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Correlation of ¹³C Chemical Shifts and CNDO/2 Charge Distributions in Phenylcarbenium Ions and Related Phenyl Substituted Onium Ions¹

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Abstract: The complete ¹³C NMR spectra have been obtained for 22 phenylcarbenium ions and related phenyl substituted onium ions. The ¹³C chemical shifts for these cationic, monosubstituted benzenes are discussed in relation to charge densities calculated for the systems using the CNDO/2 method and in relation to similar data for electronically neutral monosubstituted benzenes. The para carbon shifts are linearly correlated with charge over a range of 45 ppm. The phenylcarbenium ions and phenyl substituted onium ions are treated as successfully in calculations, neglecting the gegenion, as are the electronically neutral benzenes. The para carbon shifts in ions formed by protonation of a heteroatom in a substituent exhibit small deviations from the expected para shifts, which may be due to hydrogen bonding between the ion and solvent. Nonequivalent or tho shifts in several ions indicate an important shielding contribution from the γ -substituent effect at or the carbons in addition to charge effects. The nonequivalence in ortho shifts arises from slowed rotation about the substituent-ring bond due to significant double bond character. Meta carbon shifts in the cations occur in a narrow range, slightly downfield from meta carbons in electronically neutral benzenes. The shifts for the directly substituted ipso carbons, and also for sp^2 hybridized α carbons, correlate poorly with calculated charge densities, with the deviations from a correlation line showing some regularity related to the type of substituent.

The interpretation and prediction of ¹³C NMR chemical shifts is an area of much theoretical activity. However, in practice, ¹³C chemical shifts are frequently used to provide detailed information about structure, bonding, and electron distribution in organic molecules and ions with only cursory reference to theoretical treatments of chemical shifts. In our previous work, we have had considerable success in using ¹³C spectra as evidence for the existence of stable carbocations in solution and as a probe for determining the pattern of charge distributions in such ions. Now, as part of an investigation into the various possible influences on ¹³C chemical shifts, we have attempted to determine the extent to which the ¹³C shift can be used as a quantitative index of charge distribution in phenylcarbenium and phenyl substituted onium ions.

The relationship between ¹³C NMR chemical shifts in monosubstituted benzenes and the electronic effects of sub-

stituents has received considerable attention.³⁻¹¹ Particular attention has been given to the para carbon which is shielded by electron-donating substituents and deshielded by electron-withdrawing groups. The para carbon shifts give linear correlations with calculated electronic charge densities and with various chemically derived para substituent constants. Similar electronic effects are observed at ortho carbons, although the correlations with charge densities obtained from molecular orbital calculations are much less satisfactory than for the para position.^{5,8-10} It has often been assumed that substituent influences other than charge density perturbations affect the magnetic environment of the ortho carbons.^{4,5,11} Least subject to substituent influences are the meta carbons, which absorb over a narrow range; the directly substituted ipso carbons are the most sensitive.11

We now report a ¹³C NMR study of monosubstituted

 Table I.
 ¹³C Chemical Shifts^a of Monosubstituted Benzenes^b

	Substituent	C ₁	C _{2,6}	C _{3,5}	C ₄	Cα		
1a	CF,	119.5	126.3	128.8	131.7			
1 b	CH	137.4	129.2	128.4	125.6			
1c	CN	113.1	132.1	129.1	132.4			
1d	ССН	122.4	132.3	128.9	128.3			
1e	COCF,	122.9	130.3	129.2	135.2	180.5^{c}		
1f	COCH	137.6	128.6	128.5	132.7	196.0d		
1g	COCL	133.1	130.9	128.5	134.7	168.5d		
1ħ	СНО	137.1	129.8	129.1	134.0	191.0d		
1i	COOH	130.6	130.0	128.5	133.6	174.9d		
1j	C1	134.7	128.9	129.8	126.6			
1k	F	163.3	115.6	129.9	124.0			
11	н	128.5						
1m	NH,	146.5	115.2	129.4	118.7			
1 n	NO,	148.5	123.7	129.4	134.3			
10	OCH,	159.9	114.1	129.5	120.8			
1p	ОН	155.4	115.8	129.9	121.2			

