Mono- and Diprotonation of a Series of Methylphenanthrenes[1]

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A series of nine methylated phenanthrenes and 4,5-ethanophenanthrene have been protonated with FSO_3H in SO_2ClF at low temperatures and the resulting phenanthrenium monocations studied by ^1H NMR. No ipso protonation was observed at all. The observed sites of non-ipso protonation are in accordance with predictions based on the localization energies obtained by simple Hückel π-electron MO calculations. The di- and tetramethylphenanthrenes and 4,5-ethanophenanthrene in FSO_3H–SbF_5 (1:1) with SO_2ClF/SO_2F_2 (1:1) as a solvent are fully diprotonated. The substrates studied were all symmetrically substituted and all yielded a symmetrical dication with the exception of 3,4,5,6-tetramethylphenanthrene which gave (in addition to 65% of the 1,8-diprotonated species) 35% of the 1,9-diprotonated species. The positions of diprotonation are (given the symmetry of the substrate) the same as those for the monoprotonation.

The electrophilic aromatic substitution of phenanthrene[2-11] and its methyl derivatives[3,11-14] has recently attracted extensive and renewed interest. The substitution is generally considered to proceed via σ complexes as metastable intermediates (so-called Wheland-type intermediates). It was therefore thought of interest to study these intermediates under more stable conditions. The σ complexes of e.g., the nitro- and sulfodeprotonation of aromatic substrates have never been observed as such, but Cannell reported UV spectroscopic evidence for the σ complex in the electrophilic bromodesulfonation of 3,5-dibromo-4-hydroxybenzenesulfonate.[15] Only very recently we observed a room-temperature-stable σ complex in the aprotic sulfonation of both 4,6,8-trimethyl- and 7-isopropyl-1,4-dimethylazulene.[16]

The most simple σ complex intermediates to study are those of aromatic hydrogen exchange, as they are stable at low temperatures. They can be obtained by protonation of the aromatic hydrocarbon substrate in an acid of sufficiently high acidity at ca. −100 °C. The structures of the methylbenzenium, methylnaphthalenium, and methylanthracenium ions obtained on protonation of the corresponding methylbenzenes,[17] methylnaphthalenes,[18,19] and methylanthracenes,[20] as determined by NMR, were established.

The UV spectra of phenanthrene in strongly acidic media were reported.[21-23] The low-temperature spectra in HF–BF_3[21] and HSO_3F–SbF_5 (10:1)[23] are different and probably do not refer to the same (mixture of) phenanthrenium ion species. Reports on the structures of cationic species formed on protonation of phenanthrene and its methyl derivatives by use of the more valuable NMR technique are to our knowledge not available in the literature. Therefore, and in relation to our sulfonation studies,[11] we now report a ^1H NMR study on the low-temperature protonation of the methylphenanthrenes in both HSO_3F and the more acidic HSO_3F–SbF_5.

The 9,9,10-trimethylphenanthrenium ion[24] and 9,9,10-trisubstituted phenanthrenium ions,[25,26] obtained by low-temperature protonation of the corresponding 9,9-dialkyl- and 9-alkyl-9-aryl-10-alkylidene-9,10-dihydrophenanthrenes were studied with ^1H NMR by Shubin and Koptyug.

Results and Discussion

Monoprotonation. A series of ten methylphenanthrenes (MPs[27]) have been protonated in the HSO_3F–SO_2ClF solvent system at −80 °C. The ^1H NMR spectra of the resulting arenium ions showed the highest resolution at −60 °C. At higher temperatures the spectra of 4-MP and the higher methylated phenanthrenes changed gradually and irreversibly, illustrating chemical conversions. The spectral data at −60 °C and the structural assignments are given in Table I (see structure 1 for numbering). Attempts to protonate phenanthrene were not successful, probably as a result of polymerization which, with this substrate, competes effectively with the

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(27) The abbreviations P, MP, DMP, TMP, and EP stand for phenanthrene, methylphenanthrene, di- and tetramethylphenanthrene, and ethanophenanthrene, respectively.

