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Oxidation of Polycyclic Arenes in SbF_5/SO_2ClF, Formation of Arene Dications and Observation of Electron Exchange with Radical Cations Based on ^{13}C Nuclear Magnetic Resonance Studies[1]

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Abstract: A series of aromatic hydrocarbons was examined for formation of arene dipositive ions in SbF_5/SO_2ClF solution. Arenes with low ionization potentials as predicted in simple Hückel π-electron molecular orbital calculations are oxidized to dications, which were detected by ^{13}C NMR spectroscopy. The ^{13}C spectra of picene and 1,2,3,4-dibenzanthracene dications show nonuniform line-broadening due to electron exchange between the dications and the radical cations. Arenes predicted to have high ionization potentials formed solid products in SbF_5/SO_2ClF, probably via the radical cations. Naphthalene was not oxidized to a dication, but a dication was observed for octamethylnaphthalene.

Introduction

Polycyclic aromatic hydrocarbons have been the subject of an extraordinary amount of research, undoubtedly due in part to the early development of π electronic theories. The carcinogenic activity of many polycyclic arenes has also been a stimulus to research in this area. Evidence has been accumulating that most chemical carcinogens are either strongly electrophilic agents per se or are converted in vivo to electrophilic agents by metabolic action.[3,4] Thus, as part of our continuing investigations of carbocationic species, we were interested in possible chemical conversions of polycyclic arenes to carbocations which obviously are potential electrophiles. In this paper, we report our observations on the chemical oxidation of polycyclic arenes to stable dipositive ions. The oxidations were carried out using SbF_5 in SO_2ClF and the dications were detected by ^{13}C NMR spectroscopy. Simple Hückel π-electron molecular orbital theory is used as a background for presenting our experimental results.

Dipositive ions of aromatic systems have been observed in electrochemical oxidations,[5] and have been implicated as intermediates in reactions of radical cations[6-8] and in ESR studies of stable radical cations.[9] The generation of arene dications from arenes in strong acid media has been reported for naphthacene by SO_3 in dimethyl sulfate,[10] for naphthacene and 1,2-benzanthracene by FSO_3H-SbF_5,[11] and for naphthacene, perylene, anthracene, and some substituted anthracenes by SbF_5 in SO_2ClF, FSO_3H, or H_2SO_4.[12] The unusual hexachlorobenzene dication has been generated in SbF_5-Cl_2 at low temperatures.[13] We now report the oxidation of an extensive series of arenes to dipositive ions, including a naphthalene dication, and we also report our observations on systems with ionization potentials too high to permit full ionization to the dication stage. ^{13}C NMR is used to demonstrate the existence of the dications because of the sensitivity of ^{13}C chemical shifts to charge development; no previous ^{13}C data are available for arene dications.

Experimental Section

All polycyclic arenes were commercially available compounds of the highest purity, with the exception of octamethylnaphthalene, which was a generous gift of Professor Harold Hart, Michigan State University. SbF_5 was distilled twice prior to use and SO_2ClF was distilled directly from a storage cylinder into the reaction flask. The typical procedure for generation of dications was to add 100–150 mg of the solid arene, in small portions, directly to a vigorously stirred (Vortex mixer) solution of 1.5 ml of SbF_5 in 2 ml of SO_2ClF kept at -10 to -40 °C by periodic cooling in an ice-salt or dry ice-acetone bath. Depending on the molecular weight of the arene, SbF_5 was present in 40- to 100-fold excess on a mole-to-mole basis. The dication solutions were transferred immediately into the NMR tubes used for ^{13}C NMR analysis. About 0.5 ml was removed by precooled pipet for examination by ^1H NMR, and then returned to the ^{13}C NMR tube if signals were detected in the ^1H NMR spectrum. ^{13}C NMR spectra were obtained on a Varian Associates Model XL100-15 spectrometer operated in the pulsed Fourier transform mode. Ion concentrations were dilute and required 1000–4000 transients for acceptable signal-to-noise ratios. The spectra were recorded at 5000–7000 Hz spectral width. Chemical shifts were measured from the Me_4Si signal of a 1.75-mm capillary of 5% ^{13}C-enriched Me_4Si. The temperature at which the spectra were measured was -10 °C except as follows (ion, temp): **16**, $-30°$; **17**, $-25°$; **18**, $-40°$; and **19**, $-40°$.

