Stable Carbocations. CLXVI.[1] Benzonortricyclyl Cations

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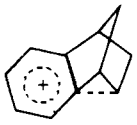
Abstract: A series of secondary 2-benzonorbornenyl precursors were studied in superacid solutions under stable-ion conditions, and the resulting carbocations were investigated by proton and carbon-13 NMR spectroscopy. The observed long-lived ions were found to be benzonortricyclyl cations (i.e., ethylenebenzenium-type ions) containing tetrahedral spiro-carbon atoms. The intermediate 2-benzonorbornenyl cations themselves were not observed as stable species. The preferential formation of tricyclic benzenium-type ions, in spite of the incorporation of substantial steric strain into the molecules, indicates π-p interaction between the benzenoid π system and the electron-deficient center.

Interested in the nature of intermediate carbocations[2] in the solvolytic reactions of 2-norbornyl derivatives,[3] Bartlett and Giddings[4] reported the solvolysis of *exo*- and *endo*-2-benzonorbornenyl brosylates. The exo epimer was found to undergo acetolysis at a rate 700 times faster than the endo brosylate to yield, exclusively, the unrearranged acetate. On the basis of the high exo:endo rate ratio and the retention of configuration, the unsymmetrical, homoallylic structure **1** was proposed for the intermediate carbocation. Giddings



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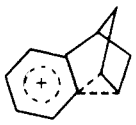

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and Dirlam further noticed that optically active *exo*-2-benzonorbornenyl brosylate actually underwent solvolysis with complete racemization, indicating symmetrically delocalized ion structure **2**,[5]

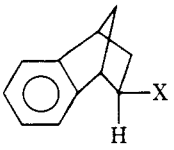
2-Benzonorbornenyl derivatives have enjoyed special attention not only because of their structural relationship to the 2-norbornyl[2] and norbornenyl-nortricyclyl[6] systems, but also because of their geometry suitable for phenyl ring π participation.[7] Extensive studies on the solvolysis of 2-benzonorbornenyl derivatives have consequently been carried out by Winstein,[8] Tanida,[9] Brown,[10] and Wiley.[11]

Winstein, based on substituent effects, concluded that acetolysis of 2-benzonorbornenyl brosylates was best interpreted by anchimerically assisted ionization of the exo isomer, involving carbon-carbon σ bond participation and anchimerically unassisted ionization of the epimeric endo brosylate.[8] On the other hand, Brown chose the 2-benzonorbornenyl system to test his hypothesis that σ delocalization (carbon-carbon bond participation) was unimportant in the solvolysis of the related 2-norbornyl derivatives.[10,12] However, the studies of substituent effects clearly established that homobenzylic participation in the transition state is indeed the dominant factor contributing to the high exo:endo rate ratio in the solvolysis of secondary 2-*exo*-benzonorbornenyl derivatives.[7] Instead of referring to 2-benzonorbornenyl systems as a model for carbon participation in the 2-norbornyl system, Brown now refers only to π participation in the solvolysis of the formers.[10a] Although other ways for aryl participation were found in the polar (electrophilic) addition to benzonorbornadienes, mainly in the work of Cristol[13] and Wilt,[14] the nature and structure of the secondary carbocationic intermediates involved in the solvolytic reactions are still unsettled.

We have recently reported that the long standing controversy as to the structure of the parent 2-norbornyl cation as studied under stable ion conditions was, in our view, unequivocally resolved in favor of the nonclassical carbonium ion.[2,15] We now report the study of a series of secondary 2-benzonorbornenyl systems in superacidic media and their spectroscopic studies, which offer significant information concerning the nature and structure of the involved carbocationic intermediates (also involved in the solvolytic reactions of their derivatives).

Results and Discussion

Benzonortricyclyl Cation. Attempted preparation of the parent, secondary 2-benzonorbornenyl cation was carried out by careful addition of benzonorbornenyl precursors (**4–6**) to either FSO_3H–SbF_5 or SbF_5 in SO_2ClF solution at



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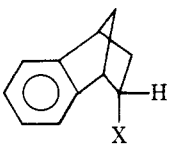

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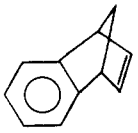

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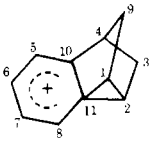

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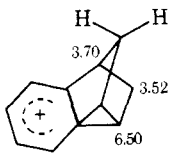
X = OH, Cl, or Br

−78°. The ^{1}H NMR (60 MHz) spectra indicated the formation of the same ion **3**. The temperature-independent (−120 to +10°) ^{1}H NMR spectrum (Figure 1A) of ion **3** consists of an AB quartet centered at δ 3.52 (four protons, $J_{H,H}$ = 12.5 Hz); a broad one-proton singlet at δ 3.70; a two-proton singlet at δ 6.50; and three sets of aromatic multiplets centered at δ 8.02 (two protons), 8.50 (doublet, one proton, J = 6.5 Hz), and 8.78 (triplet, one proton, J = 7.8 Hz). The solution of the ion is stable below +10° and slowly decomposes at higher temperatures. Within the limits of our studies, small concentration variations due to deferring samples (generally between 5–10% w/w) had no effect on the spectra.

