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AROMATIC PROTONATION—PART 2

^{1}H NMR PARAMETERS OF THE ANTHRACENIUM IONS OF SOME 9-ALKYL-, 9-ALKYL-α-CHLORO-, 9,10-DIALKYL-ANTHRACENES AND 1-CHLOROANTHRACENE. STUDY ON THE SITE OF PROTONATION AND ON THE GEOMETRY OF THE ANTHRACENIUM IONS

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Abstract—Seventeen 9-alkylanthracenes (**1–17**) and 1-chloroanthracene have been protonated with FSO_3H in SO_2ClF as cosolvent at −78°. For all substrates C(10) protonation was observed, but with some substrates in addition C(9) protonation, if that would lead to relief of steric strain between the substituent at C(9) and the substituent(s) at C(1) [and C(8)]. The C(9) protonated ions exist in the preferred conformation **IIa**. The ions resulting on *ipso*-protonation of the 9,10-dialkyl-anthracenes have a similar type of conformation. Based both on this preferred conformation and the *peri*-chloro effects of the anthracenium ions, it is concluded that these ions are best represented by the equilibirum **IIa** ⇌ **IIb**.

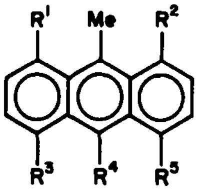
In reactions with dioxan-SO_3 a number of differences in reaction behaviour were observed between some 9-alkylanthracenes on the one hand and 9-alkylanthracenes with one or more Cl atoms at α-positions on the other hand. For example, 9-ethylanthracene yielded two sulphonic acids, viz. 1-(9'-anthryl)ethane-1-sulphonic acid and (*E*)-(9'-anthryl)ethenesulphonic acid,[2] whereas 1-chloro-9-ethylanthracene led to the formation of a dimerization type of product.[3] The difference in product formation could be explained by the assumption that initial electrophilic attack of SO_3 is at C(10) for 9-ethylanthracene and at C(9) for 1-chloro-9-ethylanthracene. It is well established that arenium ions are intermediates in aromatic substitution and we therefore thought it of interest to study the protonation of the above-mentioned substrates.

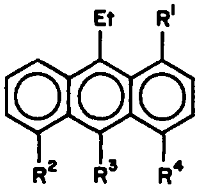
The number of studies on the protonation of anthracene and derivatives is limited.[4–6] Recently Olah reported[4] on the protonation of 9-substituted anthracenes which all yielded C(10) protonated ions. The only example of protonation at C(9) was for 1,4,5,8,9-pentamethylanthracene.[5]

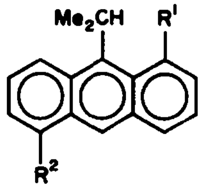
RESULTS

The 9-alkylanthracenes (**1–16**, see compound sheet), 9-propylanthracene (**17**) and 1-chloranthracene (**18**) have been protonated with FSO_3H in SO_2ClF as cosolvent at −78°. ^{1}H NMR spectra of the obtained mixtures were recorded at −40°. The ^{1}H NMR parameters (Tables 1–4) indicate that all investigated substrates (**I**) are protonated at C(10), leading to the ions **Ia**.

The substrates 9-ethyl-10-methyl-(**3**), 1,8-dichloro-9-methyl-(**7**), 1-chloro-9-ethyl-(**10**), 1,5-dichloro-9-ethyl-(**12**), 1-chloro-9-isopropyl-(**15**) and 1,5-dichloro-9-isopropyl-anthracene (**16**) yield in addition ions **Ib** resulting from protonation at C(9). The ratios between the anthracenium ions **Ia** and **Ib**, obtained from the latter five substrates, decreases upon increasing the temperature from −40° to −20°.*







