^1H and ^{13}C Nuclear Magnetic Resonance Spectra of Dimethylnaphthalenium Ions. Calculation on the Site of Protonation and Correlation between ^{13}C Chemical Shifts and Electron Density by the Hückel MO Method

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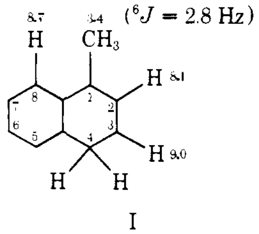
Abstract: All ten dimethylnaphthalenes have been protonated with FSO_3H-SbF_5 (1:1) in SO_2ClF. The resulting dimethylnaphthalenium ions were studied by ^1H NMR and ^{13}C NMR spectroscopy. The 1,8-dimethylnaphthalenium ion **8** isomerizes upon raising the temperature with formation of the protonated 1,7-dimethylnaphthalene **6**. The ^1H NMR spectrum of protonated 1,4-dimethylnaphthalene is temperature dependent and indicates the presence of two pairs of ions which rapidly equilibrate via simple 1,2-hydrogen shifts. One of the ions involved is the ipso protonated species **17**. The site of protonation of the dimethylnaphthalenes is as predicted from the localization energies obtained by simple Hückel π-electron molecular orbital calculations. The ^1H and ^{13}C chemical shifts of the individual ring positions of the various ions correlate with the calculated charge densities (q). A satisfactory correlation between $\Delta\delta_C$ and Δq is observed if the stabilizing features of the methyl group are accounted for. On this basis new inductive parameters for the methyl substituent are offered.

In contrast to the numerous reports on the formation and properties of stable carbocations of alkylbenzenes,[1] studies on naphthalenium ions are scarce.[2,3] In this paper we present the ^1H and ^{13}C NMR data of the σ complexes formed upon protonation of the dimethylnaphthalenes (DMNs) in superacid as an extension of an earlier study by Olah.[2] We correlate the structures of the resulting ions with the stabilities of the various σ complexes, calculated by the simple Hückel MO theory.[4] Further, the ^{13}C NMR data of the stable carbocations generated from the DMNs are correlated with π-electron densities. It is regarded as common practice to correlate ^{13}C chemical shifts with molecular orbital calculations of π or total electron densities.[5] A number of attempts on substituted naphthalenes have, however, met with limited success.[6-9] It was hoped that with the *charged* naphthalenium ions the simple Hückel method would suffice to show such a correlation.

Results and Discussion

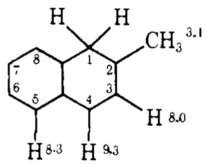
The DMNs have been protonated with FSO_3H-SbF_5 (1:1 molar ratio) dissolved in SO_2ClF (1:2 v/v) at −80 °C. The ^1H and ^{13}C NMR data of the resulting naphthalenium ions are listed in Tables I and II, respectively. Both types of NMR data of the parent hydrocarbons were reported,[6] except for the ^1H NMR parameters of 1,6-, 1,7-, and 2,7-DMN. Protonation of a given DMN resulted in the formation of one stable carbocation (Table I), except for the following three DMNs. Upon protonation of 1,6-DMN the main product is ion **4**. However, two additional ions were observed, each present in 10%. One has been tentatively assigned to have the site of protonation at position 5 (**5**).[10] Protonation of 1,7-DMN occurs mainly at C(8) and for 15% at C(4), with formation of the ions **6** and **7**.[11] The protonation of 1,4-DMN is complicated and will be discussed later.

^1H NMR Spectroscopy. The main ^1H NMR characteristics of the naphthalenium ions, listed in Table I, are summarized in I and II. Protonation "para" to the methyl substituent as in I is apparent from the long-range coupling of the very *deshielded* hydrogens of the methyl at C(1), which exhibit a triplet (J = 2.8 Hz), with the CH_2 hydrogens.[1c,2,12] These two observations also indicate considerable stabilization of I by hyperconjugation of the $CH_3(1)$ with the positive charge.[13] As to the aromatic hydrogens H(3) exhibits substantial deshielding. The coupling between H(3) and CH_2 is only weak.



I

1, **2**, **3**, **4**, **7**, and **8**



II

6, **10**, **11**, and **12**

The most shielded aromatic absorption is that of H(2) and accordingly position 2 does not carry a significant charge. The absorption of H(8) is observed at low field, indicating substantial participation in sharing the positive charge. The downfield shift of H(8) of 1-substituted naphthalenes[14] and their ions[2] was explained in terms of a peri effect.

The resonance of a methyl group "ortho" to the protonated center as in II compared to a "para" methyl as in I is considerably more shielded. Although there is coupling between CH_2 and the adjacent CH_3, it is too small to observe any fine structure on the methyl absorption. Apparently an "ortho" methyl is less stabilizing than a "para" methyl. Other characteristics of II are the low-field H(4) and the high-field H(3) absorptions in the aromatic region. As concluded for I the "meta" position of II also does not carry significant charge. In the absence of a peri methyl H(5) is observed at a more shielded position (cf. H(8) of I).