 ${}^{a}\delta_{\rm C}$, ppm from TMS. Original data converted using $\delta_{\rm C}({\rm C}_6{\rm H}_6) = 128.5$ (ref 28, p 79). ^b Data from ref 10. ^cCarbonyl resonance measured in this study. ^d Carbonyl resonance from ref 11, p 280.

benzenes in which the substituent bears a formal positive charge, specifically, phenylcarbenium and phenyl substituted onium ions. The results are discussed in relation to charge densities obtained for the systems using the CNDO/ 2 approximation¹² in all-valence-electron molecular orbital calculations and in relation to similar data for electronically neutral monosubstituted benzenes. We had several objectives in performing this study. It was of interest to establish a theoretical justification for the use of ¹³C chemical shifts in the interpretation of the electronic nature of organic cations, with neglect of the gegenion. Second, data on cationic monosubstituted benzenes permits an examination of the linearity of the relationship between para carbon ¹³C chemical shifts and calculated electron densities over a significantly wider range of shifts than previously reported. Third, we wished to determine the limitations of using chemical shift differences as indicators of charge density differences for all types of sp² hybridized carbons in these ions. The data also provide information about the electronic character of the substituents, particularly in regard to the demand by the substituents for charge stabilization through resonance interaction with the phenyl group.

Results

The ${}^{13}C$ shifts obtained by Nelson, Levy, and Cargioli for monosubstituted benzenes (1a-p) are reproduced in Table I.¹⁰ The carbon shifts found in this study for 22 cationic monosubstituted benzenes (2a-n, 3a-h) are listed in Table



11. Most of the cations were formed in SO₂ClF solution by protonation of the appropriate substrate with a superacid, HF-SbF₅ or FSO₃H-SbF₅, or by ionization of a precursor using SbF₅ or HF-SbF₅ or FSO₃H-SbF₅. The phenylammonium ion, **3f**, was an exception to the general procedure because it was not stable in superacid-SO₂ClF solutions, so it was formed by protonation of aniline in 10 N HCl. Details of the methods of preparation of these ions are given in the Experimental Section. All of the spectra reported were obtained by the pulsed, Fourier transform method on a Varian XL-100 or a modified Varian HA-100 NMR spectrometer.

Specific peak assignments were aided by running completely proton decoupled spectra and off-resonance decoupled spectra, which allowed the differentiation between C1 and carbons bearing hydrogens. Typically, C1 peaks in the completely decoupled spectra were much narrower than the other peaks. The para position, C4, could be distinguished from $C_{2,6}$ and $C_{3,5}$ resonances by consideration of the relative peak intensities. In every case, except 3f, the C₄ resonance appeared downfield of peaks for the ortho and meta positions. When ortho peaks were nonequivalent and hence of roughly the same intensity as the C₄ peak, the general downfield shift of C4 was one of the criteria used in making the assignments. In ion 2a, C-F coupling was observed for C_2 and C_6 but not C_4 . The C_4 resonance could be distinguished from the C_2 and C_6 peaks in ion 2g by their coalescence into a single $C_{2,6}$ peak at -25° , and similarly, the C_2 and C_6 peaks for ion **2f** showed significant broadening at higher temperatures. The assignments of para carbon resonances are further justified by the success of the correlation with charge densities, discussed below. The chemical shifts for the meta carbons covered a narrow range of about 4 ppm, which aided in their assignment. In the few cases in which C_{2,6} and C_{3,5} resonances were nearly equivalent and where other criteria such as similarity to other ions could not be applied, the ambiguity of the assignment has been noted.