The observed ^{1}H NMR spectrum is thus similar to those of the recently reported secondary 3-nortricyclyl cation **7**[16] and the tertiary 3-methyl-3-nortricyclyl cation **8**.[16] The 3-nortricyclyl cation **7** gives proton absorptions at δ 6.72 (broad, H_1 and H_6), 4.63 (broad, H_2), 3.65 (broad, H_4) a



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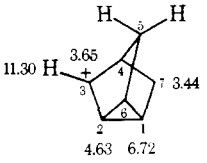

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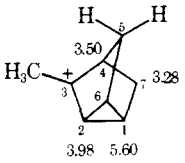

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set of AB quartet centered at δ 3.44 (H_5, H_7), and a doublet of doublets at δ 11.30 (H_3). The ^{1}H NMR shifts for **8** and their assignment are shown on the structure. In the two 3-nortricyclyl cations **7** and **8**, the methylene groups (H_5 and H_7's) should contain two different type of protons, as are the corresponding ones in **3** (H_3 and H_9's). Thus, they all

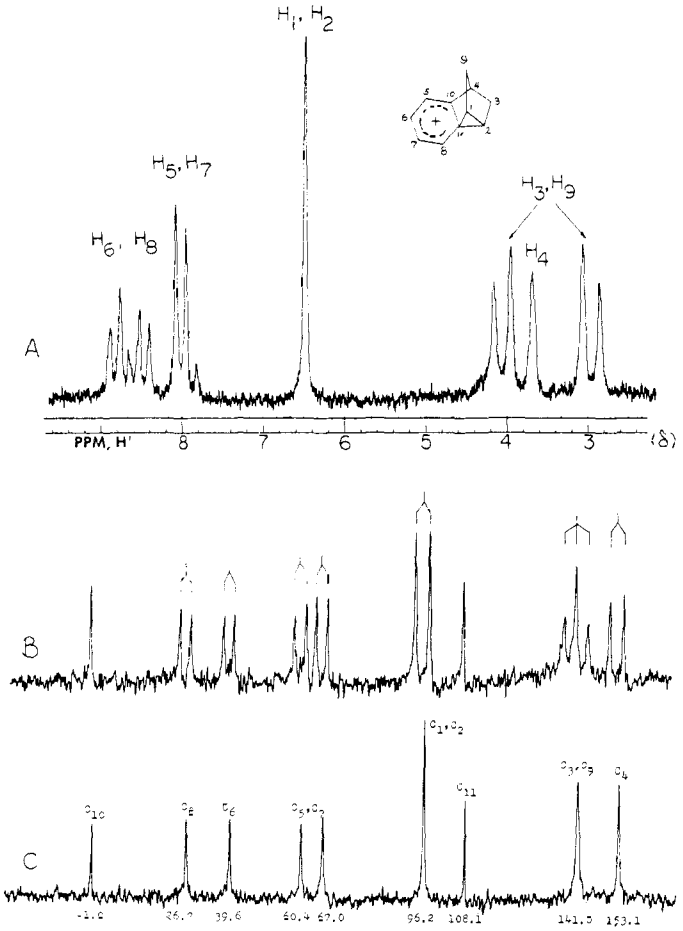
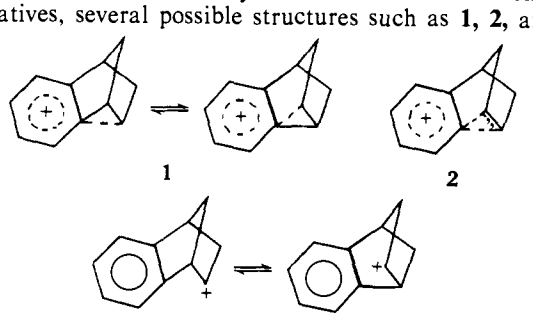


Figure 1. (A) The 60-MHz ^{1}H NMR spectrum of the parent benzonortricyclyl cation **3**, (B) Proton coupled carbon-13 NMR spectrum of **3**, (C) Proton decoupled carbon-13 NMR spectrum of **3**,

show AB type quartet coupling patterns with comparable coupling constants ($J_{H,H}$ = 12 Hz). The two cyclopropane-ring protons (H_1 and H_6) at β positions to the carbenium center in **7** and **8** are deshielded because of charge delocalization into the cyclopropyl ring, as are the corresponding protons (H_1 and H_2) in ion **3**, also deshielded by about the same extent. The bridgehead protons (H_4's) in all three ions show resonances at comparable positions.

The carbon-13 NMR spectrum (noise decoupled) for ion **3** in FSO_3H–SbF_5–SO_2ClF solution at −80° was obtained by the Fourier transform technique (Figure 1C). Carbon shifts and assignments are summarized in Table II. Assignments and coupling constants (J_{CH}, in Hz) are made with the aid of proton-coupled ^{13}C NMR spectrum (Figure 1B). There is no absorption corresponding to a typical deshielded carbenium carbon. The presence of only 9, instead of 11 carbon resonances indicates that the ion must be symmetrical.

Although based on solvolysis data of 2-benzonorbornenyl derivatives, several possible structures such as **1**, **2**, and **9**



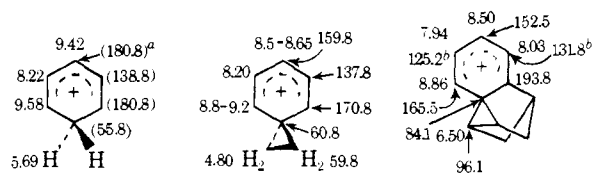
1 **2**

9a **9** **9b**

have been suggested for the 2-benzonorbornenyl cation; results of both proton and carbon-13 NMR data of the long-lived ion are incompatible with any of these. The NMR data indicate that the observed ion indeed is the benzonortricyclyl cation **3**,

The NMR data also rule out the static classical structure **9** since, for this, more complicated ^{1}H and ^{13}C NMR spectra should be expected. Rapidly equilibration pairs of classical 2-benzonorbornenyl cations (i.e., **9a** ⇌ **9b**) further are ruled out, because this would not allow much positive charge to be built up into aromatic ring and thus is contrary to the observed data showing that both homo-ortho (C_8 and C_{10}) and homo-para (C_6) ring positions experience substantial deshielding effects caused by a significant degree of charge delocalization into the aromatic ring. The dramatically different carbon resonances ($\Delta\delta_{^{13}C}$ 109.7 ppm) observed for the two fused ring carbons C_{10} ($\delta_{^{13}C}$ 193.8) and C_{11} ($\delta_{^{13}C}$ 84.1) indicate that the former is highly deshielded and the latter is shielded. One also finds that the carbon–hydrogen coupling constants for C_1 and C_2 are unusually large (J_{CH} = 190.0 Hz), indicating that these two carbon atoms display a substantial degree of bond-angle strain. The magnitude of the coupling constants is very close to those observed for the corresponding carbons in the 3-nortricyclyl cations[16] (J_{CH} = 185. Hz for **7**, and J_{CH} = 198.0 Hz for **8**).