Our assignments differ in some cases from those of a previous report.[2] The ion obtained from 1,5-DMN may be discussed as a typical example. Extensive double-resonance measurements have revealed that the methylene protons couple weakly ($J \approx 1.5$ Hz) with the most deshielded doublet at δ 9.18 (J = 8.5 Hz), assigned to H(3), and with the $CH_3(1)$ signal at δ 3.50 (^6J = 2.8 Hz). Irradiation of H(3) revealed the absorption of H(2) to be at δ 8.18 (and not at δ 8.74[2]). The doublet (J = 8 Hz) at δ 8.74 has to be assigned to H(8), in agreement with the absorption of H(8) of the ions **1**, **2**, and **4**. The present assignment differs from the previous one[2] in that those of H(2), H(8), and H(6) are replaced by H(8), H(6), and H(2), respectively (see Table I).

Protonation of 1,8-DMN at −80 °C yields the stable ion **8**. Similarly acenaphthene is protonated to give the analogous ion **13**. In agreement with the assignment of H(8) of I the low-field resonance at δ 8.7 is absent for these ions. On warming up the

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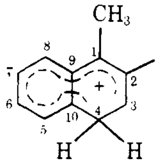
Table I. ^{1}H NMR Parameters of Dimethylnaphthalenium Ions[a]

compd	methyl substituents	position of protonation	δ(CH_3)[b]	δ(CH_2)	δ(ring positions)[c] 2	3	4	5	6	7	8
1	1,2-	4	3.39 (t, 1) J = 2.5 2.68 (s, 2)	4.95 (s, br)		8.93 (s)		8.17 (m)	8.17 (m)	8.17 (m)	8.84 (d) J = 8
2	1,3-	4	3.36 (t, 1) J = 2.8 3.02 (s, 3)	4.90 (s, br)	8.00 (s)			8.14 (m)	8.14 (m)	8.14 (m)	8.68 (d) J = 8
3	1,5-	4	3.50 (t, 1) J = 2.8 2.75 (s, 5)	4.76 (s, br)	8.18 (d) J = 8.5	9.18 (d, t) J = 8.5 and 1.5			8.24 (d, br) J = 8	8.00 (t) J = 8	8.74 (d, br) J = 8
4	1,6-	4	3.39 (t, 1) J = 2.8 2.82 (s, 6)	4.87 (s, br)	7.98 (m)	8.90 (d, t) J = 9 and 2.5		7.98 (m)		7.98 (m)	8.67 (d) J = 8.5
6	1,7-	8	3.13 (s, 7) 2.70 (s, 1)	4.83 (s)	8.16 (d) J = 7	7.90 (t) J = 7 and 8	8.30 (d) J = 8	9.42 (d, t) J = 8 and 1.8	8.04 (d) J = 8		
7	1,7-	4	3.44 (t, 1) J = 2.8 2.72 (s, 7)	4.94 (s, br)	8.09 (m)	9.07 (d, br) J = 8		8.09 (m)	8.09 (m)		8.57 (s)
8	1,8-	4	3.50 (t, 1) J = 3.2 3.10 (s, 8)	4.95 (s, br)	8.00 (m)	8.89 (d, t) J = 9 and ~2		8.00 (m)	8.00 (m)	8.00 (m)	
10	2,3-	1	3.04 (s, 2) 2.64 (s, 3)	5.16 (s, br)			9.29 (s) J = 1	8.2 (m)	8.2 (m)	8.2 (m)	8.2 (m)
11	2,6-	1	3.09 (s, 2) 2.68 (s, 6)	5.05 (s)		8.02 (d) J = 8	9.37 (d) J = 8 and 1.5	8.21 (s)		8.10 (m)	8.10 (m)
12	2,7-	1	3.01 (s, 2) 2.79 (s, 7)	4.93 (s)		7.88 (d) J = 8	9.28 (d) J = 8	8.29 (d) J = 8	7.83 (d) J = 8		7.96 (s)
13[d]		4	3.97 3.77	4.77 (s, br)	8.05 (m)	8.87 (d, t) J = 9 and 2.5		8.05 (m)	8.41 (t) J = 8	8.05 (m)	

[a] Proton chemical shifts (in parts per million) are referred to external capillary Me_4Si. J values are in hertz. [b] The number in parentheses indicates the methyl ring position. [c] The δ of (m) resonance represents the center of the (overlapping) unresolved multiplet. [d] For reasons of convenience, the aromatic ring positions of the acenaphthenium ion have been numbered as for the naphthalenium ions; the bridge methylene resonances are given in the column for methyl absorptions.



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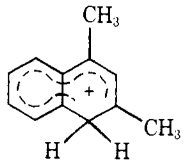

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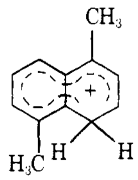

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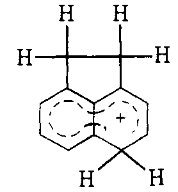

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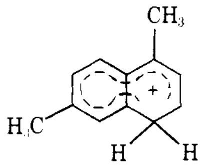

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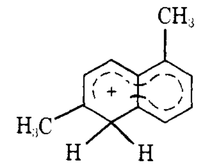

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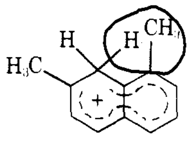

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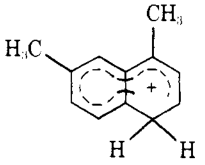

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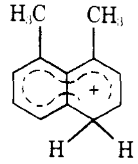

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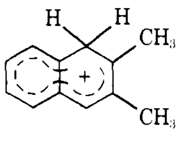

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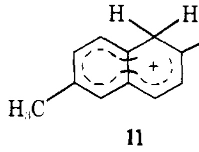