Molecular wave functions for monosubstituted benzenes were calculated using the CNDO/2 method, employing the original parameterization of Pople,¹² For calculations involving second-row elements, the sp basis set of Santry and Segal was used.¹³ Electron populations obtained from the diagonal elements of the density matrix were converted to charge densities by subtracting the electron populations from the number of atomic orbitals involved. Table III lists the total charge densities for the ring carbon atoms and for the α carbon when it is sp² hybridized. Table IV lists the π charge densities. These calculations differ slightly from previous CNDO/2 calculations on some of the same monosubstituted benzenes due to differences in the chosen molecular geometries.^{8,10,14}

Two previous studies^{8,10} of carbon shieldings in substituted benzenes successfully made use of the CNDO/2 method. In the present study, standard bond lengths and angles¹⁵ were used to estimate geometries, since reliable experimental geometries are available for only a few monosubstituted benzenes, and none of the ions. CNDO/2 calculations were performed for the electronically neutral benzenes in addition to the phenyl carbenium and phenyl substituted onium ions, using the standard geometries to provide a consistent basis for comparison. Although the use of standard bond lengths and angles will result in some deviations from the true geometries, we felt that the use of a well-defined geometric model was preferable to making arbitrary adjustments in individual geometries and was more practical than optimizing geometries through calculations. For instance, the bond from the α carbon to the ring is expected to decrease in length as carbenium-type substituents become more electron withdrawing, but the use of a standard bond length will still allow the MO calculations to represent the effect on charge distributions of a systematic increase in electron-withdrawing capability of substituents.

Conformations were chosen to minimize steric interactions and so that substituents would be coplanar with the ring when the atom bound to the ring was sp^2 hybridized. For protonated substituents, the same bond lengths were used as in the unprotonated form, with the exception of protonated benzoic acid in which both C-O bonds were given the carbonyl bond length (1.22 Å). The C(sp²)-Cl bond length was taken as 1.70 Å and the C(sp²)-S and C(sp³)-S

Table II. ¹³C Chemical Shifts^a of Cationic Monosubstituted Benzenes^b

	Substituents								
Ion	R	R'	C1	C ₂₍₆₎	C.	C _{3,5}	C4	С _а	
 2a	F	Н	129.3	155.3	142.4	134.6	163.5	203.7	
2b	Ċ	H	142.3	153.5	142.3	134.8	163.2	210.7	
	0.					133.8			
2c ^c	CH.	н	141.5	155.1	143.6	133.8	161.6	230.4	
$2d^d$	C.H.	н	138.3	149.1	143.4	133.7	150.9	200.6	
2ed	c-C.H.	Н	137.6	145.2	136.4	132.2	149.0	226.3	
2f	OH	Н	128.4	146.1	133.7	131.8	148.9	204.7	
$2g^e$	ОН	CH.	129.0	138.5	133.0	130.9	145.3	219.5	
201	OH	CH	129.1	135.8		131.0	145.2	219.5	
2h	OH	CH,CH,	127.9	137.8	133.3	131.1	145.4	222.9	
2i	OH	CF,	122.9	143.5	139.6	133.3	154.2	190.9	
		5				132.6			
2j	F	F	110.9	145.5		134.5	160.0	178.5	
2k	C1	C1	140.4	143.9		133.7	160.1	212.1	
21d	СН₃	CH3	140.0	142.4		133.3	155.9	254.3	
2m	ОН	OH	120.4	133.0		130.8	141.5	181.9	
2n	OH	OCH3	121.3	131.8		130.6	140.9	181.9	
3a8	CO ⁺ CNH ⁺ N ₂ ⁺		87.7	141.3		132.9	149.4		
3b			99.6	136.3		130.5	140.3		
3ch			115.8	134.5 ⁱ		134.2^{i}	144.5		
3d	N(C	$(H_3)_3^+$	145.8	119.0		130.9	130.9		
3e	N(C	$(H_3)_2H^+$	141.2	119.6		131.1	131.1		
3ť	NH3	+	130.8	124.5		131.3	130.8		
3g	NO	,H+	141.8	128.9		132.2	146.7		
 3h	S(C)	$H_{3})_{2}^{+}$	125.6	130.3 ⁱ		132.5 ⁱ	136.1		

 ${}^{a}\delta_{C}$, ppm from TMS. ^b Recorded in SO₂ClF solution at -60 to -80°. See Experimental Section for details of preparation. ^cC_a previously reported: G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Am. Chem. Soc.*, 93, 464 (1971). ^dG. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, 95, 7530 (1973). ^e -80°. ^f -25°. ^gG. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, 95, 3706 (1973). ^hG. A. Olah and J. Grant, *ibid.*, 97, 1546 (1975). ⁱ Ortho and meta shifts may be reversed. ^j Reported in different solvent system, ref 10.

