# Stable Carbocations. CXL.[1] Naphthalenium Ions

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**Abstract:** Protonation of naphthalene, methyl-, halo-, hydroxy-, and methoxynaphthalenes in superacid (HF–SbF$_5$–SO$_2$ClF or SbF$_5$–FSO$_3$H–SO$_2$ClF) solutions leads to the formation of the stable naphthalenium ion and methyl-, halo-, hydroxy-, and methoxynaphthalenium ions, respectively. The direct observation of these arenium ions by means of nmr spectroscopy is reported. The pmr spectrum of naphthalenium ion is temperature dependent indicating the presence of rapidly equilibrating ions (1-protonated and 2-protonated naphthalenium ions) *via* simple, 1,2-hydrogen shift. The activation energy, $E_a$, of 14.5 ± 0.9 kcal/mol and the preexponential factor, $A$, of $10^{16\pm0.8}$ sec$^{-1}$ were estimated for this process. Protonation of isomeric methyl-, fluoro-, hydroxy-, and methoxynaphthalenes in superacid gave only one kind of ion, while from chloro-, bromo-, and iodonaphthalenes, two isomeric ions were formed. These results are discussed in terms of halogen size and proton affinity, as well as in terms of a repulsive interaction of the p (halogen) and $\pi$ (ring) electrons. Substantial peri effect was observed in 1-halo-, -hydroxy-, and -methoxynaphthalenium ions. The carbon-13 Fourier-transform nmr spectra of 1,5-dimethylnaphthalene and its corresponding ion are also reported.

As expected, in the series of homologous arenes, benzene (with its ideal "aromatic sextet") is the most difficult to protonate. The "frozen" benzenium ion **1** can be observed only in the strongest superacid media[2] and only at temperatures below −130°. Anthracene derivatives (for example, 9,10-dimethylanthracene) easily give anthracenium ions **2** even in CF$_3$COOH–H$_2$O–BF$_3$ solutions.[3] There is no report in the literature on the direct observation of protonated naphthalene **3a**. It was therefore of interest to study the
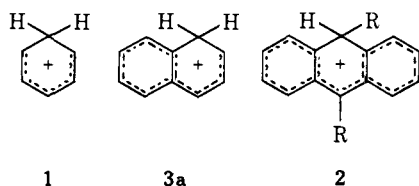


naphthalenium ion in order to complete the series of simple parent arenium ions.[3] The study of protonation of substituted naphthalenes is also of interest. It adds further insight into the chemistry of substituted arenium ions when compared with the previously described monoalkyl-, halo-, hydroxy-, and alkoxybenzenium ions.[3,4]

## Results and Discussion

Naphthalene and methyl-, halo-, hydroxy-, and methoxynaphthalenes were protonated in a superacid HF–SbF$_5$ (1:1 molar ratio)–SO$_2$ClF solution. The pmr parameters of the protonated species are summarized in Table I.

**Naphthalenium Ion.** The preparation of the stable naphthalenium ion **3a** was achieved when naphthalene **3** was treated with fluoroantimonic acid (HF–SbF$_5$ 1:1 molar ratio) dissolved in SO$_2$ClF (1:1 v/v) at low temperature. The naphthalenium ion **3a** is almost as diffi-

cult to prepare as the benzenium ion. A saturated solution of naphthalene in SO$_2$ClF was carefully added in small portions to the vigorously stirred HF–SbF$_5$–SO$_2$ClF or FSO$_3$H–SbF$_5$–SO$_2$ClF solution at −78°. Development of a dark red color was immediately observed.[5] Alternatively, the superacid solution was carefully added directly to naphthalene in an nmr tube which was cooled at −78°. The mixture was then stirred at this temperature until a clear, deep red solution was formed. The 100-MHz pmr spectrum of the clear solution (Figure 1) is consistent with structure **3a** of protonated naphthalene. One can easily recognize the methylene peak at δ 5.27.[6] The ortho (2) and para (4) positions with respect to the protonation site are, as expected, the most deshielded ones. Both signals appear as doublets at δ 9.51 ($J_{2,3} = 7.8$ Hz) and 9.81 ($J_{3,4} = 7.2$ Hz), respectively, with further unresolved splittings. This type of proton–proton coupling has also been observed in other arenium ions.[3,4] All these data are consistent with the results of a nmr study of monoalkylbenzenium ions.[3,4a] The meta-proton (3) signal overlaps with those of the B-ring protons (5–8).

The pmr spectrum of the naphthalenium ion **3a** is temperature dependent (Figure 2). The methylene and the ortho-proton signals broaden with increasing temperatures. The ortho-proton absorption broadens more rapidly than the methylene proton absorption. No change of para, meta, and B-ring proton absorptions is noticeable in the range −83 to −10°. The temperature-dependent pmr spectra clearly indicate the presence of the rapidly equilibrating ions **3a** ⇌ **4** *via* simple 1,2-hydrogen shift. This pattern has also been observed in other arenium ions[3,4] and is in agreement with the chemistry of naphthalene. The 1,2-hydrogen shift is assumed to proceed through a three-center bond benzonium ion transition state **4b**.[7]

(1) Part CXXXIX: G. A. Olah, H. Lin, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3667 (1972).

(2) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *ibid.*, **92**, 2546 (1970).

(3) A detailed discussion on arenium ions is presented by D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, p 837.

(4) (a) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972); (b) G. A. Olah and Y. K. Mo, *ibid.*, **94**, 5341 (1972).

(5) Adding the naphthalene–SO$_2$ClF solution at higher temperatures results only in tar formation. Once formed, however, at low temperature, ion 3a is stable up to −10° (the pmr spectrum displays reversible changes between −83 and −10°).

(6) The methylene protons of arenium ions generally appear between δ 4.0 and 6.0; see also ref 3.

(7) For a differentiation of trivalent carbenium ions from tetra- or pentacoordinated carbonium ions and a discussion of the general concept and naming of carbocations, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

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**Table I.** Pmr Parameters in Naphthalene, Methyl-, Halo-, Hydroxy-, and Methoxynaphthalenes, and Their Protonated Species[a]