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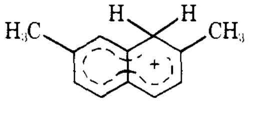

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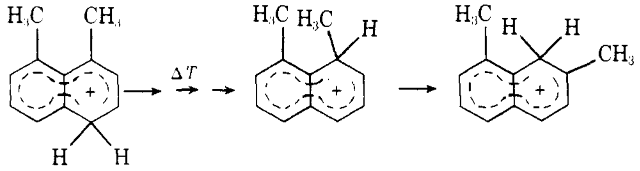
solution of **8** the ^{1}H NMR spectrum gradually changed until ultimately at −40 °C a totally different one was observed. This latter spectrum is identical with that obtained on protonation of 1,7-DMN (Figure 1), and which has been assigned to the presence of the ions **6** and **7**. Confirmation for this changeover was found by ^{13}C NMR (Figure 2). All the ^{13}C chemical shifts beside those assigned to **8** were identical with those of a separately recorded spectrum of protonated 1,7-DMN. The conversion of **8** into **6** may be explained in terms of three subsequent 1,2-hydrogen shifts yielding ion **9**, a 1,2-methyl shift, and finally a 1,2-hydrogen shift to give **6**.[15] The third 1,2-hydrogen shift and the subsequent 1,2-methyl shift are accompanied by relief of steric strain of the two peri methyl



8 **9** **6**

Table II. Carbon-13 Chemical Shifts[a] of Dimethylnaphthalenium Ions

compd	ring carbon[b] 1	2	3	4	5	6	7	8	9	10	methyl carbons[c]	
1	200.8	144.2	176.9	42.8	129.9	141.2	130.8	133.0	133.9	153.4	22.6 (1)	20.0 (2)
2	195.9	135.8	203.0	46.4	129.4	140.2	130.4	132.2	132.1	151.0	25.0 (1)	27.0 (3)
3	199.7	136.1	177.9	41.3	138.9	144.0	130.7	132.0	133.6	152.1	26.0 (1)	18.4 (5)
4	197.0	135.3	174.9	42.0	130.5	158.0	132.6	133.4	131.8	154.6	25.2 (1)	22.7 (6)
6	177.3	132.6	208.4	46.1	138.6	143.8	130.7	137.3	132.6	151.1	28.0 (3)	17.9 (5)
8	201.2	138.4	175.4	43.8	128.8	141.5	134.9	149.4	134.3	156.3	33.0 (1)	27.4 (8)
10	177.6	142.4	208.3	49.5	128.7	140.3	130.7	137.2	133.0	152.4	17.8 (2)	26.4 (3)
11	176.7	132.8	208.6	47.7	129.2	143.7	142.0	137.5	132.8	151.5	27.8 (3)	20.3 (7)
12	175.3	131.5	204.0	46.8	130.1	157.7	132.4	138.5	130.9	154.0	27.3 (3)	22.8 (6)

[a] Relative to Me_4Si. [b] The carbon ring numbering is given in **18**. [c] Number in parentheses indicates methyl position.

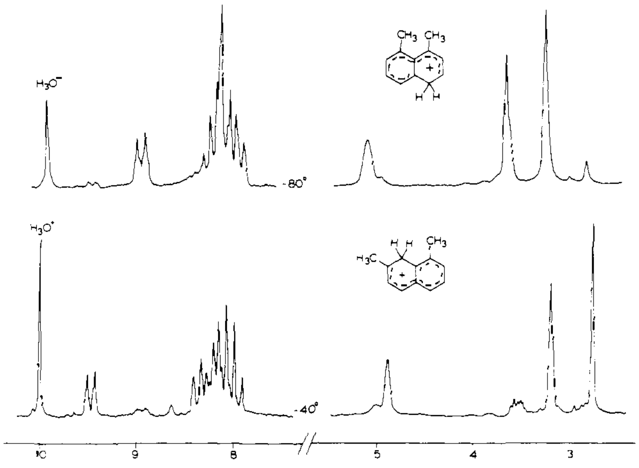


Figure 1. Temperature-dependent ^1H NMR spectra of the 1,8-dimethylnaphthalenium ion at −80 and −40 °C.

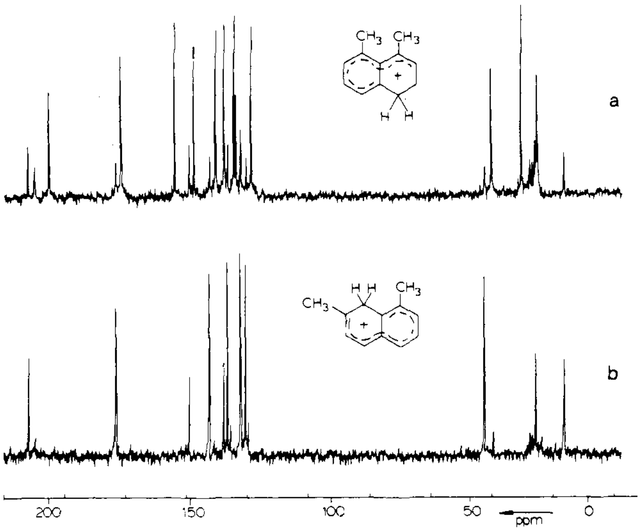
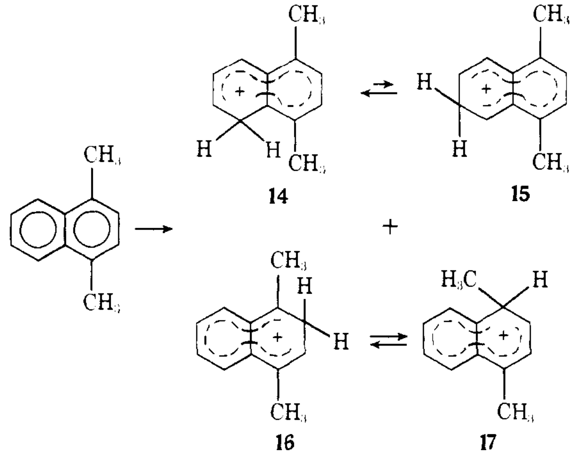


