–$CHCl_2F$ at ca. −100 °C with $CHCl_2F$ (δ 98.6) as internal standard.

Scheme II



6 9 9 3b



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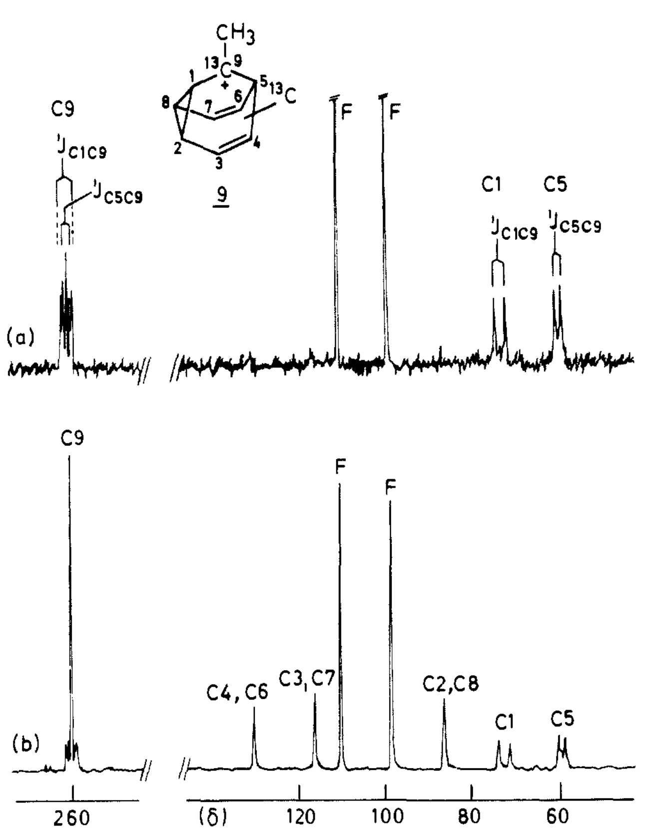


Figure 2. Proton-noise-decoupled ^{13}C NMR spectra for the 9-methyl-9-[$^{13}C_2$]barbaralyl cation (**9**) in $FSO_3H-SO_2ClF-SO_2F_2-CHCl_2F$ with $CHCl_2F$ (δ 98.6, 110.3, marked F) as internal standard. (a) Initial spectrum obtained at −140 °C. (b) Spectrum obtained after 30 min at −131 °C.

previous results[14] and indicated an approximate sp^2-hybridization of all carbons.

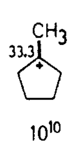
The tertiary alcohol **6**, at −135 °C, gave the 9-methyl-9-barbaralyl cation **9**(Scheme II), with ^{13}C labels exclusively at C9 (90%) and C1,C5 (45% each), as observed by ^{13}C NMR at −140 °C (Figure 2a). Rapid degenerate divinylcyclopropylcarbinyl cation rearrangements equilibrate C1 with C5 and C2,C8 with C4,C6.[11] We obtained two C–C coupling constants in **9**: $^1J_{C1C9}$ = 60.6 Hz and $^1J_{C5C9}$ = 35.2 Hz.

At −131 °C, the label at C1,C5 was simultaneously scrambled to the remaining carbon skeletal positions C2, C3, C4, C6, C7, and C8 with a first-order rate constant of $3.3 \times 10^{-4}\ s^{-1}$ (Figure 2b). This previously unobserved degenerate rearrangement of **9** has a barrier ($\Delta G^{\ddagger}$) of 10.4 ± 0.1 kcal mol^{-1} (43.4 ± 0.3 kJ mol^{-1}).

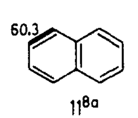
At −112 °C, **9** rearranged rapidly to the 1-methyl-1,4-bishomotropylium ion (**3b**),[5] with 90% ^{13}C at C1 and the remaining label distributed evenly over C2–C9. Positions close to C1 were observed as doublets in the ^{13}C NMR spectrum ($^1J_{C1C2} = {}^1J_{C1C9}$ = 29.3 Hz, $^1J_{C1CH_3}$ = 42 Hz), and C6 formed an AB pattern with C1 ($^1J_{C1C6}$ = 38.1 Hz). Two long-range couplings were observed (J_{C1C3} = 2.9 Hz and J_{C1C8} = 4.9 Hz), and previous assignments were partially revised[5b] (Figure 1b).