	R^1	R^2	R^3	R^4	R^5		R^1	R^2	R^3	R^4		R^1	R^2
1	H	H	H	H	H	**8**	H	H	H	H	**14**	H	H
2	H	H	H	Me	H	**9**	H	H	Et	H	**15**	Cl	H
3	H	H	H	Et	H	**10**	Cl	H	H	H	**16**	Cl	Cl
4	H	Cl	H	H	H	**11**	H	H	H	Cl			
5	H	Cl	Cl	H	H	**12**	Cl	Cl	H	H			
6	H	H	Cl	H	Cl	**13**	H	Cl	H	Cl			
7	Cl	Cl	H	H	H								

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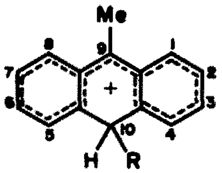
*For the protonation of 3, the variation of the ratio of the ions **3a** and **3b** in HF with temperature was studied extensively by Brouwer.[6]

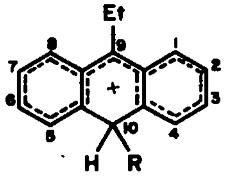
Table 1. ^1H NMR parameters of 9-methyl-10-anthracenium ions



Carbenium ion			Chemical shifts[a] (p.p.m.) and multiplicities						
R	substituents		H(1)[b]	H(8)[b]	H(10)	CH_3	R=H	H-C(α)[c]	H-C(β)[c]
H		1a	8.86	8.86	5.00(s)	3.68(s)	5.00(s)		
Me		2a	8.83	8.83	4.98(m)	3.67(s)		1.71(d,J=7Hz)	
Et		3a	8.93	8.93	5.1(m)	3.76(s)		2.67(m)	0.46(t,J=7Hz)
H	1-Cl	4a		8.86	5.07(s)	3.98(s)	5.07(s)		
H	1,5-Cl_2	5a		8.86	5.08(s)	4.04(s)	5.08(s)		
H	4,5-Cl_2	6a		8.86	5.00(s)	3.90(s)	5.00(s)		
H	1,8-Cl_2	7a			5.00(s)	4.14(s)	5.00(s)		

[a] The absorptions for the protons H(2,3,4,5,6,7) (if present) exhibit multiplets in between 8.8-7.8 p.p.m. [b] All doublets with J=8Hz. [c] The notation H-(γ) refers to the protons at C (γ) of the alkyl group R[C(10)-C(α)-C(β)].

Table 2. ^{1}H NMR parameters of 9-ethyl-10-anthracenium ions

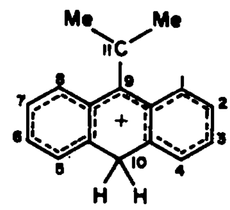


Carbenium ion			Chemical shifts^a (p.p.m.) and multiplicities							
R	substituents		H(1)^b	H(8)^b	H(10)	CH$_2$^{c}	CH$_3$^{d}	R=H	H-C(α)^e	H-C(β)^e
H		8a	8.95	8.95	5.14(s)	4.22	1.84	5.14(s)		
Me		3b	8.91	8.91	5.1(m)	4.14	1.84		1.80(d,J=7Hz)	
Et		9a	8.84	8.84	5.16(t,J=4Hz)	4.12	1.86		2.57(m)	0.21(d)
H	1-Cl	10a		8.91	5.10(s)	4.47	1.85	5.10(s)		
H	4-Cl	11a	ca.8.9	ca.8.9	5.06(s)	4.21	1.83	5.06(s)		
H	1,5-Cl$_2$	12a		8.95	5.13(s)	4.56	1.92	5.13(s)		
H	4,5-Cl$_2$	13a	9.04	9.04	5.00(s)	4.30	1.89	5.00(s)		

[a,b] See the corresponding subscript of Table 1. [c] All quartets with J=7Hz. [d] All triplets with J=7Hz.

[e] See subscript [c] of Table 1.