Figure 2. ^{13}C NMR spectra at −80 °C (a) of a mixture of **6** and **8** obtained upon short temperature increase of **8** and (b) of **6** separately.

groups.[16] It cannot be excluded that ion **9** is formed from **8** by intermolecular proton exchange.

An interesting behavior is observed on protonation of 1,4-DMN. From the temperature-dependent ^1H NMR spectrum it appears that there exist two independent equilibria, viz., **14** $\rightleftharpoons$ **15** and **16** $\rightleftharpoons$ **17**. Protonation in the unmethylated ring is

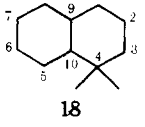


evident from the two sharp temperature-independent methyl absorptions at δ 2.70 and 3.03. At −95 °C the equilibrium is frozen out and **14** is present (30%). The $CH_2(5)$ protons give a sharp absorption at δ 4.88. The chemical shifts of H(6) and H(8) are δ 9.47 (J = 9 Hz) and 10.0 (this resonance is overlapped by that of the H_3O^+ ion), respectively; they are comparable with those of H(2) (δ 9.51) and H(4) (δ 9.81) of the 1-naphthalenium ion.[2] The H(8) is somewhat more deshielded as result of a small peri effect. With increasing temperatures the CH_2 signal broadens and the H(6) resonance disappears while the absorption at δ 10.0 remains unchanged. These observations are indicative of the rapidly equilibrating ions **14** $\rightleftharpoons$ **15** via intramolecular 1,2-hydrogen shift. Similar equilibria were reported for the naphthalenium ion[2] and for alkyl- and fluorine-substituted benzenium ions.[1c,f]

The occurrence of the second equilibrium **16** $\rightleftarrows$ **17** is concluded from the variation of the remaining methylene and the two methyl signals with temperature in the complex ^1H NMR spectrum (see Figure 3). On decreasing the temperature from −50 to −95 °C the signal at δ 5.33, due to the sites of protonation, shifts to δ 5.14 and the methyl signals from δ 3.10 and 2.90 to δ 3.24 and 2.85, respectively. The view that at −50 °C one of the two separate ions is observed, because of the sharpness of the signals just mentioned, is opposed by (1) the absence of a downfield aromatic resonance due either to H(3) of **16** or H(2) of **17** and (2) the small difference in chemical shift of the two methyl groups (Δδ = 20 Hz). Apparently at this temperature sizable amounts of **16** and **17** are in rapid equilibrium. An attempt to "freeze out" the equilibrium in favor of one of the ions by lowering the temperature to −95 °C was considered to be unsuccessful based on the broad absorption at δ 5.14. From the variation in the difference of the chemical shifts of the two methyls (from 20 Hz at −50 °C to 39 Hz at −95 °C) it may tentatively be concluded that the initial site of attack at low temperatures is the 2 position. From the absence of a sharp methylene signal at −95 °C it must be concluded that even at that temperature a sizable amount of **17** exists in equilibrium with **16**.[17] The presence of ipso protonation of 1,4-DMN is in accordance with a nitration study.[18] The absence of a 1,2-H shift between the 2 and 3 position in the temperature range studied [leading to an (average) methyl signal] indicates that the free-energy barrier for this process is substantially higher than that for the 1,2-H shift between the 2 and 1 position. This observation is different from that of the 1,2-H shifts of the *o*- and *p*-xylenium ions,[1e,f] for which the ipso-protonated ions were not considered as intermediates. Our results contradict those of Olah, who reported that 1,4-DMN is protonated at the 2 position to give ion **16**, which isomerizes to **2**, and then stated that "the final equilibrium at −55 °C is established in favor of the rearranged ion whose concentration is more than 50%".[2] We found, however, no ^1H NMR evidence for the involvement of **2** in the equilibria.

Calculated Site of Protonation. From the data on the sulfonation,[19] bromination,[20] and hydrogen exchange[21] of DMNs it appears that one of the features governing the substitution pattern is the relative stability of the σ complexes.[4] It is interesting to test whether the carbocations obtained upon protonation, and which are in fact the "frozen out" σ complexes, follow the calculated σ-complex stability order. The localization energies (L_r^+) of the various positions (r) of the ten dimethylnaphthalenes were calculated with the simple Hückel molecular orbital treatment,[4] utilizing the inductive model for the methyl substituent with $\delta\alpha_r = -0.3$.[21a,22] The calculated site of protonation of 1,2-, 1,3-, 1,5-, and 1,8-DMN is at C(4) and that for the three β,β-disubstituted DMNs at C(1). This is in full agreement with the experiments. For 1,7-DMN it is predicted that the protonation at C(8) is slightly more favored than at C(4) ($\Delta L^+_{8,4} = 0.0073\beta^{22}$), and this is in fact reflected by the appearance of 85% of **6** and 15% of **7**. Only for 1,6-DMN there is a contradiction. The MO calculations predict ion **5** to be slightly more stable than ion **4**, whereas the latter is in fact the major product. The isomerization of **9** to **6**, which have about the same L^+,[22] can be rationalized in terms of the release of steric strain between the two methyls of **9**. For 1,4-DMN it was calculated that the ipso protonation is strongly favored, whereas in fact the rapid equilibrium between substantial amounts of both **16** and **17** is observed. However, attention should be called to the fact that the protonated center is neglected in this type of MO calculations, which results in overestimating the degree of ipso attack.[23] The smaller L_r^+ for **14** than **15** is in accordance with the actual observation at −95 °C.

