to remove deuterium from the aromatic carbons. The resulting product analyzed for 96% deuterium at the methyl carbons (78% d_6, 20% d_5, 2% d_4). These labeled samples of *p*-xylene were converted to the acetyl nitrate adducts **1**-d_4 and **1**-d_6 by the method described, and configurational isomers were separated by column chromatography.

1,4-Dimethyl-4-nitrocyclohexadienol (3). The preparation and chromatographic separation of the configurational isomers of **3** by reaction of 4-methyl-4-nitrocyclohexadienone with methyllithium and subsequent column chromatography has been described.[15] The first eluting isomer of **3**, mp 52 °C, was converted to **1b** by treatment of a stirred pyridine solution of the nitrodienol with a methylene chloride solution of acetyl chloride at −40 °C and a 2-day reaction period at −10 °C. The second eluting isomer of **3**, mp 114 °C, was converted to **1a** by the same procedure.

Pyrolysis of 1,4-Dimethyl-4-nitrocyclohexadienyl Acetates. Stock solutions containing carefully weighed amounts of the nitrodienyl acetate **1a** (mp 51–52 °C) and **1b** (mp 59–60 °C) and an internal standard, 1,2-dimethyl-4-nitrobenzene, were prepared in cyclohexane at a concentration of about 30 mg mL^{-1}. Portions of these solutions were injected into the gas chromatograph with an inlet temperature of 210 ± 5 °C and a Silar 10-C column (10 ft × 0.125 in.) which was held at 50 °C for 10 min and programmed thereafter at 20 °C min^{-1} to a maximum temperature of 150 °C. Under these conditions *p*-xylene had a retention time of 6.8 min, and the internal standard had a retention time of 26.7 min. A large number of minor product peaks were detected, but only the yield of *p*-xylene was quantified. Under these pyrolytic conditions **1a** gave 71 ± 4% *p*-xylene and **1b** gave 89 ± 3% of the same hydrocarbon.

Kinetics of Solvolytic Elimination in Aqueous Ethanol. Rates of solvolytic rearomatization of the nitrodienyl acetates were followed by monitoring the UV absorption maxima of 2,5-dimethylphenyl acetate (262 nm). The typical procedure involved weighing about 3 mg of one of the adducts in a capillary tube, dissolving the sample in absolute ethanol (40 μL), and injecting 2–5 μL of the stock solution into a series of temperature-equilibrated cells containing 3–4 mL of the appropriate solvent. Plots of log $(A_\infty - A_t)$ vs. time were generally linear over 80–90% of reaction. Final values of rate constants were obtained by least-squares treatment of data. Rate constant data and kinetic isotope effects are collected in Table I. Activation parameters are tabulated in Table III. Product analyses of kinetic reaction solutions conducted after more than 9 half-lives revealed only 2,5-dimethylphenyl acetate. The conditions of GLC analysis were such that less than 0.5 mol % of 2,4-dimethylphenyl acetate or *p*-methylbenzyl acetate would have been detected.

Kinetics of solvolytic rearomatization of **3** in aqueous ethanol were followed in a similar way by monitoring the growth of the absorption maxima at 275 nm. It was necessary to use quite dilute solutions ($\sim 1 \times 10^{-4}$ M) and add 0.02 M urea to the solvent in order to obtain stable infinity values. The spectral yield of phenolic product, however, was found to be 30–40% of the calculated value. It was found, however, that acidification of the system after a stable infinity value had been reached led to a new burst of absorption at 275 nm with an absorbance that stabilized near the calculated value. Silylation of the product mixture from a kinetic run conducted without acidification of the reaction mixture and subsequent GLC analysis revealed silylated 2,4-dimethylphenol and 2,5-dimethylphenol, but the significance of this finding is doubtful since capture product, such as 1,4-dimethylcyclohexadiene-1,4-diol, would certainly aromatize under the GLC conditions. NMR spectral studies of the products of aqueous solvolysis indicated that the 2,4-isomer predominated. The kinetic data obtained from the uncatalyzed formation of dimethylphenol are listed in Table I, and activation parameters derived from these data are listed in Table III. These data are taken to represent the rate of decomposition of **3** in the reaction system.

Solvolysis of 1 and 1-d_6 in Sulfuric Acid Solutions. Stock solutions were prepared by dissolving carefully weighed samples of the adduct together with an internal standard (*p*-nitrotoluene or 4-nitro-*o*-xylene) in chloroform. The ^{1}H NMR spectrum of the stock solution was recorded and integrated as a check on the composition. Approximately 30-μL portions of the stock solution were added to 2.0-mL portions of acid solutions contained in vials fitted with screw caps and Teflon liners, and the mixture was vigorously mixed for a 1-h period with the use of a Vortex mixing apparatus. The mixtures were quenched in ice and water, and organic products were partitioned into cyclohexane by repeated extraction. The dried cyclohexane extract was analyzed by GLC with the use of a HiEff-8BP or a Silar 10-C column.

Acknowledgment. We thank the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants supporting this work.

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Protonation of Polymethylnaphthalenes and Hexahydropyrene. Formation of Stable Naphthalenium Ions and Observation of Isomerizations Based on ^{1}H and ^{13}C Nuclear Magnetic Resonance Studies[1]

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Abstract: Some tri- and tetramethylnaphthalenes and hexahydropyrene have been protonated with FSO$_3$H–SbF$_5$ (1:1) and/or FSO$_3$H in SO$_2$ClF, and the results have been classified in terms of distinct equilibria, isomerization processes, and the formation of selected stable naphthalenium ions, as determined by ^{1}H and ^{13}C NMR spectroscopy. The formation of stable "free" α-, ipso α-, and "free" β-naphthalenium ions and a β,β-naphthalenium dication are reported and the electronic features of the ions discussed on the basis of the ^{13}C NMR data. Both 1,4,5-tri- and 1,4,5,8-tetramethylnaphthalene are subject to kinetic vs. thermodynamically controlled protonation and 1,2-methyl migration occurs in the ions upon temperature changes. For the temperature-dependent protonation of 1,4,6,7-tetramethylnaphthalene a dynamic proton exchange and isomerization cycle is proposed.

Previously the protonation of dimethylnaphthalenes was reported[2] as an extension on the large body of research on the protonated alkylbenzenes.[3] Here we wish to go into detail on some special features of some polymethylnaphthalenium ions.

Naphthalene[4,5] and its mono-[4,5] and dimethylderivatives[2,4] are known to be protonated at an unsubstituted ("free") α-position.

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(1) Carbenium Ions. 5. As previous parts in this series are regarded: Part 1, see ref 2. Part 2, see ref 17. Part 3, Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257. Part 4, Lammertsma, K.; Cerfontain, H. *Ibid.* **1980**, *102*, 4528.

(2) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1979**, *101*, 3618.

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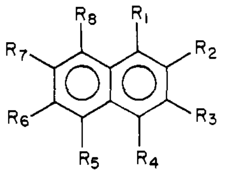
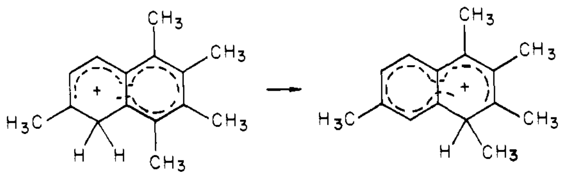
For naphthalene itself, it was demonstrated that the α-naphthalenium ion equilibrates rapidly with the β-naphthalenium ion at temperatures above −50 °C.[4] The protonation of 1,4-dimethylnaphthalene was reported to result in two sets of equilibria, one of which is similar to the naphthalene case.[2] For the other the initial site of protonation is at the β-position of the methylated ring (at C_2), where the resulting ion is in rapid equilibrium with the ion resulting from ipso α-protonation (at C_1).[2] Apparently only in these cases some β-protonation could be induced.[6] Here we present an example of the exclusive formation of a stable β-naphthalenium ion.