Results and Discussion

Eighteen unsubstituted aromatic hydrocarbons were examined, using ^{13}C NMR, for the formation of stable dipositive ions when dissolved in SbF_5/SO_2ClF. The results are summarized in Table I. The arene systems in Table I are listed in the order of increasing energy level of the highest occupied π

Table I, Arene Species in SbF_5/SO_2ClF Solution

Arene	E_{HOMO} $(\beta)^a$	Species[b] in SbF_5/SO_2ClF	Color of dication solution
Benzene (**1**)	1.0000	$C_6H_7^+$	
Triphenylene (**2**)	0.6840	(+·)	
Naphthalene (**3**)	0.6180	(+·)	
Phenanthrene (**4**)	0.6052	(+·)	
Coronene (**5**)	0.5392	(+·)	
Chrysene (**6**)	0.5201	(+·)	
Tetrabenznaphthalene (**7**)	0.5115	++	Blue
Picene (**8**)	0.5019	+· ⇌ ++	Green-black
1,2,3,4-Dibenzanthracene (**9**)	0.4991	+· ⇌ ++	Blue-black
1,2,5,6-Dibenzanthracene (**10**)	0.4735	++	Green
1,2-Benzanthracene (**11**)	0.4523	++	Blue-green
Pyrene (**12**)	0.4450	++	Green-black
1,12-Benzperylene (**13**)	0.4392	++	Purple
Anthracene (**14**)	0.4142	++	Purple
1,2-Benzpyrene (**15**)	0.3711	++	Blue
Perylene (**16**)	0.3473	++	Purple
Naphthacene (**17**)	0.2950	++	Green
Pentacene (**18**)	0.2197	++[c]	Green
Octamethylnaphthalene (**19**)		++	Red
7,12-Dimethylbenzanthracene (**20**)		++	Blue-green

[a] Energy of the highest occupied molecular orbital in the Hückel method (ref 14). [b] Dication indicated by ++, monopositive ion by +·. [c] Dication formed in SbF_5/SO_2, but not in SbF_5/SO_2ClF; SbF_5/SO_2 is a weaker oxidizing agent due to complexation of SbF_5 with SO_2. Possibly **18** is ionized to the paramagnetic trication in SbF_5/SO_2ClF.

molecular orbital (HOMO) as calculated in the simple Hückel molecular orbital method.[14] The systems with HOMO's at the higher energy levels (smaller E_{HOMO} values) should be the easiest to oxidize to dipositive ions. The arenes with low-lying HOMO's should be more difficult to ionize, with benzene being the most difficult.

If benzene were oxidized to the dipositive ion, the ion would probably be a triplet with two electrons occupying degenerate orbitals, as has recently been reported for the dipositive ion of hexachlorobenzene.[13] The ^{13}C spectrum of benzene in SbF_5/SO_2ClF at −70 °C shows a broad singlet at δ_C 145.7, at the identical position of the broad singlet in the spectrum of protonated benzene (benzenium ion) in FSO_3H-SbF_5/SO_2ClF. The ^1H NMR consists of a singlet at δ 8.1; both NMR data are indicative of the $C_6H_7^+$ benzenium ion undergoing rapid equilibration of the protons.[15] A trace of a proton-donating acid in the SbF_5/SO_2ClF apparently leads to formation of this product, although protonation of other arenes under these conditions was not observed.

