ON THE ^{1}H-NMR SPECTRA OF HIGHLY CHARGED MULTI-TRIPHENYLMETHYLIUM IONS

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Summary: Relative to their neutral precursors, highly charged multi-tritylium ions show typical downfield ^{1}H-NMR shifts, whereas the corresponding phenylfluorenylium ions show upfield shifts. A Hückel based model is presented that accounts for this contrasting behavior in terms of antiaromatic ring current in the five-membered ring of the fluorenyl system with essentially null ring currents in the two six-membered rings.

In a recent study of the UV/VIS- and ^{1}H-NMR-spectroscopical properties of multitritylium ions we showed that the mono- through tetracations **1-4** not only reveal interesting variations in their colors (i.e., their longest wavelength electronic absorptions), but also characteristic charge-related deshieldings relative to their carbinol-ether precursors.[1] The downfield shifts of the *p*-protons was quite marked. In striking contrast, the corresponding phenylfluorenylium ions **5-8** experience strong upfield shifts of their fluorenylium protons relative to the carbinol-ether precursors. The contrasting behavior of the fluorenylium and tritylium ions could be taken as evidence for considerable paratropic ring current contributions in the fluorenylium systems[2]. It was of interest, therefore, to investigate whether these contrasting NMR shifts could be reproduced by a model that has proved quite successful in correlating the ring-current dominated chemical shifts of neutral aromatic and antiaromatic hydrocarbons[3]. Appropriate modifications of the model would have to be made to account for the charge-induced shifts.

The model employed is based on an iterated Hückel model in which the bond lengths are taken to be a linear function of the bond order and the resonance integrals (betas) are taken to be an exponentially decreasing function of the bond length, all iterated to self-consistency. Ring currents were calculated by the McWeeny method[3] using the iterated bond orders and the chemical shifts due to these currents were calculated using the Biot-Savart formalism.[5] With this model over a 100 chemical shifts of neutral hydrocarbons could be reproduced with a standard deviation of about 0.2 ppm for shifts ranging from 3.6 to 9.3 ppm.

To adapt this model to hydrocarbon cations it was extended by adding four parameters. Three of the parameters determined the change in alpha(i) (Coulomb integral) for a charge on a carbon atom i, the charge on an adjacent carbon (i+1), and the charge on the next removed carbon atom (i+2). The fourth parameter is the proportionality constant between chemical shift and the electric field gradient at a proton due to all of the charges on the carbons. The parameters were determined by fitting the para chemical shift of triphenylmethyl cation exactly and the ortho and meta protons approximately. The problem is underdetermined and, therefore, infinitely varied combinations of parameters are possible. The constraint

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**Table 1 Observed and Calculated ^{1}H-NMR Chemical Shifts for Cations 1-8**

Cation		calculated 0°	calculated 32°	observed[a,b]
1	a	8.40	7.71	7.77
	b	7.87	7.81	7.95
	c	8.43	8.34	8.34
2	a	8.90	8.28	8.03
	d	8.42	7.60	7.92
	e	8.00	7.93	8.07
	f	8.70	8.59	8.50
3	a	8.72	8.41	8.22
	b	8.53	8.31	8.30
	d	8.08	7.71	8.04
	e	7.94	7.99	8.17
	f	8.70	8.67	8.61
	h	8.93	7.78	8.32
	i	8.51	8.09	8.35
	j	9.18	8.86	8.84
4	a	8.72	8.53	8.57
	b	8.34	8.35	8.38
	d	8.20	7.69	8.14
	e	7.99	8.02	8.22
	f	8.82	8.75	8.68

Cation				
5	a	8.09	8.18	8.00
	b	7.79	7.68	7.88
	c	8.52	8.09	8.20
	d	7.79	7.49	7.38
	e	7.06	6.87	7.00
	f	7.60	7.56	7.42
	g	7.28	6.96	7.02
6	a	8.67	8.61	8.17
	d	7.15	7.16	7.19
	e	6.81	6.81	6.86
	f	7.56	7.64	7.37
	g	6.94	6.96	6.85
7	a	8.92	8.83	8.19
	b	8.40	8.07	8.08
	d	7.14	7.11	7.17
	e	6.83	6.83	6.79
	f	7.67	7.73	7.34
	g	7.06	7.03	6.84
	h	7.90	7.61	8.06
	i	8.05	8.01	8.17
	j	8.97	8.78	8.71
8	a	8.99	8.91	8.28
	b	8.33	8.01	8.28
	d	6.93	6.95	7.20
	e	6.80	6.80	6.80
	f	7.68	7.77	7.36
	g	7.04	7.07	6.80

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[a]Bruker 200, 300, or 500 Mhz
[b]All cations were generated by dissolving the corresponding carbinol ethyl ethers (prepared by standard methods[7]) in mixtures of CD_2Cl_2, trifluoroacetic and trifluoromethanesulfonic acid. The ether precursors show only uncharacteristically spread multiplets between δ ($CDCl_3$) = 7.1-7.6.