Table III.	CNDO/2 Calculated	Total Charge De	ensities for Monosubstituted Benzenes $(\times 10^3)$)
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			Orthoa		Meta ^a			
Ion or mole	ecule Ipso C ₁	C ₂	C ₆	C ₃	C ₅	Para C_4	Cα	
1a	-44	28		4		21		
1b	43	-12		10		-5		
1c	39	10		6		10		
1d	55	0		7		2		
1e ^b	-6	26	15	1	4	24	173	
$1f^b$	-20	22	12	0	1	17	244	
1gb	-22	32	24	-1	0	26	346	
1ħ ^b	-13	23	16	0	0	19	228	
lib	-30	29	23	-2	-1	22	380	
11	134	-19		18		-2		
-j Ik	229	-50		26		-13		
11	5							
1m	160	-61		31		-33		
ln	35	22		5		29		
10 ^b	186	-64	-53	27	27	-22		
1p ^b	186	-62	-50	28	27	-23		
2a	-30	97	102	6	-7	122	447	
2b	-11	94	92	-7	-6	118	295	
2c	-18	90	84	9	-8	111	271	
2d	-7	79	-3	-9	-1	92	225	
2e	-18	86	91	-10	-9	106	233	
2f	-50	77	70	2	5	88	372	
2g	-58	65	62	4	6	77	392	
2h	-60	64	62	4	5	75	384	
2i	-51	72	70	6	6	90	318	
2j	-53	97		-1		114	641	
2k	-20	85		-3		106	346	
21	-29	73		-5		94	284	
2m	-72	68	60	6	9	72	531	
2n	-74	64	57	7	9	69	519	
3a	-17	76		10		80		
3b	-7	60		11		66		
3c	71	43		21		60		
3d	85	-20		34		20		
3e	76	-10		32		27		
3f	68	2		32		35		
3g	42	47	45	18	18	71		
3h	103	4		33		27		

^aBlank for entry indicates equivalence to preceding entry for the same species. ^bCarbonyl oxygen or O-X substituent is syn to C_2 .

Table IV. CNDO/2 Calculated π Charge Densities for Monosubstituted Benzenes (×10³)

		Ort	Ortho ^a		ta ^a		
Ion or molecule	Ipso C ₁	C ₂	C ₆	C ₃	C _s	Para C ₄	C_{α}
1a	50	19		0		25	
16	29	-24		11		-16	
1c	-2	0		5		8	
1 d	17	-12		8		-5	
1e ^b	-32	28	23	-2	-1	32	114
1 f ^b	-15	25	14	$^{-2}$	3	20	162
$1 g^b$	-36	30	31	-5	-4	34	180
1ħ ^b	-15	24	18	-3	-3	22	155
1i ^b	-30	29	26	-5	5	27	190
1j	5	-22		11		-10	
1k	31	-48		21		-26	
11	0						
1m	75	-89		34		-61	
1n	-68	34		-3		41	
10 ^b	51	-69	-63	28	26	-42	
1p ^b	55	-70	-64	28	27	-43	
2a	-96	135	144	-13	-13	200	493
2 b	-79	135	134	14	-12	193	493
2c	-85	137	125	-16	-14	181	551
2d	-66	125	92	-13	-4	153	428
2e	-78	133	123	-16	-15	173	469
2f	-115	101	80	-1	-1	141	422
2g	-113	82	72	1	1	1.22	422
2h	-111	79	71	2	1	119	423
2i	-116	100	82	2	0	145	393
2j	-126	125		-8		186	452
2k	-93	117		-9		173	453
21	-94	110		-10		153	539
2m	-132	79	59	5	3	114	361
2n	-125	74	55	5	4	107	347
3a	-152	73		6		128	
3b	-127	56		8		104	
3c	-150	42		16		99	
3d	-64	-31		36		29	
3e	-87	18		32		41	
3f	-115	-5		31		55	
3g	-144	58	59	10	10	116	
3ň	94	-9		24		42	

^aBlank for entry indicates equivalence to preceding entry for the same species. ^bCarbonyl oxygen or O-X substituent is syn to C_2 .