Ipso α-protonation occurs exclusively with 1,2,3,4-tetra-,[7] 1,2,3,4,5,6-hexa-,[8] 1,2,3,4,5,8-hexa-,[8] and octamethylnaphthalene.[7,8] Recently Koptyug et al.[7] observed a remarkable feature for the protonation of 1,2,3,4,6-penta-, 1,2,3,4,6,7-hexa-, and 1,2,3,4,5,6,7-heptamethylnaphthalene (**1**, **2**, and **3**, respectively). They found the initial site of protonation to be (in part) the "free" α-position, but the resulting ions to convert irreversibly to the thermodynamically more stable ipso α-protonated species (see e.g., **4** → **5**). This report contains additional examples of this process.

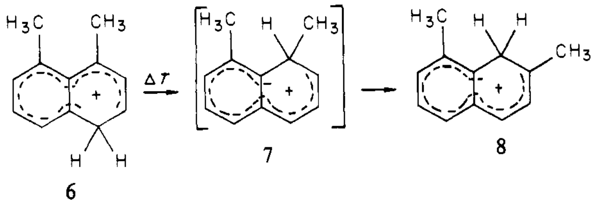


1, $R_{1-4,6} = CH_3$, $R_{5,7,8} = H$
2, $R_{1-4,6,7} = CH_3$, $R_{5,8} = H$
3, $R_{1-7} = CH_3$, $R_8 = H$
10, $R_{1-3} = CH_3$, $R_{4-8} = H$
11, $R_{1,4,5} = CH_3$, $R_{2,3,6-8} = H$
12, $R_{1-4} = CH_3$, $R_{5-8} = H$
13, $R_{1,4,5,8} = CH_3$, $R_{2,3,6,7} = H$
14, $R_{1,4,6,7} = CH_3$, $R_{2,3,5,8} = H$
15, $R_{1,8} = R_{4,5} = (CH_2)_3$, $R_{2,3,6,7} = H$



4 **5**

Isomerization of methyl-substituted benzenium ions by successive intramolecular 1,2-hydrogen and 1,2-methyl shifts are well-known.[3a] Although polymethylnaphthalenes are known to isomerize in CF_3CO_2H,[9] at present only one example has been investigated with respect to carbenium ions, viz., the ion formed on protonation of 1,8-dimethylnaphthalene (see **6** → **7** → **8**).[2] In this report new interesting examples of similar isomerizations are presented.



6 **7** **8**

It thus appears that the methylated naphthalenium ions may be subject to the following four processes.

$$\text{"free" } \alpha\text{-ion} \rightleftarrows \text{"free" } \beta\text{-ion} \tag{1}$$

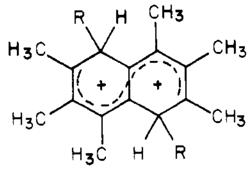
$$\text{ipso } \alpha\text{-ion} \rightleftarrows \text{"free" } \beta\text{-ion} \tag{2}$$

$$\text{"free" } \alpha\text{-ion} \rightarrow \text{ipso } \alpha\text{-ion} \tag{3}$$

$$\text{ipso } \alpha\text{-ion} \overset{\text{1,2-Me}}{-\!\!\circ\!\!\rightarrow} \text{"free" } \alpha\text{-ion} \tag{4}$$

All these processes might be well explained by rapid intra- and/or intermolecular hydrogen shifts,[2,3a,4] although, in principle, process 3 may also operate through the intermediate formation of a dication.[7]

Stable dications have been observed for the protonation of 1,2,3,5,6,7-hexa- and octamethylnaphthalene.[7,10] The observed dications (**9a** and **9b**, respectively) posses a 4,8 orientation with regard to the protonated centers. The observation of a stable β,β-naphthalenium dication is now reported.



9a, R = H
9b, $R = CH_3$

In order to clarify in more detail the scope of protonated alkylnaphthalenes, we present examples of different protonated naphthalenes and will furthermore elaborate on the isomerization processes of **3** and **4**.

Results and Discussion

Protonation of 1,2,3-tri- (**10**) and 1,4,5-tri- (**11**), 1,2,3,4-tetra- (**12**), 1,4,5,8-tetra- (**13**), and 1,4,6,7-tetramethylnaphthalene (**14**) and hexahydropyrene (**15**) was accomplished with FSO_3H and/or magic acid (FSO_3H-SbF_5, 1:1 molar ratio) in SO_2ClF (1:2, v/v) at −80 °C or lower temperatures. The ^1H and ^{13}C NMR data of the resulting naphthalenium ions and the rearranged ions (obtained by increase of the temperature) are listed in Tables I and II, respectively. The ^{13}C chemical shifts of the parent hydrocarbons (**10**–**15**) are also listed in Table II. The ^1H and ^{13}C NMR spectral assignments of the various ions, bearing an α-protonated center, were considerably facilitated by comparison with the NMR characteristics of the dimethylnaphthalenium ions, which were used as standards, and are summarized in structures I and II (^1H NMR) and III and IV (^{13}C NMR).[2]

The assignment of the NMR signals of most of the naphthalenium ions was also facilitated by investigation of the ^{13}C-substituent chemical shifts, listed in Table III. In particular, for the α-naphthalenium ions, comparison of these data with those reported for the dimethylnaphthalenium ions (summarized in

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(3) For an excellent review and discussion of arenium ions see: (a) Brouwer, D. M.; Mackor, E. L.; Maclean, C. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Ed.; Wiley: New York, 1970; Vol. 2, p 837. For more recent studies see: (b) Olah, G. A.; Schlosberg, R. H.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2546. (c) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *Ibid.* **1972**, *94*, 2034. (d) Olah, G. A.; Spear, R. J.; Messina, G.; Westerman, P. W. *Ibid.* **1975**, *97*, 4051. (e) Olah, G. A.; Mo. Y. K. *Ibid.* **1972**, *94*, 9241. (f) *J. Org. Chem.* **1973**, *38*, 3212. (g) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284. (h) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *Ibid.* **1977**, *99*, 2615. (i) Devlin, J. L.; III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *Ibid.* **1976**, *98*, 1990. (j) Hünig, S.; Schilling, P. *Chem. Ber.* **1975**, *108*, 3355.

(4) Olah, G. A.; Mateescu, G. D.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 1865.

(5) Olah, G. A.; Staral, J. S.; Asensio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

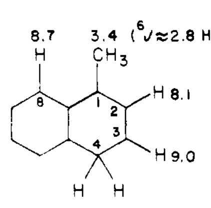
(6) For both the 1- and 2-halonaphthalenes increasing amounts of β-protonation was observed, by ^1H NMR spectroscopy, in the order I > Br > Cl.[4]

(7) Bodoev, N. V.; Mamatyuk, V. I.; Krysin, A. P.; Koptyug, V. A. *J. Org. Chem. USSR* (*Engl. Transl.*) **1978**, *14*, 1789.

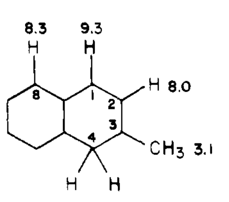
(8) Hart, H.; Oku, A. *J. Org. Chem.* **1972**, *37*, 4269.