Discussion

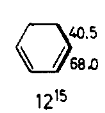
Structure Evaluation Using C–C Coupling Constants of Model Substances. The relevant $^1J_{CC}$ reference material on polycyclic delocalized carbocations is limited. Some of the most useful structures and their coupling constants are summarized below.



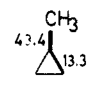
10[10]



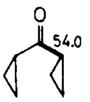
11[8a]



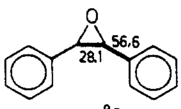
12[15]



13[8c]

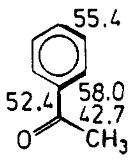


14[8a]

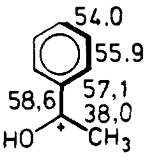


15[8a]

9-Methyl-9-barbaralyl Cation (9). The observed coupling constants are 60.6 and 35.2 Hz for C1–C9 and C5–C9, respectively. According to previous structural assignments, **9** is stabilized via cyclopropylcarbinyl cationic resonance with a partial double bond at C1–C9.[11,12] The coupling constant of this bond supports this view, being even higher than $^1J_{COC1}$ = 58.6 Hz of **16b**, reflecting the excellent ability of the properly aligned cyclopropane ring to stabilize positive charge.



16a[9b]



16b[9b]

The C5–C9 bond has a coupling only slightly higher than the C^+-CH_3 coupling of **10**, which is reasonable since C5 is higher substituted.[8]

Thus, the observed couplings of **9** are in excellent agreement with its proposed structure.

1,4-Bishomotropylium Ions 3a and 3b. The two proposed structures **3** and **4** have been optimized in quantum chemical calculations, using the semiempirical methods MINDO/3 and MNDO. The $^1J_{CC}$ values can therefore be discussed in relation to a reasonable knowledge of bond lengths, bond orders, charge distributions, etc., in the two species under scrutiny. From calculations the bridgehead region is expected to provide the most decisive characters distinguishing between these two structures, but the multiple bond system in the six-membered ring is also undergoing considerable changes.[7]

The $C1-CH_3$ coupling of **3b** (42 Hz) is larger than the corresponding value of neopentane (37 Hz),[8a] being closer to methylcyclopropane (**13**) or propene (41.9 Hz).[8] This indicates a substantial rehybridization of the bridgehead carbons approaching the sp^2-hybridization characterizing bonds to three-membered rings. Such a view is also in agreement with the observed C1–H coupling in **3a** ($^1J_{CH}$ = 164 Hz), which gives a hybridization index of 2.0. The calculated geometry of **3a** with a dihedral angle of 68.5° between the six- and five-membered rings fits these data much better than that of **4**, where the corresponding dihedral angle is 132.6° (MINDO/3).[7a]

This rehybridization is also reflected in the C1–C2 and C1–C9 bonds ($^1J_{CC} \sim 29$ Hz), both being considerably smaller than reasonable models for **4**. Thus C1–C2 in **4** is similar to the C1–C6 bond in cyclohexadiene (**12**) with $^1J_{CC}$ = 40.5 Hz, and C1–C9 resembles C5–C9 in **9** ($^1J_{CC}$ = 35.2 Hz), also being a delocalized charged center bonded to a bridgehead carbon. It is interesting to note how the discrepancy between measured values and the models for **4** *increases* with distance from the charged fragment C7–C8–C9, making **4** a weak candidate structure. Since C–C couplings within partially formed three-membered rings have not been measured previously, we are left without adequate models for **3a** and **3b**. However, even if 29 Hz higher than $^1J_{CC}$ of a normal cyclopropane ring such as **13**, it is similar to the C–C coupling in an oxirane **15**, placing the measured value in the range of three-membered rings.[16] In the MO calculations for ion **3** both

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[13] Roberts, J. M. Ph.D. Thesis, University of California, Los Angeles, 1971.

[14] Jonsäll, G.; Engdahl, C.; Ahlberg, P., to be published.

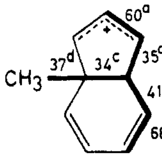
[15] Zobl-Ruh, S.; von Philipsborn, W. *Helv. Chim. Acta* **1981**, *64*, 2378–2382.