Figure 1. Para carbon shift vs. para total charge density. Symbols: O, electronically neutral benzenes; \Box , cationic benzenes; Δ , cationic benzenes formed by protonation of a heteroatom. Correlation line does not include Δ points.

bonds were 1.74 and 1.81 Å, respectively. All other geometric parameters could be defined by the standard geometric model.¹⁵

Discussion

Para Carbons. The ¹³C NMR chemical shifts for para carbons in monosubstituted benzenes are plotted vs. CNDO/2 total charge densities for the para carbons in Fig-

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ure 1. A good linear correlation is observed for all the data (slope $(m) = 282.1 \pm 9.7$; intercept $(i) = 126.7 \pm 0.6$; correlation coefficient (r) = 0.980; standard deviation (SD) = 2.6). An equally good correlation is observed if only the π charge densities are considered $(m = 166.6 \pm 5.8; i = 127.8 \pm 0.6; r = 0.979;$ SD = 2.6). The data point for ion **2e**, which contains a cyclopropyl group, was omitted from the correlations because of the failure of the CNDO/2 method in adequately treating small ring systems.¹⁶

The observation of a good linear relation between carbon chemical shifts and charge densities covering a range of 45 ppm and a total of 37 substituents is a clear indication that factors other than charge density differences must be of minor importance in determining differences in the magnetic environment at the para carbon. The fact that π charge densities are as good as total charge densities in the correlation suggests that π -system resonance and polarization interactions with the substituents are the dominant influences on para carbon charge densities. The slope of the line for the dependence of ¹³C shifts on π charge density (167 ppm/ π electron) is close to the proportionality constant of 160 ppm/ π electron previously observed for monocyclic aromatic systems¹⁷ and para-substituted benzenes.¹⁸

Although the correlation of shifts with charge densities is good for all points, a systematic deviation is detectable for those points corresponding to the cationic monosubstituted benzenes formed by protonation of a heteroatom in a substituent. There are ten protonated systems (2f-i, 2m, 2n, 3b, 3e-g) and all but 2i lie above the line shown in Figure 1 es-