Table 3. ^{1}H NMR parameters of 9-isopropyl-10-anthracenium ions



Carbenium ion		Chemical shifts[a] (p.p.m.) and multiplicities				
Substituent		H(1)[b]	H(8)[b]	H(10)	H(11)	CH_3
	14a	9.09	9.00	4.89(s)	4.86(m)	2.04(d,J=7Hz)
1-Cl	**15a**		9.05	4.99(s)	4.91(m)	2.03(d,J=7Hz)
1,5-Cl_2	**16a**		9.04	4.99(s)	4.93(m)	2.03(d,J=7Hz)

[a,b] See the corresponding subscripts of Table 1.

More detailed studies on the temperature dependence have been carried out with the mixtures resulting on protonation of 7 and 12. At temperatures below *ca.* −40° exclusively the ions **ia** are formed. Upon cooling a mixture of **ia** and **ib** from −20° to −80° it appeared that at −80° no reformation of **ia** from **ib** takes place. It further appeared that with each of the two substrates different ratios of the ions **ia** to **ib** were found for "differently prepared" protonating mixtures.[§]

The protonation of 9-propylanthracene (17) with FSO_3H yielded the C(10) protonated anthracenium ion (**17a**) {^{1}H NMR: 8.86[d, $J = 8$ Hz, H(1, 8)], 8.5–7.8[m, H(2,3,4,5,6,7)], 5.09[s, $H_2C(10)$], 4.09[m, protons at C(α)], 2.14[m, protons at C(β)] and 1.44[t, $J = 7$ Hz, Me protons]}. On lowering the temperature from −20° to −85°, the ring methylene absorption of **17a** (at 5.09 ppm) broadens, and remains unresolved, even in a 360 MHz spectrum. This broadening, however, is larger than the band width broadening due to the increase of the viscosity of the solution, as can be seen by comparing the half-width of this band with those of the other absorptions of the same sample.

1-Chloroanthracene (**18**) on protonation yielded two different ions, viz. **18a** protonated at C(10) {^{1}H NMR: 10.46[s, H(9)], 5.21[s, $H_2C(10)$], 8.8–8.0(m, other aromatic protons)}, and **18b** protonated at C(9) {10.06[s, H(10)], 5.13[s, $H_2C(9)$], 8.8–8.0(m, other aromatic protons)} in a ratio of *ca.* 0.11. These assignments are based on the absorptions at 10.46 and 10.06 which on the basis of the *peri*-chloro effect (see Discussion) are ascribed to H(9) of **18a** and H(10) of **18b** respectively.

The ^{1}H NMR data of the carbenium ions obtained from 9-methyl-, 9 - ethyl-, 9,10 - dimethyl- and 9 - ethyl - 10 - methyl - anthracene (by protonation in HF) were reported by Brouwer[6] and the ^{13}C NMR data of the ions of the first two substrates (by protonation with FSO_3H) by Olah.[4] The ^{1}H NMR data of these four ions have also been ascertained in the presently employed solvent mixture and have been included for comparison with the other presently investigated substrates.

DISCUSSION

Position of protonation. From a protiodetritiation study on anthracene[7] it appeared that the 9-position is far more reactive than the 1- and 2-positions, the partial rate factors being 1.27 × 10^7, 7.900 and 1.135 respectively. Protonation of anthracene occurs exclusively at C(9).[4] For the 9 - alkyl- and 9,10 - dialkyl - anthracenes electrophilic attack is expected to take place at C(10) as the then resulting carbenium ions are stabilized hyperconjugatively by the 9-alkyl group. In fact with 9-methyl-, 9-ethyl-, 9-propyl- and 9-isopropyl - anthracene C(10) protonation is observed, and with 9,10 - dimethyl-, 9,10-diethyl- and 9 - ethyl - 10 - methyl - anthracene *ipso*-protonation.