(9) Oku, A.; Yuzen, Y. *J. Org. Chem.* **1975**, *40*, 3850.

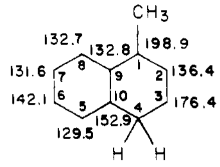
(10) (a) Mamatyuk, V. I.; Krysin, A. P.; Bodoev, N. V.; Koptyug, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 2392. (b) Bodoev, N. V.; Krysin, A. P.; Mamatyuk, V. I.; Koptyug, V. A. *Ibid.* **1976**, 1899.



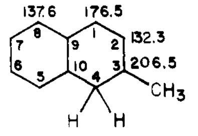
I



II

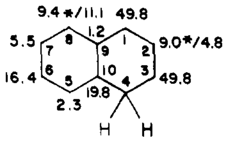


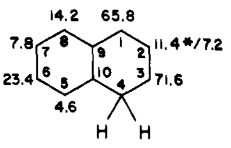
III



IV

structures V and VI) was found helpful.[2,11]





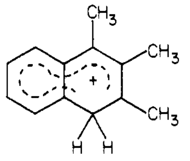
V unsubstituted carbons

VI methylated carbons

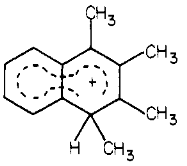
the asterisk represents $\Delta\delta_C$ upon 1-methylation

For reasons of simplicity and consistency all the α-naphthalenium ions in this report were taken to have the protonated center at position 4 and the assignments were made accordingly.

Stable Naphthalenium Ions. Protonation of 1,2,3-trimethylnaphthalene (**10**) with magic acid occurs exclusively at the "free" α-position 4, to give ion **16**, as can be concluded unequivocally from the ^1H and ^{13}C NMR data (see Tables I–III). The data demonstrate the same characteristics as depicted in structures I–VI. Protonation at position 4 was, in fact, to be anticipated, because of the conjugative stabilization of the positive charge by the methyl groups in the same ring.



16



17

When one ring is fully methyl substituted, i.e., in 1,2,3,4-tetramethylnaphthalene (**12**), protonation occurs exclusively at the ipso α-position to give ion **17**. Its ^1H NMR spectrum is in agreement with that reported in the literature.[7] We have found that ion **17** is stable up to the boiling point of SO_2ClF (7 °C), and no other ions were detected. The ^1H and ^{13}C NMR spectral data of **17** (see Tables I and II) follow reasonably well the NMR characteristics for "free" α-protonated dimethylnaphthalenes, given in structures I–IV. The larger deviations for $\Delta\delta_C$ for C_3, C_5, and C_{10} (see Table III and structures V and VI) might be attributed to steric and electronic factors due to ipso protonation.

Protonation of hexahydropyrene (**15**) with FSO_3H at −80 °C resulted in the exclusive formation of ion **18**, which is the first observed stable β-protonated hydrocarbon-substituted naphthalene.[6] The ^1H and ^{13}C NMR spectra are shown in Figure 1. Of the three aromatic hydrogens (Table I) H_3 has the most shielded absorption! Similarly the ^{13}C chemical shift of C_3 also appears to be rather shielded (see Table II). Apparently position 3, next to the protonated center, does not carry significant positive charge, as mesomeric structures of **18** might suggest. From the very deshielded absorption of C_1 at δ_C 219.0 it is concluded that the positive charge is located to a large extent at position 1. A similar observation was made for ortho-protonated ethylbenzene, i.e., δ_{C_α} 215.0.[12] The $\Delta\delta_C$ values (see Table III) show that although the positive charge is mainly located at position 1 ($\Delta\delta_{C_1}$ 83.4), there is to some extent alternation of positive charge throughout the naphthalenium skeleton.

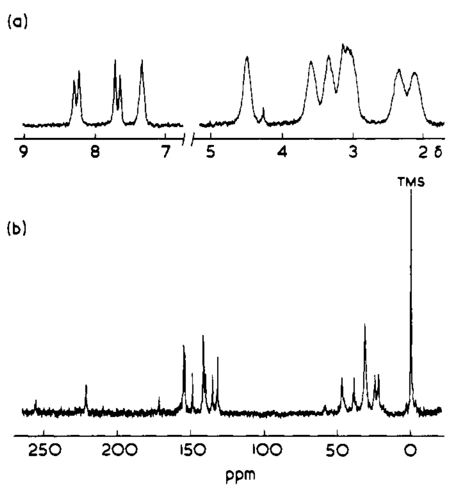


Figure 1. ^1H and ^{13}C NMR spectra a and b, respectively, of **18** at −80 °C.

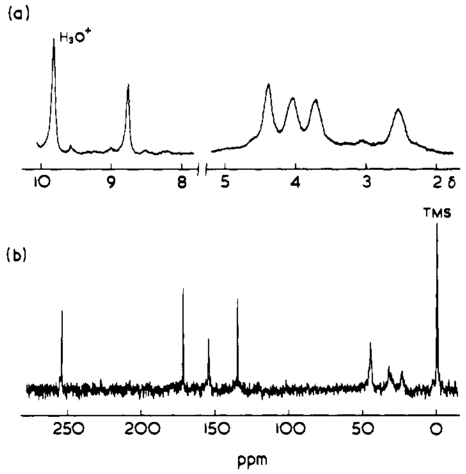
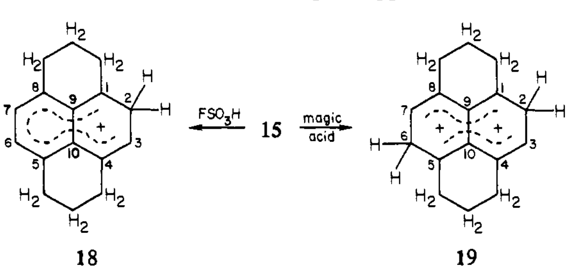


Figure 2. ^1H and ^{13}C NMR spectra a and b, respectively, of **19** at −80 °C.



18 **19**

With the stronger acid, FSO_3H-SbF_5, **15** is diprotonated at −80 °C to give ion **19**, which is the first example of a β,β-diprotonated naphthalene derivative. The ^1H and ^{13}C NMR spectra are shown in Figure 2. The four aromatic ^{13}C chemical shifts

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[11] This can for example be demonstrated for the reported ^{13}C chemical shifts of the 1- and 2-methylnaphthalenium ions and the parent ion itself. The data in Table II of ref 5 are in good agreement with those of structures III and IV if the following tentative assignments are reversed, viz., for all three ions C_8 and C_{10} and for the 1-methylnaphthalenium ion also C_2 and C_7 (the numbering is the same as in ref 5). This is in particular substantiated on comparison of the calculated $\Delta\delta_C$ values, with the use of ^{13}C chemical shifts of the parent compounds reported by: Wilson, N. K.; Stothers, J. B. *J. Magn. Reson.* **1974**, *15*, 31 with those of structures V and VI.

[12] Fărçasiu, D.; Melchior, M. T.; Craine, L. *Angew. Chem.* **1977**, *89*, 323.