Two other arenes, triphenylene and coronene, are also predicted to have triplet dipositive ions on the basis of degenerate HOMO's in simple Hückel theory. The *dinegative* triphenylene ion has been observed as a triplet.[16] However, triphenylene and coronene have relatively low-lying HOMO's, and therefore, higher ionization potentials than any of the species for which dications were observed. Three other arenes (naphthalene, phenanthrene, and chrysene) with HOMO's at similar energy levels also did not give dications. Lewis and Singer reported the oxidation of all five of these arenes to monopositive ions in $SbCl_5/CH_2Cl_2$.[9] Our observations in SbF_5/SO_2ClF are probably best explained also by oxidation just to the monopositive stage: highly colored solutions are formed immediately upon the addition of a few milligrams of arene to the solution, but attempts to raise the concentration to the level required for NMR measurements result in the formation of solids. The solid products were not investigated further, so it is not known whether paramagnetic solids were formed, as observed by Lewis and Singer.[9] No signals were detectable in ^1H NMR spectra of the supernatant liquids or suspensions.

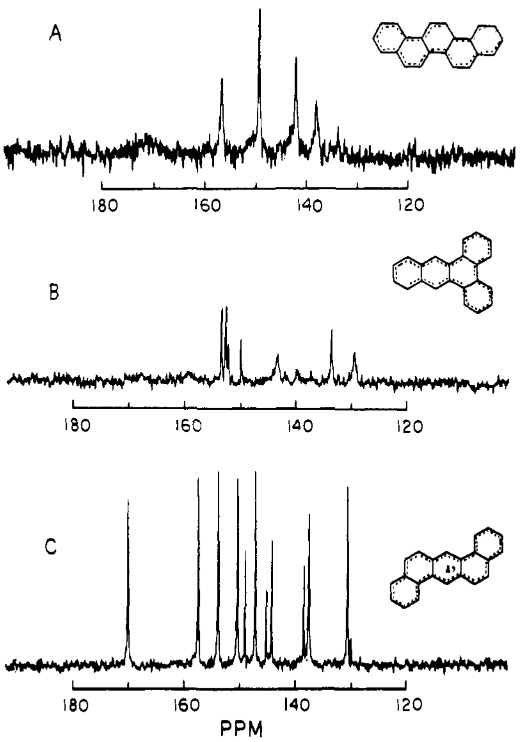
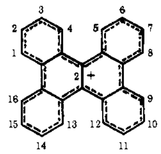
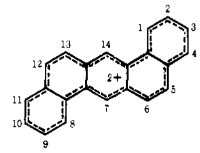
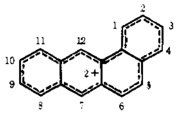
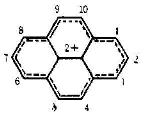
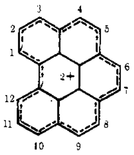
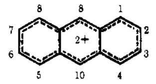
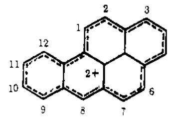
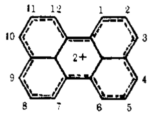
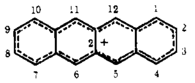
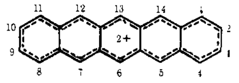


Figure 1, Spectrum A: ^{13}C NMR of picene in SbF_5/SO_2ClF, showing dication undergoing electron exchange. Spectrum B: ^{13}C NMR of 1,2,3,4-dibenzanthracene in SbF_5/SO_2ClF, showing dication undergoing electron exchange. Spectrum C: ^{13}C NMR of 1,2,5,6-dibenzanthracene in SbF_5/SO_2ClF, showing all 11 resonances for the dication. Spectral conditions were as follows. A: spectral width (SW) 5500 Hz, acquisition time (AT) 0.73 s, pulse delay (PD) 0.70 s, pulse width (PW) 20 μs, 4700 transients. B: SW 5000 Hz, AT 0.80 s, PD 0.40 s, PW 25 μs, 1862 transients. C: SW 5000 Hz, AT 0.80 s, PD 0.70 s, PW 25 μs, 2637 transients.