| Compd | Substituent position | δ(CH₃) | δ(CH₂) | δ (ring protons) 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 | | | | 7.73c | 7.37c | 7.37c | 7.73c | 7.73c | 7.37c | 7.37c | 7.73c |
| 3a | | | 5.27 (s, br) | | 9.51 (d, J = 7.8) | 8.4b | 9.81 (d, J = 7.2) | 8.4b | 8.4b | 8.4b | 8.4b |
| 5a | 1-CH₃ | 2.34 (s)d | | | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) |
| 6a | 1-CH₅ | 3.62 (t), J = 2.5 | 5.20 (s, br) | | 8.92 (d), J = 8 | 9.26 (d), J = 8 | | 8.4 (m) | 8.4 (m) | 8.4 (m) | 8.4 (m) |
| 5b | 2-CH₂ | 2.60 (s) | | 7.6 (m) | | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) |
| 6b | 2-CH₂ | 3.26 (s) | | 5.24 (s, br) | | 8.3 (m)b | 9.63 (d, t), J = 8 and 2 | 8.3 (m)b | 8.3 (m)b | 8.3 (m)b | 8.3 (m)b |
| 7 | 1,5-(CH₃)₂ | 2.63 (s) | | | 7.2 (m)b | 7.2 (m)b | | | 7.2 (m)b | 7.2 (m)b | 7.2 (m)b |
| 7a | 1,5-(CH₃)₂ | 3.70 (t, 1), J = 3; 2.94 (s, 5) | 4.95 (s, br) | | 8.93 (d), J = 8.4 | 9.36 (d, t), J = 8.4 and 1.3 | | | 8.4 (m)b | 8.4 (m)b | 8.4 (m)b |
| 8 | 2,6-(CH₃)₂ | 2.46 (s) | | 7.44 (s) | | 7.15 (m) | 7.55 (d), J = 7 | 7.44 (s) | | 7.15 (m) | 7.55 (d), J = 7 |
| 8a | 2,6-(CH₃)₂ | 3.17 (s, 2); 2.76 (s, 6) | 5.16 (d), J = 1.6 | | | 8.2 (m)b | 9.44 (d), J = 8 | 8.2 (m)b | | 8.2 (m)b | 8.2 (m)b |
| 9 | 2,3-(CH₃)₂ | 2.27 (s) | | 7.39 (s) | | | 7.39 (s) | 7.56 (m)b | 7.24 (m)b | 7.24 (m)b | 7.56 (m)b |
| 9a | 2,3-(CH₃)₂ | 3.14 (s, 2); 2.95 (s, 3) | 5.28 (s) | | | | 9.43 (t), J = 1 | 8.4 (m)b | 8.4 (m)b | 8.4 (m)b | 8.4 (m)b |
| 10 | 1,3-(CH₃)₂ | 2.53 (s, 1); 2.38 (s, 3) | | | 7.5 (m)b | | 7.5 (m)b | 7.5 (m)b | 7.5 (m)b | 7.5 (m)b | 7.5 (m)b |
| 10a | 1,3-(CH₃)₂ | 3.40 (t, 1), J = 3.2; 3.06 (s, 3) | 4.95 (s, br) | | 8.1b | | 8.1b | 8.1b | 8.1b | 8.1b | 8.1b |
| 11 | 1,4-(CH₃)₂ | 2.38 (s) | | | 7.15 (s) | 7.15 (s) | | 8.05 (m) | 7.55 (m) | 7.55 (s) | 8.05 (m) |
| 12 | 1,4-(CH₃)₂ | 3.40 (s, 1); 2.88 (s, 4) | 5.38 (s, br) | | 8.9 (m)b | | | 8.9 (m)b | 8.9 (m)b | 8.9 (m)b | 8.9 (m)b |
| 13-F | 1-F | | | φ 124.5 (m) (F) | 7.6b | 7.6b | 7.6b | 7.6b | 7.6b | 7.6b | 8.0b |
| 14-F | 1-F | | 5.50 (d), JHF = 7 | φ 24.2 (m) (F) | 8.31 (t), J = 9 | 9.9 (m) | | 8.3 (m) | 8.3 (m) | 8.3 (m) | 9.3 (d), J = 8 |
| 13-Cl | 1-Cl | | | | 7.5b | 7.5b | 7.5b | 7.5b | 7.5b | 7.5b | 8.3 (m) |
| 14-Cl | 1-Cl | | 5.38 (s) | | 8.6b | 9.6 (d), J = 8 | | 8.6b | 8.6b | 8.6b | 9.3 (d), J = 8 |
| 13-Br | 1-Br | | | | 7.6b | 7.6b | 7.6b | 7.6b | 7.6b | 7.6b | 8.3 (m) |
| 14-Br | 1-Br | | 5.0 (s, br) | | 8.6 (m) | 10.3 (d) | | 8.6d | 8.6b | 8.6b | 9.2 (d), J = 8 |
| 15-Br | 1-Br | | 5.4 (s, br) | | | 9.7 | 8.6b | 8.6b | 8.6b | 8.6b | 8.6b |
| 13-I | 1-I | | | | 8.0b | 8.0b | 8.0b | 8.0b | 8.0b | 8.0b | 8.6 |
| 15-I | 1-I | | 5.4 (s, br) | | | 9.8 (br) | 8.6 (br)b | 8.6b | 8.6b | 8.6b | 8.6b |
| 13-OH | 1-OH | | | 6.0 (s) (OH) | 7.9b | 7.9b | 7.9b | 7.9b | 7.9b | 7.9b | 8.4 (m) |
| 14-OH | 1-OH | | 4.7 (s) | e | 7.70 (d), J = 9 | 8.9e | 8.2 (m) | 8.2 (m) | 8.2 (m) | 8.2 (m) | 8.9 (d), J = 7 |
| 13-OCH₃ | 1-OCH₃ | | | 3.80 (s) (OCH₃) | 7.8 (m) | 7.5 (m) | 7.5 (m) | 7.5 (m) | 7.5 (m) | 7.5 (m) | 8.3 (m)b |
| 14-OCH₄ | 1-OCH₃ | | 4.90 (s) | 5.04 (s) (OCH₃) | 8.00 (d), J = 10 | 9.20 (d, t), J = 10 and 3 | | 8.2 (m) | 8.2 (m) | 8.2 (m) | 8.9 (d), J = 7 |
| 16-F | 2-F | | | 7.6 (m) | φ 107.3 (m) (F) | 7.6 (m) | 7.6 (m) | 7.4 (m) | 7.4 (m) | 7.4 (m) | 8.7 (m) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 17-F | 2-F | 5.4 (d) $J = 8$ | | $\phi$ 8.44 (m) (F) | 8.03 (t) $J = 8$ | 10.2 (m) | 8.5 (m) | 8.5 (m) | 8.5 (m) | 8.5 (m) |
| 16-Cl | 2-Cl | | 7.8 (m) | | 7.8 (m) | 7.8 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) | 7.6 (m) |
| 17-Cl | 2-Cl | 5.5 (s) | | | 8.54 (d) $J = 8$ | 9.91 (d) $J = 8$ | 8.6 (m) | 8.6 (m) | 8.6 (m) | 8.6 (m) |
| 18-Cl | 2-Cl | 5.4[f] | 8.5[f] | | | 9.5 (s) | 8.6 (m) | 8.6 (m) | 8.6 (m) | 8.6 (m) |
| 16-Br | 2-Br | | 7.8 (m) | | 7.8 (m) | 7.8 (m) | 7.8 (m) | 7.8 (m) | 7.8 (m) | 7.8 (m) |
| 17-Br | 2-Br | 5.50 (s) | | | 8.5 (m)[g] | 9.74 (d) $J = 8$ | 8.5 (m) | 8.5 (m) | 8.5 (m) | 8.5 (m) |
| 18-Br | 2-Br | 5.4[f] | 8.5[f] (m) | | | 10.0 (s, br) | 8.5 (m) | 8.5 (m) | 8.5 (m) | 8.5 (m) |
| 16-I | 2-I | | 8.7 (s) | | 8.0 (m) | 8.0 (m) | 8.0 (m) | 8.0 (m) | 8.0 (m) | 8.0 (m) |
| 17-I | 2-I | 5.2 (s) | | | 8.5[g] | 9.4 (d) $J = 8$ | 8.5 (m) | 8.5 (m) | 8.5 (m) | 8.5 (m) |
| 18-I | 2-I | 5.2 (s) | 8.5[g] (m) | | | 9.2 (t) $J = 2$ | 8.5 (m) | 8.5 (m) | 8.5 (m) | 8.5 (m) |
| 16-OH | 2-OH | | 8.2 (m) | 5.8 (s) (OH) | 8.2 (m) | 8.2 (m) | 8.0 (m) | 8.0 (m) | 8.0 (m) | 8.0 (m) |
| 17-OH | 2-OH | 5.10 (s) | | e | 7.57 (d) $J = 9$ | 9.51 (d) $J = 9$ | 8.3 (m) | 8.3 (m) | 8.3 (m) | 8.3 (m) |
| 16-OCH₃ | 2-OCH₃ | | 7.9 (m) | 3.95 (s) (OCH₃) | 7.9 (m) | 7.9 (m) | 7.4 (m) | 7.4 (m) | 7.4 (m) | 7.4 (m) |
| 17-OCH₃ | 2-OCH₃ | 5.00 (s) | | 4.92 (s) (OCH₃) | 7.63 (d) $J = 9$ | 9.40[e] | 8.3 (m) | 8.3 (m) | 8.3 (m) | 8.3 (m) |

[a] Proton chemical shifts are referred to external capillary TMS in parts per million, and fluorine shifts are referred to external capillary CFCl₃ in parts per millions. [b] Center of the overlapping, unresolved multiplet. [c] Doublet of doublets ($J = 3$ and 6 Hz). [d] Number in parentheses indicates methyl position. [e] See text. [f] Shelter. [g] Proton buried under ring-B proton region.
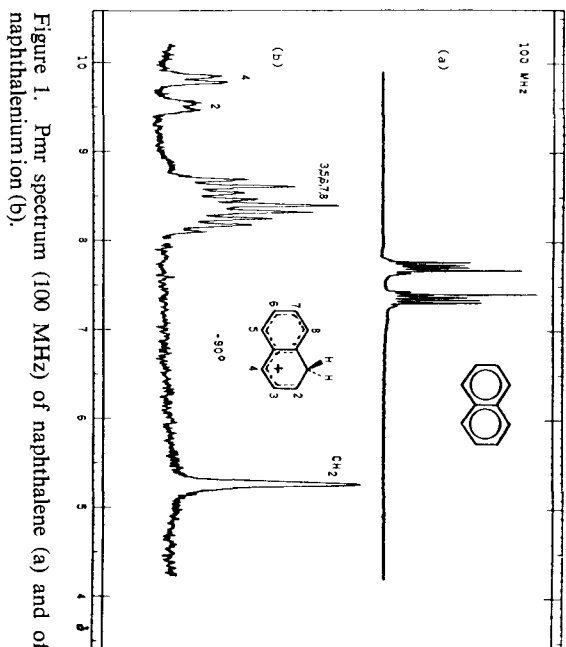