[16] Interpretation of C–C couplings in three-membered rings is complicated by the large negative $^2J_{CC}$ contribution sensitive to structural changes (cf. **15**).[8b]

C1–C2 and C1–C9 came out as weak bonds, with overlap populations smaller than ordinary single bonds.[7b]

The coupling between the bridgehead carbons C1–C6 was observed to be 38.1 Hz within the range of an ordinary single bond. A coupling between carbons in two three-membered rings such as in structure **3** might have been expected to yield a much higher value, but MO calculations showed that both the length (1.53 Å) and overlap population (0.374) of this bond are normal for a single bond.[7] Thus the observed $^1J_{C1-C6}$ can fit both of our candidate structures.

The C2–C3 coupling (60.4 Hz) is substantially reduced compared with the corresponding bond of cyclohexadiene ($^1J_{C1-C2}$ = 68 Hz), used as a model of the six-membered ring in **4**. Even if C=C polarization could have reduced this value,[17b] the magnitude of such an effect is expected to be much smaller, since even in a conjugated system like **16**, the charge rarely introduces a change of more than 2 Hz.[9b] However, 60.4 Hz is close to the C1–C9 coupling in **9**, which could serve as a model for a charged center bonded to a three-membered ring as in structure **3**. It is also similar to the value of naphthalene (**11**), in agreement with the proposed delocalized structure of ion **3**. In MO calculations the C2–C3 bond of **3** turned out as intermediate between a single and a double bond.[7]



16

It is most difficult to find proper models for the C7–C8 bond ($^1J_{C7-C8}$ = 51.9 Hz) related to the structures **3** and **4**. Either $^1J_{C1-C9}$ (60.6 Hz) in **9** or the coupling between the carbonyl carbon and the cyclopropane rings in **14** (54 Hz) could be tried to mimic **3** (with a reasonable agreement), but in the absence of a proper allyl cation model, ion **4** could not be evaluated. This is also a part of the molecule where π-transmitted components should have a large influence, making even higher demands on the choice of models.[8d]

The accumulated data give valuable information on the bonding within the carbon framework of these ions and provide strong support for cyclically delocalized 1,4-bishomotropylium ions. The large C1–CH$_3$ and the accompanying small C1–C2 and C1–C9 couplings clearly indicate the formation of partial three-membered rings. Other explanations, such as hyperconjugative effects in a structure like **4**, ought to decrease both J_{C1CH_3} and J_{C1C2}.[17b] The formation of homoaromatic bridges between C2 and C9 (C5–C7) could not in this study be evaluated by direct measurement (^1J < 11 Hz),[17a] but these bonds are expected to be weak considering results from MO calculations.[7]

Estimation of s-Character of Carbon Hybrids. We have applied the general relationships between C–C and C–H coupling constants and fractional s-characters in contributing carbon hybrids to the delocalized carbocations **3a** and **3b**. The relationships $^1J_{CC} = 550(s_{1(2)})(s_{2(1)})$ and $(s_C) = {}^1J_{CH}/500$ have been shown to be valid for neutral molecules, including systems containing small rings.[18] This made is possible to estimate the fractional s-character in each of the carbon hybrids in 1,4-bishomotropylium ions by using measured C–C and C–H coupling constants. CH$_3$ was assumed to be sp^3-hybridized, and the total s-character was supposed to be 1 on all carbon atoms. C1–C6 is assumed to be symmetric in **3b**, giving C hybrids on C1 and C6 the same s-character, and C3 is expected to have equal s-character in its bonding hybrids to C2 and C4, respectively (see Table I).

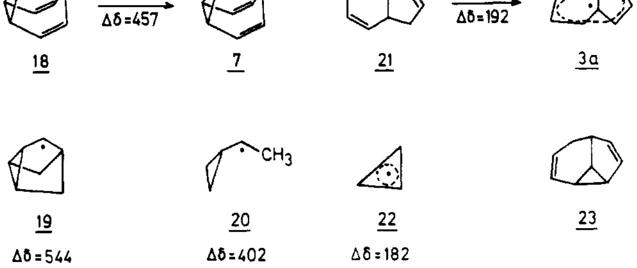
Table I. Calculated Fractional s-Character of Carbon–Carbon Bonds in 1,4-Bishomotropylium Ions