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Table I. ^{1}H NMR Data of Phenanthrenium Ions in HSO_3F/SO_2ClF at −60 °C[a,b]

phenanthrene substituents	site of protonation	chemical shift, ppm										content of ion, %
		1	2	3	4	5	6	7	8	9	10	
1-methyl	9	2.94 (s)	7.50 (d)		8.16 (d)	8.27 (d)				4.10 (br s)	7.96 (s)	>95
3-methyl	4			3.48 (s)	4.85 (br s)							25
	9			3.29 (s)						4.35 (br s)		75
4-methyl[c]	1	4.77 (br s)	8.71 (d)	7.97	3.58 (s)							70
	10[d]				3.46 (s)						4.55 (br s)	30
9-methyl	10									3.09 (s)	4.44 (br s)	>95
1,8-dimethyl	4	3.47 (br s)	8.09 (d)	8.94 (d)	5.26 (br s)	8.60 (d)	7.95 (t)	7.9	2.92 (s)	8.45 (s)	8.45 (s)	>95
4,5-dimethyl	1	4.89 (br s)	8.66 (d)[e]		3.10 (d, J = 2.8 Hz)	2.77 (s)				8.37 (d)[e]		80
	9	8.79 (d)			2.70 (s)	2.87 (s)				4.50 (br s)		20
4,5-ethano	1	4.96 (br s)	8.76 (d)[e]		3.87 (br s)	3.6				8.81 (d)[e]		88
	9				3.6	3.6				4.60 (br s)		12
9,10-dimethyl	1	4.45 (d)								2.97 (s)	2.46 (s)	33
	4	8.67 (d)	8.28 (m)	8.67 (d)	4.85 (br s)	8.28 (d)				2.65 (br s)	2.65 (br s)	67
2,4,5,7-tetramethyl	1	4.77 (br s)	2.81 (s)	7.80 (s)[e]	2.99 (br s)	2.70 (s)	7.45 (s)	2.70 (s)	7.93 (s)[e]	8.48 (d)	7.84 (d)	>95
3,4,5,6-tetramethyl	1	4.84 (br s)	8.18 (s)[e]	2.75 (s)	2.99 (br s)	2.57 (s)	2.67 (s)	7.89 (d)	8.14 (d)	8.57 (d)[e]	7.89 (d)	>95

[a] All the ortho $J_{H,H}$'s are ca. 8 Hz. [b] The unassigned absorptions of protonated 1-, 3-, 4-, and 9-MP, 4,5- and 9,10-DMP, and 4,5-EP are in the ranges 7.7–8.0, 7.5–9.0, 7.5–9.0, 7.1–8.5, 7.7–8.3, 7.8–8.3, and 7.8–8.2 ppm, respectively. [c] 4-MP contained some phenanthrene as an impurity, as evidenced by field-desorption mass spectrometry. [d] With 4-MP, the 9-position as the site of protonation cannot be excluded by the NMR data. However, the 10-position is preferred in view of the lower localization energy.[11] [e] The assignment may be the reverse.

Table II. Protonation of Methylphenanthrenes

phenanthrene substituents	sites of protonation (%)		
	mono		
	obsd	predicted by MO calculations[a]	di
		9 > 1 >> 4 >> others	
1-methyl	9 (>95)	*1* >> 9 ≈ 4 >> others	
3-methyl	4 (25), 9 (75)	*3* >> 4 ≈ 9 >> others	
4-methyl	1 (70), 10 (30)	*4* >> 1 >> 10 > 9 >> others	
9-methyl	10 (>95)	*9* >> 10 >> others	
1,8-dimethyl	4 (>95)	*1* >> 9 ≈ 4 >> others	4 + 5 (>95)
4,5-dimethyl	1 (80), 9 (20)	*4* >> 1 >> 9 >> others	1 + 8 (>95)
4,5-ethano	1 (88), 9 (12)		1 + 8 (>95)
9,10-dimethyl	1 (33), 4 (67)	*9* >> 1 >> 4 >> others	
2,4,5,7-tetramethyl	1 (>95)	*4* >> 1 >> *2* >> others	1 + 8 (>95)
3,4,5,6-tetramethyl	1 (>95)	*5* >> *3* >> 1 >> 9 > others	1 + 8 (65), 1 + 9 (35)

[a] The reactivity order was obtained from the complete list of localization energies given in ref 11. The peri positions are italicized. The signs ≈, >, and >> correspond with $0.00 < \Delta L^+ < 0.07\beta$, $0.07\beta < \Delta L^+ < 0.30\beta$, and $0.30\beta < \Delta L^+$, respectively.

