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CHARGE DISTRIBUTION IN DICARBONIUM IONS

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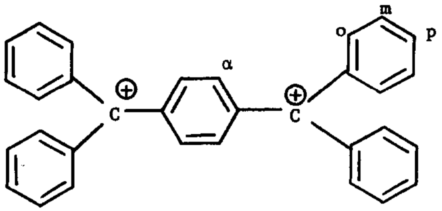
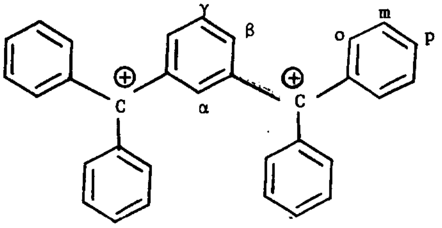
Nmr chemical shifts in charged species are proportional to tne charge density (1). Charge distribution in arylcarbonium ions has been probed using this tool (2,3), and it has been shown that chemical shifts of para protons parallel m.o. predictions, whereas ring currents of adjacent aryl groups seriously affect ortho protons (and, to a lesser extent, meta protons). Thus in the triphenylmethyl cation, para protons appear at lowest field, but ortho protons appear at highest field (4).

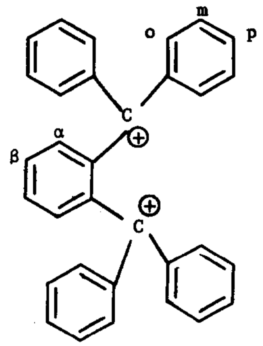
We wish to report here the first assignment of chemical shifts of protons in dicarbonium ions. Spectra and $pK_{R^{++}}$'s of ions I-III were reported earlier (5). I-III were synthesized with deuterium in the positions shown in Table I. From the nmr spectra of the



I



II



III

TABLE I. Labelled Dicarbonium Ions

Ion	o	m	p	α	β	γ
I	D	D	H	D		
	D	D	D	H		
	H	H	D	D		
II	H	H	H	D	D	D
	D	D	D	H	H	H
	D	D	D	H	H	D
III	H	H	D	H	H	
	D	D	D	H	H	
	D	D	D	H	D,H	

unlabelled and labelled ions in 98% D_2SO_4 with tetramethylammonium ion as an internal reference (τ 6.87), the chemical shifts of the various types of protons were deduced (6). These are presented in Table II, together with charge densities calculated by the ω-technique (7) using designated models for the geometry of the ions.

One can draw the following conclusions from these results:

1. The same sequence of chemical shifts is observed in the 'outer' rings of dicarbonium ions I-III as is observed in the trityl cation; i.e., p>m>o. The value of $\tau_m-\tau_p$ and $\tau_o-\tau_p$ are respectively 20 and 30 cps, about the same as in the trityl cation. However, all the protons appear at lower field, as expected for a dication.

2. The 'outer' rings of I are predicted to, and do carry more positive charge than those of II.

3. Protons in the ortho positions of the 'outer' rings, and in similar locations on the 'central' ring, appear at considerably higher field than predicted by m.o. calculations,

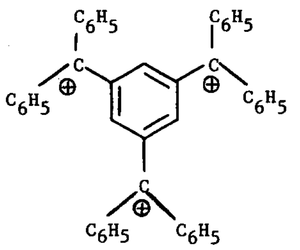
TABLE II. Chemical Shifts and
Calculated Charge Densities

	I			II			III			Trityl	
Position	τ	ρ_{flat}	$\rho_{30°}$	τ	ρ_{flat}	$\rho_{30°}$	τ	$\rho_{30°}$	$\rho_{45°}$	τ	$\rho_{30°}$
o	2.12	.065	.061	2.23	.063	.059	2.25	.060	.054	2.31	.057
m	1.95	.025	.024	2.10	.024	.023	2.08	.024	.022	2.13	.022
p	1.60	.070	.067	1.77	.066	.063	1.75	.065	.060	1.76	.061
α	2.03	.069	.065	2.40	.121	.114	2.03	.080	.073		
β				1.77	.109	.103	1.52	.071	.066		
γ				1.77	.041	.039					

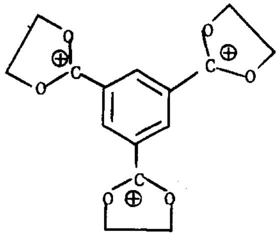
due to shielding by neighboring aryl rings. Particularly striking is the α proton of II, which appears at highest field, though predicted from m.o. calculations of charge density to appear at lowest field. Although the α proton presumably has twice the positive charge of the para protons in II, the two appear at opposite extremes of the nmr spectrum. The β protons in II are also strongly shielded from their expected position.

4. When shielding by ring currents of neighboring aryl groups should not be very large, the chemical shifts are in approximate accord with m.o. predictions. An example is the β proton in III which, as predicted even for a highly twisted model, appears at lower field than the para protons. Compare also the γ *vs* meta protons in II. The γ proton does, however, appear at somewhat lower field than expected, by comparison with the para protons.

Finally, attention is called to the possible advantage of using the nmr spectra of 1,3-dioxolenium cations in preference to those of arylmethyl cations to test predictions of m.o. theory regarding charge densities. For example, in IV, the three protons on the 'central' ring appear at higher field than any other protons in the ion, at τ 2.57 (8); the corresponding protons in V, where ring currents do not interfere, appear at τ 0.42 (9),



IV



V

although delocalization of charge to the oxygens in V should be even greater than delocalization to the 'outer' phenyls in IV (10).

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6. Labeling did not have to be unique for each type of proton present. Assignments could be made making use of incomplete exchange, since the chance that the few hydrogens not replaced by deuterium would appear in the same molecule was small; thus these hydrogens appeared as fairly sharp singlets.
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