Although naphthalene could not be ionized to the dipositive ion, the presence of methyl groups in 1,2,3,4,5,6,7,8-octamethylnaphthalene lowers the ionization potential to the point where the stable dication can be formed in SbF_5/SO_2ClF (^{13}C spectrum in Table II). The average (weighted) position of the *ring* carbon resonances in the octamethylnaphthalene dication is δ_C 181.4, which is 48.9 ppm downfield from the average δ_C for the ring carbons of octamethylnaphthalene in $CDCl_3$.[17] The deshielding amounts to 244.7 ppm/e^-, which is an unusually large proportionality factor for the relation between ^{13}C chemical shifts and charge, but the ring deshielding is also affected by the methyl groups, which produce greater deshielding at positively charged carbons than at neutral carbon atoms.[18] Steric interactions undoubtedly also influence chemical shifts in this crowded system.[19]

The most interesting behavior is observed in the borderline region between compounds which are fully oxidized to dications and those described above which are apparently oxidized only to the monopositive stage. Picene (**8**) and 1,2,3,4-dibenzanthracene (**9**) give ^{13}C spectra in which some lines are "missing", i.e., broadened into the baseline, some are broadened slightly, and some lines remain sharp. Figure 1 compares the spectra of **8** and **9** in SbF_5/SO_2ClF with the dipositive ion of 1,2,5,6-dibenzanthracene (**10**), an isomeric polycyclic arene with a lower ionization potential. Each dication spectrum should show 11 lines, but clearly that condition is fulfilled only for **10**, The nonuniform broadening of the NMR lines for **8** and **9** is characteristic behavior expected for a diamagnetic molecule (i.e., the dication) which is undergoing "weak" exchange of electrons with its paramagnetic precursor (the radical cation).[20] The ^{13}C NMR spectra of the **8** and **9** dications are ap-

Table II. ^{13}C Chemical Shifts of Arene Dications[a,b]

		δ_C for C–H positions	δ_C for ring junctions
7		157.1 (C(4)),[c] 154.1 (C(2)),[c] 135.6 (C(1)),[d] 134.6 (C(3))[d]	210.2 (C94b)), 140.6, 138.4
10		170.0 (C(7)), 157.3, 153.7, 150.3, 147.0, 137.4, 130.4 (C(1))	148.9, 145.0, 144.1, 138.3
11		184.0 (C(7)), 165.4, 163.9, 162.6, 161.7, 161.0, 160.1, 153.5, 145.4, 145.4, 140.0, 130.3 (C(1))	149.6, 149.6, 145.0, 143.8, 142.1, 136.7
12		184.0 (C(1), J = 172 Hz), 156.2 (C(4), J = 176 Hz), 143.3 (C(2), J = 185 Hz)	145.1 (C(3a)), 133.9 (C(10b))
13		170.8, 165.5, 155.3, 143.3, 142.0, 140.4	155.2, 139.2, 139.2, 134.7, 128.6
14		188.6 (C(9), J = 177 Hz), 166.6 (C(1), J = 178 Hz, 155.0 (C(2)), J = 179 Hz)	140.9 (C(4a))
15		186.0 (C(8)), 173.5, 165.4, 164.3, 160.5, 158.1, 152.6, 150.0, 140.1, 140.0, 137.5, 134.8	148.8, 144.9, 144.0, 142.0, 141.7, 138.4, 131.6, 129.8
16		167.8 (C(3)), 151.7 (C(1)), 139.0 (C(2))	138.2 (C(6a)), 135.0, 124.0
17		173.7 (C(5)), 150.1 (C(1)), 138.5 (C(2))	147.9 (C(2)), 134.7 (C(5a))
18		171.6 (C(6), J = 173 Hz), 163.4 (C(5), J = 172 Hz), 144.1 (C(1), J = 170 Hz),[e] 142.9 (C(2), J = 168 Hz)[e]	139.8, 134.5
	19	205.3 (C(1)), 165.2 (C(2)), 28.4 (C(1)–CH_3), 18.1 (C(2)–CH_3)	165.9 (C(4a))
	20	211.3 (C(7)), 191.3 (C(12)), 160.7, 158.2, 154.9, 153.3, 147.1, 144.8, 143.8, 143.5, 138.3, 135.0, 27.1 (C(7)–CH_3), 22.1 (C(12)–CH_3)	151.1, 147.1, 146.8, 146.4, 144.6, 139.7