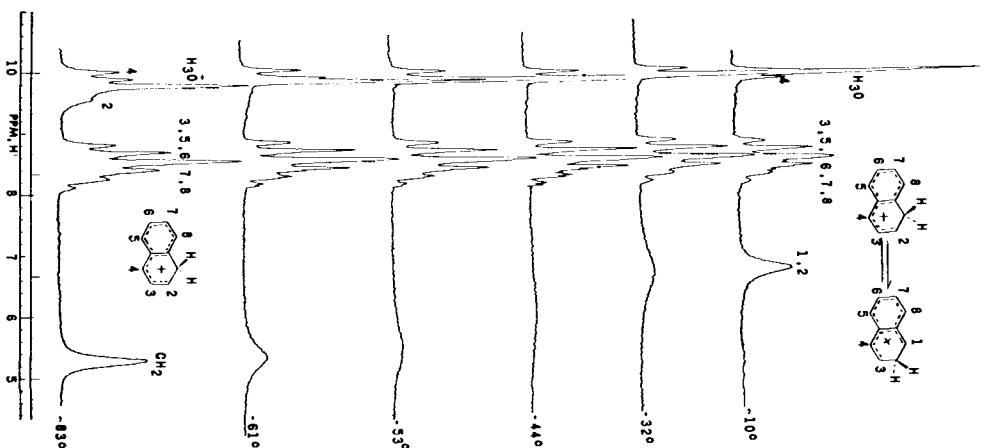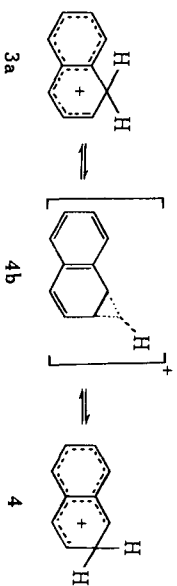Figure 1. Pmr spectrum (100 MHz) of naphthalene (a) and of naphthalenium ion (b).



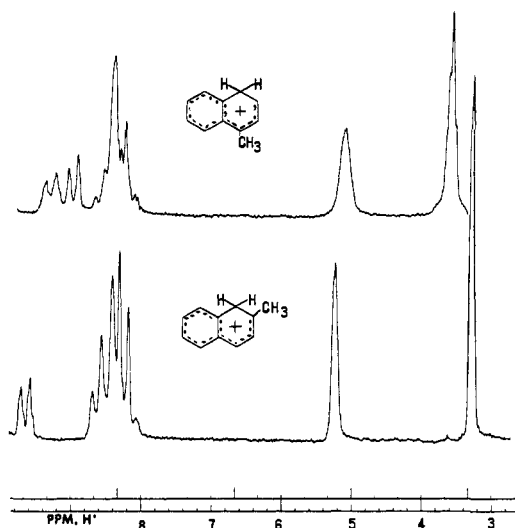Figure 2. Temperature-dependent pmr spectra (60 MHz) of naphthalenium ion 3a.

Figure 3. Pmr spectrum (60 MHz) of protonated 1-methylnaphthalene (upper trace) and 2-methylnaphthalene (lower trace).
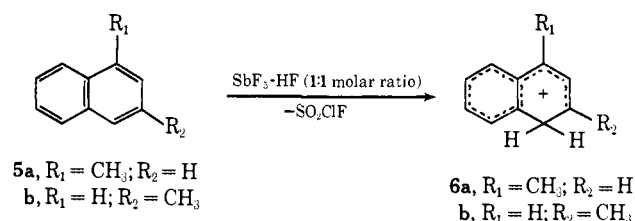
In the case of the benzenium and alkylbenzenium ions,[2,3,4a] observation of both intra- and intermolecular proton exchange was reported (simple 1,2-hydrogen shift and proton exchange with superacid occur simultaneously). The higher coalescence temperature of the signals of $CH_2$ and C(2)-H proton (at $\delta$ 6.76) as well as the fact that the other proton signals do not undergo an observable modification show that in the case of the naphthalenium ion **3a** intermolecular exchange does not occur even at $-10°$. The value of $\delta$ 6.76 is in good agreement with that calculated for the intramolecular exchange of $CH_2$ and C(2)-H protons $(5.27 \times 2 + 9.81)/3 = 6.78$. Besides the pmr data, evidence for the intramolecular process was obtained when naphthalene was deuterated in $FSO_3D–SbF_5–SO_2ClF$ solution at $-78°$. Deuteration was found to take place at both carbon 1 and carbon 2 as shown by the integration of the pmr spectrum. The methylene signal shows a pmr absorption of less than two protons and the carbon-2 proton peak corresponds to slightly less than one proton. The remainder of the spectrum is essentially unchanged compared with that of protonated naphthalene. 1,2-Hydrogen shift is most probably responsible for this D repartition, although direct deuteration at carbon 2 is also possible. When the solution was heated to $-50°$ for 1 min and then cooled back to $-85°$, the methylene signal displayed an intensity corresponding to 1.33 protons and the carbon-2 proton absorption integrated for 0.67 proton. Meanwhile, the intensity of the acid peak (due to the presence of a small amount of protic acid impurity in the $FSO_3D–SbF_5–SO_2ClF$ solution) was not affected. This result clearly indicates that deuterium is incorporated almost exclusively at carbons 1 and 2.

On the other hand, when the solution of naphthalenium ion **3a** (in $FSO_3H–SbF_5$) was heated to $0°$, the methylene and aromatic proton absorptions considerably broadened. These results may indicate an intermolecular proton exchange (as shown by the shifting of the acid peak to higher field), but they are also compatible with an intramolecular 2,3-hydrogen shift (which, however, should have a lower probability than the 2,1 shift). At $10°$, extensive decomposition (tar formation) took place and the pmr lines broadened considerably, almost

merging into the base line. Recently the formation of naphthylfluoroantimony compounds has been demonstrated in the reaction of naphthalene with antimony pentafluoride.[8]

The temperature dependence of the pmr spectrum was used to calculate the rate constant and activation parameters of the 1,2-hydrogen shift. The line shapes for various rate constants were calculated by means of a multiple-site exchange program.[9] Fitting the data to the Arrhenius equation gave an activation energy, $E_a$, of $14.5 \pm 0.9$ kcal/mol and a preexponential factor, $A$, of $10^{16} \pm 0.8$ sec$^{-1}$. Both the values of $E_a$ and $A$ are higher than those of benzenium[2] and methylbenzenium ions.[3] The 1,2 shift in **3a** is strongly endothermic, whereas those studies with benzenium ions are shifts between equally stable positions.

**Monomethylnaphthalenium Ions.** 1- and 2-methylnaphthalenes (**5a** and **5b**) were smoothly protonated in superacid $SbF_5–HF(1:1$ molar ratio)$–SO_2ClF(1:1$ v/v) solution at $-60°$ to give the 4- and 2-methylnaphthalenium ions (**6a** and **6b**), respectively. The 60-MHz



SbF$_5$-HF (1:1 molar ratio)
$-SO_2ClF$

**5a**, $R_1 = CH_3$; $R_2 = H$
**b**, $R_1 = H$; $R_2 = CH_3$

**6a**, $R_1 = CH_3$; $R_2 = H$
**b**, $R_1 = H$; $R_2 = CH_3$

pmr spectra of ions **6a** and **6b** are shown in Figure 3. The methyl protons of ion **6a** are coupled to the methylene protons and show a triplet at $\delta$ 3.62 $(J = 2.5$ Hz). This kind of long-range (through 6 bonds) coupling has been observed in monoalkylbenzenium ions.[3,4a] As a result of the coupling, the methylene proton absorption (at $\delta$ 5.20) is broadened. Double irradiation of the $CH_3$ resonance caused substantial sharpening of the methylene signal, but fine structure was not observed. Obviously, the methylene protons are also coupled to the ortho proton. This is also indicated by the slight broadening of the ortho-proton doublet at $\delta$ 9.26 $(J = 8$ Hz). The meta proton gives a doublet at $\delta$ 8.92 $(J_{o,m} = 8$ Hz). It is rather surprising that the meta proton is more deshielded (by 0.6 ppm) than the B-ring protons. Usually the meta position essentially carries no significant charge. The best evidence for this argument comes from the carbon-13 nmr study of monoalkylbenzenium ions.[4a] For comparison, the meta-proton absorption of ion **6b** is overlapping with the B-ring absorptions. The para proton of ion **6b** is a doublet of triplets at $\delta$ 9.63 $(J_{vic} = 8$ Hz and $J^5 = 2$ Hz). Double irradiation of the $CH_2$ (at $\delta$ 5.24) also caused the sharpening of the doublet of triplets.