Table I. ^{1}H NMR Parameters of Naphthalenium Ions[a]

compd	CH_3 or CH_2 substituent position	δ(CH_2 or CH)[b]	δ(ring position) 2	3	5	6	7	8	δ(CH_3 or CH_2 substituents)[c]
16	1,2,3	4.97 (s, br)			8.05 (m)	8.05 (m)	8.05 (m)	8.69 (d, $J = 8$)	3.31 (t, 1, $J = 2$), 2.60 (s, 2), 2.97 (s, 3)
17	1,2,3,4	4.68 (q, br)			8.05 (m)	8.05 (m)	8.05 (m)	3.71 (d, br, $J = 8$)	3.33 (d, 1, $J = 2$), 2.62 (s, 2), 3.00 (s, 3), 1.88 (d, 4, $J = 8$)
18	1,4,5,8	4.50 (br)		7.35 (s, br)		8.27 (d, $J = 7$)	7.68 (d, $J = 7$)		3.60 (br, α_1), 3.1 (br, α_4 and α_5), 3.35 (br, α_8), 2.35 and 2.15 (br, β)
19	1,4,5,8	4.40 (s, br)		8.77 (s)			8.77 (s)		4.05 (br, α_1 and α_5), 3.75 (br, α_4 and α_8), 2.60 (br, β)
20	1,5,8	4.57 (s, br)	7.9 (m)	8.9 (br)		8.1 (m)	7.9 (m)		3.45 (s, br, 1), 2.60 (s, 5), 3.03 (s, br, 8)
21	1,4,5	4.90 (br)	7.90 (d, $J = 9$)	9.04 (dd, $J = 9, 4$)		8.17 (d, $J \approx 7$)	7.89 (t, $J \approx 8$)	8.65 (d, $J = 8$)	3.39 (d, 1, $J = 2$), 1.61 (d, 4, $J = 8$), 2.78 (s, 5)
22	1,3,5	4.63 (s, br)	7.97 (s)			8.08 (d, br, $J = 7$)	7.87 (t, $J = 7$)	8.54 (dd, $J = 7, 1$)	3.33 (t, 1, $J = 2$), 3.02 (s, 3), 2.67 (s, 5)
23	1,4,5,8	4.85 (br)	7.74 (d, $J = 9$)	8.80 (dd, $J = 9, 4$)		8.01 (d, $J = 8$)	7.76 $J = 8$)		3.42 (d, 1, $J = 2$), 1.55 (d, 4, $J = 8$), 2.64 (s, 5), 3.04 (s, 8)
24	1,3,5,8	4.55 (s, br)	7.86 (s)			7.96 (d, $J = 8$)	7.73 ($J = 8$)		3.40 (t, 1, $J \approx 2$), 3.05 (d, 3, $J \approx 1$), 2.63 (s, 5), 2.95 (s, 8)
26	1,3,5,7	4.59 (s, br)	7.96 (s)			7.96 (s)		8.36 (s)	3.43 (t, 1, $J \approx 2$), 3.02 (s, 3), 2.69 (s, 5), 2.67 (s, 7)
27	2,3,5,8	4.74 (s, br)	9.50 (s)[d]			7.93 (d, $J = 8$)	7.67 ($J = 8$)		2.96 (s, 3), 2.60 (s, 2 and 5), 2.89 (s, 8)

[a] Chemical shifts (in parts per million) are referred to external capillary Me_4Si. *J* values are in hertz. Multiplicities are in parentheses: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = center of the (overlapping) unresolved multiplet. [b] The protonated center is at position 4, except for 18 (position 2) and 19 (positions 2 and 6). [c] The number in parentheses indicates the methyl or methylene ring position. [d] This is the chemical shift of H(1). Position 2 carries no hydrogen.

Table II. Carbon-13 Chemical Shifts[a] of Naphthalenium Ions and Some of Their Neutral Precursors

compd	ring carbon[b]										methyl or methylene carbons[c]			
	1	2	3	4	5	6	7	8	9	10				
10	130.6	131.9	131.4	124.6	127.4	124.3	125.7	123.5	132.8	134.8	14.7 (1)	16.1 (2)	21.4 (3)	
11	133.3*	125.9	129.0	135.8	134.2	128.8	124.7	123.2	132.7	133.0*	20.3 (1)	26.1 (4)	26.1 (5)	
12	131.2	128.4	128.4	131.2	124.2	124.1	124.1	124.2	132.7	132.7	17.3 (1)	15.1 (2)	15.1 (3)	17.3 (4)
13	135.9	130.9	130.9	135.9	135.9	130.9	130.9	135.9	137.4	137.4	28.4 (1)	28.4 (4)	28.4 (5)	28.4 (8)
14[d]	124.2	134.5	134.5	124.2	131.1*	125.3	125.3	131.1*	131.4*	131.4*	20.3 (2)	20.3 (3)	19.3 (5)	19.3 (8)
15	135.6	125.0	125.0	135.6	135.6	125.0	125.0	135.6	131.6	131.6	33.0 (α)	24.8 (β)		
16	195.4	143.2	199.4	48.6	129.6	139.6	130.9	132.5	133.6	150.6	22.8 (1)	15.8 (2)	26.9 (3)	
17	195.7	142.1	205.9	51.9	129.7	140.3	130.7	133.7	132.5	157.1	27.1 (1)	22.9 (2)	24.3 (3)	15.8 (4)
18	219.0	46.7	139.7*	139.3*	138.7	152.8	130.2	152.0**	133.9	147.0**	38.5 (α_1); 30.5, 30.9, and 31.1 ($\alpha_{4,5,8}$); 21.8 and 24.3 (β)			
19	252.4	45.0	153.4	134.1	252.4	45.0	153.4	134.1	170.5	170.5	45.0 ($\alpha_{1,5}$); 32.8 ($\alpha_{4,8}$); 23.5 (β)			
20	200.3	138.5	174.4	42.1	137.3	144.0	135.1	148.3	134.5	153.9	33.6 (1)	19.6 (5)	28.0 (8)	
21	201.1	134.1	185.2	45.5	139.4	145.7	130.8	133.9	133.3	157.6	26.7 (1)	16.7 (4)	18.9 (5)	
22	196.1	136.2	201.5	45.2	138.8	142.7	130.7	131.3	132.7	149.6	25.7 (1)	27.6 (3)	18.9 (5)	
23	201.3	136.1	180.0	45.4	137.4	145.5	134.9	150.6	133.9	159.6	33.6 (1)	18.4 (4)	18.6 (5)	28.2 (8)
24	196.1*	138.0	197.5*	45.6	136.9	142.9	134.9	147.0	133.3	151.4	32.6 (1)	26.5 (3)**	19.4 (5)	27.4 (8)**
26	195.3	136.0	199.7	45.0	138.5	144.6	141.7	130.7	133.0	147.7	25.6 (1)	29.8 (3)	18.7 (5)	20.9 (7)
27	174.1	146.2	203.4	48.4	136.2	143.4	132.3	141.5	132.9	152.1	18.5 (2)	26.3 (3)	18.5 (5)	18.9 (8)

[a] Chemical shifts (in parts per million) are referred to external capillary Me_4Si. Resonances within a spectrum which are labeled with an equivalent number of asterisks have interchangeable assignments. [b] The protonated center is at position 4, except for 18 (position 2) and 19 (positions 2 and 6). [c] The number in parentheses indicates the methyl or methylene ring position. [d] For reasons of convenience the assignment of 14 is that of 2,3,5,8-tetramethylnaphthalene, allowing a simpler comparison with ion 27.