$^1J_{CC}$, Hz	restraints	calculated s-character
$^1J_{C1CH_3} = 42$	$s_{CH_3(1)} = 0.25$[a]	$s_{1(CH_3)} = 0.30$
$^1J_{C1C6} = 38.1$	$s_{1(6)} = s_{(6)1}$,[b] $s_{1(2)} =$	$s_{1(6)} = s_{6(1)} = 0.26$
	$s_{1(9)}$, $\sum s_{C1} = 1$[c]	$s_{1(2)} = s_{1(9)} = 0.22$
$^1J_{C1C2} = {}^1J_{C1C9} = 29.3$		$s_{2(1)} = s_{9(1)} = 0.24$
$^1J_{C8C9} = 51.9$	$s_{8(H)} = 0.36$,[d]	$s_{8(7)} = s_{8(9)} = 0.32$
	$\sum s_{C8} = 1$[c]	$s_{9(8)} = s_{7(8)} = 0.29$
$^1J_{C2C3} = 60.4$	$s_{3(H)} = 0.34$,[d]	$s_{3(2)} = s_{3(4)} = 0.33$[e]
	$\sum s_{C3} = 1$[c]	$s_{2(3)} = 0.33$

[a] sp^3 methyl is assumed. [b] C1–C6 is assumed to be symmetric in **3b**. [c] A total s-character of 1 is assumed on all carbons. [d] From observed C–H couplings (ref 14). [e] C3 is assumed to have equal s-character in its bonds to C2 and C4.

Thus, we can now estimate the s-character of the C2–C9 bond by using the calculated values of all other bonds to C2 and C9, including the C–H bonds ($s_{C2(H)}$ = 0.34 and $s_{C9(H)}$ = 0.36).[14] The values obtained are $s_{2(9)}$ = 0.09 and $s_{9(2)}$ = 0.11. An s-character of 0.1, compared with the 0.16–0.22 obtained for methylcyclopropane (**13**) ($^1J_{CC}$ = 13.3 Hz but $^2J_{CC}$ can be as large as −15 Hz, cf. **15**),[8b] suggests at least 50% cyclopropane character in the homoaromatic C2–C9 (C5–C7) bonds. The C1–C2 and C1–C9 bonds have ca. 23% s-character, somewhat less than in sp^3-hybrids. Our results are in agreement with recent theoretical studies of **1**, indicating a weak homoaromatic bond and the two other bonds in the three-membered ring as almost normal single bonds with a small curvature.[19]

Application of the Additivity of ^{13}C Chemical Shift Analysis. As a test for carbocation structure, we applied the ^{13}C chemical shift additivity criterion proposed by Schleyer et al.[20] to ion **3a** and the parent 9-barbaralyl cation (**7**). The ^{13}C chemical shift sum of **7** is 1062 ppm, to be compared with its hydrocarbon counterpart barbaralane (**18**) with 605 ppm,[21] a difference (Δδ) of 457 ppm. This difference is clearly in the range of classical ions, intermediate between values observed for nortricyclyl (**19**) and cyclopropylcarbinyl cations (**20**).[20]



The 1,4-bishomotropylium ion (**3a**), on the other hand, has a total ^{13}C chemical shift of 1075 ppm,[5b] only 192 ppm higher than dihydroindene (**21**, 883 ppm),[22] close to the value observed for the homocyclopropenium ion (**22**) compared with cyclobutene (Δδ = 182 ppm).[20] This suggests strongly that **4** is an inadequate model structure for 1,4-bishomotropylium ions in superacid. This is in agreement with C–C coupling results. For other hydrocarbons presumed to be better representations of the 1,4-bishomoaromatic carbon skeleton (e.g., homosemibullvalene, **23**), ^{13}C NMR data have not been reported.

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(17) (a) One referee has pointed out the possibility of measuring J_{C2-C9} by using the INADEQUATE pulse sequence, which "would substantially improve the paper". However, with the estimated s-contributions this one-bond coupling should be approximately 5 Hz, which is expected to be reduced even further from $^2J_{CC}$ influence. Thus such a coupling would be difficult for one to evaluate not knowing also the sign of the coupling constant (cf. note 16). (b) One referee suggested that C–C hyperconjugation and C=C polarization in structure **4** could affect the C1–C2 and C2–C3 couplings, respectively.