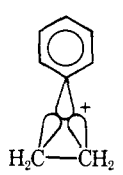
In addition, both proton and carbon-13 NMR data of the fused benzene ring in **3** show a charge-distribution pattern characteristic of either benzenium **10**[17] or ethylenebenzenium **11**[18] ions. Both **10** and **11** have been shown to exist as



10 **11** **3**

[a] Values in parentheses are estimated from ethylenebenzenium ion **11** and reported substituted arenium ions. [b] ^{13}C NMR shifts were assigned based on analogy with model compounds. The C_5 and C_7 shifts could not on this basis be differentiated and must be considered interchangable.

typical carbenium ions, i.e., benzenium and spiro[2.5]octadienyl (or ethylenebenzenium) type ions, respectively, under stable-ion conditions.[17,18] The related nonclassical ethylenephenonium ion **12**[2,7] is yet unknown and would represent bonding interaction of the phenyl cation sp^2 orbital

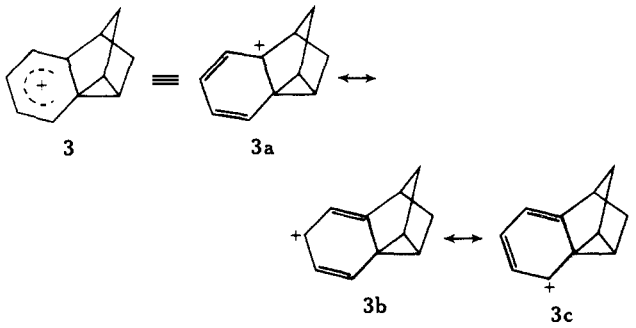


12

with the ethylene π bond. Carbon-shift differences between the spiro carbon (C_1) and ortho carbon (C_2) in **11** and that between C_{11} (spiro carbon) and C_{10} (ortho carbon) in **3** are of the same magnitude ($\Delta\delta_{^{13}C}$ 110 and 109.1, respectively). The aliphatic nature of the spiro carbon in **3** is therefore clearly established. Because of the substituent effect at C_{10} in **3** and the incorporation of strained cyclopropyl ring, positive-charge distribution in this ion is expected to be slightly different from that in **11**. This is shown by the slight shielding of the homo-para carbon (C_6) in **3** (about 7 ppm) over that in **11**. Para carbon shifts in arylcarbenium ions have been utilized to estimate the charge-distribution pattern into the ring since the para position is remote from electron-deficient center so that no significant steric effect

should contribute to its carbon (or proton) resonance shift. A difference in para shifts, in a series of related arylcarbenium ions, therefore indicates the trend in charge distribution in aryl rings.[19] The more strained cyclopropyl ring in **3** apparently delocalizes more positive charge into the three-membered ring than that in **11**, as we have previously shown that charge delocalization between cyclopropyl C–C bonds and neighboring electron-deficient centers (i.e., carbenium centers) depends not only on the orientation of the cyclopropyl ring but also on the degree of strain in the ring.[16,20,21]

Considering all facts, the structure of the ion obtained from secondary 2-benzonorbornenyl precursors under stable-ion conditions can be assigned only as the benzonortricyclyl cation **3**, with a significant contribution from the ca-



3 **3a** **3b** **3c**

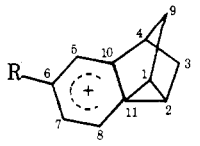
nonical form **3a**, Ion **3** does not show, based on comparison of ^{13}C NMR parameters between **3** and **14**, resemblance to the 2-norbornyl cation **14**,[15] which would indicate nonclassical structure **13**, The benzonortricyclyl cation, on the

13 **14**

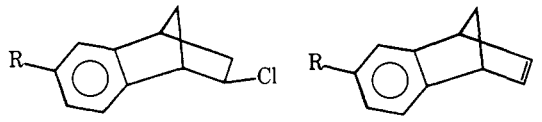
other hand, shows similarity to the ethylenebenzenium ion **11** and 3-nortricyclyl cations **7** and **8** containing a tetrahedral spiro-carbon atom (C_{11}) and a nortricyclyl-type framework.

C_6-Substituted Benzonortricyclyl Cations. The effect of substituents in the aromatic ring on the solvolysis of 2-benzonorbornenyl derivatives was first noticed by Wiley[11] and followed by related work by Winstein,[8] Tanida,[9] and Brown.[10] The formation of the benzonortricyclyl cation from 2-benzonorbornenyl precursors under stable-ion conditions indicates the higher stability of the former system (despite increased ring strain), and that considerable positive charge delocalizes into the benzene ring. The presence of substituents on the aromatic ring should therefore affect charge distribution and consequently should be reflected in the chemical shifts. For comparison and in order to further study substituted analogs of **3**, we have prepared three ring-substituted ions (**3-R**).

6-Methyl-, 6-methoxy-, and 6-chloro-2-benzonortricyclyl cations were prepared from their respective 2-benzonorbornenyl chloride precursors **15-R**[22] in either SbF_5–SO_2ClF or FSO_3H–SbF_5–SO_2ClF solution at −78°. Proton and car-



3-R



15-R **16-R**

R = CH_3, OCH_3, and Cl

bon-13 parameters for **13-R** are summarized in Tables I and II, respectively, along with their assignments.