[a] Chemical shifts in parts per million from external (capillary) Me_4Si. One-bond C–H coupling constants given in hertz. Tentative assignments were made as described in text. [b] Average (weighted) δ_C are **7**, 145.6; **10**, 147.5; **11**, 152.2; **12**, 156.0; **13**, 146.7; **14**, 159.1; **15**, 149.2; **16**, 144.8, **17**, 150.6; and **18**, 147.4. [c,d,e] Interchangeable assignments.

parently affected by the paramagnetic pulses experienced by the carbons during the time that each molecule contains an unpaired electron in the radical cation form. The ^1H NMR of both **8** and **9** in SbF_5/SO_2ClF consists of a very broad absorption, which rises only slightly above the baseline. The dications of **8** and **9** must exist in equilibrium with the radical cations: $Ar^{2+} \rightleftarrows Ar\cdot^+$. Lewis and Singer previously postulated electron exchange reactions between mono- and dipositive ions as a source of loss of resolution in the hyperfine structure in ESR spectra of the radical cations,[9] and the uv spectrum of naphthacene in dimethyl sulfate plus SO_3 indicated the presence of both mono- and dipositive ions.[10]

Potentially, a great deal of useful information could be derived from ^{13}C spectra in which partial relaxation occurs due to electron exchange, such as the rate of exchange, and the sign and magnitude of spin densities at ring positions in the radical cations. However, relaxation times for the carbons in dications can vary substantially even in the absence of electron exchange. In particular, carbons at ring junction positions which are not bonded to protons typically have longer relaxation times than carbons bonded to protons, due to lesser ^{13}C–^1H dipole-dipole relaxation.[21] More important in relation to the interpretation

Table III. Assignment of ^{13}C Chemical Shifts in Arene Dications by Comparison with Hyperfine Splitting Constants (a_H) of Monopositive Ions and Hückel Charge Densities (q_i)

Arene	Position	a_H[a]	q_i[b]	δ_C dication
7	1	0.60	0.054	135.6[c]
	2	1.99	0.112	154.1[d]
	3	<0.03	0.004	134.6[c]
	4	2.28	0.134	157.1[d]
12	1	5.38	0.272	184.0
	2	1.18	0.000	143.3
	4	2.12	0.175	156.2
14	1	3.08	0.193	166.6
	2	1.38	0.097	155.0
	9	6.49	0.387	188.6
16	1	3.04	0.167	151.2
	2	0.44	0.026	138.6
	3	4.04	0.216	167.4
17	1	1.68	0.112	150.1
	2	1.02	0.067	138.5
	5	5.01	0.295	173.7
18	1	0.98	0.071	144.1[e]
	2	0.76	0.047	142.9[e]
	5	3.56	0.212	163.4
	6	5.08	0.282	171.6
19[f]	1	5.54	0.362	205.3
	2	2.06	0.138	165.2

[a] Data for radical cations from ref 9. [b] Positive charge densities for dications in simple Hückel MO calculations. [c,d,e] Interchangeable values. [f] Radical cation data is for naphthalene; shifts for 19 not included in correlation in Figure 3.