Table III. ^{1}H NMR Data of Dications Resulting from Diprotonation of Methylphenanthrenes in HSO_3F–$SbF_5/SO_2ClF/SO_2F_2$ at −60 °C[a]

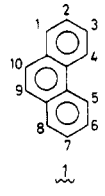
phenanthrene substituents	sites of protonation	chemical shifts, ppm										content of dication, %
		1	2	3	4	5	6	7	8	9	10	
1,8-dimethyl	4 + 5	3.88 (s)	8.81 (d)	9.97 (d)	5.50 (br s)					9.26 (s)		>95
4,5-dimethyl	1 + 8	5.59 (br s)	9.76 (d)	8.60 (d)	3.58 (br s)					8.79 (s)		>95
4,5-ethano	1 + 8	5.63 (br s)	9.72 (d)	8.65 (d)	4.49 (br s)					9.06 (s)		>95
2,4,5,7-tetramethyl	1 + 8	5.30 (br s)	3.24 (s)	8.34 (s)	3.35 (br s)					8.55 (s)		>95
3,4,5,6-tetramethyl	1 + 8	5.49 (br s)	8.83 (s)	2.94 (s)	3.37 (br s)					8.67 (s)		65
	1 + 9[b]	5.49 (br s)	9.29 (s)	*c*	3.26 (br s)	*c*	*c*	8.52 (d)	9.69 (d)	5.68 (br s)	9.34 (s)	35

[a] All the ortho $J_{H,H}$'s are ca. 8 Hz. [b] The diprotonation at the positions 1 + 10 cannot be excluded; however, it is much less likely, as the charge dissipation in the resulting dication will be less than in the one resulting from the 1 + 9 diprotonation. [c] Three methyl absorptions at 3.00, 3.50, and 3.65 ppm.

Table IV. Quenching Products of Phenanthrenium Monocations

phenanthrene substituents	site of protonation	content of ion, %	quenching products, assayed by FDMS (m/z, rel signal intens)	
			at zero time at −80 °C	after NMR measurement at −40 °C
1-methyl	9	>95	MP (192, 100)	MP (192, 90), P (178, 10)
3-methyl	4	25	MP (192, 100)	MP (192, 100)
	9	75		
4-methyl[a]	1	70	MP (192, 55); P (178, 40)[a]	(291,[b] 70), (173, 10), (157, 20)
	10[c]	30		
9-methyl	10	>95	MP (192, 100)	
1,8-dimethyl	4	>95	DMP (206, 100)	DMP (206, 80), MP (192, 5), P (178, 15)
4,5-dimethyl	1	80	DMP (206, 100)	
	9	20		
4,5-ethano	1	88	4,5-EP (204, 90), P (178, 10)	
	9	12		
9,10-dimethyl	1	33	DMP (206, 5), (172, 70)	(291,[b] 40), (157, 40), (425, 20)
	4	67		
2,4,5,7-tetramethyl	1	>95		(291,[b] 40), (157, 40), (425, 20)
3,4,5,6-tetramethyl	1	>95	TMP (234, 5), (172, 70)	

[a] 4-MP contained some phenanthrene as an impurity, as evidenced by field-desorption mass spectrometry. [b] The m/z 291 corresponds with in the mass spectrometer protonated dimethyldihydrophenanthrenesulfonyl fluoride. [c] With 4-MP, the 9-position as the site of protonation cannot be excluded by the NMR data. However, the 10-position is preferred in view of the lower localization energy.[11]



protonation. The assignments are based in part on Brouwer's observation in the benzene series that the chemical shift of both the ring hydrogens and the methyl hydrogens increase in the order "meta" < "ortho" < "para" with respect to the methylene group resulting from protonation.[17] Further, protonation "para" to a methyl group, as with 4-MP, 1,8-DMP, 2,4,5,7-TMP and 3,4,5,6-TMP, is apparent from the significant broadening of the signal of this methyl, due to long-range coupling ($^6J_{H,H}$) of the methylene hydrogens, similarly as observed with 1-methylnaphthalenes protonated at C(4) for which $^6J_{H,H}$ = 2.8 Hz.[18] This coupling was in fact observed on the 4-methyl signal of the cation resulting from protonation of 4,5-DMP at the 1-position. The protonation "para" to a methyl group is known to lead to a higher degree of stabilization of the arenium ion by hyperconjugation than protonation "ortho" or "meta" to this methyl.[28]

The localization energies (L_r^+) of the various positions (r) of the methylphenanthrenes, which are a measure for the relative stabilities of the various arenium ions, were calculated with the simple Hückel MO treatment by utilizing the inductive model for the methyl substituent with $\delta\ \alpha_r = -0.3$.[11] The Hückel MO calculations indicate a preference for ipso protonation (Table II). Ipso protonation has in fact not been observed with any of the MPs studied. Only for 2,4,5,7-TMP is the degree of protonation at the 1-positions predicted to be between those at the ipso positions 2 and 4. It should therefore be recalled that the protonated center is neglected in the Hückel-type MO calculation which results in overestimating the degree of ipso attack.[31]