Table V. ¹³C Chemical Shifts^a of Some Disubstituted Benzenes^b

	Ion or							
	molecule	C ₁	C ₂	C ₆	C _{3,5}	C4	C_{α}	
	p-OCH ₃ -1h	129.7	131.8	131.8	114.1	164.6	190.6	
	p-OCH ₃ -1h ^c	129.0	136.2	127.3	115.2	164.2	191.0	
					112.4			
	<i>p</i> -OCH ₃ -2f	121.3	148.6	136.3	119.6	176.3	193.2	
					116.2			
	<i>p</i> -CH ₃ -2f	126.0	146.2	133.8	133.1	165.9	200.3	
	5				132.5			
	<i>p</i> -OCH ₃ -2g	121.7	141.8	136.3	117.3	173.5	208.9	
					116.0			
	p-CH ₃ -2g	126.5	138.7	133.1	131.8	160.6	216.0	
	p-F-2g	125.7	143.0	137.4	118.8	173.6	216.7	
	p-C1-2g	127.3	139.3	134.1	131.4	153.1	218.1	
-				~~~				-

 ${}^{a}\delta_{C}$, ppm from TMS. b Measured in SO₂ClF solution at -60° . ${}^{c}-105^{\circ}$.

tablished by the para carbons of the other substituted benzenes, i.e., the para carbons in protonated systems are not as deshielded as would be anticipated from the calculated charge densities. When the protonated systems are excluded, the correlation improves significantly in the plot of shieldings vs. total charge density ($m = 293.0 \pm 5.3$; i = 127.4 ± 0.3 ; r = 0.996; SD = 1.3). The correlation with π charge densities shows similar improvement ($m = 172.5 \pm$ 3.4; $i = 128.6 \pm 0.3$; r = 0.995; SD = 1.4). Actually, the magnitude of the deviations has been minimized by using the unaltered carbonyl bond lengths in the protonated systems; the use of a longer bond length in the calculations gives a larger deviation.

The source of the deviation of protonated systems is not clear. The substituents are fully protonated, as indicated by proton NMR spectra in which separate resonances were observed for the protons bound to the substituents. For protonated benzaldehyde and the other aldehydes listed in Table V, the PMR peaks for the hydroxylic proton and the aldehydic proton are doublets due to mutual coupling, which indicates that intermolecular exchange is slow. However, if hydrogen bonding between the protonated species and the solvent or gegenion occurred to any extent, it would reduce the demand for charge stabilization by the benzene ring and hence lower the expected charge density at the para position. On the other hand, the standard geometric models or the CNDO/2 method may be inadequate for proper representation of the protonated systems. Good examples of these deviations are the phenylammonium ions **3d-f**, for which the calculations show significantly different charge densities but have nearly identical C4 shifts. Regardless of the cause of the deviation, the conclusion that the ¹³C chemical shift is linearly related to charge density at the para position is not negated by this observation of a systematic deviation for a specific group of compounds.

Ortho Carbons. The ortho carbon chemical shifts are particularly interesting. In most monosubstituted benzene derivatives, the ortho carbons are magnetically equivalent due to symmetry in the substituent or fast rotation about the single bond between the substituent and ipso ring carbon. However, the ortho carbons in several of the charged systems listed in Table II are not equivalent, differing by as much as 13 ppm. Resonance forms of the type shown below for the styryl cation, **2c**, in which the C_1-C_{α} bond acquires double bond character as charge is delocalized into the ring, are clearly important contributors to the structure of these ions. The increased bond order results in slow rotation about the C_1-C_{α} bond on the NMR time scale, and the ortho carbons no longer experience the same magnetic environment.

The importance of such resonance forms is expected to depend upon the demand for charge stabilization. In keep-



Figure 2. Carbon-fluorine coupling constants (Hz) for selected ions.



ing with this expectation, we found that protonated benzaldehyde, **2f**, maintains two ortho resonances up to 37°, while protonated acetophenone, **2g**, in which the charge is additionally stabilized by a methyl substituent on C_{α} , shows coalescence of the ortho peaks in the ¹³C NMR spectrum at -25° . Similarly, increased availability of electrons from the π system should slow the rotation about C_1-C_{α} . As noted in Table V, the rotation in neutral *p*-methoxybenzaldehyde was "frozen out" at -105° , creating nonequivalent ortho carbons, but we were not able to freeze out rotation in benzaldehyde or α, α, α -trifluoroacetophenone in which no electron donating substituents were present.

The assignment of ortho carbon resonances was made primarily on the basis of the well known γ -substituent effect. In alkanes, a substituent other than hydrogen attached to the γ carbon has a shielding effect on the α carbon in a syn or gauche conformation relative to the anti conformation.²⁰ A similar shielding effect by an atom or group in a syn relationship has been observed in compounds such as 1fluoronaphthalene²¹ and phenanthrene,²² and in alkylbenzenes,²³ oximes,²⁴ alkenes,²⁵ and formamides.^{24a} In the charged monosubstituted benzenes examined here, the restricted rotation about the C₁-C_{α} bond creates separate ortho carbon resonances presumably because the same γ substituent effect is operative, and therefore the more shielded carbon is assumed to be syn to X-C_{α} and the less shielded carbon anti to X-C_{α}.



