Carbon-13 NMR Spectroscopic Study of Substituted Anthracene Dications[1]

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A series of substituted anthracenes (2–10 and 20–21) were oxidized by SbF$_5$/SO$_2$ClF at 0 to −30 °C to their dications (11–19 and 22–23), which were observed by carbon-13 NMR spectroscopy. In the studied anthracene dications substantial positive charge was found to be localized at C$_9$ and C$_{10}$ positions. Methyl substitution in these dications was found to deshield the α-carbons as compared to their shielding effect in the corresponding monocations. The proportionality factor of ^{13}C chemical shift to electron density was found to be 174.1–217.0 ppm/e$^-$, clearly proving the dicationic nature of the ions.

Introduction

Polycyclic aromatic hydrocarbons continue to be the subject of extensive research, significantly due to their carcinogenic activity. Experimental evidence for the chemical binding of polycyclic aromatic hydrocarbons to cellular constituents was known as early as the 1940s. In the subsequent years ample evidence has been obtained indicating that polycyclic arenes bind to proteins, DNA, and RNA. A critical problem is to learn what site in the cell is involved in interaction with the carcinogen and the nature of the binding. A number of alternate possibilities are considered including protein binding and nucleic acid binding. Arene oxides have also been postulated as the intermediates in the metabolism of aromatic hydrocarbons. Evidence has been accumulating that most chemical carcinogens act as strongly electrophilic agents or are concerted in vivo to electrophilic agents by metabolic action.[2] This leads to the possibility of involvement of carbocationic reactive intermediates derived from arenes, as potential electrophiles of carcinogenic activity. As part of our continuing investigation of potential biological alkylating agents of carbocationic nature, we continued to study the in vitro chemical conversion of model polyarenes, such as substituted anthracenes to carbocationic species. In the present study we report their two electron oxidation to their related carbodications and the study of their structure by ^{13}C NMR spectroscopy to determine the charge distribution pattern which in turn shows the sites of highest possible electrophilic reactivity.

The ability of superacids to protonate, as well as in certain cases oxidize unsaturated hydrocarbons to produce carbocations and dications is well established.[3] A combination of the nature of the unsaturated hydrocarbon and the superacid used has been found to have a profound effect on the formation of carbocations.[4,5] It is well-known that polynuclear aromatic hydrocarbons such as perylene, naphthacene, and anthracene are oxidized to their monopositive radical ions by strong acids.[6] Dipositive ions of aromatic systems have been observed in electrochemical oxidations[7] and have been implicated as intermediates in reactions of radical cations[8–10] and in ESR studies of stable radical cations.[11] The generation of arene dications from arenes in strong acid media has been reported for naphthacene by SO$_3$ in dimethyl sulfate[6c] and for naphthacene and 1,2-benzanthracene by FSO$_3$H–SbF$_5$.[12] The unusual hexachlorobenzene dication[13] has been generated in SbF$_5$–Cl$_2$ at low temperature. More recently, tetramethylnaphthalene and octamethylnaphthalene were oxidized to their corresponding dications in SbF$_5$–SO$_2$ClF.[14]

(1) Stable Carbocations. 251. For Part 250 see: Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Krishnamurthy, V. V.; Narang, S. C. *J. Am. Chem. Soc.*, submitted for publication.

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Table I

dication	temp, °C[a]	color of ion solution
11	0	red-violet
12	0	violet
13	0	blue
14	0	blue
15	0	greenish-blue
16	0	greenish-blue
17	0	blue
18	−30	blue
19	−30	deep blue
22	0	blue
23	0	blue

[a] Temperature at which the ion was prepared.

Unlike benzene and naphthalene, anthracene has a relatively low ionization potential and can be readily converted to the corresponding carbodication.[15] Brouwer and van Doorn[16] have reported the ^{1}H NMR spectroscopic study of different arene dipositive ions, including some substituted anthracene dications formed by oxidation with SbF_5–SO_2ClF or FSO_3H–SbF_5. ^{1}H NMR spectroscopic data, however, can give only limited information about these ions.