^{13}C NMR Spectroscopy. The number of ^{13}C NMR studies of naphthalene derivatives is rapidly augmenting.[6,9,25] No systematic study on the naphthalenium ions has, however, been reported. Some data are available on protonated (poly)alkylbenzenes[1] and polymethylnaphthalenes.[2,3a] In this section for reasons of simplicity and consistency the numbering of the naphthalenium skeleton as shown in **18** will be used. (The protonated center of each ion is chosen to be position 4.) The data are presented in Table II. The assignment of the resonances was found to be straightforward, and was based on (1) off-resonance noise decoupling, (2) fully ^1H coupled spectra by use of the gated noise technique, (3) selective decoupling with the aid of the ^1H NMR spectra, (4) the long-range spin-spin coupling constants, and (5) the peak positions in relation with related compounds. For the various carbocations the chemical shifts of a given position are nearly the same (Table II). The largest differences then observed are those between the methyl- and hydrogen-substituted carbons, but for these two substituents they are about equal for a given position. The data for the hydrogen-substituted ring carbons are summarized in III and IV. The most deshielded are the ring carbons which are formally conjugated with the positive charge, and this also applies to the methylated ring carbons and the methyl carbons. The resonance of the methylated C(1) compares well with the chemical shifts reported for the toluenium ion (δ_C 201.0) and the mesitylenium ion (δ_C 196.0).[1c] The special influence of the CH_3(1) group is evident on comparing III with IV and correlates with the ^1H NMR observations (cf. I with II). It leads to deshielding of H(8) and to shielding of C(8). Apparently the H(8) is electron releasing to C(8). Whether this effect is the result of peri steric repulsion by or the field effect of CH_3(1) is unkown; the average value for $^1J_{C(8)H}$, which is 167.1 Hz and thus normal, tends to direct to the field effect.[26] The largest deviations in chemical shift for the positions 2, 7, 9, and 10 are found for **8**. Similar large deviations were observed with the corresponding hydrocarbon 1,8-DMN.[6] They are accordingly ascribed to the interaction between the two peri methyls.[6,16]



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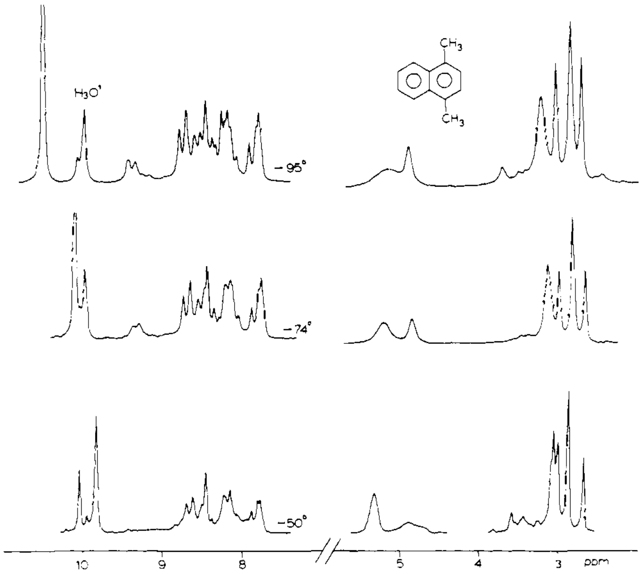
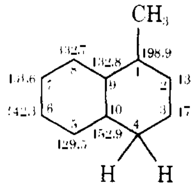


Figure 3. Temperature-dependent ^1H NMR spectra of 1,4-dimethylnaphthalenium ions.



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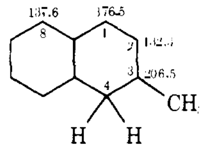
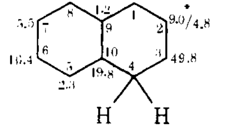
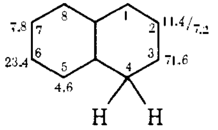


IV

In order to obtain a better measure of the (neat) influence of the positive charge of the naphthalenium structure the ^{13}C NMR chemical shift differences between the various naphthalenium ions and the corresponding DMNs ($\Delta\delta_c$) have been determined, using the reported ^{13}C NMR data of the DMNs in $CDCl_3$.[6] The results are in Table III and summarized in V and VI. The positions which are formally conjugated with the positive charge have the largest $\Delta\delta_C$. The effect of alternating



V



VI

*$\Delta\delta_C$ upon 1-methylation.