Proton NMR spectra of **3-R** closely resemble those of the parent ion **3**, The two cyclopropane-type protons (H_1 and H_2) in **3-CH_3** and **3-Cl** show similar resonances, and those of **3-OCH_3** are shielded by about 1 ppm (Figure 2). The two sets of methylene protons (H_3 and H_9) in all three ions

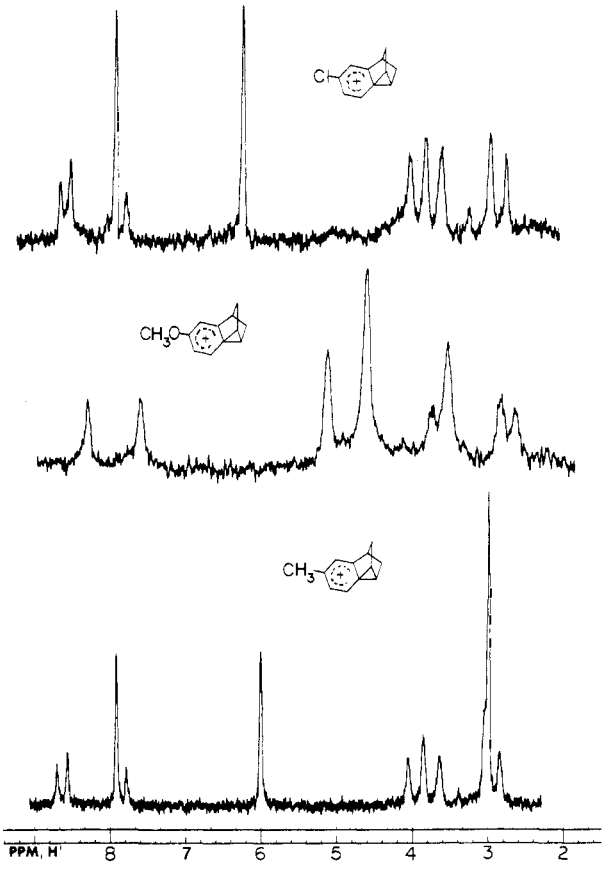


Figure 2. The 60-MHz ^1H NMR spectra of **3-CH_3** (bottom trace), **3-OCH_3** (middle trace), and **3-Cl** (top trace).

Table I, Proton NMR Parameters of the Benzonortricyclyl Cations[a]

Ion	H_1,H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	CH_3	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$
3	6.50, s	3.52[b]	3.70, s	8.03, d	8.50, dd	7.94, dd	8.86, d	3.52[b]		7.4	7.0	8.0
3-CH_3	6.02, s	3.40[c]	3.68, s	7.95, s		7.86, d	8.60, d	3.40[c]	3.02, s			8.2
3-Cl	6,32, s	3,45[c]	3.68, s	8.02, s		7.94, d	8.68, d	3.45[c]				8.0
3-OCH_3	5.15, s	3.22[c]	3.55, s	7.60, s		7.60, s	8.34, s	3.22[c]	3.62, s			
17-Cl	6.38, s	3.80[b]	3.98, s	8.20, d	8.82, dd	8.18, dd	8.92, d	5.70, s		7.6	8.0	8.8
17-Br	6.08, s	3.68[c]	5.02, s		8.40, s			5.02, s				

[a] ^1H NMR shifts (δ) are given in parts per million from external Me_4Si (capillary). Multiplicities: d = doublet; dd = doublet of doublet; s = singlet. [b] AB quarter, J = 12.5 Hz. [c] AB quartet, J = 12.0 Hz.

display an AB quartet pattern with similar coupling constants ($J_{H,H} \simeq 12$ Hz). Again ^{1}H NMR resonances for ion **3**-OCH_3 appear at higher field than those in the methyl- and chloro-substituted ions. The assignments for the benzene ring protons are straightforward, The sharp singlets at δ 7.95 and 8.02 are assigned to H_5 protons in **3**-CH_3 and **3**-Cl, respectively. The H_7 and H_8 protons in these two ions are doublets, with the higher field doublets assigned to the H_7 protons. The benzene-ring protons in **3**-OCH_3 are different from those in **3**-CH_3 or **3**-Cl and do not show coupling patterns similar to those found in the latter.

Carbon-13 NMR spectra of **3**-R are all very similar to that of the parent ion **3**, showing nine carbon resonances characteristic of the benzonortricyclyl structure, in addition to those of the methyl or methoxy carbons. C_6 carbons in ring-substituted ions **3**-R become singlets in their off-resonance spectra and could be assigned accordingly. Table II reveals that carbon shifts of methyl- and chloro-substituted ions **3**-CH_3 and **3**-Cl are of similar magnitude but are quite different (especially for the cyclopropyl-ring, homo-ortho and homo-para carbon resonances) from those in **3**-OCH_3. Carbon shifts in **3**-OCH_3 are therefore found shielded from the corresponding shifts in **3**-CH_3, which in turn show resonances shielded from those in **3**-Cl.

Based on both ^{1}H and ^{13}C NMR data, resonance forms of the type **3a**-R–**3c**-R, as discussed in the case of the parent ion **3**, are clearly important contributors to the benzonortricyclyl ions. Particular attention is directed to the carbon resonances of C_1 (and C_2), homo-para carbons C_6 and homo-ortho carbons C_8 (and C_{10}). The deshielding effects observed for the presently studied series of 2-benzonortricyclyl cations at the cyclopropane ring, as well as of the homo-ortho and homo-para carbons, apparently show that positive charge has been shared between the cyclopropyl and benzenium rings. The results of substituent effects in the solvolysis of *exo*- and *endo*-2-benzonorbornenyl derivatives showed that the exo epimers solvolyzed in an anchimerically assisted manner because of carbon–carbon σ- and π-aryl participation, whereas the endo epimers solvolyzed without assistance.[8-11] Substitution at C_6 in the presently studied 2-benzonorbornenyl systems under stable-ion conditions also shows the predominant importance of the benzene-ring participation in the benzonortricyclyl ions. A variation of the electron-releasing ability of substituents apparently makes the cyclopropyl ring to share positive charge to a varying degree. We have previously reported ^{13}C NMR spectra of a series of cyclopropylcarbenium ions in both open-chain and strained systems.[16,23] When charge delocalization into the cyclopropyl ring becomes more significant, $C_{1(2)}$ becomes further deshielded. Differences in chemical shifts (proton and carbon) therefore reflect the trend of the relative degree of charge delocalization into either the cyclopropyl or benzenium ring. Cyclopropyl carbons in **3**-OCH_3 are the least deshielded, followed by those in **3**-CH_3, **3**-Cl, and finally those in **3** which are the most deshielded.