No carbon-13 NMR study of substituted dications, which could give significant information about the structure and substitution effect was reported in the literature except for our preceding report[15] of the parent anthracene dication (1). In continuation of our studies on carbo-
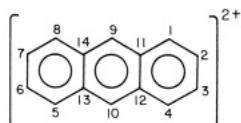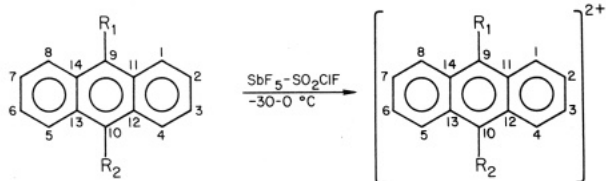
1

C_9, δ 188.6; C_1, δ 166.6; C_2, δ 155.0; C_{11}, δ 140.9

dications we now wish to report the two electron oxidation of an extensive series of mono- and disubstituted anthracenes in SbF_5–SO_2ClF medium and the carbon-13 NMR spectroscopic study of the obtained substituted anthracene dications, including unequivocal demonstration of the dicationic nature of these species.

Results and Discussion

A series of mono- and disubstituted anthracenes (2–10)

2, R_1 = CH_3; R_2 = H
3, R_1 = R_2 = CH_3
4, R_1 = Cl; R_2 = H
5, R_1 = Br; R_2 = H
6, R_1 = R_2 = Cl
7, R_1 = R_2 = Br
8, R_1 = Cl; R_2 = CH_3
9, R_1 = Ph; R_2 = H
10, R_1 = R_2 = Ph

11, R_1 = CH_3; R_2 = H
12, R_1 = R_2 = CH_3
13, R_1 = Cl; R_2 = H
14, R_1 = Br; R_2 = H
15, R_1 = R_2 = Cl
16, R_1 = R_2 = Br
17, R_1 = Cl; R_2 = CH_2
18, R_1 = Ph; R_2 = H
19, R_1 = R_2 = Ph

were readily oxidized to their dipositive ions (11–19) by adding them to a solution of excess SbF_5–SO_2ClF at temperatures ranging between −30° and 0 °C. The reaction temperatures and the colors of the solutions of the formed

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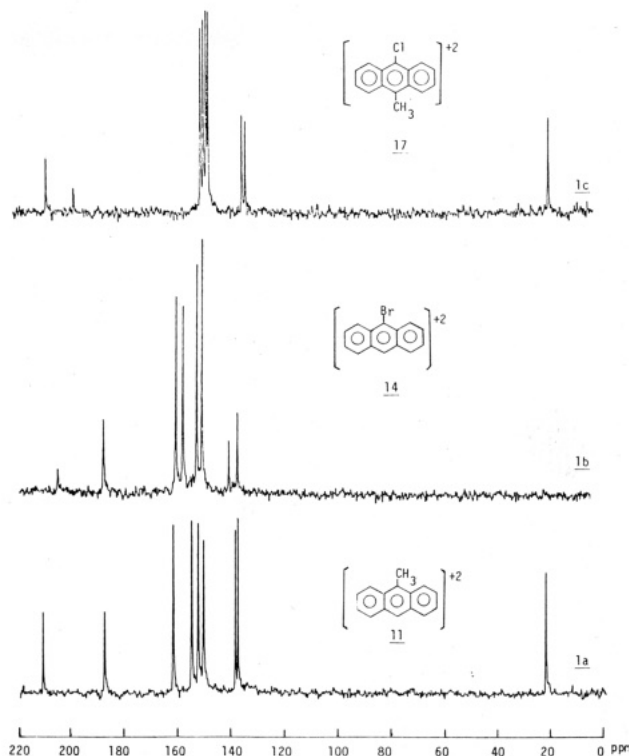

Figure 1. Carbon-13 NMR's of ions 11, 14, and 17.