Besides effects of stabilization by alkyl substituents steric effects are of importance in determining the site of protonation. For example, protonation of **18** yields two both "secondary" carbenium ions, viz. for *ca.* 90% **18b**, which results on protonation at C(9) and for *ca.* 10% **18a**, which results on protonation at C(10). Despite the mesomeric stabilization of the positive charge in **18a** by the 1-chloro substituent which is absent in **18b**, the ratio of **18a** to **18b** is *ca.* 0.11. The preference for the carbenium ion **18b** over **18a** is ascribed to a predominating steric effect, viz. relief of steric strain between H(9) and the chlorine-atom on forming ion **18b** (*cf* Ref. 8). Thus, the steric interactions of a chloro substituent at an α-position of the anthryl group are of greater importance than its electronic effects in determining the site of protonation.

At temperatures above −40° 1,5 - dichloro - 9 - ethylanthracene (**12**) yields two carbenium ions, viz. **12a**, protonated at C(10), and **12b** protonated at C(9). The formation of both these ions is the result of competition between the mesomeric stabilization of the resulting carbenium ion (in **12a** "tertiary" and in **12b** "secondary") and the stabilization as result of relief of steric strain (between chloro and ethyl on forming **12b** vs between chloro and hydrogen on forming **12a**). The formation of **12b**, despite the preference of a carbenium ion being tertiary rather than secondary, illustrates the importance

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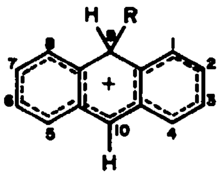
[§] No **ia** to **ib** ratios are reported in this paper in view of the large variations in the **ia** to **ib** ratios observed both for "differently prepared" protonating mixtures (which infers different quantities of FSO_3H and SO_2ClF relative to the aromatic substrate) and for different temperatures.

Table 4. ^1H NMR parameters of 9-alkyl-9-anthracenium ions



Carbenium ion		Chemical shifts[a] (p.p.m.) and multiplicities						
Substituents		H(4)	H(5)	H(9)	H(10)	H-C(α)[b]	H-C(β)[b]	H-C(α')[b]
e 1,8-Cl_2	<u>7b</u>	8.66(d,J=8Hz)	8.66(d,J=8Hz)	5.69(q,J=7Hz)	9.95(s)	1.73(d,J=7Hz)		
t 1-Cl	<u>10b</u>	ca.8.6	ca.8.5	5.49(t,J=5Hz)	9.84(s)	2.63(m)	0.30(t,J=7Hz)	
t 1,5-Cl_2	<u>12b</u>	8.63(d,J=8Hz)		5.56(t,J=5Hz)	10.35(s)	2.65(m)	0.42(t,J=7Hz)	
Pr 1-Cl	<u>15b</u>	8.52(d,J=8Hz)	8.64(d,J=8Hz)	5.40(d,J=3Hz)	9.87(s)	3.03(m)	0.06(d,J=7Hz)	1.57(d,J=7Hz)
Pr 1,5-Cl_2	<u>16b</u>	8.58(d,J=8Hz)		5.39(d,J=3Hz)	10.29(s)	ca.3.1(m)	0.10(d,J=7Hz)	1.54(d,J=7Hz)

The protons H(1,2,3,4,5,8) (if present) exhibit multiplet absorptions in between 8.8-7.8 p.p.m.

The notation H-C(γ) refers to the protons at C(γ) of the alkyl group R $[C(9)-\underset{\displaystyle C(\alpha')}{\underset{|}{C}}(\alpha)-C(\beta)]$.

of the relief of steric strain between the ethyl and the chloro substituent.

From the study on the temperature dependence on the composition of the protonation mixtures of 7 and 12 it follows that the formation of the ions 7a and 12a is kinetically controlled, but that 7b and 12b are the thermodynamically most stable ions. The same applies in all likelihood to the ions resulting from 10, 15 and 16.