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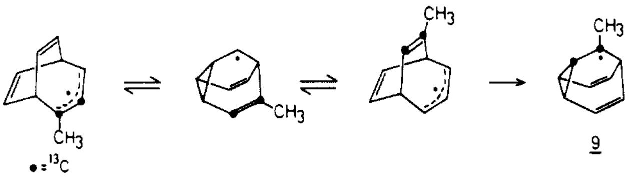
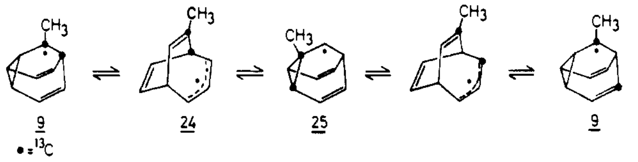
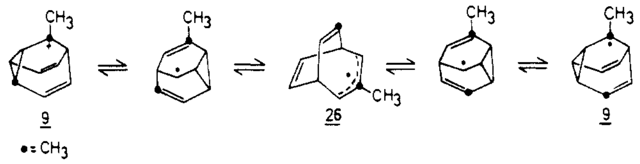
Scheme III



Scheme IV



Scheme V



Degenerate Rearrangements of the 9-Methyl-9-[$^{13}C_2$]barbaralyl Cation (9). The 9-barbaralyl cations have previously been observed to undergo rapid degenerate rearrangements via reversible ring openings to bicyclo[3.2.2]nonatrienyl cations and divinylcyclopropylcarbinyl cationic rearrangements.[23] The latter mechanism has been proposed to operate in the Cope-mimicking rearrangement of **9**, where C1 is interchanged with C5 and C2,C8 with C4,C6, with a barrier of 7.6 kcal mol^{-1}.[11]

The first-formed 9-methyl-9-[$^{13}C_2$]barbaralyl cation (**9**) has one label associated with CH_3 at C9 and the other exclusively shared between C1 and C5 (Figure 2a). This suggests a rapid, essentially irreversible formation of **9** via a series of ring-closure ring-opening reactions at the low temperature of ion preparation (−136 °C) outlined in Scheme III. The rapid Cope-mimicking divinylcyclopropylcarbinyl cationic rearrangement will then scramble the label between C1 and C5. Scrambling to other positions must proceed via the reopening of **9** to **24**, followed by formation of barbaralyl cations with both labels at one end of the molecule (e.g., **25**), since only these isomers can separate the two labels. This rearrangement is outlined in Scheme IV.

This mechanism, coupled with the rapid divinylcyclopropylcarbinyl cation rearrangement, gives scrambling almost exclusively to C2, C4, C6, and C8, and formation of **24** is proposed to be the rate-limiting process ($\Delta G^{\ddagger}$ = 10.4 kcal mol^{-1}). This value is close to the sum of $\Delta G^{\ddagger}$ for the divinylcyclopropylcarbinyl cation rearrangement of **9** (7.6 kcal mol^{-1}; cf. step one in Scheme V)[11] and the energy difference between secondary 9-barbaralyl and bicyclo[3.2.2]nonatrienyl cations (ca. 4 kcal mol^{-1}).[7a,12]

However, we observed a simultaneous scrambling to C2, C3, C4, C6, C7, and C8 at −131 °C, which suggests another mechanism rapidly scrambling the carbons in the basal six-membered ring, as in the 1,9-dimethyl-9-barbaralyl cation.[11] This is most simply effected by ring opening of **9** to the 3-methylbicyclo-[3.2.2]nonatrienyl cation (**26**), where the methyl group is expected to be more stabilizing than in **24** (Scheme V).

Conclusions. One-bond ^{13}C-^{13}C coupling constants have been shown to provide detailed structural information on chemical bonding in delocalized carbocations. The agreement with neutral reference systems and reasonable values obtained for s-contributions to C–C bonds suggest that the relationship between hybridization and coupling obtained for neutral systems is valid also for charged species. Thus, C–C couplings promise long-desired information of carbon frameworks in reactive intermediates, especially if further progress is multiple quantum coherence techniques can eliminate the need for tedious isotopic labeling procedures.[9b]

The C–C couplings in 1,4-bishomotropylium ions (**3a** and **3b**) have clearly revealed delocalized structures. Partial rehybridization of both the bridgehead and the adjacent carbons have provided ca. 10% s-contribution to the homoaromatic bonds (C2–C9 and C5–C7) forming partial three-membered rings. Dihydroindeyl cations have been excluded as relevant representations for **3a** and **3b** in superacidic solutions both from C–C couplings and from total ^{13}C chemical shift arguments.