dications (11–19) are given in Table I.
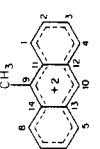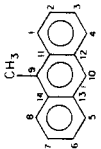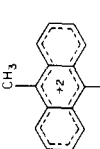
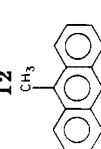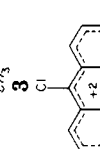The carbon-13 NMR parameters of the studied anthracene dications (11–19) as well as their neutral precursors (2–10) are summarized in Table II. The assignments of the different carbon resonances in the carbon-13 NMR spectra of the ions (11–19) are based on three criteria: (a) the multiplicities of different carbon resonances in the proton-coupled spectra; (b) relative peak intensities in relation to the number of equivalent carbons giving rise to the peaks (this is, however, not an entirely unequivocal criterion because of possible differences in relaxation times, but generally the positions with the fewest number of equivalent carbons are also at the junctions of the rings, farthest removed from protons, so that the smaller peaks would be expected both on the basis of fewer carbons and longer relaxation times); (c) comparison with the parent anthracene dication (1).
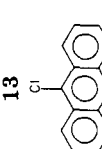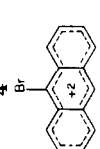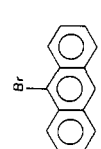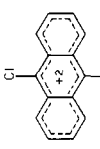
The 9-methylanthracene dication (11) showed nine peaks in its carbon-13 NMR (Figure 1a) at 0 °C. The lowest field peak at $\delta^{13}C$ 212.1 (s) was assigned to C_9 and the peak at $\delta^{13}C$ 188.8 (d) to C_{10}. The assignments of the additional carbon atoms is shown in Table II. The 9,10-Dimethylanthracene dication (12) (a symmetrical ion) showed only five peaks. The most deshielded peak at $\delta^{13}C$ 212.3 was assigned to the C_9, C_{10} carbons. It is significant to point out that mono- or disubstitution of anthracene dication at the C_9 and C_{10} position, as in ions 11 and 12, does not cause any apparent difference in the chemical shifts of these carbons (see Table II). The 9-halogen substituted anthracene dications 13 and 14 (Figure 1b) showed eight peaks in their carbon-13 spectra and the lowest field peaks at $\delta^{13}C$ 201.8 and 206.3 were assigned to C_9 for ions 13 and 14, respectively. Bromine substitution at C_9 as in ion 14 causes more deshielding of the C_9 chemical shift than does chlorine substitution in ion 13 (Table II). This deshielding effect of bromine is quite opposite to its general shielding effect in neutral molecules. The C_{10} chemical shifts of ions 13 and 14 were found at $\delta^{13}C$ 188.6 and 188.9, respectively, which are again identical to the C_9 chemical shift of ion 1. It is clear from these ions,

Table II.   Carbon-13 Chemical Shifts^a of Substituted Anthracene Dications and Related Neutral Compounds

substrate	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	others
11	162.8 (d)	153.5 (d)	155.8 (d)	151.3 (d)	151.3 (d)	155.8 (d)	153.5 (d)	162.8 (d)	212.1 (s)	188.8 (d)	139.2 (s)	138.3 (s)	138.3 (s)	139.2 (s)	21.1 (q)
2	124.7 (d)	125.1 (d)	124.6 (d)	129.0 (d)	129.0 (d)	124.6 (d)	125.1 (d)	124.7 (d)	130.0 (s)	125.2 (d)	130.0 (s)	131.4 (s)	131.4 (s)	130.0 (s)	13.8 (q)
12	153.3 (d)	151.1 (d)	151.1 (d)	153.3 (d)	153.3 (d)	151.1 (d)	151.1 (d)	153.3 (d)	212.3 (s)	212.3 (s)	138.1 (s)	138.1 (s)	138.1 (s)	138.1 (s)	21.4 (q)
3	125.3 (d)	124.6 (d)	124.6 (d)	125.3 (d)	125.3 (d)	124.6 (d)	124.6 (d)	125.3 (d)	128.3 (s)	128.3 (s)	129.8 (s)	129.8 (s)	129.8 (s)	129.8 (s)	14.0 (q)
13	162.4 (d)	153.6 (d)	156.4 (d)	152.2 (d)	152.2 (d)	156.4 (d)	153.6 (d)	162.4 (d)	201.8 (s)	188.6 (d)	138.5 (s)	138.5 (s)	138.5 (s)	138.5 (s)	
4	128.6 (d)	126.9 (d)	125.7 (d)	124.8 (d)	124.8 (d)	125.7 (d)	126.9 (d)	128.6 (d)	125.2 (s)	126.1 (d)	132.0 (s)	127.1 (s)	127.1 (s)	132.0 (s)	
14	161.5 (d)	153.7 (d)	158.9 (d)	151.7 (d)	151.7 (d)	158.9 (d)	153.7 (d)	161.5 (d)	206.3 (s)	188.9 (d)	141.3 (s)	138.0 (s)	138.0 (s)	141.3 (s)	
5	128.6 (d)	127.6 (d)	127.2 (d)	125.6 (d)	125.6 (d)	127.2 (d)	127.6 (d)	128.6 (d)	122.4 (s)	127.2 (d)	132.1 (s)	130.6 (s)	130.6 (s)	132.1 (s)	
15	153.6 (d)	151.9 (d)	151.9 (d)	153.6 (d)	153.6 (d)	151.9 (d)	151.9 (d)	153.6 (d)	202.2 (s)	202.2 (s)	137.0 (s)	137.0 (s)	137.0 (s)	137.0 (s)	