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

	ring carbon[b]										methyl carbons[c]	
compd	1	2	3	4	5	6	7	8	9	10		
1	70.0	11.4	48.1	−82.8	1.6	16.9	5.3	9.5	1.2	21.2	8.2 (1)	−0.6 (2)
2	62.2	7.1	68.2	−78.7	1.7	14.8	5.8	8.5	3.1	17.3	5.9 (1)	5.5 (3)
3	65.2	9.9	52.8	−80.9	4.4	17.8	5.6	9.8	1.1	19.6	6.3 (1)	−1.3 (5)
4	63.4	9.8	49.6	−83.6	3.2	23.3	5.0	9.7	1.2	20.9	6.1 (1)	1.3 (6)
6	49.2	5.2	73.4	−76.9	4.8	17.2	6.3	11.4	0.9	20.9	6.5 (3)	−1.3 (5)
8	66.0	9.2	50.6	−83.9	1.1	16.7	5.7	14.2	1.4	18.5	7.1 (1)	1.5 (8)
10	50.3	7.2	73.1	−77.8	2.0	15.5	5.8	10.5	0.2	20.2	−2.3 (2)	6.3 (3)
11	49.7	4.8	74.4	−78.8	2.2	15.7	7.8	11.0	0.9	19.6	6.2 (3)	−1.3 (7)
12	48.4	4.4	68.9	−79.2	4.1	22.6	4.6	11.6	1.2	20.4	5.6 (3)	1.1 (6)

[a] Defined as the difference (ppm) between the ^{13}C chemical shifts of the dimethylnaphthalenium ion and the unprotonated species.[6] Positive values indicate increased deshielding. [b] The carbon ring numbering is given in **18.** [c] Number in parentheses indicates methyl position.

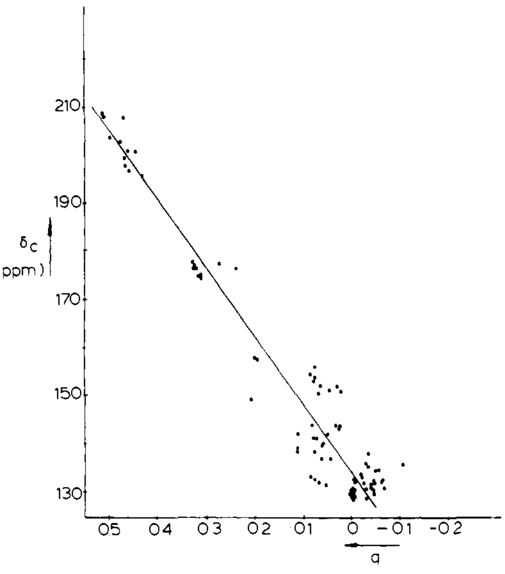


Figure 4. Correlation for individual positions of the dimethylnaphthalenium ions of δ_C with charge density (q).

the positive charge is now more pronounced than on comparing δ_C. Accordingly the delocalization occurs over the two rings of the naphthalenium structure. The $\Delta\delta_C$'s of the other carbons, i.e., C(2), C(5), C(7), and C(9), are only small and reflect that these carbons do not carry much charge. The apparent difference between $CH_3(1)$ and $CH_3(3)$ will be discussed in the following section.

Correlation with Calculated Charge Densities. The carbon chemical shifts of aromatic systems were found to be proportional to π-electron densities.[5] For monocyclic aromatic systems the proportionality constant is ca. 160 ppm/electron.[27] O'Brien et al. reported the correlation line for monocyclic and conjugated π systems to be $\delta_{C_{av}} = 289.5 - 156.3\rho_{av}$ (ρ_{av} is the average local π-electron charge).[28] We have calculated from Wilson and Stothers's ^{13}C NMR data of the DMNs in $CDCl_3$[6] an average δ_C for the π carbons of 128.9 (SD 0.67) ppm, which is comparable with $\delta_{C_{av}}$ 128.7 for benzene,[5b] and in reasonable agreement with the value of 133.2 predicted from the correlation line of O'Brien.[28] The average δ_C for the 81 π carbons of all the dimethylnaphthalenium ions of Table II is 150.1 (SD 0.57) ppm, which accords excellently with the $\delta_{C_{av}}$ 150.5 predicted by O'Brien's correlation line. Thus the dimethylnaphthalenium ions, which are *bicyclic ionic π systems*, also fit the general linear correlation for ionic π systems.

The spread in the chemical shifts of the ring carbon is about 70 ppm (see Table II). It is therefore of interest to find out whether the correlation between δ_C and π-electron density also exists *within* the naphthalenium skeleton. Future assignments of arenium ions might then be facilitated by the use of the (very simple) Hückel MO treatment. A plot of δ_c vs. the charge density q (Figure 4) is linear with a slope of 140.9 ppm/e$^-$ and an intercept of 134.5 ppm ($r = 0.9627$). Similar data were obtained by Olah and Forsyth for the dications of unsubstituted polycyclic arenes, viz., slope 143 ppm/e$^-$ and intercept 135.2 ppm.[29] The observed correlation is only approximate as expected from a similar study on the parent DMNs using CNDO/2, which showed that other factors besides charge distribution are important.[6,30] In order to eliminate these factors and to investigate the "neat" influence of the positive charge of the naphthalenium ion system a correlation was sought between $\Delta\delta_C$ and Δq. In fact two correlation lines have been found,[31] one for the methyl-substituted ring carbons (slope 167.8, intercept 7.6, $r = 0.9955$), and one for the hydrogen-carrying ring carbons (slope 147.2, intercept 3.5, $r = 0.9665$). Obviously the methyl substituent plays a role in stabilizing the positive charge.