The only other available evidence relating to the specific assignments of ortho carbon resonances is the observation of ${}^{13}\text{C}{}^{-19}\text{F}$ spin-spin coupling in ion **2a**. The coupling constants differ substantially for the two carbons (Figure 2), although both are quite large for three-bond CCCF coupling. The coupling constants could be of use in verifying

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Figure 3. Ortho carbon shift vs. ortho total charge density. Symbols are as in Figure 1. The solid line is the correlation line for para carbons, from Figure 1, not a correlation line for ortho carbons.

the assignment if it were possible to distinguish between cisand trans-CCCF coupling. A model compound, protonated 1-fluoro-2,3,4,5,6-pentamethylbenzene (4, Figure 2), does exhibit trans-CCCF coupling of the magnitude seen in ion $2a.^{26}$ In order to generate a similar model compound which would have both cis- and trans-CCCF couplings in the π system, we prepared and measured the ¹³C spectrum of protonated 1-fluoronaphthalene, $5.^{27}$ Both trans-CCCF couplings (28 and 18 Hz) in 5 are larger than the cis-CCCF coupling (15 Hz), although the difference is small in one case. CCCF couplings in the two model ions 4 and 5 are supportive of the assignment for 2a in which the carbon anti to fluorine has the larger coupling constant and appears downfield of the other ortho carbon.

The specific assignments suggested for ions 2g-i were made on the basis of comparison between similar systems. Protonated acetophenone, 2g, and protonated propiophenone, 2h, show nearly identical chemical shifts for C₄, C_{3,5}, and one of the ortho carbons. The other ortho carbon differs by about 1 ppm in the two systems, which indicates that it is the carbon syn to the alkyl group, as the γ -substituent effect probably differs somewhat between a methyl and ethyl substituent. The assignment in 2i was made in analogy to 2gand 2h.

The ¹³C chemical shifts for ortho carbons of monosubstituted benzenes are plotted vs. CNDO/2 total charge densities in Figure 3. It is obvious that the points show a great deal more scatter than in Figure 1, although the same overall trend of the dependence of shielding on charge is evident. The line in Figure 3 is the line from Figure 1 for the neutral benzenes and the ions formed other than by protonation. A plot using π charge densities gave a similar pattern of point distribution.

Most of the points corresponding to the charged derivatives lie above the line in Figure 3, i.e., the ortho carbons are more shielded than predicted by the relationship to charge densities established for the para carbons. The five points in the lower right portion of Figure 3 which lie within 2 ppm of the line are, in each case, for the less shielded of the two nonequivalent ortho carbons in a charged species (2a-d, 2f) in which one of the substituents on C_{α} is a hydrogen. In each of these cases, we have assigned this downfield resonance to the ortho carbon which is anti to the C_{α} -X substituent. The proximity of these points to the line is a strong indication that the γ -substituent effect is completely absent in the anti configuration.

Most of the deviations of the ortho carbon chemical shifts in charged, monosubstituted benzenes from a linear rela-

tionship with calculated charge densities can be attributed to the γ -substituent effect. The same effect should influence the ortho carbon shifts in electronically neutral benzene derivatives. For instance, the C_2 and C_6 shifts in benzaldehyde would differ by about 9 ppm if the C_1-C_{α} rotation were frozen out; 9 ppm is the observed difference in *p*-anisaldehyde, and the examples of protonated p-substituted benzaldehydes and acetophenones in Table V indicate that the C_2, C_6 difference does not vary with para substituents. With fast rotation between planar conformations in benzaldehyde, the expected ortho carbon deviation from a charge density correlation due to the γ -substituent effect would be an averaged value of 4.5 ppm. It is significant that the ortho carbon resonances for the neutral benzenes substituted by a group capable of exerting a γ -substituent effect (the nitro-, trifluoromethyl-, and carbonyl-containing substituents) are all shielded relative to the line in Figure 3.