(Table rotated 90° on the page; ^{13}C NMR chemical shifts listed per compound. Structures drawn at the base of each column.)
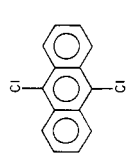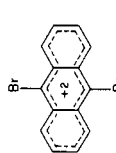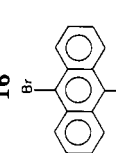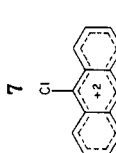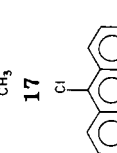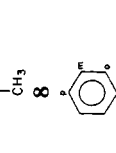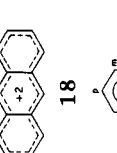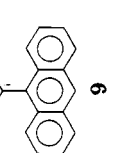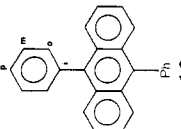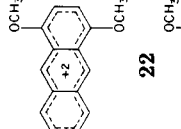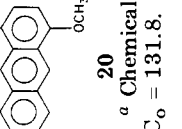
Compd	Chemical shifts
6 (Cl, Cl)	127.1 (d), 125.2 (d), 127.1 (d), 125.2 (d), 128.2 (s), 129.1 (s), 129.1 (s), 129.1 (s)
16 (Br, Br, +2)	155.8 (d), 151.7 (d), 155.8 (d), 151.7 (d), 206.8 (s), 139.8 (s), 139.8 (s), 139.8 (s)
7 (Br, Br)	128.3 (d), 127.4 (d), 128.3 (d), 127.4 (d), 123.5 (s), 131.0 (s), 131.0 (s)
17 (Cl, CH₃, +2)	153.8 (d), 151.5 (d), 150.8 (d), 152.7 (d), 212.1 (s), 201.1 (s), 153.8 (d), 136.5 (s), 137.8 (s), 21.5 (q)
8 (Cl, CH₃)	126.2 (d), 125.4 (d), 124.9 (d), 125.4 (d), 127.2 (s), 129.8 (s), 126.2 (d), 128.4 (s), 130.5 (s), 14.1 (q)
18 (p,m,o-C₆H₄, +2)	160.1 (d), 152.2 (d), 148.9 (d), 159.9 (d), 189.2 (s), 152.2 (d), 185.6 (d), 138.0 (s), 137.6 (s), b
9 (p,m,o-C₆H₄)	131.2 (d), 128.3 (d), 125.3 (d), 126.8 (d), 137.0 (s), 130.1 (d), 131.2 (d), 126.5 (s), 131.3 (s), c
19 (p,m,o-C₆H₄, Ph, +2)	157.8 (d), 145.2 (d), 157.8 (d), 145.2 (d), 191.8 (s), 157.8 (d), 145.2 (d), 135.7 (s), 135.7 (s), d

Table II (Continued)

carbon-13 chemical shifts and multiplicities

substrate	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	others
10	131.3 (d)	127.0 (d)	127.0 (d)	131.3 (d)	131.3 (d)	127.0 (d)	127.0 (d)	131.3 (d)	137.2 (s)	137.2 (s)	129.9 (s)	129.9 (s)	129.9 (s)	129.9 (s)	e
22	184.6 (s)	142.3 (d)	142.3 (d)	184.6 (s)	142.1 (d)	138.1 (d)	138.1 (d)	142.1 (d)	154.3 (d)	154.3 (d)	123.4 (s)	123.4 (s)	135.7 (s)	135.7 (s)	65.9
20	149.4 (s)	125.5 (d)	125.5 (d)	149.4 (s)	120.8 (d)	100.8 (d)	100.8 (d)	120.8 (d)	128.5 (d)	128.5 (d)	131.5 (d)	131.5 (d)	100.3 (s)	100.3 (s)	55.5

^{a} Chemical shifts are in parts per million from external Me_4Si. Multiplicities are in parentheses: s = singlet, d = doublet, q = quartet. ^{b} C_p = 151.8, C_m = 146.3, C_i = 135.7, C_o = 131.8. ^{c} C_p = 127.4, C_m = 128.3, C_i = 138.7, C_o = 125.0. ^{d} C_p = 143.1, C_m = 138.0, C_i = 135.0, C_o = 130.1. ^{e} C_p = 127.5, C_m = 128.5, C_i = 139.1, C_o = 125.0.