The double ^{13}C labeling of the 9-methyl-9-barbaralyl cation (**9**) revealed a new degenerate rearrangement, with a barrier ($\Delta G^{\ddagger}$) of 10.4 kcal mol^{-1}, proposed to proceed via reversible ring opening to the 6-methylbicyclo[3.2.2]nonatrienyl cation (**24**).

Experimental Section

The proton-noise-decoupled ^{13}C NMR spectra were recorded with a JEOL-FX 100 spectrometer equipped with a variable temperature 5-mm $^{1}H/^{13}C$ dual probe, an external ^{7}Li lock, and a quadrature phase detector using the FAFT 70-791221 and FAFT 80/81 programs. CD_2Cl_2 (δ_c 53.8 ppm) and $CHCl_2F$ (δ_c 98.6 ppm) were used as internal standards. The NMR probe temperature was determined with a precalibrated chemical shift thermometer (CH_3OH in $CHCl_2F$–$CDClF_2$, 1:1, v/v) within ±1 °C.

We used the following parameters in the study of **3a**, **3b**, and **9** (the latter two within parentheses): pulse width 45°, spectral width 5 kHz (**3b**, 4 kHz; **9**, 8 kHz), 16 384 (8192) data points when accumulating the spectra, acquisition time 0.7 s (**3b**, 1.0 s; **9**, 0.5 s), pulse delay 1 s (0.5 s), and 5000–6000 scans accumulated. The measured coupling constants are accurate within ±0.6 Hz for **3a**, ±1.0 Hz for **3b**, and ±2.0 Hz for **9** (the distance between two data points).

Preparative gas chromatography (GLC) was carried out with a Varian 90-P, and the column was a 0.65 m × $^{3}/_{8}$ in. copper tube with 20% Reoplex on Chromosorb W (60/80 mesh). The carrier gas flow (He) was 70 mL min^{-1} and the column temperature 144 °C. For analytical GLC, an HP 5880 A instrument was used with a 1.5 m × 2.5 mm glass column with 10% Carbowax 20 M and 1% KOH on Chromosorb W and a column temperature program from 80 to 160 °C. TLC was performed on precoated TLC plates with silica gel 60 F-254 (Merck); the solvent was diethyl ether/petroleum ether (7:3).

Tropylium tetrafluoroborate was prepared by the procedure of Conrow.[24] [1,2,3-$^{13}C_3$]Malonic acid (Prochem, 90% ^{13}C), oxalyl chloride (Merck, "Zur Synthese", 97%), lithium aluminum hydride (Merck, "Zur Synthese", 90%), and lithium wire (Merck, "Zur Synthese", 0.5% Na) were used as purchased. Pyridine (Kebo Grave, purum) was distilled, and triethylamine (Baker, >99%) was distilled over sodium. They, as well as methylene chloride (Merck, analytically pure), *n*-heptane (Merck, analytically pure), and methyl iodide (Riedel, prosynthesis, 99%), were stored over molecular sieves. Diethyl ether (May & Baker, anhydrous) was dried over sodium, and tetrahydrofuran (Fisons, HPLC grade) was distilled from lithium aluminum hydride. All reactions were carried out under dry nitrogen (or when noted, argon (AGA, SR)) in glassware dried at 120 °C (or in a vacuum oven at 50 °C/0.01 mm) overnight.

Cyclohepta-2,4,6-trien-1-yl[1,2-$^{13}C_2$]acetic Acid (27).[12] Tropylium tetrafluoroborate (0.400 g, 2.25 mmol) was reacted with [1,2,3-$^{13}C_3$]-malonic acid (0.23 g, 2.2 mmol) in refluxing pyridine for 45 h and worked up by the normal procedure, leaving 0.33 g (2.2 mmol, 100%) of **27** as crude product.

Cyclohepta-2,4,6-trien-1-yl[1,2-$^{13}C_2$]acetyl Chloride (28).[12] Treatment of the crude **27** with 1 mL of oxalyl chloride in methylene chloride containing one drop of pyridine at room temperature for 7 h followed by evaporation of solvent and hydrogen chloride under vacuum gave 0.36 g (2.0 mmol, 95%) of crude **28**.