For similar reasons as just given for 12, 1 - chloro - 9 - ethylanthracene (10) also yields two carbenium ions (10a and 10b). There exists no steric strain between the chloro- and the ethyl -group in 4- and 4,5 - di - chloro - 9 - ethylanthracene (11 and 13 respectively) and these substrates do yield, just like 9-ethylanthracene, exclusively the C(10) protonated ions 11a and 13a.

1-Chloro- and 1,5 - dichloro - 9 - methylanthracene (4 and 5 respectively) yield, just like 9-methylanthracene, only the tertiary [C(10) protonated] carbenium ions. Apparently the relief of steric strain which would result on C(9) protonation of 4 and 5 (both having one *peri* methyl-chloro interaction) is not sufficiently large to obtain the less stable secondary [C(9) protonated] ion. This relief of steric strain becomes sufficiently large with 1,8 - dichloro - 9 - methylanthracene (7), which has two *peri* methyl-chloro interactions as now in addition to the ion 7a the ion 7b is formed. In accordance with the behaviour of 13, 4,5 - dichloro - 9 - methylanthracene (6) only yields the C(10) protonated carbenium ion 6a.

The two chlorinated 9-isopropylanthracenes 15 and 16 yield both the C(10) and the C(9) protonated carbenium ions, again as the result of relief of steric strain between the 9-isopropyl and 1-chloro substituents.

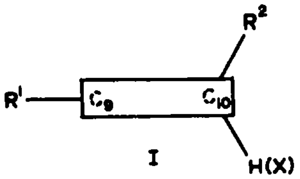
At very low temperatures the protonation of the 9-alkylanthracenes only takes place at C(10) yielding the ions Ia. The occurrence of the two types of ions Ia and Ib at higher temperatures is the result of the conversion of Ia into Ib. The variation in the ratio of these two ions for the "differently prepared" protonating mixtures of a given substrate at a given temperature is ascribed to differences in the FSO_3H concentration. This conversion is accordingly an intermolecular process and proceeds by $\mathrm{Ia} \rightleftharpoons \mathrm{I} + H^+ \rightarrow \mathrm{Ib}$.

On the geometry of the anthracenium ions. The structure of the anthracenium ions will be discussed as to the geometry of the central ring on the basis of the two possible structures, suggested for the 4-methylbenzenium ion from ^1H NMR studies,[9] viz. a close to planar cyclohexadienyl ring system, and two—even at −115° rapidly equilibrating—nonplanar cyclohexadienyls. As to the anthracenium ions the former conforms to a close to planar dibenzocyclohexadienyl system (I) with all its substituents in the molecular plane with exception of those at the sp^3 C(10) [or C(9)] which are above and below that plane, as shown in I,[c] whereas the latter conforms with the equilibrium IIa⇌IIb.[c]

In the 360 MHz ^1H NMR spectrum of 9-propylanthracene at −85° no fine structure of the ring methylene absorption was observed; this in in agreement with both these structural possibilities.

In the anthracenium ions under study there is a difference in chemical shift between the proton [or the α-proton(s) of an alkyl substituent] at C(9) or C(10) which has (have) a chloro- and which has (have) a hydrogen-substituent at the neighbouring α-position of the anthryl group. This so called *peri*-chloro effect[10] is mainly due to the very small distance between the substituent and the *peri* Cl-atom,[d] the distance between C(9) and C(1) in anthracene being only 2.40 Å, i.e. equal to the sum of the van der Waals radii of two hydrogens.[12] The *peri*-chloro effects for the different substituents are expressed as the differences in the chemical shifts of the appropriately chosen substrates. The *peri*-chloro effects for the anthracene derivatives (*cf* Table 5) amount to 49 Hz for hydrogen,[e] 31 Hz for methyl,[e] 40 Hz for the CH_2 of an Et group, and 57 Hz for the CH of the i-Pr group. It should be realized that in this approach to the *peri*-chloro effect all other effects of the substituent and any deviations from planarity of the anthracene ring are overlooked.