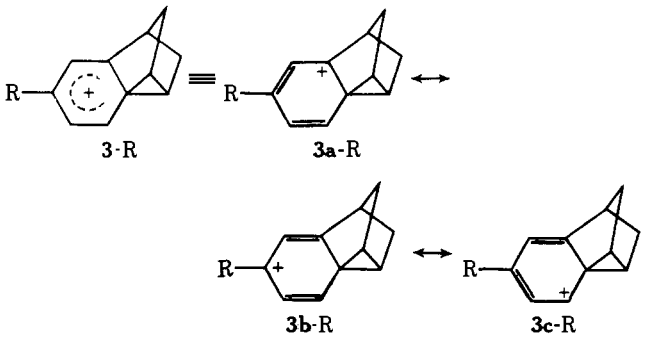


Table II. Carbon-13 NMR Parameters of the Benzonortricyclyl Cations[a]

Ion	C_1,C_2	C_3	C_4	C_5[c]	C_6	C_7[c]	C_8	C_9	C_{10}	C_{11}	CH_3	Δ[b]
3	96.1 (d, 190.0)	51.2 (dd, 139.0, 142.0)	39.1 (d, 160.7)	131.8 (d, 164.7)	152.6 (d, 164.2)	125.2 (d, 172.8)	165.5 (d, 178.6)	51.2 (as C_3)	193.8 (s)	84.1 (s)		109.7
3-CH_3	86.0 (d, 188.1)	49.7 (dd, 145.1, 141.9)	38.8 (d, 157.1)	133.5 (d, 171.2)	172.6 (s)	126.8 (d, 165.9)	164.8 (d, 173.7)	49.7 (as C_3)	194.1 (s)	75.6 (s)	24.2 (q, 129.9)	118.5
3-Cl	93.6 (d, 190.0)	50.3 (dd, 140.0, 135.0)	39.4 (d, 160.0)	133.0 (d, 152.5)	163.1 (s)	126.8 (d, 155.0)	165.1 (d, 175.0)	50.3 (as C_3)	193.4 (s)	80.9 (s)		112.5
3-OCH_3	70.5 (d, 189.4)	47.2 (dd, 141.5, 144.8)	38.9 (d, 158.8)	127.4 (d, 174.4)	177.2 (s)	110.5 (d, 164.8)	159.3 (d, 173.5)	47.2 (as C_3)	189.2 (s)	61.3 (s)	60.2 (q, 132.7)	132.9
17-Cl	89.3 (d, 194.0)	47.5 (dd, 133.0, 140.0)	45.5 (d, 161.2)	133.7 (d, 166.1)	165.3 (d, 172.6)	126.9 (d, 169.5)	156.1 (d, 167.0)	64.9 (d, 174.1)	188.1 (s)	80.9 (s)		107.2
17-Br	88.3 (d, 194.8)	47.3 (dd, 133.5, 141.0)	45.8 (d, 160.5)	134.7 (d, 165.8)	166.8 (d, 170.4)	128.0 (d, 168.5)	158.7 (d, 167.5)	78.9 (d, 183.1)	186.3 (s)	76.6 (s)		109.7

[a] ^{13}C NMR shifts ($\delta_{^{13}C}$) are given in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (J_{CH}, in Hz) are given in parentheses. d = doublet, dd = doublet of doublet, s = singlet, q = quartet. [b] $\Delta = \delta_{^{13}C_{10}} - \delta_{^{13}C_{11}}$. [c] Interchangeable values.

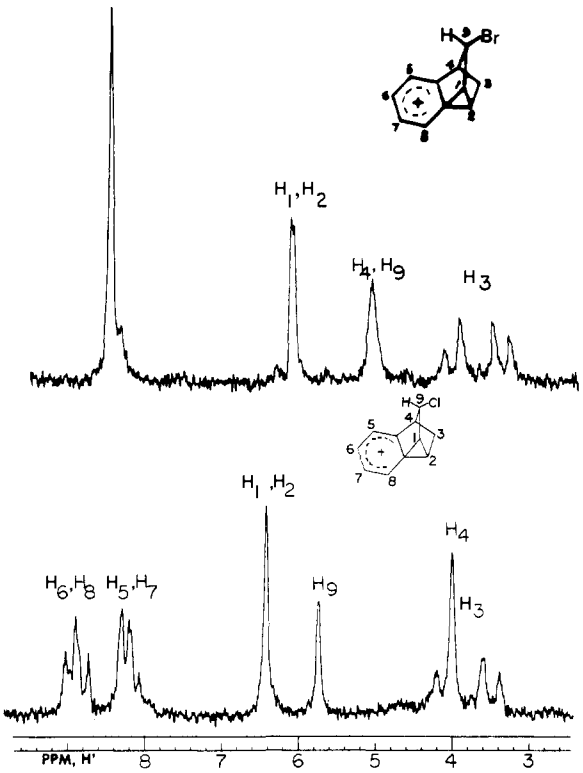
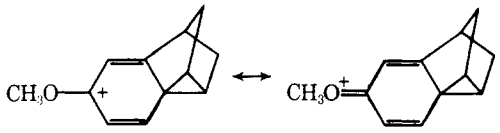


Figure 3, The 60-MHz ^{1}H NMR spectra of **17**-Cl (bottom trace) and **17**-Br.