[2,3-$^{13}C_2$]Bicyclo[3.2.2]nona-3,6,8-trien-2-one (29).[12] The crude acid chloride **28** was dissolved in *n*-heptane and added dropwise to a refluxing solution of 1.1 mL of triethylamine in 25 mL of *n*-heptane over a 19-h period. Triethylamine was added (0.5 mL), the reflux was continued for 20 h, and the product was worked up by the normal procedure and separated by preparative GLC. Yield of **29**: 59.1 mg (0.44 mmol, 21% overall). Yield of [1,2-$^{13}C_2$]indan-1-one (**30**): 76.4 mg (0.57 mmol, 27% overall). ^{1}H NMR spectra of **29** and **30** agreed with the corresponding mono-^{13}C-labeled compounds.[12] ^{13}C NMR (CD_2Cl_2) **29**: δ 189.1 (d, $^{1}J_{CC}$ = 53.7 Hz, C2), 152.9 (d, $^{1}J_{CC}$ = 64.7 Hz, C4), 138.1 (C6 and C9), 128.3 (d, $^{2}J_{CC}$ = 2.4 Hz, C7 and C8), 124.3 (d, $^{1}J_{CC}$ = 52.5 Hz, C3), 59.0 (dd, $^{1}J_{CC}$ = 36.6 Hz and $^{2}J_{CC}$ = 12.2 Hz, C1), 41.3 (C5). **30**: δ 206.8 (d, $^{1}J_{CC}$ = 39.1 Hz, C1), 155.5 (d, $^{2}J_{CC}$ = 10.7 Hz, C3a), 137.3

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(dd, $^{1}J_{CC}$ = 57.7 Hz and $^{2}J_{CC}$ = 18.6 Hz, C7a), 134.7, 127.3 (d, J_{CC} = 2.9 Hz), 127.0 (dd, J_{CC} = 3.9 Hz and J_{CC} = 1.9 Hz), 123.5, 36.4 (d, $^{1}J_{CC}$ = 39.1 Hz, C2), 25.9 (dd, $^{1}J_{CC}$ = 35.2 Hz and $^{2}J_{CC}$ = 2.9 Hz, C3).

[2,3-$^{13}C_2$]Bicyclo[3.2.2]nona-3,6,8-trien-2-ol (5).[12] The ketone **29** was reduced with lithium aluminum hydride in diethyl ether at −80 °C and worked up as usual to yield 88% **5**. ^{1}H NMR (CD_2Cl_2): δ 6.88–6.63 (m, 2 H), 6.40–6.06 (m, 3 H), 4.98 (dd, m, $^{1}J_{CH}$ = 157.2 Hz and J_{HH} = 10.7 Hz, 0.9 H; d, m, J_{CH} = 10.6 Hz, 0.1 H), 4.01 (br d, $^{1}J_{CH}$ = 147 Hz, 0.9 H; br, 0.1 H), 3.49 (m, 1 H), 3.25 (m, J = 7 Hz, 1 H), 2.20 (br, 1 H). ^{13}C NMR: δ 141.9 (C6 or C9), 140.7 (C6 or C9), 136.6 (d, $^{1}J_{CC}$ = 70.8 Hz, C4), 128.9 (d, $^{1}J_{CC}$ = 46.4 Hz, C3), 65.1 (d, $^{1}J_{CC}$ = 46.4 Hz, C2), 44.6 (d, $^{1}J_{CC}$ = 35.4 Hz, C1), 37.3 (C5).

2-Methyl[2,3-$^{13}C_2$]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (6).[11a] Methyllithium was prepared by the addition of methyl iodide to lithium wire in ether under argon[25] and was titrated with 1,3-diphenyl-2-propanone tosylhydrazone (Ventron) in tetrahydrofuran, [CH_3Li] = 0.9 M.

The ketone **29** (20 mg, 0.15 mmol) was dissolved in diethyl ether, added to methyllithium (1 mL, 0.9 M) in diethyl ether at 0 °C, and stirred for 4 min. The reaction was quenched with ice and saturated NH_4Cl, extracted with diethyl ether, dried over K_2CO_3, and evaporated, to give 18 mg (0.12 mmol, 80%) of **6**. Analysis with TLC and GLC revealed some minor impurities (<2% each). ^{1}H NMR (CD_2Cl_2): δ 6.9–6.5 (d, t, 2 H), 6.3–6.0 (m, 3 H), 4.82 (ddd, $^{1}J_{CH}$ = 156.6 Hz and J_{HH} = 10.7, 2.2 Hz, 0.9 H; dd, J_{HH} = 10.7, 2.2 Hz, 0.1 H), 3.31 (m, 2 H), 1.91 (br, 1 H), 1.28 (m, 3 H). ^{13}C NMR: δ 141.5 (C6 or C9), 139.3 (C6 or C9), 134.4 (d, $^{1}J_{CC}$ = 46.4 Hz, C3), 130.8 (C7 or C8), 130.1 (C7 or C8), 68.4 (d, $^{1}J_{CC}$ = 46.4 Hz, C2), 49.6 (d, $^{1}J_{CC}$ = 34 Hz, C1), 37.3 (C5), 27.4 (d, $^{1}J_{CC}$ = 41.5 Hz, CH_3).