It is also worthwhile to mention that the signal separation between $CH_2$ and $CH_3$ (also para proton) is smaller in ion **6a** than in ion **6b**. Similar observations are also found in other dimethylnaphthalenium ions (see subsequent discussion).

**Dimethylnaphthalenium Ions.** A complete nmr ($^1$H

(8) G. A. Olah and P. Schilling, submitted for publication in *J. Org. Chem.*

(9) The theoretical spectra were calculated by means of a multiple-site exchange program based on equation of H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956). The program was obtained originally from Dr. T. Gerig and was adapted to the Univac 1108 by Dr. W. E. Heyd.
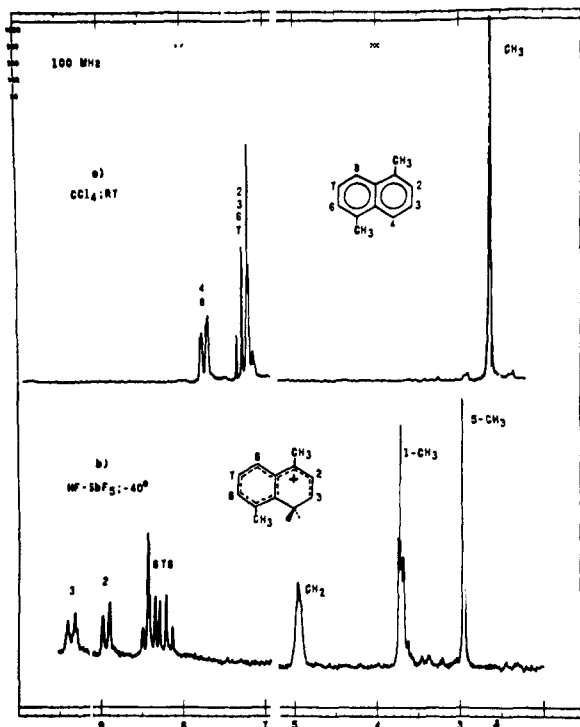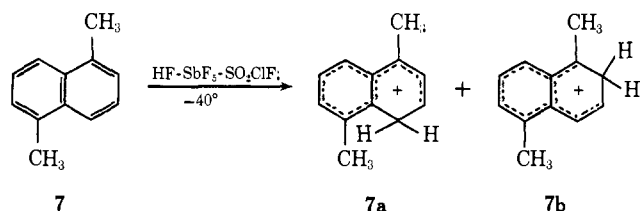
Figure 4. Pmr spectrum (100 MHz) of 1,5-dimethylnaphthalene 7 (a) and of its protonated species 7a (b) in HF–SbF$_5$–SO$_2$ClF at −40°.



Figure 5. The first-order pattern of the 300-MHz proton spectrum of 1,5-dimethylnaphthalenium ion 7a (aromatic region).

and $^{13}$C) analysis of the 1,5-dimethylnaphthalenium ion 7a has been carried out. Figure 4a shows the 100-MHz spectrum of the precursor: the two equivalent methyl groups absorb at δ 2.63. The double resonance experiment reveals the approximately equal coupling ($J \sim 0.6$ Hz) of the methyl protons with at least two ring protons. One of these is the proton in the para position (4 or 8, respectively). The aromatic protons adsorb between δ 7 and 8.

The cation, prepared in a similar manner as the naphthalenium ion, exhibits the spectrum shown in Figure 4a.[10] The two methyl groups, which are no longer



7   7a   7b

equivalent, serve as excellent "labels" for identifying the site of protonation (determined by their own inductive effect). The upper field peak (δ 2.94) is assigned to the 5-CH$_3$ group. Its deshielding of 0.3 ppm (δ 2.94 cation − δ 2.63 precursor) is indicative of participation of the unprotonated ring in sharing the positive charge. A dramatic change is observed in the position and pattern of the 1-CH$_3$ signal (Figure 4a). It shows a substantial deshielding (δ 3.70 cation − δ 2.63 precursor = 1.07 ppm), and it is split into a triplet due

(10) This spectrum is consistent only with cation 7a. There is no spectral evidence for the presence of 7b. The methyl substitution enhances particularly the basicity of the carbon atom in para position. Probably this enhancement is also assisted by the other methyl group (a "peri" effect). However, when HFSO$_3$–SbF$_5$ is used, a small amount of 7b is observed after heating the solution at −20 and cooling it back to −60°.
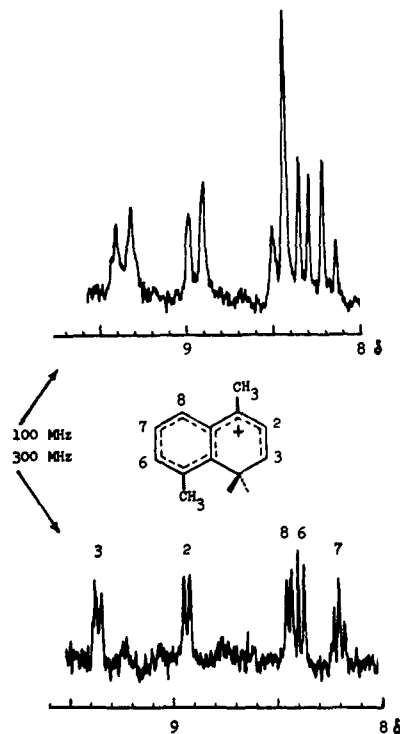
to a surprisingly large long-range coupling (through six bonds) with the methylene protons ($^6J = 3.1$ Hz). This assignment was confirmed by double resonance experiments and by comparison with the pmr spectra of 2,6-dimethylnaphthalenium ion 8a and 2,3-dimethyl-naphthalenium ion 9a (vide infra). As the temperature is increased and the methylene protons exchange more rapidly, this coupling diminishes. At −10°, it is less than 2 Hz. At this temperature the sample starts to decompose and the process can no longer be followed. This large long-range coupling is obviously a consequence of the drastic modification of the electronic structure of the ring. The long-range coupling takes place through the π framework of a molecule and is rather small in an aromatic 6-π system. It appears that the structure of cyclohexadienyl cation is particularly favorable for unusual long-range coupling.[3]

The methylene absorption at δ 4.95 is an unresolved multiplet which, by decoupling of 1-CH$_3$ protons, is still displaying a slight broadening due to the weak interaction with protons 3 and (perhaps) 2. The coupling with proton 3 can be directly found in the signal of the latter, a doublet ($J_{23} = 8.4$ Hz) of triplets ($J_{34} \sim 1.3$ Hz) at δ 9.36. The doublet assigned to proton 2 (δ 8.94) exhibits only a slight broadening. It is very weakly coupled to the methylene and methyl protons. The overlapping absorptions of the remaining three protons (6, 7, and 8) cover the region δ 8–8.5 and cannot be resolved by a first-order approximation. This is, however, possible when the spectrum is taken at a much higher magnetic field intensity, specifically at 70.46 kG (300 MHz). The 300-MHz pmr spectrum of the 1,5-dimethylnaphthalenium ion 7a is compared with the corresponding 100-MHz spectrum in Figure 5. The assignments are now straightforward. The chemical shifts are given in Table I.