Table III. ^{13}C Substituent Chemical Shifts[a] of Naphthalenium Ions

compd	ring carbon										methyl or methylene carbons[b]			
	1	2	3	4	5	6	7	8	9	10				
16	64.8	11.3	68.0	−76.0	2.2	15.3	5.2	9.0	0.8	15.8	8.1 (1)	−0.3 (2)	5.5 (3)	
17	64.5	13.7	76.6	−79.3	5.5	16.2	6.6	9.5	−0.2	24.4	9.8 (1)	7.8 (2)	9.2 (3)	−1.5 (4)
18	83.4	−79.3	14.7	3.7	3.1	27.8	5.2	16.4	2.3	15.6	5.5 (α_1); −1.9, −2.1, −2.5 ($\alpha_{4,5,8}$); −0.5, −2.2 (β)			
19	116.8	−80.0	28.4	−1.5	116.8	−80.0	28.4	−1.5	38.9	38.9	12.0 ($\alpha_{1,5}$); −0.2 ($\alpha_{4,8}$); −1.3 (β)			
20	66.1	9.7	49.7	−81.1	4.0	18.1	6.1	12.5	1.5	21.2	7.5 (1)	−0.7 (5)	1.9 (8)	
21	67.8	8.2	56.2	−90.3	5.2	16.9	6.1	10.7	0.6	24.6	6.4 (1)	−9.4 (4)	−7.2 (5)	
23	65.9	5.7	49.6	−90.2	2.0	15.0	4.5	15.2	−3.0	22.8	5.2 (1)	−10.0 (4)	−9.8 (5)	−0.2 (8)
27	49.9	11.7	68.9	−75.8	5.1	18.1	7.0	10.4	1.5	20.7	−1.8 (2)	6.0 (3)	−0.8 (5)	−0.4 (8)

[a] Defined as the difference (ppm) between the ^{13}C chemical shifts of the naphthalenium ions and the unprotonated species, given in Table II. Positive values indicate increased deshielding. [b] Number in parentheses indicates methyl or methylene ring position.

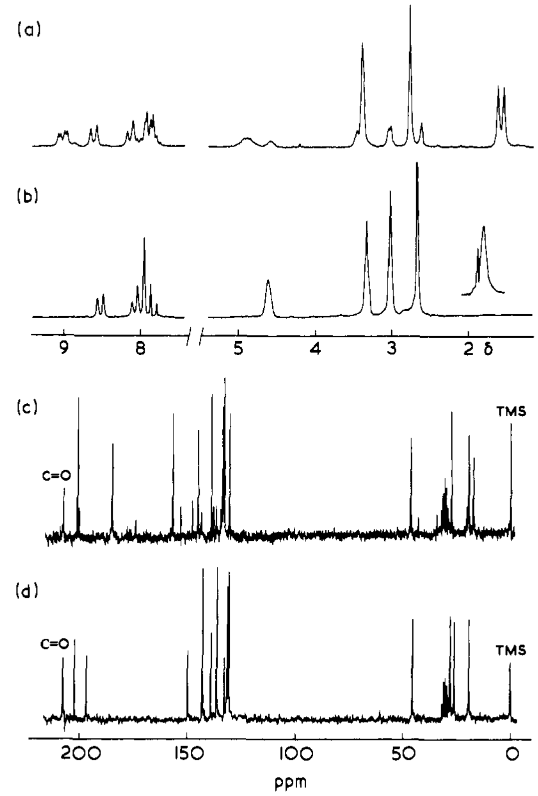
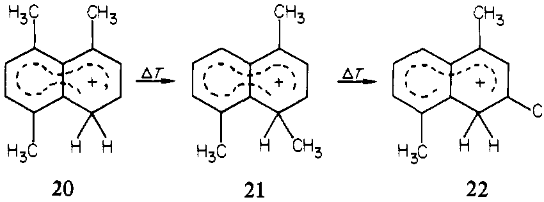


Figure 3. Temperature dependence of 1,4,5-trimethylnaphthalenium ions: ^1H NMR spectra of (a) the mixture of **20** and **21** at -70 °C and (b) ion **22** at -50 °C, with the insert at -10 °C; ^{13}C NMR spectra of (c) the mixture of **20** and **21** at -80 °C and (d) ion **22** at -20 °C.

indicate a 2,6 orientation of the protonated centers; a 2,7 orientation should display five absorptions in the aromatic region. The positive charge in **19** (as in **18**) is mainly located at C_1 (and C_5), as may be concluded from the very deshielded ^{13}C chemical shift at δ_C 252.4 (see Table II) and the $\Delta\delta_{C_1}$ value of 116.8 (see Table III). It is noteworthy that C_4 (and C_8) are shielded by 1.5 ppm (see Table III) relative to the neutral precursor, despite the double-positive charge present in **19**. Both the ^1H and ^{13}C NMR spectra (see Figure 2) display broad signals for the hydrogens and carbons of the aliphatic bridges, which may indicate restricted flexibility.

Isomerizations. Protonation of 1,4,5-trimethylnaphthalene (**11**) with FSO_3H at -90 °C resulted in a mixture of the ions **20** and **21**, in a ratio of 1:4, as concluded from the ^1H NMR spectrum (see Figure 3).[13] Both the ions **20** and **21** are characterized on the basis of the ^1H and ^{13}C NMR data (Tables I–III) and by comparison with the NMR characteristics given in structures I–VI. The ipso α-protonated center in ion **21** is established by the doublet splitting of the methyl absorption at δ_H 1.61, and in particular the resonances of H_8 at δ_H 8.65 and C_8 at δ_C 133.9 indicate that the methine hydrogen is located at position 4 (see I and III). When the temperature is increased from -90 to -70 °C, ion **20** is converted irreversibly into ion **21** (see Figure 3); lowering of the temperature back to -90 °C did not lead to reappearance of ion **20**. The conversion of **20** → **21** represents an example of process 3, mentioned before.



20 21 22

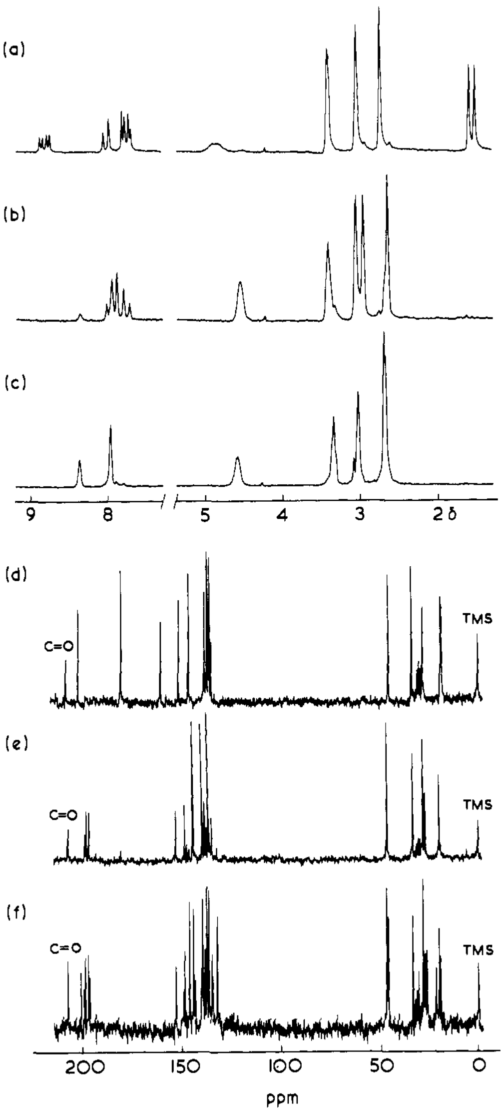


Figure 4. Temperature dependence of 1,4,5,8-tetramethylnaphthalenium ions: ^1H NMR spectra of (a) **23** at -60 °C, (b) **24** at -15 °C, and (c) **26** at -50 °C after recooling from -5 °C; ^{13}C NMR spectra of (d) **23** at -80 °C, (e) **24** at -15 °C, and (f) a mixture of **24** and **26** after longer time exposure to -15 °C.