It is common practice to regard the methyl substituent attached to a sp^2-hybridized carbon as electron releasing, relative to hydrogen, both inductively and hyperconjugatively.[32] One of the suggested stabilizing factors of substituents on carbenium ion stabilities is the capability of electron donation to a positive center. However, it is also recognized by some molecular orbital treatments that upon substitution of a methyl group for hydrogen the positive charge of the α carbon may increase.[13,33] This discrepancy was scrutinized by Olah, who studied the effect of the replacement of a hydrogen by methyl on the electronic charge distribution of the concerned sp^2 carbon (C_α) in carbocations. The order of deshielding of C_α observed in ^{13}C NMR was related to an increasing electron donation from the methyl via hyperconjugation accompanied by a simultaneous increase in magnitude of the negative inductive effect.[33] It was also shown that in extended π systems the electron donation was "polarized away" from the positive center.[33] To account for the effect on the charge distribution in the protonated naphthalene ring system in the simple Hückel MO calculation, an increase of the combined hyperconjugative and negative inductive effect may be represented by an increase in the inductive parameter of the methyl, the result of which will be an increase in positive charge of such a methylated ring carbon position, with the electron density "polarized away".

The inductive parameters of the Hückel MO treatment have been adjusted by trial and error to obtain a linear correlation between $\Delta\delta_C$ and Δq to yield the following best set: for $CH_3(1)$ $\delta\alpha_1 = -0.5$, for $CH_3(3)$ $\delta\alpha_3 = -0.4$, for all other methyl-carrying ring carbons $\delta\alpha = -0.3$, and for C(10) $\delta\alpha_{10} = -0.1$. Using this set the plot of $\Delta\delta_C$ vs. Δq for *all π carbons* was found to be linear (Figure 5) with a slope of 158.1 ppm/e$^-$ (intercept 4.0, $r = 0.979$). This value is in excellent agreement with the generally accepted value of 160 ppm/e$^-$ [27] and that of 156.3 ppm/e$^-$ reported by O'Brien.[28] The order of the in-

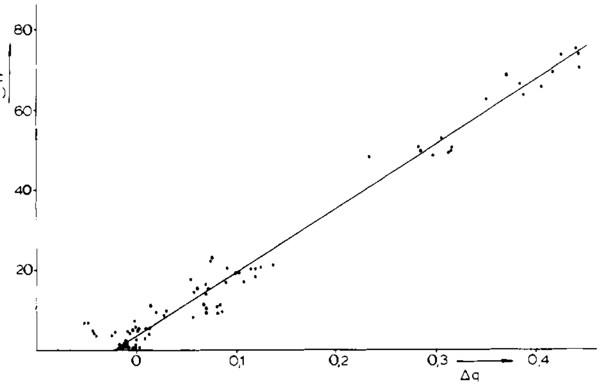


Figure 5. Correlation for the individual positions of the dimethylnaphthalenium ions of $\Delta\delta_C$ with the change in charge density calculated with modified parameters.

ductive methyl parameters could in fact have been anticipated. Stabilization of the positive charge is significantly stronger for $CH_3(1)$ than for $CH_3(3)$, as was concluded from the NMR data (see before).[34] Protonation at C(4) changes its hybridization from sp^2 to sp^3 and might thus itself participate in stabilizing the positive charge.[36] The geometric flexibility of the C(10) junction carbon will be far less for C(10) than for C(3) and accordingly there is hyperconjugation from CH_2 toward the former.

Experimental Section

Materials. The high-purity organic compounds were obtained commercially. Magic acid was obtained from Aldrich and used without further purification.

Preparation of Ions. The dimethylnaphthalenium ions were prepared by dropwise addition of a precooled 1:1 (by volume) solution of FSO_3H-SbF_5 (1:1) in SO_2ClF (1 mL) to the hydrocarbon precursor (150 mg) in SO_2ClF (1 mL) at −78 °C under vigorous shaking. Directly after formation of the ions about 0.5 mL was transferred using a precooled pipet into 5-mm tubes for ^1H NMR examination. For ^{13}C NMR the ions were generated directly in 12-mm tubes. Quenching of the ion solutions resulted in the re-formation of the precursors as concluded from ^1H NMR analysis. Workup of the rearranged ion solution of **8** resulted in 1,7-DMN.

Nuclear Magnetic Resonance. ^1H NMR spectra were obtained using a Varian HA-100 NMR spectrometer equipped with a variable-temperature probe. External Me_4Si (capillary) was used as reference. The double and triple resonance technique was used extensively for the assignment of the ^1H NMR spectra. ^{13}C NMR spectra were obtained using a Varian XL-100 NMR spectrometer with 12-mm tubes, at 25.2 MHz with proton noise decoupling. Chemical shifts (δ_C) in parts per million were determined relative to external hexadeuterioacetone (5-mm concentric tube in 12-mm sample tube) and converted to the Me_4Si scale using $\delta_{\text{acetone-}d_6}$ 29.2. The ^2H resonance of acetone-d_6 was used for field-frequency lock. A high-power pulse amplifier supplied 68° rf pulses of 22 μs at 1-s intervals. The free induction decays were averaged in a Varian 620 i computer employing a 5500-Hz sweep width in 8192 data points. When necessary definitive assignments were obtained by comparing the nondecoupled spectra with the spectra that were made by single frequency decoupling at low power, with the decoupler frequency set at the value for each individual proton resonance.