The *peri*-chloro effects of the proton(s) of the substituents at the unprotonated meso-carbon of the anth-



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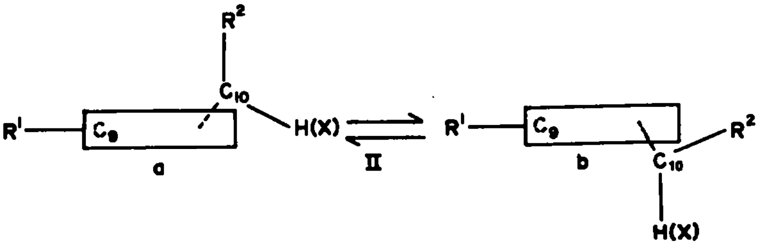

II

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[c] In I and II the numbers of C(9) and C(10) are interchangeable dependent on the site of protonation.

[d] For example the differences in ^1H chemical shifts of benzene and chlorobenzene are only small because the shift differences induced by the inductive and mesomeric effect of the chlorine atom are in opposite directions: the *ortho*-, *meta*- and *para*-hydrogens of chlorobenzene absorb at 7.25, 7.20 and 7.15 ppm respectively vs those of benzene at 7.25 ppm.[11]

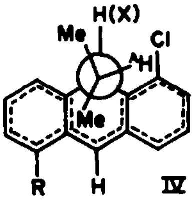
[e] If a substituent at C(9) or C(10) has two neighbouring chlorine atoms then the resulting effect of the *peri*-chlorines on hydrogen is additive, e.g. the positions of H(10) of 9-ethyl-, 4-chloro-9-ethyl- and 4,5 - dichloro - 9 - ethyl - anthracene are at 8.23, 8.67 and 9.06 ppm respectively. However, non-additivity is observed for the methyl protons of 1,8 - dichloro - 9 - methylanthracene, most likely as result of the deviation from planarity of the anthracene ring induced by the repulsion between the Me and the Cl substituents.[12]

racenium ions, determined similarly, are of the same size as those of the substrates, viz. 33, 31 and 35 Hz for hydrogen, Me and the CH_2 of an Et group respectively. However the value for the CH of the i-Pr group is only 6 Hz. The similarity of the various *peri*-chloro effects in the substrates and the anthracenium ions is thought to be related to the close geometric resemblance of the C(1)–C(9)–C(8) [or C(4)–C(10)–C(5)]moiety of the substrates and the unprotonated side of the anthracenium ions.[f] These *peri*-chloro effects of the anthracenium ions are explainable in terms of both the structures I and II and do not discriminate between them. No *peri*-chloro effect is observed on the ring methylene protons of the anthracenium ions and this is in agreement with the longer chlorine-methylene hydrogen(s) distance. This is also in agreement with both the structures I and II. If protonation of an 9-alkylanthracene occurs at C(9) a *peri*-chloro effect is found for the ring-methine proton (see later).

The spectra of the ions **9a**, **10b** and **12b** exhibit, just like the spectrum of **3a**,[6] a number of remarkable features: (i) the Et-Me groups are unusually strongly shielded and appear at a field as high as *ca.* 0.36 ppm and (ii) the coupling between the C(10)H and the CH_2 protons is rather weak (*ca.* 5 Hz). These features can be accounted for by assuming the conformation III (shown in Newman projection along the $MeCH_2$–C(9)H bond) to be the strongly preferred one, as proposed by Brouwer for **3a** (for an extensive discussion on this subject, see Ref.[6]). Brouwer observed a comparable shielding of the Et-Me protons of the aliphatically bonded Et group of the hexaethylbenzenium ion as in **3a**. He attributed this shielding primarily to the conjugated π-electron system of the central ring rather than to the ring currents of the adjacent rings. Our observation of a triplet splitting of the protons H(X) in the ions **9a**, **10b** and **12b** infers equal values for J_{AX} and J_{BX}, which indicates that the two dihedral angles are (about) equal. This triplet splitting pattern is explainable in terms of conformation III; it thus supports Brouwers proposition that the shielding of the Et-Me protons is attributed primarily to the conjugated π-electron system of the central ring.