Preparation of Ions. Ions were prepared in 5-mm NMR tubes with the ion-generation apparatus of Ahlberg and Engdahl.[11b] Precursor alcohols (ca. 8 mg) were dissolved in $CHCl_2F$ (ca. 100 μL) at −10 °C in a syringe and added to a mixture of FSO_3H–SO_2ClF–SO_2F_2–$CHCl_2F$ (2:7:7:2, v/v/v/v) under nitrogen gas at ca. −135 °C.[12] Rapid mixing gave pale-yellow solutions, which were sealed and stored in liquid nitrogen.

Acknowledgment. We thank the Swedish Natural Science Research Council for support, including a predoctoral fellowship for G.J.

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Communications to the Editor

Remarkably Facile Synthesis of an Isoelectronic and Isostructural Boron Analogue of Acetylcholine

Bernard F. Spielvogel,* Fahim U. Ahmed, and Andrew T. McPhail

P. M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706

Received October 3, 1985

We are interested in the synthesis and characterization of isoelectronic and isostructural boron analogues of biologically important molecules. These may be of use to probe fundamental biochemical events at the molecular level as well as to provide entirely new classes of compounds of potential pharmacological value. Along these lines we have prepared some of the first examples of boron analogues of the α-amino acids[1-3] and their related precursors[4,5] and derivatives.[6,7] These analogues, typified by the protonated glycine analogue[1] $H_3NBH_2CO_2H$, contain 4-coordinate boron and possess appreciable air and hydrolytic stability. They have been found to possess significant pharmacological activity, in particular, antitumor,[8-10] antiarthritic,[11] and hypolipidemic[12,13] activity in animal model studies.

Boron analogues of other important biologically active molecules such as neurotransmitters can be envisioned. In this paper, we wish to report a remarkably facile synthesis of (2-acetoxyethyl)dimethylamine–borane (**1**), an isoelectronic and isostructural boron analogue of the important neurotransmitter the acetylcholine (ACh) cation (**2**).

$$H_3B{-}N(CH_2)_2CH_2CH_2OC({=}O)CH_3$$

1

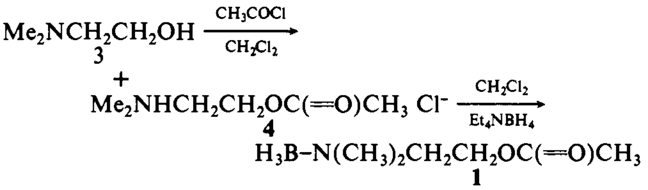
$$[H_3CN(CH_3)_2CH_2CH_2OC({=}O)CH_3]^+$$

2

This boron analogue of ACh is a molecular species since the boron and nitrogen atoms bear canceling formal negative and positive charges, respectively. Thus this analogue may be useful in studies designed to probe the importance of the so-called "anionic" subsite of acetylcholinesterase and ACh receptors. Although **1** belongs to the relatively well-known class of compounds, the amine–boranes, viewed as an analogue of ACh, suggests examination of its activity in novel areas.[14]

(2-Acetoxyethyl)dimethylamine–borane, **1** was prepared by an efficient synthesis shown below in Scheme I.

Scheme I



$$\underset{\mathbf{3}}{Me_2NCH_2CH_2OH} \xrightarrow[CH_2Cl_2]{CH_3COCl}$$

$$+\; \underset{\mathbf{4}}{Me_2NHCH_2CH_2OC({=}O)CH_3\ Cl^-} \xrightarrow[Et_4NBH_4]{CH_2Cl_2} \underset{\mathbf{1}}{H_3B{-}N(CH_3)_2CH_2CH_2OC({=}O)CH_3}$$

The ester hydrochloride **4** was prepared by adding $CH_3C(O)Cl$[15] (10% mol excess) dropwise to an ice-cold solution of

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