used here was that the ratios of the three parameters that determined the alpha of each carbon fell off approximately as the ratios of the electron repulsion integrals appearing in Pariser-Parr-Pople SCF calculations.[6]

$$-\alpha(i) = 0.5\, q(i) + 0.4\, q(i+1) + 0.2\, q(i+2)$$
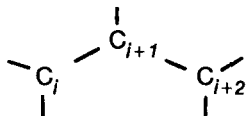
charge shift at proton j = 14.339 x electric field gradient at proton j

In these calculations it was assumed, as with the tripenylmethyl cation, that the plane of each phenyl group is rotated by 32°. The calculations for the fully planar cations are included to illustrate the sensitivity of the shifts to torsional angles. As approximate as the model is, it is able to correlate 44 additional chemical shifts of hydrocarbon cations bearing 1-4 positive charges with a standard deviation of 0.26 ppm (Table 1). A least squares fit of the calculated and observed data gave a slope of 1.0000 (sigma 0.0048) and a correlation coefficient of 0.91. If the full set of data were used to calibrate the parameters, the fit would undoubtedly improve.
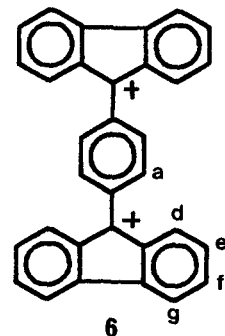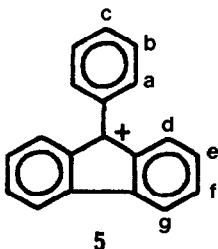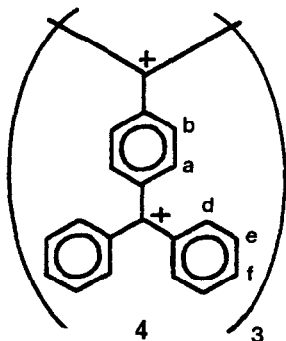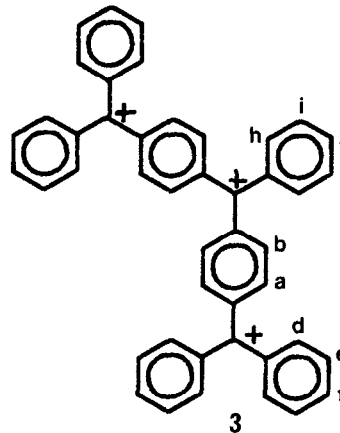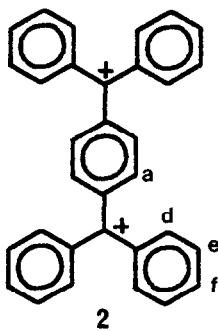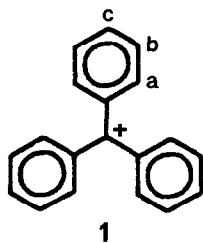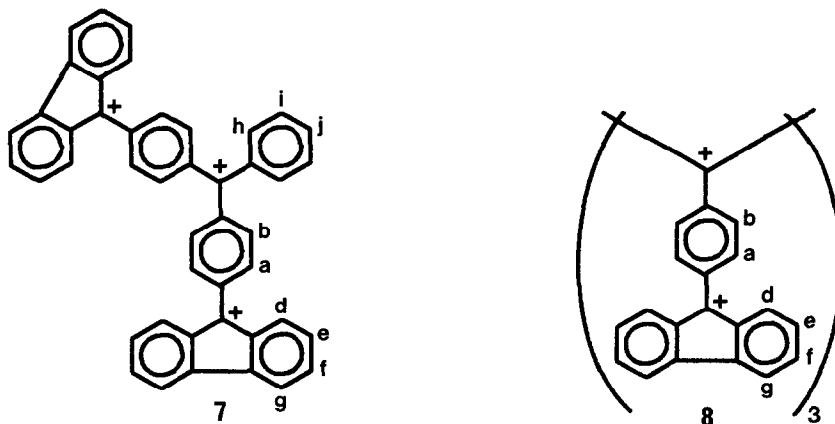
The two cations that initiated this study are **5** and **6**. In **5** the protons on the phenyl ring come at about the same positions as in the triphenylmethyl cation, **1**. However the meta and para protons of the fluorenyl ring are displaced upfield by an average of 0.93 ppm. According to the model this upfield shift is a direct result of the very small diatropic ring current calculated for benzo rings (0.147) and the strongly paratropic ring current in the central five-membered ring (-1.045). In fact, the protons would come even further upfield than those in **1** except for the fact that the electric field induced downfield shifts in **5** are somewhat larger than in **1**. A similar analysis applies to cations **6**, **7** and **8**. In **6** the protons on the fluorenyl ring are about 1.2 ppm upfield relative those in **2**; the six-membered ring of the fluorenyl system are calculated to have almost no ring current (0.029), while the five-membered ring is strongly paratropic (-1.148). As with **5** the charge-induced downfield contributions in **6** are slightly larger than the charge effects. In **7** the six-membered rings of the fluorenyl system have almost no ring currents (0.001), while the five-membered rings are strongly papratropic (-1.169). In **8** the ring currents are slightly paratropic (-0.018), while the five-membered rings are strongly so (-1.186). In **5-8** it is primarily the absence of the usual diatropic ring currents in the six-membered rings that account for the upfield displacements of the attached protons. The paratropic ring current of the adjacent five-membered rings also make a further upfield contribution.

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