In the preferred conformation III of the ions **3a**, **9a**, **10b** and **12b** the proton H(X) will be in the plane defined by the carbons C(1), C(8) and their substituents and accordingly a *peri*-chloro effect should be possible for H(X). This is in fact observed as the chemical shifts of H(X) for **3a** and **9a** are at 5.1 and 5.16 ppm respectively, whereas in **10b** and **12b** they are at 5.49 and 5.56 ppm respectively. A *peri*-chloro effect on H(X) is also apparent on comparing the anthracenium ion **7b** with **2a** and **3b** obtained respectively from 1,8-dichloro-9-methyl-, 9,10-dimethyl- and 9-ethyl-10-methyl-anthracene, as H(X) of **2a** and **3b** absorb at 4.98 and 5.1 respectively vs for **7b** at 5.69 ppm.

The isopropyl methyls of the anthracenium ions **15b** and **16b** appear quite unexpectedly as two doublets at *ca.* 1.55 and *ca.* 0.08 ppm. The observed difference of 1.47 ppm is certainly not consistent with a simple diastereotropic relationship involving a freely rotating i-Pr group.[14] This observed difference in shielding of the methyls may be explained in terms of the preferred conformation IV (shown in Newman projection along the Me_2CH–C(9)H bond). This conformation also explains



15b: R = H
16b: R = Cl

the relative small coupling constant ($J_{AX} = 3$ Hz) as result of a dihedral angle of *ca.* 80°.[15] A comparable preferred conformation is observed for *cis*-1,4-dimethyl-9,10-diisopropyl-9,10-dihydroanthracene (for a complete discussion on the conformation of this hydrocarbon and its ^1H NMR spectrum see Ref. 16).

The observations of the preferred conformations III and IV together with the *peri*-chloro effects on H(X) render structure II for the anthracenium ions more likely than structure I. They further indicate that for R^2 = alkyl IIa is preferred over IIb. For R^2=H the equilibrium IIa ⇌ IIb is rapid [with **17a** there is no fine structure of the ring methylene absorption (not even at −85°) and no *peri*-chloro effect on the ring methylene hydrogens].

EXPERIMENTAL

Materials. 9-Methyl-, 9,10-methyl-, 1-chloro-anthracene, fluorosulfuric acid and sulfurylchloride fluoride were commercially available reagents. 9,10-Diethylanthracene was prepared from 9,10-diethyl-9,10-dihydroanthracene by reaction

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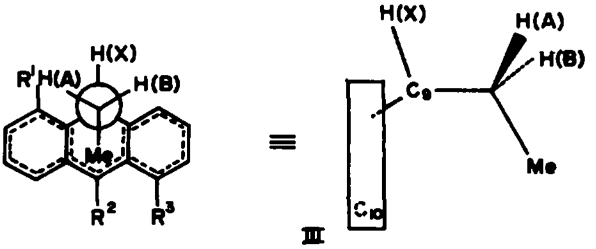
[f] Small differences in the distance between the proton, or the α-proton(s) of the substituent at C(9), and the chlorine-atom at C(1) lead to large differences in the chemical shift of these proton(s) (and accordingly in the *peri*-chloro effects), as the ^1H chemical shift difference induced by an adjacent Cl atom is proportional to the distance between the proton and that Cl atom to the sixth power.[13]



III

3a: $R^1 = R^3 = H$; $R^2 = Me$
9a: $R^1 = R^3 = H$; $R^2 = Et$
10b: $R^1 = R^3 = H$; $R^1 = Cl$
12b: $R^2 = H$; $R^1 = R^3 = Cl$