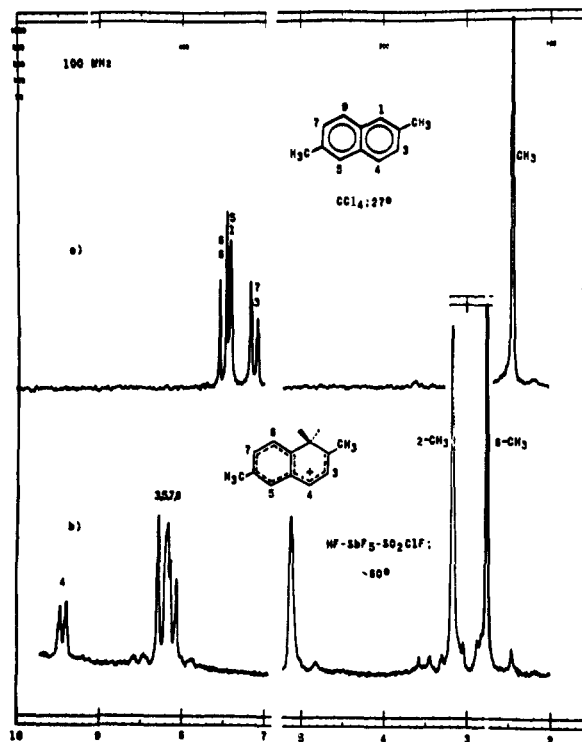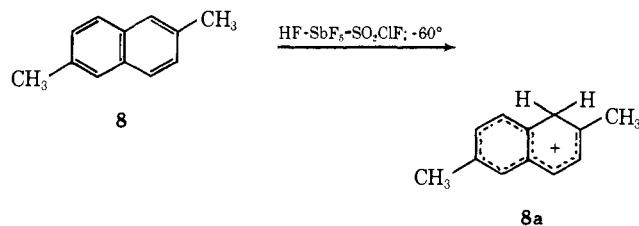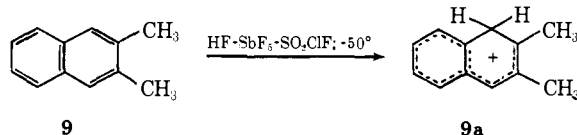The 100-MHz spectrum of 2,6-dimethylnaphthalenium

Figure 6. Pmr spectrum (100 MHz) of 2,6-dimethylnaphthalene (a) and its protonated species 8a (b).

ion 8a (Figure 6) displays, in contrast with that of its iso-



8

8a

mer 7a (1,5-dimethylnaphthalenium ion), narrower $CH_2$ and $CH_3$ signals. The relative position of these groups is no longer favorable for a strong interaction. The long-range coupling over five bonds, $CH_2$ to H-4, is significantly smaller ($^5J \simeq 1.6$ Hz) than the $^6J = 3.1$ Hz mentioned above. This also indicates that the geometry factor is playing an important role in this type of interaction. The shifts toward lower field of the $CH_2$ ($\delta$ 5.16) group and of the para proton ($\delta$ 9.44), as compared with the corresponding shifts in 1,5-dimethylnaphthalenium ion 7a, indicate that methyl groups in the $\beta$ position have less stabilizing power than those situated in the $\alpha$ position. The pmr parameters of 8a are given in Table I.

The effect of having two methyl groups attached to the protonated ring varies with the relative positions of these groups. Thus in the 2,3-dimethylnaphthalenium ion 9a (Figure 7a), the $CH_2$–$H_4$ coupling is slightly en-



9

9a

hanced ($^5J \simeq 2.2$ Hz). The $CH_3$–$CH_2$ and $CH_3$–$H_4$ proton–proton coupling is 0.5 Hz or less. In the 1,3-
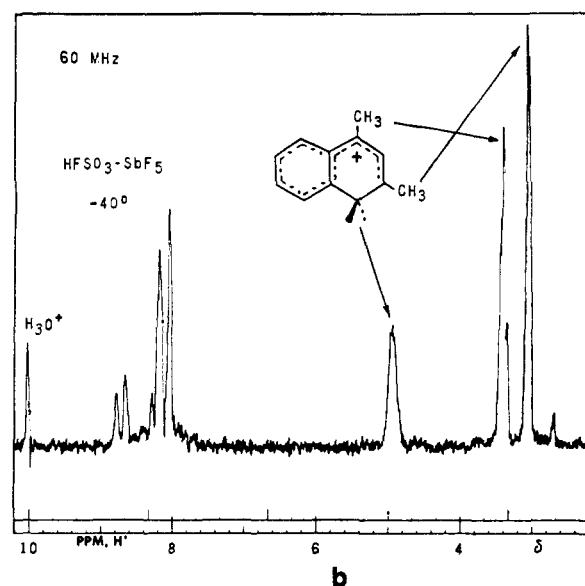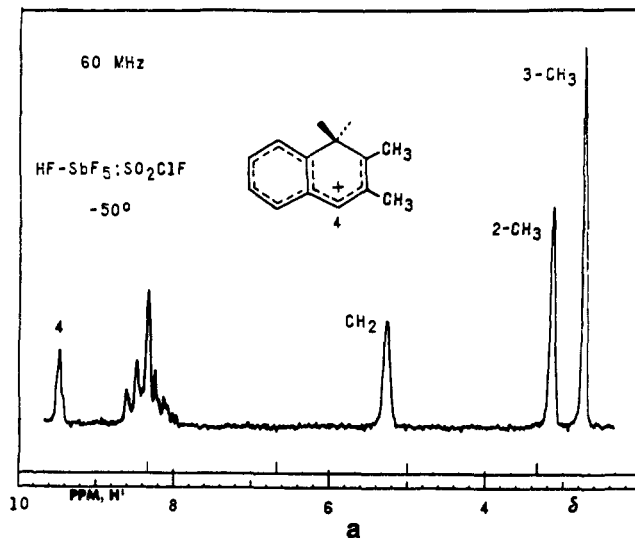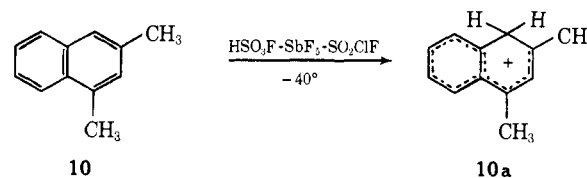


a



b

Figure 7. (a) Pmr spectrum (60 MHz) of 2,3-dimethylnaphthalenium ion 9a. (b) Pmr spectrum (60 MHz) of 1,3-dimethylnaphthalenium ion 10a.

dimethylnaphthalenium ion 10a (Figure 7b), the 1-$CH_3$



10

10a

group exhibits the same long-range coupling ($^6J = 3.2$ Hz) as its 1,5 isomer 7a.

An interesting behavior is observed in the case of the protonation of 1,4-dimethylnaphthalene (11). Since the best stabilization of the ion is achieved when the electron-deficient methylene group is assisted from both ortho and para positions, a 1,2 methyl shift and a 1,2-hydrogen shift take place. The final equilibrium at −55° is established in favor of the rearranged ion whose concentration is more than 50%.

It is interesting to note that in going from one ion to another the methylene and methyl group signals always shift in opposite directions. Usually the lowest field
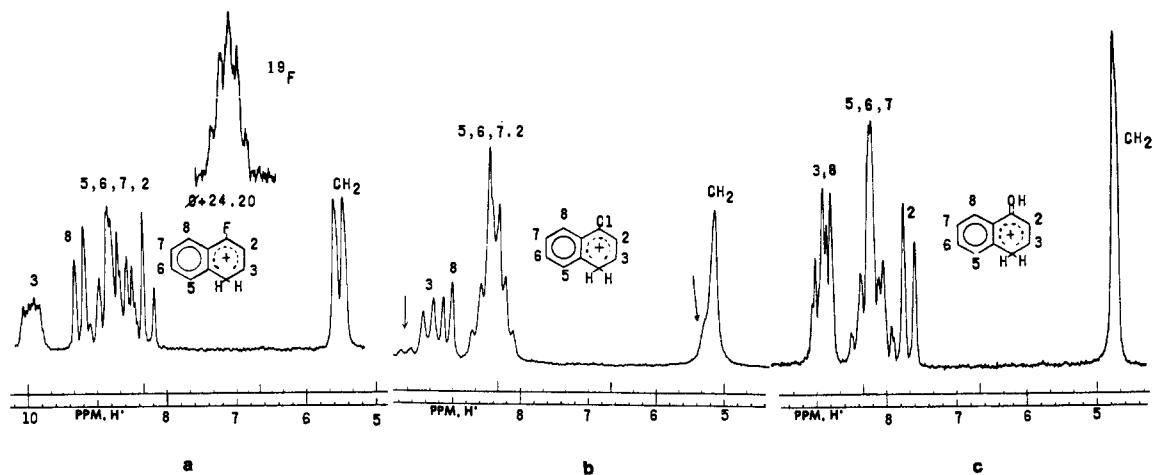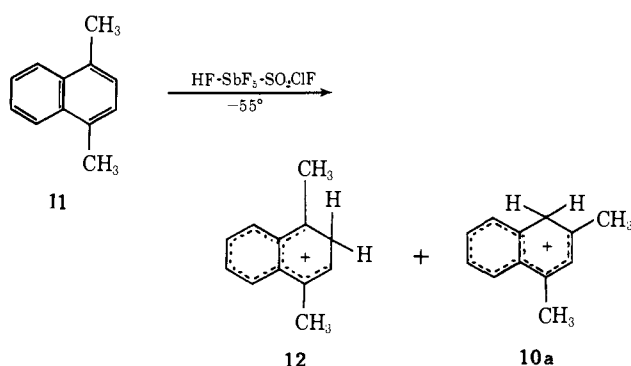
Figure 8. (a) Proton and fluorine nmr spectra of protonated 1-fluoronaphthalene; (b) pmr spectrum of protonated 1-chloronaphthalene; and (c) pmr spectrum of protonated 1-naphthol.



peak in the spectrum (the most deshielded ring proton) shifts in the same direction as the methylene group. This suggests that the closer the methylene and methyl group signals (the smaller $\Delta\delta$), the better delocalization of the charge, i.e., the better stabilizing effect. The pmr spectra indicate the following stabilizing order for different substitutions studies: 1,5 (**7a**, $\Delta\delta$ = 1.25 ppm) > 1,3 (**10a**, $\Delta\delta$ = 1.55) > 2.6 (**8a**, $\Delta\delta$ = 1.95) > 1,4 (**12**, $\Delta\delta$ = 1.98) > 2,3 (**9a**, $\Delta\delta$ = 2.14).