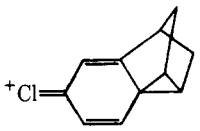
Charge delocalization into the cyclopropyl ring is therefore indicated in the decreasing order

$$3 > 3\text{-Cl} > 3\text{-CH}_3 > 3\text{-OCH}_3$$

The methoxy group in **3**-OCH_3 apparently draws substantial positive charge away from the cyclopropyl ring. The C_1 carbon-shift difference between **3** and **3**-OCH_3 is significant, 25.6 ppm. Resonance form **3b**-OCH_3 is there-



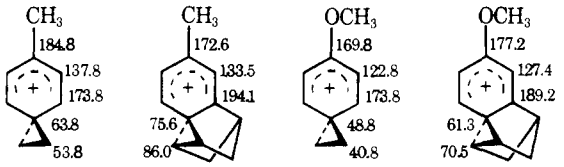
3b-OCH_3



3b-Cl

fore an important contributor to he structure of the 6-methoxy-2-benzonortricyclyl cation. Methyl substitution apparently causes a similar effect as the methoxy group. Chlorine substitution, however, shows only a minor effect on the chemical shifts. Halogen "back-donation" is well known in acyclic and cyclic halocarbenium ions.[24] Chlorine "back-donation" is never, however, as important as that of fluorine. Resonance form **3b**-Cl should therefore only be a minor contributor to **3**-Cl. The increase in bond order between C_6 and R is thus more significant for the methoxy group than for the chlorine atom.

We have previously compared the ^{13}C NMR spectra of the parent benzonortricyclyl and ethylenebenzenium ions, **3** and **11**, respectively, The aliphatic spiro carbon (C_{11}) in **3** is clearly shown by its ^{13}C NMR resonance and coupling constant (J_{CH}). A comparison of ^{13}C NMR shifts between ring-substituted ethylenebenzenium ions **11**-R (R = CH_3,

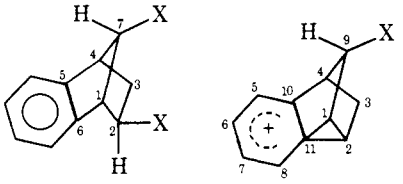


11-CH_3 **3**-CH_3 **11**-OCH_3 **3**-OCH_3

and OCH_3)[18] with their corresponding benzonortricyclyl cations **3**-R also indicate the presence of aliphatic spiro-carbon atoms in the latter.

The benzonortricyclyl structures of **3**-R are further supported by the observation of unusually large coupling constants (J_{CH} in Hz, see Table II) for the cyclopropyl-type carbons (C_1 and C_2). The coupling constants are in the order of 190 Hz. The substituted benzonortricyclyl cations **3**-R are thus essentially very similar in nature to the ethylenebenzenium ions **11**-R and 3-nortricyclyl cations having a tetrahedral spiro-carbon atom and a nortricyclyl skeleton.

C_9-Substituted Benzonortricyclyl Cations. In addition to the preparation of the parent and ring-substituted benzonortricyclyl cations, we have also prepared two C_9 halogen-substituted ions **17**-X (X = Cl and Br). These ions were prepared via ionization of *exo*-2-*anti*-7-dihalobenzonorbornenes **18**-X in SbF_5-SO_2ClF (or FSO_3H-SbF_5) solution at −78°.



18-X **17**-X

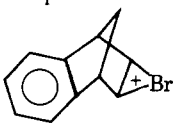
X = Cl and Br

^{1}H NMR spectra of 9-chloro- and 9-bromobenzonortricyclyl cations are shown in Figure 3. ^{1}H and ^{13}C NMR parameters for these ions are summarized in Tables I and II, respectively. The ^{1}H NMR spectrum of **17**-Cl (Figure 3) showed a pattern similar to that of the parent benzonortricyclyl cation **3**. The methylene protons (H_3's) showed a typical AB quartet with J = 12.5 Hz as those in other benzonortricyclyl cations shown in Table I. H_9 in **17**-Cl becomes a singlet and is deshielded. The cyclopropane-type protons (H_1 and H_2) in **17**-Cl resonate at δ 6.38 as a broad singlet, in the approximate region of those in other benzonortricyclyl cations. The benzenium protons also display a typical pattern indicating charge delocalization.

The ^{13}C NMR spectrum of **17**-Cl showed ten carbon resonances, characteristic of a benzonortricyclyl structure. C_3 and C_9 became nonequivalent because of chlorine substituent at C_9. The two cyclopropyl-type carbons C_1 and C_2, are however identical. Both ^{1}H and ^{13}C NMR data, therefore, confirmed the benzonortricyclyl structure of **17**-Cl.

The ^{1}H NMR spectrum of the bromo analog **17**-Br is somewhat different from that of **17**-Cl, especially the aromatic protons, which are only displayed as a broad absorption, centered at δ 8.40 (four protons). In addition, there are two broad singlets at δ 6.08 (two protons) and 5,02 (two protons) and a AB quartet centered at δ 3.68 (J = 12 Hz).

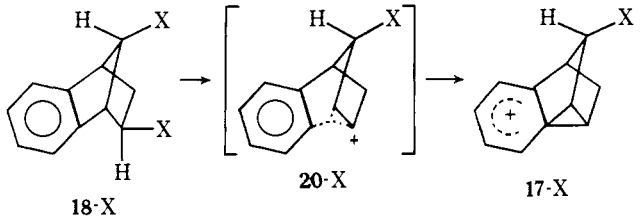
Based on the ^{1}H NMR spectrum of the bromobenzonortricyclyl caton, a symmetrical structure such as **19** could be assumed for **17**-Br, as the apparent symmetrical ^{1}H NMR spectrum seems to correspond to such a structure **19**. When



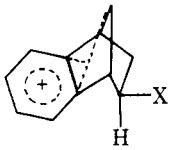
19

the ^{13}C NMR spectrum (Table II) of the same ion was, however, obtained, a characteristic benzonortricyclyl pattern was observed. There are ten carbon resonances indicative of an unsymmetrical structure, such as **17**-Cl. H_3 and H_4 in **17**-Br are accidentally magnetically equivalent. It is not clear why H_4 (the bridgehead proton) became so much deshielded, and the aromatic protons are all magnetically equivalent. However, clearly **17**-Br can also be assigned the benzonortricyclyl cation structure.