Upon further temperature increase from -70 to -60 °C the subsequent isomerization of ion **21** to **22** is complete (see Figure 3), as can be concluded from the ^1H and ^{13}C NMR data (see Tables I and II). The comparison of these data with those of "free" α-protonated dimethylnaphthalenes in structures I–IV is good. The chemical shifts at δ_H 3.02 and δ_C 201.5 indicate the presence of a methyl group at position 3 "ortho" to the α-protonated center. The conversion of **21** → **22** nicely illustrates process 4.

Protonation of 1,4,5,8-tetramethylnaphthalene (**13**) with FSO_3H at -90 °C occurs exclusively at the ipso α-position, resulting in ion **23** (see Figure 4), as can be concluded unequivocally on the basis of the ^1H and ^{13}C NMR data (see Tables I–III) and comparison with the data of structures I–VI. The features due to ipso α-protonation are similar to those observed for **17** and **21**, e.g., doublet splittings for signals of both methyl groups at C_4 (J = 8 Hz) and at C_1 (J = 2 Hz) in the ^1H NMR spectrum; the deviations for the $\Delta\delta_C$ values (see Table III) from those in structures V and VI are only those of C_9 and C_{10}.

When the temperature is increased to -40 °C, ion **23** isomerizes to ion **24** (see Figure 4) and represents another example of process 4, similar to the conversion of **21** to **22**. The ^1H and ^{13}C NMR data (see Tables I and II) fully assist the structural assignment

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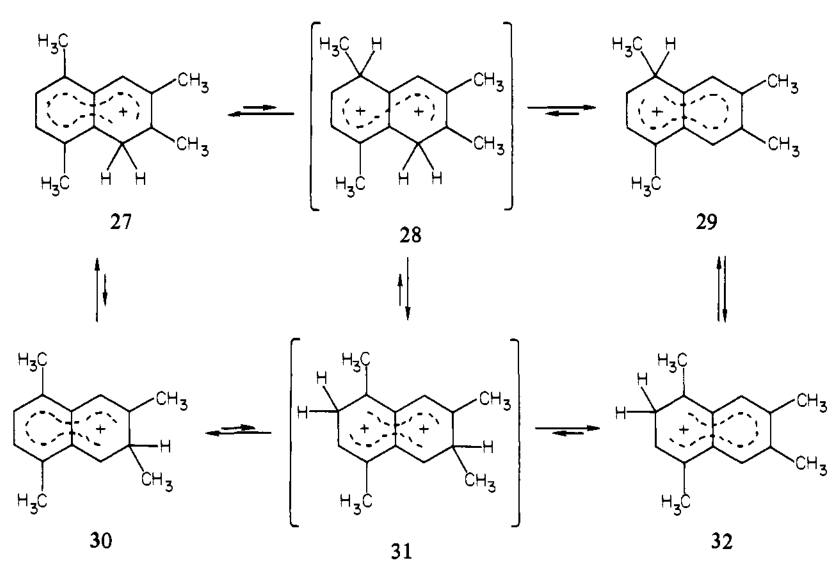
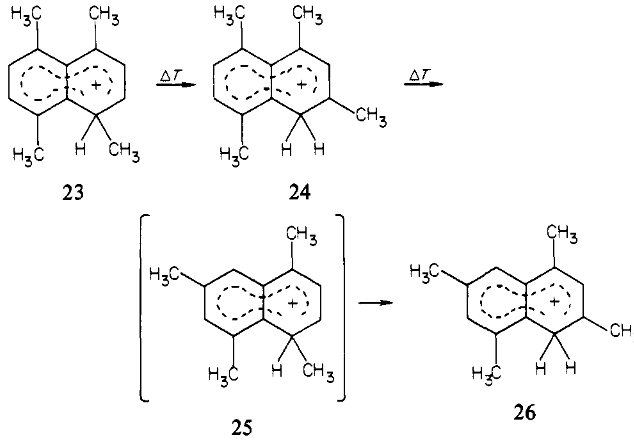
(13) The ratio did not change significantly within 1–2 h at this temperature. Preparation of the ion solution at -120 °C and immediate recording at -90 °C gave the same isomer ratio.

Scheme I



of **24**. In particular, they reveal the presence of an "ortho" and a "para" methyl group to the "free" α-protonated center by comparison with the data in structures I–IV.



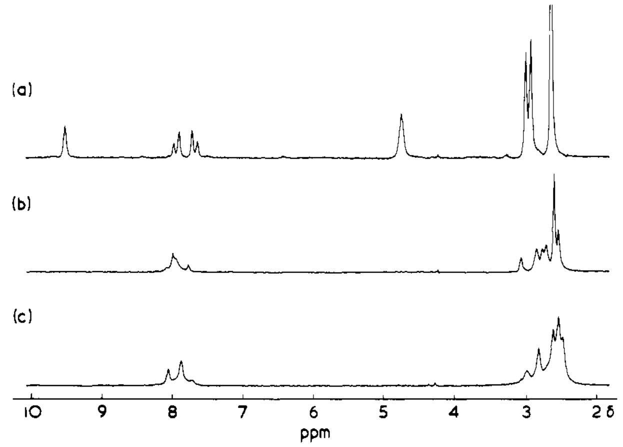


Figure 5. Temperature-dependent ^1H NMR spectra of protonated 1,4,6,7-tetramethylnaphthalene: (a) ion **27** at −70 °C; spectra after "heating" to −30 °C and ca. 2 h (b) at −5 °C, and (c) at −60 °C.

Additional increase of the temperature to ca. −15 °C results in the subsequent isomerization of **24** to ion **26** (see Figure 4). The ^1H and ^{13}C NMR data (see Tables I and II) in combination with the NMR characteristics of structures I–IV are fully consistent with the structural assignment of **26**; the second methyl migration is obvious from both the resonances of H_8 at δ_H 8.36 (s) and C_8 at δ_C 130.7. In this particular case workup of the ion solution afforded no conclusive evidence for the existence of **26**, because of the instability of the ion solution.[14] On the basis of the above-mentioned isomerizations it is likely that the conversion **24** → **26** operates through the intermediacy of ion **25**, thus representing examples of both process 3 and process 4.

Protonation of 1,4,6,7-tetramethylnaphthalene (**14**) with FSO_3H at −80 °C occurs exclusively at the "free" α-position, resulting in the formation of ion **27** (see Figure 5), as can be concluded unequivocally on the basis of the ^1H and ^{13}C NMR data (see Tables I–III) and comparison with those of structures I–VI.