**Halo-, Hydroxy-, and Methoxynaphthalenium Ions.** 1-Substituted naphthalenes **13-X** were smoothly protonated in either $SbF_5$–HF–$SO_2ClF$ (1 : 1 molar ratio) or $SbF_5$–$FSO_3H$–$SO_2ClF$ (1 : 1 molar ratio) solution to give the stable naphthalenium ions **14-X** and **15-X**.
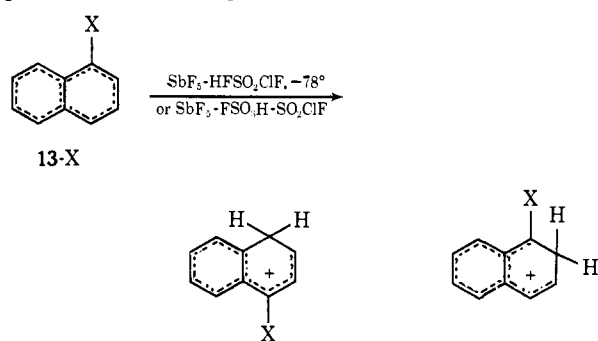


| | |
|---|---|
| 14-F, X = F (100%) | 15-F, X = F (0%) |
| 14-Cl, X = Cl (90%) | 15-Cl, X = Cl (10%) |
| 14-Br, X = Br (60%) | 15-Br, X = Br (40%) |
| 14-I, X = I (0%) | 15-I, X = I (100%) |
| 14-OH, X = OH (100%) | 15-OH, X = OH (0%) |
| 14-OCH₃, X = OCH₃ (100%) | 15-OCH₃, X = OCH₃ (0%) |

The nmr ($^1$H and $^{19}$F) spectra of representative ions **14-F**, **14-Cl**, and **14-OH** are shown in Figures 8a–c, respectively. The methylene protons of ion **14-F** show a slightly broadened doublet at $\delta$ 5.50 with $^5J_{HF}$ = 7 Hz. This kind of long-range coupling has also been observed in other fluoroarenium ions.[11] The ortho proton displays a multiplet at $\delta$ 9.9 since it couples to the meta proton, $CH_2$, and also the fluorine atom. The chemical shift ($\delta$ 9.9) is similar to the ortho protons' in the fluorobenzenium ion.[11] The $C_8$ proton of the B ring is deshielded by a (fluorine) peri effect[12] and shows a doublet at $\delta$ 9.2 ($J_{HF}$ = 8 Hz). The $^{19}$F nmr spectrum of ion **14-F** shows a multiplet at $\phi$ 24.20 (100.3 ppm lower field than the precursor). The fluorine chemical shift, however, is slightly smaller than that of fluorobenzenium ion ($\phi$ 11.2) indicating partial charge delocalization into the B ring.

The pmr spectrum of 1-chloronaphthalene in $SbF_5$–$FSO_3H$–$SO_2ClF$ solution at $-60°$ shows that ion **14-Cl** is formed (Figure 8b). The slightly broadened singlet at $\delta$ 5.83 is assigned to the methylene protons. The deshielded ortho proton displays a slightly broadened doublet at $\delta$ 9.6 ($J_{HH}$ = 8 Hz). Similarly, the $C_8$ proton of the B ring is deshielded by a peri effect and shows a doublet at $\delta$ 9.3 ($J_{HH}$ = 8 Hz). The presence of a shoulder on the methylene signal and that of a small doublet at 9.7 (see arrow in Figure 8b) are tentatively interpreted as due to the formation of ion **15-Cl** (10%), since the remainder of the absorption lines of ion **15-Cl** are obscured by those of ion **14-Cl**.

In the case of 1-bromonaphthalene, two isomeric ions **14-Br** and **15-Br**, in a ratio of 3 : 2, were formed. There are two methylene resonances at $\delta$ 5.0 and 5.4, respectively, in the pmr spectrum of 1-bromonaphthalene in $SbF_5$–HF–$SO_2ClF$ solution at $-60°$. Due to the viscosity of the solution, only broad spectral lines are observed for the remainder of the protons. On the other hand, the pmr spectrum of 1-iodonaphthalene in $SbF_5$–HF–$SO_2ClF$ solution shows a broadened singlet absorption at $\delta$ 5.4 indicating that only one iodonaphthalenium ion is formed. Due to the high viscosity of the system at $-90°$, only a poorly resolved spectrum

(11) G. A. Olah and T. E. Kiovsky, J. Amer. Chem. Soc., **89**, 5692 (1967).

(12) (a) R. H. Martin, N. Defay, and F. Greets-Evrard, Tetrahedron, **20**, 1505 (1964); (b) G. O. Dudek, Spectrochim. Acta, **19**, 691 (1963).
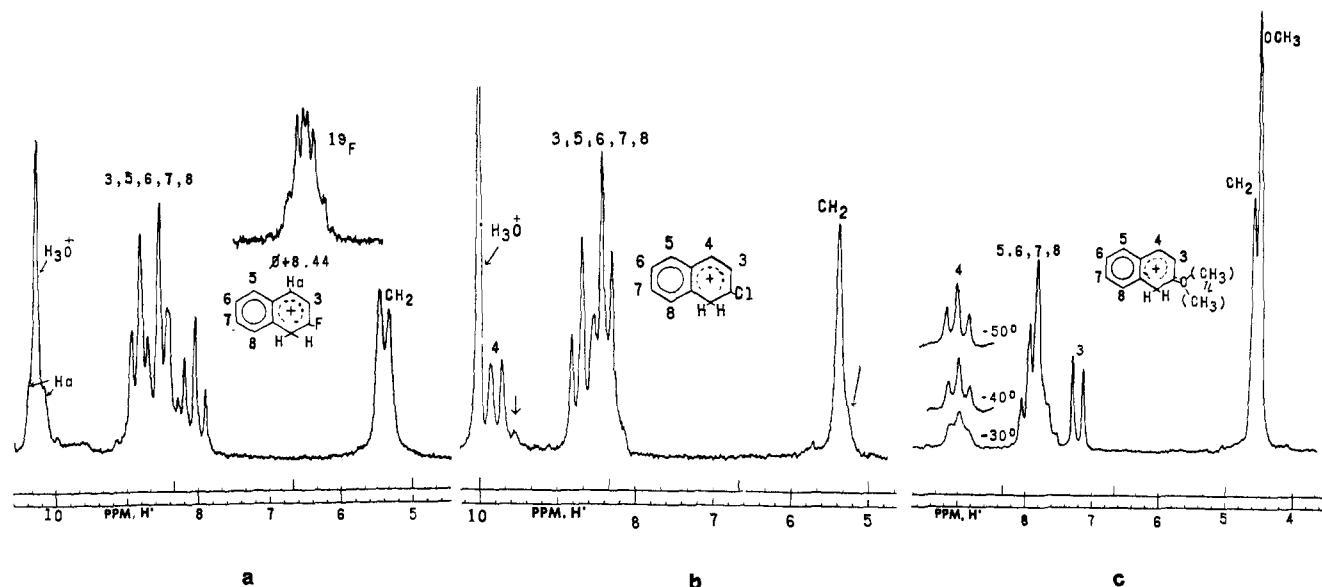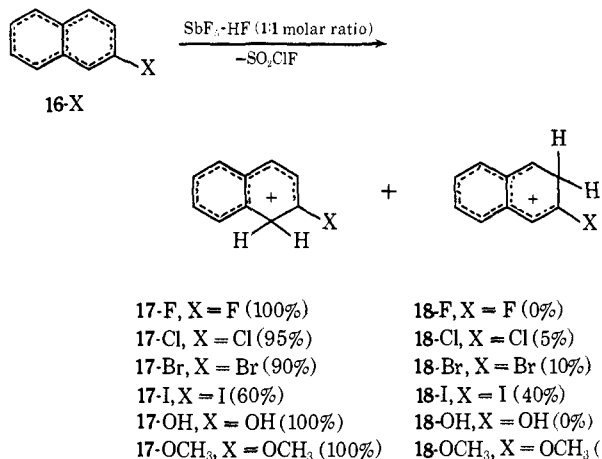
Figure 9. (a) Proton and fluorine nmr spectra of protonated 2-fluoronaphthalene; (b) pmr spectrum of protonated 2-chloronaphthalene; and (c) pmr spectrum of 2-metpoxynaphthalene.