Ionization of *exo*-2-*anti*-7-dihalobenzonorbornenes **18**-X might involve direct cleavage of C_2–X bond to form ion **20** which would give **17**-X via simultaneous ring closure form-



ing the benzonortricyclyl system. Ionization, however, should not be limited to only the C_2–X bond. The C_9–X bond could also undergo ionization. If so, the 2-halo-9-benzonorbornenyl ion **21**-X should be formed. The large differ-



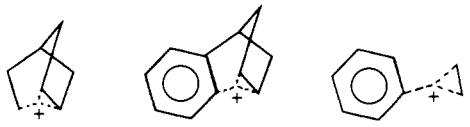
21-X

ence in carbon shift (109.7 ppm) between C_{10} and C_{11}, however, rules out **21** since carbon shifts for these two carbons are not expected to be very different.

Conclusions

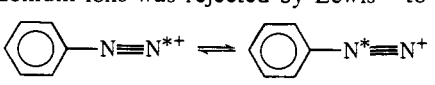
The benzonorbornenyl system offers several advantages for the study of neighboring aryl π participation, which thus far has been studied in related phenylethyl systems,[25] and also in cyclic[26,27] and polycyclic systems.[7] The observation that β-phenylethyl derivatives form, via phenyl π participation, spiro[2.5]octadienyl (ethylenebenzenium) ions under stable conditions,[18] provided direct structural evidence for Cram's bridged "phenonium" ion intermediates involved in the facile solvolysis of β-phenylethyl derivatives.[28] It should be clear, however, that these ions **11**-R have no nonclassical nature, and the related nonclassical ions, i.e., **13**, are still unknown. The present study of 2-benzonorbornenyl derivatives in superacidic media has also not resulted in the observation of a nonclassical bridged ion **13**, only the more stable subsequently formed benzonortricyclyl cations **3**, **3**-R, and **17**-X were obtained. All these ions contain aliphatic, spirocarbon atoms (C_{11}).[29]

Ion **13** could be considered not only an analog of the 2-norbornyl cation **14**, but at the same time of a nonclassical phenonium ion, of the type **12**. This may explain why **14** is

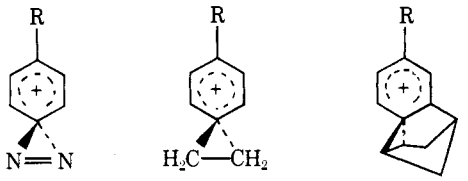


14 13 12

not observable as a long-lived species and immediately gives **3**. A further aspect worthwhile mentioning is that the nitrogen "turn around" observed in scrambling of nitrogen label in aryldiazonium ions was rejected by Lewis[30] to involve a

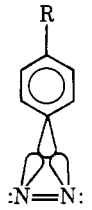


nitrogen-bridged intermediate, because such an intermediate was expected to be an analog of Cram's phenonium ions,[28] but para substituents in the two systems gave no



22 11-R 3-R

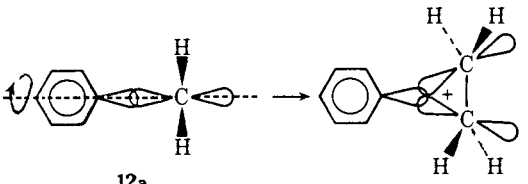
comparable effects. However, if the species involved in the nitrogen turn-around is a side-on π bonded, thus nonclassical ion (instead of the end-on bonded spiro-diazenium ion derivative) **23**—then the substituent effects would be differ-



23

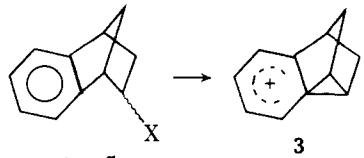
ent, because the model systems for the latter would not be of type **11**, but **12**.[31] Conjugative effects would dominate in the former, but inductive ones in the latter.

Considerable theoretical interest is involved in the differentiation between the bisected form of ethylenebenzenium ion **11** containing a tetrahedral sp^3 type tetravalent carbon and the nonclassical form **12** containing a sp^2 type planar tetracoordinated carbon.[32] The latter can be considered as having a two-electron, three-centered bond formed between the empty sp^2 orbital of the phenyl ring (a phenyl cation) and the π orbital of ethylene. Shanshal has shown that the rotation of the phenyl ring (or the ethylene residue) around the molecular axis is accompanied by considerable change of geometry in the three-membered ring.[32f] The energy difference between **11** and **12** is also shown by calculation to be large (ca. 22 kcal/mol).[32f,33] Whether the favorable conformation of the nonclassical ethylenephenonium ion should be planar or bisected (**12b** and **12a**, respectively) is yet un-



12a 12b

known. The present NMR spectroscopic data clearly indicate that the benzonortricyclyl cations are classical ions (ethylenebenzenium-type ions **11**) containing sp^3 tetravalent carbon atoms. If the formation of benzonortricyclyl cations from 2-benzonorbornenyl derivatives is assumed to proceed through initial σ-bond delocalization via nonclassical ion **13** (although we do not at present have direct evidence to prove such an assumption), then this ion must adopt a conformation resembling **12a** since free rotation is impossible in this case because of geometrical rigidity. Whether this implies that the ethylenephenonium ion **12** should also adopt such a conformation as its stable form **12a**, however, cannot be presently answered. The present data certainly show that π participation leading to the formation of highly strained benzonortricyclyl framework is favorable under stable-ion conditions, via either consecutive



or concerted π alkylation. The results are also in accordance with the solvolytic study showing that delocalization of positive charge to the aryl ring in the transition state is significant.[4-11]

Experimental Section

Materials, 2-Benzonorbornadiene **6** was prepared according to the procedure reported by Wittig and Knauss,[34] bp 80-82° (10 mm).

exo-2-Halobenzonorbornenes **4-X** were prepared from the addition of hydrogen halide to **6** in ether solution at room temperature according to Cristol.[13]

exo- and *endo*-2-benzonorbornenols **4-OH** and **5-OH** were prepared from **6** and 2-benzonorbornanone[4] according to Bartlett.[4]

Samples of 6-methyl-, 6-chloro-, and 6-methoxybenzonorbornadienes **16-R** were kindly provided by Dr. H. Tanida.[22] The corresponding chlorides **15-R** were prepared by shaking the mixture of **16-R** and concentrated HCl at room temperature in a sealed ampoule for 48 hr.

exo-2-*anti*-7-Dihalobenzonorbornenes **18-X** were prepared by halogenation of benzonornadiene according to Cristol.[13]

Preparation of Carbocations, In general, benzonortricyclyl cations were prepared by addition of appropriate benzonorbornenyl precursors in SO_2ClF to a freshly prepared FSO_3H-SbF_5 (or SbF_5) solution in SO_2ClF at Dry Ice-acetone temperature (ca. −78°) with vigorous stirring. The resulting light-brown colored solutions were immediately transferred to precooled NMR tube for NMR measurement. The variation of the concentration of the ion does not change or affect spectroscopic data, neither does the change in temperature.