Acknowledgments. The authors are indebted to Dr. J. W. Verhoeven for many helpful discussions in the course of this research. We also acknowledge Professor H. Wynberg and Dr. P. H. Gore for samples of 2,7-DMN and Mr. C. Kruk and Mr. R. H. Fokkens for assistance in obtaining the NMR data.

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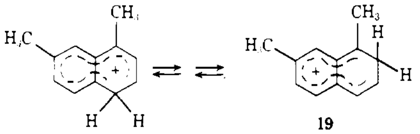

7 **19**

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Electron Transfer Reactions Involving Porphyrins and Chlorophyll *a*[1]

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Abstract: Electron transfer reactions involving porphyrins (P) and quinones (Q) have been studied by pulse radiolysis. The porphyrins used were tetraphenylporphyrin (H_2TPP), its tetracarboxy derivative (H_2TCPP), the sodium and zinc compounds (Na_2TPP and ZnTPP), and chlorophyll *a* (Chl *a*). These compounds were found to be rapidly reduced by electron transfer from $(CH_3)_2\dot{C}O^-$. Reduction by $(CH_3)_2\dot{C}OH$ was rapid in aqueous solutions but relatively slow in *i*-PrOH solutions. Transient spectra of the anion radicals were determined and, in the case of $H_2TCPP^-\cdot$, a pK = 9.7 was derived for its protonation. Electron-transfer reactions from the anion radical of H_2TCPP to benzoquinone, duroquinone, 9,10-anthraquinone 2-sulfonate, and methylviologen occur in aqueous solutions with rate constants $\sim 10^7$-10^9 M^{-1} s^{-1} which depend on the pH and the quinone reduction potential. Reactions of $Na_2TPP^-\cdot$, $ZnTPP^-\cdot$, and Chl $a^-\cdot$ with anthraquinone in basic *i*-PrOH solutions occur with rate constants $\sim 10^9$ M^{-1} s^{-1}. The spectral changes associated with these electron-transfer reactions as observed over a period of ~1 ms indicated, in some cases, the formation of an intermediate complex $[P\cdots Q^-\cdot]$.

Introduction

Electron-transfer reactions have been the subject of extensive studies in recent years. Particular attention has been drawn to those systems which bear specific relation to primary photosynthetic processes.[5-10] Two types of electron-transfer reactions are generally studies by fast kinetic techniques. In the system of porphyrins (P) and quinones (Q) these reactions are

$$P^* + Q \rightarrow P^+\cdot + Q^-\cdot \quad (1)$$

$$P^-\cdot + Q \rightarrow P + Q^-\cdot \quad (2)$$

In the first case, the donor molecule is promoted to an excited electronic state which subsequently undergoes an electron-transfer reaction with an acceptor molecule. Either the photoexcited singlet or the photoexcited triplet serves as precursor for the intermediate radical pair ($P^+\cdot Q^-\cdot$) which is formed following the excitation. It is expected that the efficiency of charge separation would be higher in the case of a triplet precursor, as indeed has been confirmed in recent studies on model compounds.[6,9-11] In bacterial photosynthesis, however, it is known that the preceding state for photochemistry is the singlet and the reason for this apparent contradiction is as yet unknown.

Another approach to the study of photosynthetic electron transfer reactions is to follow reaction 2. This type of reaction, although studied quite extensively in many systems, has rarely been applied to porphyrins and their biological analogues. It is the purpose of the present study to show some examples of electron-transfer reactions between anion radicals of various porphyrins and different acceptors in aqueous and alcoholic solutions. In the first part we discuss the reduction of porphyrins and the acid-base equilibria of some anion radicals. The second part deals with electron transfer to various acceptors. This electron transfer was found to be more complicated than that formulated in reaction 2. In order to account for our findings we invoke the possible participation of an intermediate complex $[P\cdots Q^-\cdot]$.

Experimental Section

The porphyrins used in this study were the following. Mesotetra(4-carboxyphenyl)porphyrin (H_2TCPP) was obtained from Strem Chemicals, and mesotetraphenylporphyrin (H_2TPP) from Aldrich. Zinc tetraphenylporphyrin (ZnTPP) was kindly supplied by Professor A. D. Adler, and chlorophyll *a* (Chl *a*) was extracted and purified by the method described.[12]

The H_2TCPP was used for experiments in aqueous solutions. It was dissolved (1×10^{-5} to 1×10^{-4} M) in slightly alkaline solutions (pH ~11) which were then adjusted to the pH required for the experiments. Sodium phosphates and sodium tetraborate were used as buffers for pH 6-8 and 8-10, respectively. The solutions contained also 0.1-0.4 M of 2-propanol (*i*-PrOH) or *tert*-butyl alcohol (*t*-BuOH) as scavengers for OH radicals. The alcohols and the inorganic compounds were all Baker Analyzed reagents, and the water was doubly purified by a Millipore Milli-Q system.

The other porphyrins are not sufficiently soluble in water to allow meaningful radiolytic experiments. They were, therefore, studied only in alcoholic solutions. First they were dissolved in a minimal amount of tetrahydrofuran (THF, refluxed over $LiAlH_4$ and distilled). This solution was then diluted into a large volume of *i*-PrOH. A stock solution containing ~0.1 M *i*-PrO^-Na^+, prepared by dissolving sodium metal in *i*-PrOH, was used for experiments in basic alcoholic solutions.

Since the porphyrins are quite sensitive to light, their solutions were

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