Table 5. ^{1}H NMR parameters of the substrates 1-16 in $CDCl_3$

Compd.	Chemical shifts[a] (p.p.m.) and multiplicities								
	H(1)	H(4)	H(5)	H(8)	H(10)	α-CH_3[b]	CH	CH_2	β-CH_3[b]
1	8.20(m)	7.91(m)	7.91(m)	8.20(m)	8.24(s)	3.00(s)			
2	8.25(m)	8.25(m)	8.25(m)	8.25(m)		3.01(s)			
3	8.28(m)	8.28(m)	8.28(m)	8.28(m)		3.04(s)		3.61(q)	1.42(t)
4		7.79(d)	7.88(m)	8.26(m)	8.21(s)	3.40(s)			
5		7.78(d)		8.05(d)	8.54(s)	3.27(s)			
6	8.11(d)			8.11(d)	9.13(s)	3.00(s)			
7		7.73(d)	7.73(d)		8.10(s)	3.32(s)			
8	8.20(m)	7.90(m)	7.90(m)	8.20(m)	8.23(s)			3.55(q)	1.48(t)
9	8.28(m)	8.28(m)	8.28(m)	8.28(m)				3.69(q)	1.42(t)
10		7.59(d)	7.71(m)	8.19(m)	8.00(s)			3.87(q)	1.50(t)
11	8.02(d)		7.93(m)	8.11(m)	8.67(s)			3.42(q)	1.30(t)
12		7.90(d)		8.25(d)	8.70(s)			3.99(q)	1.59(t)
13	7.97(d)			7.97(d)	9.06(s)			3.39(q)	1.28(t)
14	8.41(m)	7.92(m)	7.92(m)	8.41(m)	8.25(s)		4.52(m)		1.70(d)
15		7.75(d)	7.88(m)	8.52(m)	8.16(s)		5.10(m)		1.68(d)
16		7.85(d)		8.45(d)	8.68(s)		5.08(m)		1.68(d)

[a] The protons H(2,3,6,7) exhibit multiplet absorptions in between 7.0 and 8.0 p.p.m.

[b] α- and β-CH_3 represent the methyls attached to the anthryl group and those of the ethyl- and isopropyl group respectively.

with n - butyl - lithium - N,N,N′,N′ - tetramethylethylenediamine complex and subsequent addition of cadium(II)chloride.[17] 9,10 - Diethyl - 9,10 - dihydroanthracene was prepared from anthracene and EtLi.[18] The other compounds were prepared from reaction of the appropriate Grignard reagents with the appropriate anthrones, as described before.[2] The anthrones were obtained from reduction of the commercial available anthraquinones according to literature procedures.[19]

The ^{1}H NMR data of the substrates 1-16 in $CDCl_3$ are given in Table 5, those of 17 and 18 ($CDCl_3$) are: 17 {8.22[s, H(10)], 8.19[m, H(1,8)], 7.90[m, H(4,5)], 7.88[m, H(2,3,6,7)], 3.51[m, Ar-$C\underline{H}_2$], 2.79[m, $C\underline{H}_2$-CH_3], 1.08[t, CH_3]} and of 18 {8.79[s, H(9)], 8.45[s, H(10)], 7.98[m, H(5.8)], 7.84[d, H(4)] and 7.6-7.2[m; H(2,3,6,7)]}

Preparation of the anthracenium ions. Solns containing these ions were prepared by addition of *ca.* 1 ml FSO_3H cooled to *ca.* −78° to a cooled slurry of the hydrocarbon in *ca.* 1 ml SO_2ClF at −78°; the resulting mixture was stirred vigorously until a clear soln was obtained.

^{1}H NMR analysis. The 100 MHz spectra were recorded with a Varian HA-100 or XL100 spectrometer, equipped with a variable temp probe. The chemical shifts (δ_H) are for the protonation mixtures relative to external neat TMS (capillary) and for the substrates relative to internal TMS. The 360 MHz spectra have been recorded on a Bruker HX-360 spectrometer also equipped with a variable temp probe.

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