11, 13, and 14 that substitution at C_9 by a methyl, chlorine, or bromine group does not have any effect on the chemical shift of C_{10} centers which means that C_9 and C_{10} centers are independent of each other in these anthracene dications. The 9,10-dihaloanthracene dications 15 and 16 were found symmetrical and each showed four peaks. The most deshielded peak at $\delta^{13}C$ 202.2 in ion 15 was assigned to the C_9, C_{10} cabons and similarly the peak at $\delta^{13}C$ 206.8 in ion 16 was assigned to C_9, C_{10}. The rest of the peak assignments in ions 15 and 16 are shown in Table II.

An interesting case is dication 17 formed from 9-chloro-10-methylanthracene (8) at 0 °C which showed nine peaks in its carbon-13 NMR (Figure 1c). The lowest field peak at $\delta^{13}C$ 212.1 was assigned to C_{10} carrying a methyl group which is the same as the C_9 chemical shift of ion 11. The peak at $\delta^{13}C$ 201.1 was assigned to C_9 substituted by a chlorine atom which is the same as the C_9 chemical shift of ion 13. These centers are independent of each other in all the substituted anthracene dications.

Similarly, 9-phenyl- and 9,10-diphenylanthracene 9 and 10 were oxidized in SbF_5–SO_2ClF at –30 °C to the corresponding dications 18 and 19, respectively. The chemical shifts of C_9 in ion 18 and C_9, C_{10} in ion 19 were found to be $\delta^{13}C$ 189.2 and 191.8, respectively. The assignments of the additional peaks are summarized in Table II. We were also able to oxidize 1,4-dimethoxyanthracene (20) and

2-methylanthracene (21) with SbF_5–SO_2ClF at 0 °C to the corresponding dications 22 and 23, respectively. The carbon-13 spectrum of ion 22 showed eight peaks of which the peak at $\delta^{13}C$ 184.9 was assigned to the C_1, C_4 carbons. The carbon-13 spectrum of ion 23 was found difficult to assign completely, however, we could readily assign the peaks at $\delta^{13}C$ 187.7, 182.3, and 177.1 to C_9, C_{10}, and C_2, respectively. The assignments of the additional peaks are only tentative (Table II).

Methyl substituents in arenium ions (protonated arenes) cause shielding[4,17] of effected carbons in accord with their electron-donating ability. In the case of substituted anthracene dications methyl as well as halogen substitutions at C_9 and C_{10} were found to have a deshielding effect on the affected ring carbons (specially the α-carbons on the same side or the opposite side of the substitution (see Table II). Carbon-13 NMR shifts of aromatic systems have been demonstrated to be primarily dependent upon the π-electron density (e) at the individual carbon atoms. Least square analysis of the data obtained for the 2π-, 6π-, and 10π-electron monocyclic aromatics indicates a relationship[18] of π-electron densities with chemical shifts (Spiesecke–Schneider relationship) of $\delta^{13}C$ = 159.5p + 288.5. O'Brien, Hart, and Russell have extended the scope

(17) Review by Brouwer, D. M.; Mackor, E. L.; MacLean, C. In "Carbonium Ions"; Olah, G. A.; Schleyer, P. v. R., Eds.; Interscience: New York, 1970; Vol. II, Chapter 20.