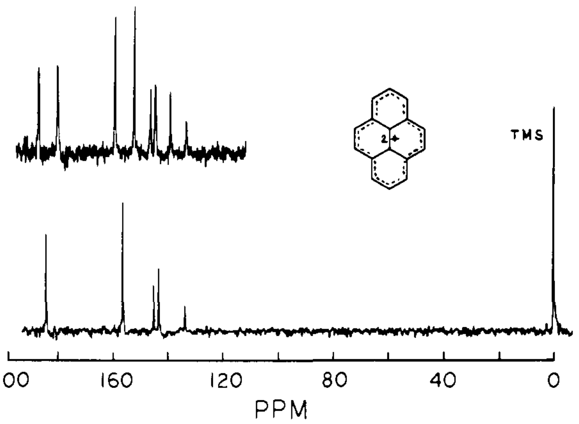


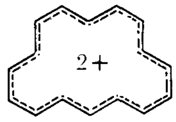
Figure 2. ^{13}C NMR spectrum of pyrene dication in SbF_5/SO_2ClF. Lower spectrum is proton decoupled, upper spectrum is fully coupled. Spectral conditions: SW 5000 Hz, AT 0.80 s, PD 0.70 s, PW 25 μs, 2469 transients.

of the present observations is the fact that limiting conditions are used to generate the dications. A large excess of SbF_5 is employed, so that oxidation occurs to the full extent possible with this reagent. Therefore, carbon chemical shifts for the **8** and **9** dications in the absence of electron exchange are not known, nor can reliable assignments be made for the peaks that are observed. As far as future studies are concerned, it would probably be more useful to study a well-defined arene dipositive ion and attempt to create a situation of partial oxidation by using a lesser amount of SbF_5; a similar procedure of partial reduction is effective in ^{1}H NMR studies of radical anions.[20] Corrections to chemical shifts have not been made here for bulk susceptibility, which would be affected to some extent by the presence of paramagnetic species of unknown concentration. Despite these limitations, it is noteworthy that any peaks downfield of ca. δ_C 156 in the spectra of **8** and **9** are either missing or highly broadened. The downfield peaks in ^{13}C NMR spectra of arene dications correspond to the carbons with the greatest positive charge density and these carbons should also be the centers of concentration of unpaired electron density in the radical cations, since both densities are determined by the coefficients of the HOMO of the arene in simple Hückel theory. The carbons in the dications which have the largest spin density in the radical cation form will experience the most relaxation, due to the electron exchange process. Similar nonuniform line broadening was noted by Lawler and Ristagno in a ^{1}H NMR study of arene dianions, although few details were given.[22]

Another arene which is predicted by Hückel theory to have an ionization potential similar to **8** and **9** is tetrabenznaphthalene (**7**), which gave a well-resolved ^{13}C spectrum of the dipositive ion with no evidence of electron exchange. However, during the 1.5 h at −10° necessary to obtain the pulsed FT spectrum, the solution turned from a homogeneous liquid to a solid gel. Formation of solids was typical of the arenes with higher ionization potentials; typical solutions of dications were stable for hours at −10° and indefinitely (weeks) at ca. −60°.

Stable dipositive ions were observed for the nine arenes in Table I which have the highest lying HOMO's. A typical result is illustrated by the ^{13}C spectrum of the pyrene (**12**) dication, shown in Figure 2. Carbon chemical shifts for the dications are listed in Table II, along with tentative assignments (vide infra). The line positions are considerably downfield from resonances typical of neutral aromatic hydrocarbons (δ_C 122–134).[23] For instance, the average (weighted) δ_C for anthracene dication is 159.1 ppm, compared to an average δ_C of 128.0 for anthracene in $CDCl_3$.[23] The total change in δ_C for all 14 carbons is 434.6 ppm, or 217.3 ppm/e$^-$. The δ_C for neutral **10**,[23] **11**,[23] and **12**[24] are also known, and these species give shifts in position amounting to 218.7, 220.2, and 226.8 ppm/e$^-$. Although δ_C's are not known for the other neutral arenes, a rough indication of the generality of this magnitude of charge dependence for the dications can be seen from the slope of 200 ppm/e$^-$ (intercept = 129 ppm; SD = 2.3) found for a plot of average δ_C vs. average charge (2/no. of carbons), considering the average δ_C's for all of the unsubstituted dications in Table II. The average δ_C's cover a range of 15 ppm. The large deshielding is strong evidence for the dipositive character of these species.