Upon temperature increase an interesting observation was made. At ca. −30 °C all signals in the ^1H NMR spectrum broadened considerably, but after ca. 1 h at this temperature a completely different and well-resolved spectrum was obtained (see Figure 5),[15] showing the following phenomena: (1) no signal of (a) methylene or methine hydrogen(s) of (a) protonated center(s) was detected between −5 and −80 °C; (2) the aliphatic region displays two sets of four methyl signals, all rather shielded (δ_H 2.5 −3.0), and the aromatic part shows two sets of three signals, again rather shielded (δ_H 7.7–8.1), with a relative intensity ratio between the two regions of 1 (aromatic):4–5 (aliphatic); (3) the resonances of all the methyl groups experience upfield shifts to a different degree upon temperature decrease, accompanied by both up- and downfield shifts of the aromatic signals; (4) the relative intensity ratios of the two different sets of signals diminishes on both temperature increase and prolonged time exposure, e.g., ratios are 1:3 at −60 °C and 1:1.5 at −5 °C (both after ca. 3 h) and 1:4 at −20 °C, directly after formation, as calculated from the methyl absorptions; (5) the ion solution is green, whereas **27** is orange;[16] (6) no proper ^{13}C NMR spectrum could be obtained within the temperature range of −5 to −80 °C.[18] Workup of the ion solution did not result in the sole reformation of **14**, which may be due to the complexity of the ions involved.[14]

The above observations indicate that ion **27** merges into a dynamic process, for which the following conclusions may be

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(14) Alternatively it may also be argued that the proton abstraction in the quenching process (see Experimental Section) is liable to steric factors, which may cause additional isomerizations, eventually resulting in differently substituted naphthalenes. However, it has been shown that **13** isomerizes in CF_3CO_2H to 1,3,5,7-tetramethylnaphthalene in 87% yield.[9]

(15) Several repetitions demonstrated the consistency of this process. With use of the stronger acid FSO_3H–SbF_5, however, ion **27** was stable for a short time even at −20 °C; additional and uncharacterized signals were then observed, accompanied by polymerization.

(16) All the monoprotonated naphthalenes have an orange or red color. Dication **19** and the dication obtained from **13**, by oxidation with SbF_5,[17] have a green color. See also ref 27.

(17) Lammertsma, K.; Olah, G. A.; Berke, C. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6658.

(18) At −80 °C the ^{13}C NMR spectrum just showed the presence of **27** in addition to one or two other ions, which could not be characterized because of the bad resolution.

drawn: (1) the total absence of (a) protonated center(s) in a 75 °C temperature range indicates that intermolecular proton exchange plays an important role; (2) that this process is likely to operate through diprotonated **14** (also apparent from the green color); (3) the temperature-dependent chemical shifts of both the methyl and aromatic resonances indicate the involvement of intramolecular proton shifts, (4) the temperature-dependent ratios of the two sets of signals, in both the aromatic and aliphatic regions, reveal two distinct equilibria, mutually related; (5) invoking (in part) the possible oxidation of the aromatic species to a radical cation or a dication[17,19] can be excluded on the basis of the ^{1}H chemical shifts and their behavior. On the basis of these conclusions, we tentatively propose the protonation cycle, given in Scheme I, for the dynamic protonation behavior of **14**.

Mechanistic Considerations. In the preceeding sections we have been primarily concerned with the characterization of different protonated naphthalene derivatives and with the detection of the isomerization processes 3 and 4, mentioned in the introduction. It is of relevance to examine more closely some of the aspects invoked in these isomerizations. The equilibria 1 and 2 were previously reported in detail in the literature[2,4] and hence will not be discussed here.

Process 4 is the transformation of an ipso α-naphthalenium ion to a "free" α-naphthalenium ion with, effectively, a 1,2 migration of the ipso methyl group. Three examples have been observed, viz. **21** → **22**, **23** → **24**, and [**25**] → **26**, in addition to the reported one,[2] i.e., [**7**] → **8**. These isomerizations are in all likelihood governed by successive 1,2-methyl and 1,2-hydrogen shifts.[3a] It is suggested that the initial 1,2-methyl shift results in significant relief of steric strain between the two peri methyl groups present in the ipso α-naphthalenium ion.[20] The resulting intermediate ipso β-naphthalenium ion is then rapidly converted to the thermodynamically more stable "free" α-naphthalenium ion via a 1,2-hydrogen shift.[21] The hyperconjugative stabilization by the methyl groups in these ions seems to overrule the steric effects, which are apparent from the splitting pattern of the methyl group "ortho" to the protonated center (see the ^{1}H NMR spectra of **22** and **26** in Figure 3b (insert) and 4c, respectively).[22]

Process 3 is the conversion of "free" α-protonation to ipso α-protonation with retention of the methylated naphthalene skeleton. One example has been observed, i.e., **20** → **21**, and two assumed, i.e., [**24**] → **25** and **27** → **29**, in addition to those reported, viz., **6** → [**7**][2] and the three observed for the protonation of **1**, **2**, and **3**.[7] The change in site of protonation may be attributed to kinetic vs. thermodynamic controlled C-protonation. The initially formed "free" α-naphthalenium ions all have either a peri methyl–methyl interaction (ions **6**, **20**, and **24**) or a substantial peri methyl–hydrogen interaction, due to buttressing of the methyl group (protonation of **1**, **2**, and **3**). Accordingly, ipso protonation of the respective methyl group will result in significant relief of steric strain from these interactions. Also, simple Hückel MO calculations indicate the preference of ipso α-protonation over "free" α-protonation.[23] For the conversion **27** → **29**, however, less energy is assumed to be gained from relief of steric strain because of lack of buttressing of the α-methyl group.

The importance of steric factors is also reflected in the different sites of protonation of **13** and **15**. The ipso protonation of the former,[23] giving **23**, results in one diminished peri methyl–methyl interaction. In contrast, similar protonation of **15** is assumed to increase the steric strain in the hydrocarbon bridge, therefore favoring the formation of the less strained β-naphthalenium ion **18**.

It is of interest to discuss the possible pathways by which process 3 may operate. In general the following three routes may be considered: (a) consecutive intramolecular 1,2-hydrogen shifts, (b) intermolecular proton exchange via the neutral precursor, and (c) intermolecular proton exchange via a dication. Route a is regarded not to be applicable to naphthalenium ions, because it would invoke the protonation of a bridgehead carbon as well as 1,2-hydrogen shifts between neighboring β-positions, neither of which has been observed. Route b has been offered as the explanation for the kinetic vs. thermodynamically controlled protonation of some anthracene derivatives[24,25] and is, in fact, supported by the observation that the methylene group of 9-alkylanthracenium ions is eventually fully deuterated with FSO_3D.[26] Hence route b might equally well be applied to the naphthalenium ion isomerizations of process 3. Formulation of route c originates from the fact that the stable dications **9a** and **9b** have been observed.[7,10] Elaborating on route c, it should be emphasized that the diprotonations could only be effected with FSO_3H–SbF_5, whereas all the conversions discussed were accomplished with the much weaker acid FSO_3H, and that for none of them the existence of a dication could be observed.[27] Methyl migrations have been found to occur even in CF_3CO_2H.[9] It is also important to stress that the dications **9a** and **9b**, reported by Koptyug et al.,[7,10] have a 4,8 orientation of the protonated centers and therefore the conversion **4** → **5**, reported by the same authors,[7] cannot be explained via a similar dication.[28] Furthermore taking into account that there must be a considerable spread in basicities for the various discussed polymethylnaphthalenes, we feel that there is no conclusive evidence for route c, although it cannot be rigorously excluded for all cases.

On the basis of the accumulated knowledge of the protonation of polymethylnaphthalenes, it is worthwile to elaborate on the tentatively postulated protonation sequence depicted in Scheme I. The conversion (in part) of **27** to **29**, via process 3, was outlined before. In comparison with the protonation of 1,4-dimethylnaphthalene[2] (ipso α-ion ⇄ "free" β-ion) it is anticipated that, in the temperature range studied, ion **29** is likely to be in equilibrium with **32** via a 1,2-hydrogen shift. Ion **32** then might be

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(19) (a) Deger, H. M.; Müllen, K.; Vogel, E. *Angew. Chem.* **1978**, *90*, 990. (b) Oth, J. F. M.; Smith, D. M.; Prange, U.; Schröder, G. *Ibid.* **1973**, *85*, 352.

(20) The peri interaction between the two methyls amounts to 7 kcal: Good, W. D. *J. Chem. Thermodyn.* **1973**, *5*, 715.