The observed order of monoprotonation of the non-ipso positions is, in general, in full agreement with the predicted order of protonation. For 3-MP and 9,10-DMP the calculations predict the observed positions of protonation, but in the reversed order. Only with 1,8-DMP is the protonation observed predominantly at the 4-position,[32] whereas the MO calculations favor the 9-position somewhat over the 4-position. The substantially higher degree of observed 4-protonation with 1,8- and 9,10-DMP as compared with the predicted one may be explained in terms of a relief of steric strain between the 4-H and 5-H in the starting substrate on protonation at the 4-position which is not accounted for by the MO calculations.[33]

Diprotonation. The di- and tetramethylphenanthrenes in the HSO_3F–SbF_5 (1:1)/SO_2ClF/SO_2F_2 solvent system at −80 °C are diprotonated. This follows from both the reduction in the number of and the increase in the chemical shhifts of the ^1H NMR signals, as compared with the monocations. Phenanthrene and the monomethylphenanthrenes failed to yield stable dications. The NMR data and the assignments are given in Table III. Again protonation "para" to a methyl group manifests itself by the broadening of the methyl signal.

The dications formed from the symmetrically substituted DMPs and TMPs are again symmetrical in that they possess a mirror plane through the middle of the C(9)–C(10) bond, perpendicular to the plane of the carbon framework, but this is not true for 3,4,5,6-TMP which also yields the nonsymmetrical dication, resulting from 1,9-diprotonation.

The sites of diprotonation are the same as those observed in the monoprotonation. The symmetrical diprotonations and the diprotonation of 3,4,5,6-TMP at positions 1 and 9 lead to a maximal charge dispersion over the whole carbon framework, just as in the dication resulting from the diprotonation of 1,2,3,6,7,8-hexahydropyrene at positions 4 and 9.[19]

Quenching of the Cations. The mono- and dication reaction mixtures have been quenched by addition to a precooled $NaHCO_3$–methanol mixture, and the organic material has been analyzed qualitatively by using field

(28) The enhanced stabilizing effect of the "para" methyl in the toluenium ions was recently established by Hehre[29] and Mulliken.[30]

(29) J. L. Devlin III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976).

(30) W. C. Ermler and R. S. Mulliken, *J. Am. Chem. Soc.*, **100**, 1647 (1978).

(31) See ref 21 and in particular ref 27 of that paper.

(32) With 1,8-DMP the 9-position can be rigorously excluded as the site of protonation in view of the observed splitting pattern and relative intensities of the NMR signals of the cation (cf. Table I).

(33) Because of the overcrowding between 4-H and 5-H, phenanthrene itself is in fact slightly distorted from complete coplanarity.[34]

(34) J. Trotter, *Acta Crystallogr.*, **16**, 605 (1963).

desorption mass spectrometry (FDMS). It should be realized that relative peak intensities with FDMS as such are not a quantitative measure for the relative concentrations of the various components in the sample analyzed[11] and that usually at the best anode temperature for desorption the peak of the component with the lower molecular weight and thus with the higher volatility prevails, relative to the others.

The FDMS data of the quenched solutions of the monocations are given in Table IV. They show in most cases the regenerated starting hydrocarbons, as evidenced from its molecular ion $ArH^{+\cdot}$, to be the predominant components. For 1-MP, 4-MP, 1,8-DMP, and 4,5-EP the presence of the m/z 178 signal is compatible with the presence of phenanthrene, illustrating dealkylation. With the monocation of 9,10-dimethylphenanthrene, no starting hydrocarbon was found, but among others a signal at m/z 291 was observed, probably from a protonated 9,10-dimethyl-9,10-dihydrophenanthrenesulfonyl fluoride. No evidence was found in any of these cases for the presence of methoxy addition compounds, illustrating that the methoxide addition is the slower process.

From the quenched solutions of the dications, the presence of the regenerated starting substrate and a dimeric product could be established only with 4,5-DMP [m/z 206 ($M^{+\cdot}$, 40%) and 411 ($(M' + 1)^{+\cdot}$, 15%)] and 2,4,5,7-TMP [m/z 234 ($M^{+\cdot}$, 20%) and 464 $(M')^{+\cdot}$, 80%)], where $M' = 2M - 2$.

Experimental Section

The origin of the methylphenanthrenes was described elsewhere.[11] Fluorosulfuric acid (Fluka), "magic" acid (HSO_3F–SbF_5, 1:1), SO_2ClF (both Aldrich), and SO_2F_2 (Matheson) were commercial products, used without purification.