Proton and Carbon-13 NMR Spectroscopy, Both proton and carbon-13 NMR spectra were obtained as previously reported.[35]

Acknowledgment, Support of our work by the National Science Foundation is gratefully acknowledged. We thank Dr. H. Tanida for samples of substituted benzonorbornadienes.

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Solvolysis of Sterically Compressed *anti*-7-Norbornenyl 3,5-Dinitrobenzoates. Evidence for the Absence of Enhanced Ionic Stabilization in Unsymmetrical (2 + 2 + 0) Laticyclic Cations

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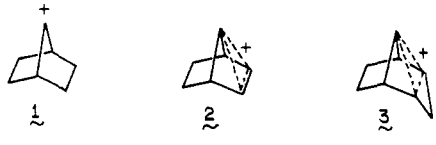
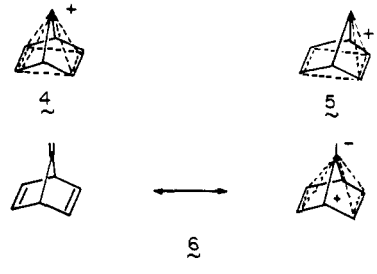
Abstract; The five dinitrobenzoates of generalized structure **24**, prepared according to Scheme I, show solvolysis rates in 80% aqueous acetone which differ by less than a factor of 5 at 114°. The dimethanonaphthadienyl system **10**, previously studied by Allred and Hinshaw, ionizes at a comparable rate. The lack of accelerating influences by the laticyclically positioned double bond, benzene ring, or oxygen atom shows that extended ionic stabilization above that associated with the *anti*-7-norbornenyl moiety is not operative. The products in all cases are the derived alcohols, and these are isolated in >95% yield. Alkyl-oxygen cleavage was established by suitable methanol reactions in one example. The inability of the remote bridges in **10** and **24** to interact during ionization contrasts with the high level of neighboring-group involvement previously observed for the structurally similar brosylates **35–37**, These major differences may derive from the prevailing wide variations in electron-deficiency demand. In the case of **36** and **37**, there is considerable need for laticyclic charge delocalization of the 7-norbornyl cation, and customary neighboring-group influences are manifested. For **10** and **24**, homoaromatic stabilization is appreciable and electron demand is very low such that neighboring-group involvement ceases, and the rate ratios are effectively leveled.

The very low level of solvolytic reactivity associated with 7-norbornyl derivatives,[1] perhaps best reflected in the enormous electron demand ($\rho = -5.64$) of the developing cation center,[2] has for at least a decade been thought to arise chiefly because of energetically unfavorable changes in angle strain upon ionization.[3] The recent theoretical study by Hoffmann and Heilbronner of the 7-norbornyl cation (**1**) has, however, unveiled the alternative possibility that the bicyclo[2.2.1]heptane skeleton with its structurally rigid-boat six-membered ring probably has a symmetry-enforced destabilizing interaction between the C_7 2p orbital and the high-lying cyclohexane σ orbitals.[4] Introduction of a double bond to arrive at the *anti*-7-norbornenyl system has a pronounced effect on the relative ease of ionization, the rate enhancement gained being on the order of 10^{11}.[2a,5] Significantly, interaction of the C_2C_3 π orbital with the vacant orbital at C_7 now permits two-electron delocalization over three centers (cf. **2**) and partially offsets some of the positive charge density at this reaction site.[6] This bishomocyclopropenyl cation interaction leads to approximately 15 kcal/mol of stabilization energy at 25°.[7] An endo-cyclopropane ring in the 2,3 position (**3**) stabilizes positive charge at C_7 to a larger extent than a double bond at the same position,[8] presumably because the vacant C_7 orbital is capable of greater conjugative (trishomoaromatic) interaction with the symmetric e_s Walsh orbital of the cyclopropane moiety than with the π_a orbital of the double bond at the same site.[9] When the double bond becomes part of an aromatic system, the ΔE_π due to bishomoaromatic delocalization is diminished in comparison to **2**.[10,11]



The introduction of a second double bond into the norbornane framework causes a further rate enhancement for ionization at C_7 of 10^3 relative to the already anchimerically accelerated *anti*-7-norbornenyl derivative.[12] The additional ~4.1 kcal/mol stabilization had been initially attributed to the favorable involvement of the double bonds as in **4**.[7] However, because the 7-norbornadienyl cation is now recognized to adopt a distorted geometry more closely resembling **5** than **4**,[13] it would seem that enhanced homoaromatic interaction is of major consequence in the stabilization of this "bicycloaromatic"[14] system. Or, as viewed by Goldstein and Hoffmann,[15] one pericyclic interaction (of the bishomoaromatic type) is favored at the expense of the other [longicyclic (2 + 2 + 0) interaction]. In any event, since the barrier to bridge flipping in **5** is greater than 19.6 kcal/mol at 45°,[13] stabilization of the *symmetrical* (C_{2v}) 7-norbornadienyl cation (**4**) must be quite small and may even be zero.[16] Nevertheless, the exceptional stability of **5**[17] is undoubtedly a function of the spatial orientation and proximity of the π orbitals such that some measurable degree of effective overlap does operate. A perhaps comparable interaction between two vinyl bridges and a C_7 p orbital within a bicyclo[2.2.1]heptyl framework has also been discovered for triene **6**,[18,19] the importance of dipolar ground-state contributions being revealed by its substantial dipole