The proportionality constant of 200 ppm/e$^-$ is larger than the approximately 160 ppm/e$^-$ found for monocyclic aromatic π systems.[25,26] Oth found that the average δ_C of 153.2 ppm for 16-annulenium dication (**21**) fell on the same correlation line of 160 ppm/e$^-$ slope.[27] O'Brien et al. reported that a proportionality constant of 156.3 ppm/e$^-$ (intercept at zero charge = 133.2 ppm) is applicable to δ_C in monocyclic systems plus the average δ_C in conjugated π systems in which all the carbons are not equivalent, e.g., acyclic- and phenyl-substituted carbanions and carbocations.[28] Dication **21** should be very similar to the arene dications generated in the present study and in fact its average δ_C falls very close to the correlation line we observe for the arene dications, in addition to fitting the 156.3 ppm/e$^-$ correlation line. One interesting aspect of the correlation line reported by O'Brien is that it passes through the middle of our arene dication average δ_C data because the lesser slope is compensated for by the higher intercept of 133.2 ppm (~4.5 ppm above δ_C for benzene[21]). Thus, despite the slope of 200 ppm/e$^-$, our dication data do not deviate greatly from the overall correlation line for ionic π systems, although it is obvious that the average δ_C for the neutral arenes will fall below this correlation line, as does benzene.



21

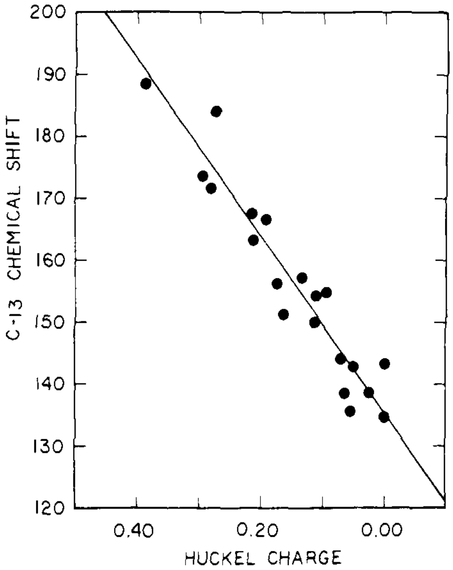


Figure 3. Correlation of δ_C for individual positions of dications vs. positive charge densities calculated in Hückel MO method (cf. Table III).

The resonances assigned to ring junction carbons in Table II were distinguished from the other ring position resonances by the lack of one-bond C–H coupling in off-resonance or fully coupled spectra. In many cases, further specific assignments of ring junction carbons could not be made. However, for **7**, **12**, **16**, **17**, and **19**, specific assignments were made on the basis of relative peak intensities in relation to the number of equivalent carbons giving rise to the peaks; this is not a completely reliable criterion because of possible differences in relaxation times, but generally the positions with the fewest numbers of equivalent carbons were also at the interior of the molecule, farthest removed from protons, so that the smaller peaks would be expected both on the basis of fewer carbons and longer relaxation times.

Assignments for carbons bonded to protons were made on the basis of peak intensities for **12**, **14**, and **17**, and by comparison with substituted derivatives in the case of **14**,[29] but the chief criterion was comparison with calculated charge densities for the dications and with experimental hyperfine splittings in ESR spectra of the radical cations, as shown in Table III. These assignments must be regarded as tentative, but generally differences were great enough (>10 ppm) between individual positions in each dication so that such assignments could be made with confidence. A plot of δ_C from Table III vs. charges calculated in the simple Hückel method is shown in Figure 3 (slope = 143 ± 11: intercept = 135.2 ± 1.9 ppm, SD = 4.9). The correlation with Hückel charges is obviously approximate, as would be expected from a method which neglects electron repulsions, but the standard deviation from the correlation line is less than half of the typical difference between shifts in any individual system where assignments were made. Further detailed theoretical studies may lead to fuller understanding of δ_C in ionic π systems, but the present brief examination suffices to demonstrate the dominant influence of charge and also to lend theoretical support to the evidence for existence of dipositive arene systems as stable species.

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