was obtained. At higher temperatures the methylene protons at δ 5.4 gradually disappeared (probably due to deprotonation). The remainder of the spectrum shows a broadened absorption at δ 8.6. It is difficult to determine which isomeric ion (14-I or 15-I) is formed. However, the absence of a doublet at δ 9.2 can rule out the para protonation (or ion 14-I formation), because the $C_8$ proton of ion 14-I (if formed) should be deshielded substantially by the peri effect. Such an effect was found in other halonaphthalenium ions (14-X, X = F, Cl, and Br). Electrophilic aromatic substitution of iodobenzene shows the preferential formation of the ortho isomer.[13] Since iodine is comparatively large, electrophiles can, in all probability, attack the iodine lone pair in the first step and then migrate to the nearest carbon. Indeed, stable alkylarylhalonium ions, in particular, iodonium ions, have been prepared and directly observed by means of nmr spectroscopy.[14] Our present results seem to indicate the involvement of initial iodine protonation (kinetically controlled process) with subsequent C protonation. It should be noted that the ortho protonation or ion 15-X formation is enhanced with the increase of the size of the halogen. Furthermore, the isomeric ion distribution (14-X and 15-X) is temperature independent in the range −80 to −20° (thermodynamically controlled process). A repulsive interaction of the p (halogen) and π (ring) electrons (which would enhance the electron density at the para position in the order F > Cl > Br > I)[15] may also explain this isomer distribution.

Since hydroxy and methoxy groups are highly activating the aromatic rings, protonation of 1-hydroxy- and 1-methoxynaphthalenes can be achieved even in weaker acid such as $FSO_3H$–$SO_2ClF$ at −40 and −35°, respectively. The pmr spectrum of ion 14-OH (Figure 8c) shows a slightly broadened singlet absorption at δ 4.7 for the methylene protons. The meta proton reveals a

well-resolved doublet at δ 7.70 ($J_{o,m}$ = 9 Hz). The ortho proton and the $C_8$ proton show complicated resonance lines centered at δ 8.8. Careful analysis shows that this region actually includes a doublet (ortho proton) and a doublet of triplets ($C_8$ proton). The substantial deshielding of the $C_8$ proton indicates that the carbon–oxygen bond (C–OH) has a double bond (C=OH) character and thus a strong peri effect is observed. The pmr spectrum of ion 14-$OCH_3$ is similar to that of ion 14-OH except that an additional peak for $OCH_3$ is observed at δ 5.04.

**Protonation of 2-substituted naphthalenes 16-X** was also studied in various superacid media. The site of protonation is found to be at the carbons 1 and 3 to give ions 17-X and 18-X, respectively. The ratio of 17-X/18-X depends on the nature of the substituent.



16-X



| 17-F, X = F (100%) | 18-F, X = F (0%) |
|---|---|
| 17-Cl, X = Cl (95%) | 18-Cl, X = Cl (5%) |
| 17-Br, X = Br (90%) | 18-Br, X = Br (10%) |
| 17-I, X = I (60%) | 18-I, X = I (40%) |
| 17-OH, X = OH (100%) | 18-OH, X = OH (0%) |
| 17-$OCH_3$, X = $OCH_3$ (100%) | 18-$OCH_3$, X = $OCH_3$ (0%) |

The nmr spectra of ions 17-F, 17-Cl, and 17-$OCH_3$ are shown in Figures 9a–c, respectively. The nmr parameters of ions 17-X and 18-X are summarized in Table I.

Protonation of 2-fluoronaphthalene in superacid $HF$–$SbF_5$ (1 : 1 molar ratio)–$SO_2ClF$ solution gave ion 17-F rather than 18-F. Evidence comes from the meta proton of ion 17-F showing the most shielded vinyl–proton triplet absorption at δ 8.03 ($J_{HH}$ = $J_{HF}$ = 8 Hz). If ion 18-F would have been formed, the meta proton

(13) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, 83, 4581 (1961).
(14) G. A. Olah and E. Melby, *ibid.*, 94, 6220 (1972).
(15) L. M. Stock, "Aromatic Substitution Reaction," Prentice-Hall, Englewood Cliffs, N. J., 1968, p 56.

should have been a doublet. The coincidence of $J_{HH}$ and $J_{HF}$ in ion **17-F** is not surprising since similar observations have been made in other fluorobenzenium ions.[11] The para proton of ion **17-F** shows multiplet resonance lines overlapping with that of the hydronium ion ($H_3O^+$). The methylene protons are coupled to the fluorine and show a doublet at δ 5.4 ($J_{HF}$ = 8 Hz). The ^{19}F nmr spectrum of ion **17-F** shows a multiplet at φ 8.44 (deshielded by 98.9 ppm in comparison with the precursor, **16-F**).

The pmr spectra of **16-Cl** and **16-Br** when protonated in HF–SbF (1:1 molar ratio)–SO₂ClF show the formation of ions **17-Cl** (95%), **18-Cl** (5%) and **17-Br** (90%), **18-Br** (10%), respectively. The para protons of ions **17-Cl** and **17-Br** show a doublet at δ 9.91 ($J_{HH}$ = 8 Hz) and δ 9.74 ($J_{HH}$ = 8 Hz), respectively. The methylene protons of both ions **17-Cl** and **17-Br** display a slightly broadened singlet at δ 5.5. In addition, there is a shoulder at δ 5.4 (e.g., Figure 9b, indicated by arrow) in the methylene proton region indicating the formation of the isomeric ions **18-Cl** and **18-Br**. Additional evidence for the formation of ions **18-Cl** and **18-Br** comes from the presence of a small broadened singlet at δ 9.5 (5%) and 10.0 (10%), respectively. These singlets are due to the ortho proton of ions **18-X** (X = Cl and Br, respectively).

Protonation of 2-iodonaphthalene in superacid SbF₅–HF (1:1 molar ratio)–SO₂ClF gave two isomeric ions, **17-I** (60%) and **18-I** (40%). The pmr spectrum of the solution shows in the methylene proton region a broadened singlet at δ 5.2 and in the vinyl proton region a multiplet centered at δ 8.5, a doublet at δ 9.4 ($J_{HH}$ = 8 Hz), and a triplet at δ 9.2 ($J_{HH}$ = 2 Hz). The doublet at δ 9.4 clearly indicates that it is the para proton of ion **17-I** when compared with the spectra of ions **17-Cl** and **17-Br**. The triplet at δ 9.2 with a small coupling (0.5 Hz) is then assigned to the ortho proton of ion **18-I**. The ratio of **17-I**/**18-I** was determined by pmr integration and was found to be 3/2. Again no temperature-dependent pmr spectra were observed for ions **17-I** and **18-I** in superacid SbF₅–HF (1:1 molar ratio)–SO₂ClF solution in the range from −80 to −20°.

These results show that protonation of 2-halonaphthalenes in superacids is similar to that of 1-naphthalenes. Initial protonation on halogen is favored in the order I > Br > Cl > F and subsequent proton transfer takes place from the n donor to the π donor.[16] Protonation and alkylation at the fluorine lone-pair level have not yet been observed in solution[17] although they have been demonstrated in the gas-phase (ion-molecular reactions).[18] These data are also in agreement with our recent study of alkylation of bromo- and iodobenzenes leading to the formation of alkylarylhalonium ions.[14] Chloro- and fluorobenzenes do not undergo such reactions.

Protonation of 2-hydroxy- and 2-methoxynaphthalenes in superacid gave exclusively ions **17-OH** and **17-OCH₃**, respectively. The structure determination of ions **17-OH** and **17-OCH₃** was based on their pmr spectra. A doublet at δ 9.51 ($J_{HH}$ = 9 Hz) indicates pro-

(16) Similar trends have been observed in the protonation of chloro and bromo substituted benzenes (see ref 3, sections II.C and VI.E).