(18) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

Table III. Comparison of Carbon Chemical Shifts in
Substituted Anthracene Dications and Their Neutrals[a]

dica-tions	total $\delta^{13}C^{2+}$, ppm	neutral sub-strates	total $\delta^{13}C$n, ppm	$\delta^{13}C^{2+}$ − $\delta^{13}C$n, ppm	total deshield/ e⁻, ppm
11	2223.8	2	1798.6	425.2	212.6
12	2237.4	3	1803.4	434.0	217.0
13	2193.6	4	1781.5	412.1	206.05
14	2205.4	5	1793.0	412.4	206.2
15	2174.2	6	1782	392.2	196.1
16	2202.8	7	1793.8	409.0	204.5
17	2200.9	8	1792.7	408.2	204.1
18	3010.5	9	2578.6	431.9	215.9
19	3766.6	10	3374.4	392.2	196.1
22	2172.8	20	1824.6	348.2	174.1
23	2238.6	21	1821.8	416.8	208.4

[a] $\delta^{13}C^{2+}$ is the chemical shift of the dication. $\delta^{13}C$n is
the chemical shift of the neutral molecule.

of the applicability of the relationship to include carbon-13
NMR shifts in fully conjugated π-systems in which all
carbons are not necessarily equivalent and found the
correlation of the average π-electron density (e_{av}) to average
^{13}C NMR chemical shifts to be $\delta^{13}C_{av} = -156.8e_{av} + 28$ 9.9.
The dicationic nature of 1 is clearly demonstrated[4] upon
comparison of the experimentally observed average car-
bon-13 NMR shielding in 1 (δ 159.0) with that predicted
for a 12π-14-carbon anthracene dication (δ 155.0). The
difficulty in precisely estimating substituent effects on ^{13}C
NMR chemical shifts, however, precludes comparison of
the average ^{13}C NMR shieldings observed in the cases of
substituted anthracene dications (11-19) with those pre-
dicted by a Spiesecke–Schneider type treatment. The
expected similarity of these substituent effects operative
in an anthracene dication and its related neutral precursor,
however, allows one to compare the total increase in ^{13}C
NMR shieldings of a substituted anthracene dication
relative to its neutral precursor with the 313.9 ppm increase
predicted by O'Brien' correlation[19] to accompany a 2π-
electron oxidation. In other words if the total increase in
the ^{13}C NMR shieldings of a cationic species relative to
its neutral precursor is about 300 ppm or more it is strongly
indicative of a dication. The observed total increases in
the ^{13}C NMR shieldings of ions 11-19 and 22 relative to
their neutral precursors 2-10 and 20 are listed in Table
III and are in accord with the dicationic nature of these
ions. The proportionality factor for the relationship be-
tween ^{13}C NMR chemical shifts and charge density in these
systems (174.1-217 ppm/π-electron), Table III, is some-
what larger than those found in the previously discussed
correlations.[18,19] However, it is in good agreement with
previous results on the oxidation of other polycyclic arenes
to their dications.[15] The large deshieldings of the sub-
stituted carbons (C_9 and C_{10}) in their ions (11-19 and
22-23), relative to those in their parent dications and their
relationship to the shifts in the neutral precursors (Table
II), further suggests that substantial positive charge is
located at the C_9 and C_{10} carbons of these dications.

Experimental Section

All substituted anthracenes were commercially available from
Aldrich except 9-chloro-10-methylanthracene, which was prepared
by the known procedure.[20] Antimony pentafluoride and SO_2ClF
used in this study were freshly distilled before use. All the
carbon-13 NMR spectra were recorded on Varian FT-80 or Varian
XL-200 spectrometers. All the dications were prepared in an air
atmosphere.

Preparation of 9-Chloro-10-methylanthracene. A vigor-
ously stirred mixture of 9-methylanthracene (26 mmol) and an-
hydrous cupric chloride (55 mmol) in benzene (1 L) was heated
under reflux for 1.5 h. The reaction mixture was cooled and
filtered. Evaporation of the solvent gave a solid residue which
was crystallized by petroleum ether: yield 80%; mp 178-179 °C
(lit.[20] mp 179-180 °C).

**General Procedure for the Preparation of Substituted
Anthracene Dications.** A solution of 1 mL of SbF_5 and 1-1.5
mL of SO_2ClF in a 5-mm Carbon-13 NMR tube was stirred at
0 to -30 °C temperature. The solid substituted anthracene
(200-300 mg) was added in small portions to the acid solution
with continuous stirring and the NMR tube was cooled. After
the completion of the addition, the solution was stirred for an
additional 1-2 min at 0 to -30 °C to get the homogeneous solution
of dication. The carbon-13 NMR tube containing the ion solution
was placed into the precooled (0 to -30 °C) probe of the Varian
FT-80 or XL-200 spectrometer to record its ^{13}C spectrum.

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