The ^1H NMR spectral data of the starting methylphenanthrenes were reported previously.[11]

Preparation of Monocations. FSO_3H (1.0 mL) cooled to −78 °C was added to a cooled slurry of 100 mg of the phenanthrene in ca. 2 mL of SO_2ClF at −100 °C with efficient stirring in order to avoid local heating. The viscous solution was then allowed to warm slowly to −80 °C with vigorous mixing, whereby a reddish brown homogeneous solution was obtained. After ca. 0.5 mL of the solution was transferred into an NMR tube cooled to −100 °C, the remaining solution was quenched at −80 °C by pouring it into a solution of sodium bicarbonate (1 g) in methanol (20 mL). The quenched solution was then allowed to warm slowly to room temperature and was filtered, and the methanol was evaporated. The residue was subjected to field desorption mass spectroscopy (FDMS) by using a Varian MAT 711 double-focussing mass spectrometer with a combined EI/FI/FD source. The samples were dissolved in a little dimethyl sulfoxide and then brought onto the emitter (10-μm activated tungsten wire) by the dipping technique. In most cases the emitter current required to desorb the sample was ca. 18 mA.

The ^1H NMR spectra of the cations were recorded on a Varian XL-100 spectrometer, equipped with a variable-temperature probe, initially at −80 °C and by increasing the temperature and recording one spectrum at 10 °C intervals until decomposition was observed or the temperature of the probe reached −30 °C. The NMR tube was then removed from the probe, similarly quenched in a sodium bicarbonate–MeOH mixture cooled at −80 °C, and after the workup (see before) subjected to FDMS.

Preparation of Dications. To a cooled slurry of 100 mg of the phenanthrene in 2 mL of SO_2ClF at ca. −100 °C was added "magic" acid (ca. 1 mL) dissolved in SO_2F_2 (ca. 1 mL) with efficient stirring in order to avoid local heating. The solution was then allowed to warm up slowly to −80 °C with vigorous mixing. The color at the solid interface was blue, and after mixing a homogeneous dark green or light brown solution resulted. The solution was then transferred into a precooled NMR tube, as described for the monocations. The first spectrum was normally recorded at −80 °C and the others at 10 °C intervals upward thereafter until the probe temperature was −50 °C (a further increase in temperature was not attempted due to the presence of very volatile SO_2F_2).

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Registry No. 1-Methylphenanthrene, 832-69-9; 3-methylphenanthrene, 832-71-3; 4-methylphenanthrene, 832-64-4; 9-methylphenanthrene, 883-20-5; 1,8-dimethylphenanthrene, 7372-87-4; 4,5-dimethylphenanthrene, 3674-69-9; 4,5-ethanophenanthrene, 6628-98-4; 9,10-dimethylphenanthrene, 604-83-1; 2,4,5,7-tetramethylphenanthrene, 7396-38-5; 3,4,5,6-tetramethylphenanthrene, 7343-06-8; 9-protonated 1-methylphenanthrene cation, 84498-70-4; 4-protonated 3-methylphenanthrene cation, 84498-71-5; 9-protonated 3-methylphenanthrene cation, 84498-72-6; 1-protonated 4-methylphenanthrene cation, 84498-73-7; 10-protonated 4-methylphenanthrene cation, 84498-74-8; 10-protonated 9-methylphenanthrene cation, 84498-75-9; 4-protonated 1,8-dimethylphenanthrene cation, 84498-76-0; 1-protonated 4,5-dimethylphenanthrene cation, 84498-77-1; 9-protonated 4,5-dimethylphenanthrene cation, 84498-78-2; 1-protonated 4,5-ethanophenanthrene cation, 84498-79-3; 9-protonated 4,5-ethanophenanthrene cation, 84498-80-6; 1-protonated 9,10-dimethylphenanthrene cation, 84498-81-7; 4-protonated 9,10-dimethylphenanthrene cation, 84498-82-8; 1-protonated 2,4,5,7-tetramethylphenanthrene cation, 84498-83-9; 1-protonated 3,4,5,6-tetramethylphenanthrene cation, 84498-84-0; 4,5-diprotonated 1,8-dimethylphenanthrene dication, 84498-85-1; 1,8-diprotonated 4,5-dimethylphenanthrene dication, 84498-86-2; 1,8-diprotonated 4,5-ethanophenanthrene dication, 84498-87-3; 1,8-diprotonated 2,4,5,7-tetramethylphenanthrene dication, 84498-88-4; 1,8-diprotonated 3,4,5,6-tetramethylphenanthrene dication, 84498-89-5; 1,9-diprotonated 3,4,5,6-tetramethylphenanthrene dication, 84520-41-2.