(21) Accordingly these isomerizations can be regarded as

$$\text{ipso } \alpha\text{-ion} \xrightarrow[\circ]{1,2\text{-Me}} \text{ipso } \beta\text{-ion (process 5)}$$

$$\text{ipso } \beta\text{-ion} \rightarrow \text{“free” } \alpha\text{-ion (process 6)}$$

(22) Instructive information is obtained from: (a) Dalling, D. K.; Ladner, K. H.; Grant, D. M.; Woolfenden, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 7142. (b) Forsyth, D. A.; Vogel, D. E.; Stanke, S. J. *Ibid.* **1978**, *100*, 5215.

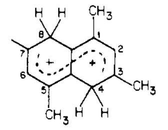
(23) It should, however, be emphasized that the simple Hückel MO calculations neglect steric factors and overestimate ipso protonation (because of neglect of the protonated center) and thus reflect their limited value in calculating the site of protonation in these very crowded systems (see also ref 2).

(24) (a) Van de Griendt, F.; Cerfontain, H. *Tetrahedron*, **1979**, *35*, 2563. (b) Brouwer, D. M.; Van Doorn, J. A. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 88.

(25) For stable (polymethyl)anthracenium ions see: (a) Van de Griendt, F.; Cerfontain, H. *Tetrahedron*, **1980**, *36*, 317. (b) Reference 5.

(26) Van de Griendt, F.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2*, in press (private communication).

(27) It is relevant to mention that protonation of **13** with FSO_3H–SbF_5 at −15 °C for 1–2 h resulted in some cases partly in the formation of a species to which the dication structure **33** was tentatively assigned. Only a ^{1}H NMR spectrum could be obtained and only at <−50 °C: δ 8.65 [s, br, 2-H, H(3), and H(6)], δ 5.45 [s, br, 4-H, $H_2(4)$, and $H_2(8)$], δ 3.48 [s, 6-H, $CH_3(1)$, and $CH_3(5)$], δ 2.73 [s, 6-H, $CH_3(3)$, and $CH_3(7)$]. At increased temperatures this spectrum emerged in the base line. In these particular cases the ion solution was greenish of color (see ref 16).



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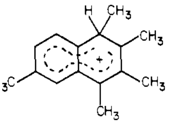
(28) Deprotonation of such a dication would lead to the formation of ion **34**, instead of the actually observed ion **5**.[7]



34

in part converted to **30** via the intermediate dication **31** (compare the protonation of **15** to **18** and **19**). Ion **30**, being an ipso β-naphthalenium ion, is assumed to equilibrate with **27** (see the discussion of process 4). Whether or not dication **28** is involved in the protonation sequence, e.g., through protonation of **27** by FSO_3H (see discussion of process 3) or by intermolecular proton exchange from **31** or alternatively via two intramolecular 1,2-hydrogen shifts from **31**, remains questionable. However, on the other hand, it is hard to believe that both the neutral precursor (**14**), and the dication **31**, would be present in the same ion solution.

^{13}C NMR Spectroscopy and Carbenium Ions. Carbon chemical shifts have been shown to be mainly dependent upon local π-electron densities of the carbon nuclei.[29] Recently O'Brien, Hart, and Russell[30] demonstrated that the Spiesecke–Schneider correlation[31] could be extended to monocyclic and conjugated π systems, in which all π-carbons are not necessarily equivalent, by the empirical relationship $\delta_{C_{av}} = 289.5 - 156.3\rho_{av}$, where ρ_{av} is the average π-electron charge. Olah et al.[5] have shown that this relationship is also applicable to the parent benzenium, naphthalenium, and anthracenium ions, being mono-, bi-, and tricyclic ionic systems, respectively. In the previous report[2] it was found that the $\delta_{C_{av}}$ value of 150.1 (standard deviation 0.57) ppm for nine stable dimethylnaphthalenium ions is in excellent agreement with that of 150.5 ppm, predicted for a 8π–9C system from O'Brien's correlation line, despite the fact that substituent effects were neglected.[29a,32] It is informative to see that the $\delta_{C_{av}}$ value of 151.7 (standard deviation 1.0) ppm for the ten highly substituted and crowded "stable" monocations in this report, including the "free" β-naphthalenium ion **18**, are also in good agreement with the predicted value. The average π-carbon chemical shift for dication **19** is $\delta_{C_{av}}$ 177.6 and comparable with those for **8a** ($\delta_{C_{av}}$ 177.7) and **8b** ($\delta_{C_{av}}$ 179.1 and 179.5),[33] calculated from their reported ^{13}C NMR spectra;[7] they are in reasonable agreement with $\delta_{C_{av}}$ 172.3, calculated for a 6π–8C system, demonstrating the fit for bicyclic dications.[34]

The cationic nature of a protonated arene can also be deduced from the total downfield shift of the ^{13}C NMR resonances of all olefinic carbons of the ion relative to those of the related carbons of the neutral precursor. These total changes in δ_C for **16**, **17**, **18**, **20**, **21**, **23**, and **27**, relative to **10**, **12**, **15**, **11**, **11**, **13**, and **14** respectively are 192.4, 217.7, 172.0, 197.9, 196.3, 173.2, and 193.3 ppm/e^-, respectively, and are in accord with the assignment of the naphthalenium monocations.[5] The spread in these values may result from substituent effects and steric factors. The total change in δ_C obtained for **19** relative to **15** amounts 365.2 ppm or 182.7 ppm/e^- and thus confirms the dicationic nature of **19**.

It is informative to mention the consistency for the δ_C and $\Delta\delta_C$ values of each particular carbon (see Tables II and III) and that there is a reasonable correlation between the $\Delta\delta_{C_i}$ and Δq_i values (being the respective change in electron density[2]), and that both these observations, in fact, relate well with those made for the less crowded dimethylnaphthalenium ions.[2] This also demonstrates that the electronic features in *all* α-naphthalenium ions are basically similar. Furthermore it emphasizes the convenient use of ^{13}C NMR data for the structural assignment of *any* (polyalkyl)naphthalenium ion.

Experimental Section

Materials. The compounds **10**, **11**, **12**, and **13** were synthesized by known procedures[36,37] with minor modifications. Compound **14** was obtained as a gift from Dr. J. G. J. van de Heuvel. Compound **15**, magic acid, fluorosulfonic acid, and SO_2ClF were obtained from the Aldrich Chemical Co. and were used without further purification.

Preparation of Ions. The ion solutions were prepared at −78 °C or lower temperatures as previously described.[2] Quenching of the ion solutions in sodium bicarbonate buffered methanol at −78 °C resulted in the reformation of the precursors or respective isomers, as concluded from ^{1}H NMR analysis. Workup of the ion solutions of protonated **13** and **14**, however, afforded also minor amounts of other uncharacterized products.

Nuclear Magnetic Resonance. The ^{1}H NMR spectra were obtained by using a Varian HA-100 NMR spectrometer and the ^{13}C NMR spectra by using Varian FT-80 and XL-100 spectrometers, all equipped with variable-temperature probes. Chemical shifts (δ_C and δ_H) in parts per million were determined relative to external (capillary) Me_4Si. The instrumentation and techniques employed have been described previously.[2] Multiplicities of carbon resonances were obtained from off-resonance ^{1}H-decoupled experiments if necessary.

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[33] Ion **9b** exists in a "cis" and a "trans" configuration.[7,10]

[34] In order to be complete it should be mentioned that a relationship similar to the O'Brien correlation was found for the dications of polynuclear arenes, obtained by oxidation.[17,35]

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