(17) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969).

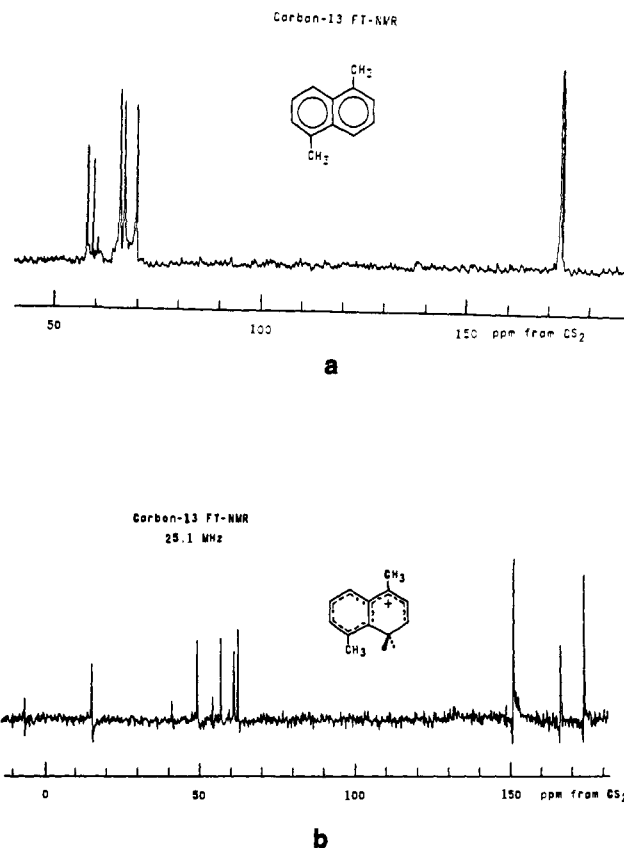(18) D. Holtz, J. C. Beauchamp, and S. D. Woodgate, *ibid.*, **92**, 7478 (1970).

Figure 10. Carbon-13 Fourier-transform nmr spectra of 1,5-dimethylnaphthalene **7** (a) and its protonated species (b).

tonation at carbon 3 with formation of ion **17-OH**. Ion **18-OH** was not observed.

The pmr spectrum of protonated 2-methoxynaphthalene (**17-OCH₃**) is temperature dependent (Figure 9c). The most deshielded one-proton triplet at δ 9.40 is due to the overlapping of two doublets of the $H_a$ proton in isomeric ions **17-OCH₂-a** and **17-OCH-b**. At
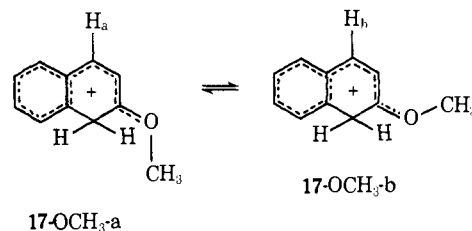


17-OCH₃-a          17-OCH₃-b

higher temperature (ca. −30°) interconversion of **17-OCH₃-a** and **17-OCH-b** is rapid and the triplet becomes broadened. Such behavior has been observed in the case of C-protonated anisole and its derivatives.[3,4b] The meta proton of both ions **17-OCH₃-a(b)** shows a doublet at δ 7.63 ($J_{HH}$ = 9 Hz) and is temperature independent. The shift is stronger for the $H_a$ proton than for the meta proton, indicating strong ortho–para interaction.

**Carbon-13 Magnetic Resonance Studies.** Since carbon-13 magnetic resonance (cmr) reflects the electronic structure and charge distribution better than proton magnetic resonance, a ^{13}C study of a selected naphthalenium ion **7a** and its precursor 1,5-dimethylnaphthalene (**7**) has been carried out. As in the proton spectra, a dramatic change occurs in the carbon spectra upon protonation of the hydrocarbon. The differ-

ences are even more remarkable because the relative spread of the chemical shifts in the case of $^{13}C$ is larger than for $^1H$. The electron-deficient carbon 1 in ion 7a exhibits a chemical shift ($\delta$ $-7.4$ ppm from $^{13}CS_2$) which is deshielded by 64.5 ppm from its position in the neutral hydrocarbon (see Figure 10). A tentative assignment of the carbon absorptions is shown below and is compared with the cmr chemical shifts found for toluenium ion 19, revealing that the unprotonated ring preserves much of its aromatic character.[4a]
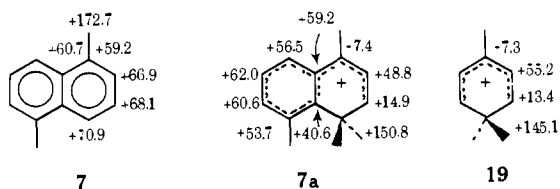


The application of the Fourier-transform natural abundance carbon nmr spectroscopy to the investigation of carbocation intermediates thus proves very useful and promises to open up a new dimension in our ability to elucidate in detail structures of even quite complicated and large ions.

## Experimental Section

**Materials.** All the organic compounds used in this study were commercially available in high purity. Antimony pentafluoride (Allied Chemical) was triply distilled; fluorosulfuric acid was doubly distilled.

**Preparation of Ions.** The solution of naphthalenium ion was prepared as reported previously in this series for protonations in superacid media and studied directly by nmr spectrometry. The quenching of solutions of naphthalenium ions and the analysis of recovered hydrocarbons (by glc and pmr) were also carried out as described.[4a]

**Nuclear Magnetic Resonance Measurement.** Spectra were obtained on Varian Associates Model A56/60A, HA100, and HR300 spectrometers. Fourier-transform spectra were recorded either with a Bruker HX-90 nmr spectrometer (22.63 MHz) or with a Varian HA-100 FT nmr spectrometer (25.16 MHz). With the Bruker instrument $^{19}F$ was used for locking the system (either $Cl_2C=CF_2$ for low-temperature or $C_6F_6$ for room-temperature measurements). With the Varian instrument, a $^{13}C$ lock ($^{13}C$-enriched $CH_3I$) was used for both low- and high-temperature measurements. In both cases a broad band (2 KHz) noise generator was used for proton noise decoupling.

# Radical Anions of 1,8-Bis-Unsaturated Naphthalene Derivatives

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Abstract: The synthesis of 7,8-dimethylenenaphtho[1',8']bicyclo[3.2.0]hept-2-ene and its conversion into 2,3-dimethyl- and 2,3-cyclobutapleiadiene are described. The epoxide derived from naphtho[1',8']bicyclo[3.2.0]-hepta-2,5-diene and the related hydrocarbon give the peri-bridged 1,8-divinylnaphthalenes resulting from cyclobutane cleavage upon pyrolysis. The esr spectra of the radical anions from six pleidaiene derivatives, 1-oxo-4-naphtho[1',8']cycloocta-2,4,7-triene, and 1,8-divinylnaphthalene are reported and discussed.

W$e$ report here the synthesis of some 1,8-bis-unsaturated derivatives of naphthalene, some limitations on the use of thermal cleavages of acenaphthene derivatives to prepare such compounds, and the esr spectra of several such radical anions. Experimental comparisons of the spin distributions of pleiadiene (1), the related enol ether 2, and 1,8-divinylnaphthalene
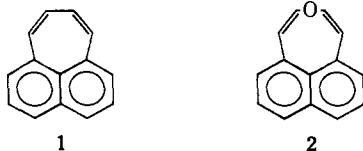


radical anions were of particular interest, to see if simple MO calculations would be successful for predictive purposes and, if not, to see what spin distributions actually result.

**Synthesis.** Several derivatives of pleiadiene (1) were prepared using the method of Meinwald and coworkers,[1] who employed the heavy-atom solvent enhanced photocycloaddition of maleic anhydride to acenaphthylene to give 3a after work-up, lead tetraacetate decarboxylation to 4a, and pyrolytic cyclobutene ring opening to give 1a. Starting the sequence with 3,6-di-*tert*-butylacenaphthene gave 1c, and preparation of 3b by base-catalyzed exchange (KOD-D$_2$O, 150°) on 3a gave 1b after completion of the sequence. We were unable to repeat the reported[1] 28% yields in the bis-decarboxylations and observed serious falling-off of the yield in runs at a larger scale than 4 g. Attempts to improve conditions showed that saturation of the reaction mixtures with oxygen[2] shortened the

(1) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Amer. Chem. Soc.*, **92**, 7604 (1970).
(2) C. M. Cimarsturi and J. Wolinsky, *ibid.*, **90**, 113 (1968).