Unfortunately for the clarity of this analysis, the ortho carbons in several benzenes which are not expected to be affected by a γ substituent fall below the line instead of on it. A line of slightly smaller slope, as suggested by the dotted line in Figure 3, would create a picture more consistent with the explanation whereby most ortho carbon deviations arise from the γ -substituent effect. The deviation of the benzal-dehyde C_{2,6} resonance from the dotted line is about 4.5 ppm, which is exactly the value expected. However, there is no real justification for using a proportionality constant for the dependence on charge density which differs from that for the para carbons, other than in noting the approximate nature of the calculations.

The γ -substituent effect is often referred to as the "steric compression shift".²⁸ The effect is too large to be due to magnetic anisotropies of substituent groups, because effects of comparable magnitude have not been observed for ${}^{1}H$ chemical shifts. Grant and Cheney proposed that the shielding was due to sterically induced polarization of the C-H bond which would increase the negative charge associated with the carbon atom.²⁹ Their proposal has recently been questioned, based on data showing that the shielding does not increase with the effective size of the γ substituent³⁰ and that similar steric crowding by δ substituents results in deshielding rather than shielding.³¹ The shielding behavior we observe in this study could be explained by a through-space effect, in which a polarization is induced in the C-H bond by the neighboring, parallel C_{α} -X bond that is highly polar itself.



A thorough discussion of γ -substituent effects is beyond the scope of this paper, but it is clear that, if the mechanism is one of polarization of the C-H bond, polarization is not reproduced in the CNDO/2 calculations. Only the extremely crowded benzhydryl cation, **2d**, shows any C-H bond polarization³² for the syn position relative to the anti position. The point for the crowded C₆ in ion **2d** falls well below the line in Figure 3, showing that the effect is overestimated; undoubtedly, alteration of bond angles from 120° and noncoplanarity of the phenyl rings relieve the strain in the actual ion.

Meta Carbons. The meta carbon chemical shifts are relatively insensitive to the nature of the substituent. Chemical shifts for $C_{3,5}$ of monosubstituted benzenes in Table I cover the narrow range from δ 128.3 to 129.9, while $C_{3,5}$ chemical



Figure 4. Ipso carbon shift vs. ipso total charge density. Symbols designate type of substituting atom: O, sp² hybridized carbon; ∇ , sp hybridized atom; Δ , neutral heteroatom; \Box , other. Line is para carbon correlation line from Figure 1.

shifts for the cations in Table II also cover a relatively small range, from δ 130.6 to 134.8. The meta carbons in the positively charged derivatives appear slightly downfield from the meta carbons in the neutral compounds.

The slight deshielding experienced by the meta carbons in the cations suggests the possibility of some positive charge delocalization to that position, although the CNDO/ 2 calculations do not indicate any systematically greater positive charge on the meta carbons in charged species relative to uncharged molecules. There is no apparent correlation between ¹³C shifts and calculated carbon charge densities at the meta position. However, substantial positive charge does appear at the meta hydrogens in the CNDO/2 calculations of charged benzene derivatives.

Streitwieser has noted that the partitioning of charge between carbon and hydrogen is highly dependent on the relative choice of parameters for carbon and hydrogen in CNDO/2 calculations;³³ CNDO results are particularly sensitive to the choice of the $\beta_{\rm H}^{0}$ bonding parameter for hydrogen.³⁴ If some of the positive charge that appears on the meta hydrogens in the CNDO/2 calculations should more properly be associated with the meta carbons, a dependence of ¹³C chemical shifts on charge would be evident at the meta position. The ¹³C chemical shifts may be a better indicator of charge densities at the meta carbons than are the calculations.³⁵ It is also possible that influences other than charge densities affect the C_{3,5} shieldings to a small extent, since two ions, **2b** and **2i**, show nonequivalent C₃ and C₅ shieldings.

Ipso Carbons. The ipso ring carbons differ from the other ring carbons in being bonded to a different substituent group in each case. If magnetic anisotropies of substituent groups or other neighboring group effects have any significant influence on ¹³C chemical shifts, the effect will be important at the ipso carbon. Diamagnetic shielding effects due to electrons on the substituting atom have been postulated to be important.³⁶ In addition, calculated charge densities at the ipso carbon are more sensitive to the choice of geometry than at the other positions.¹⁰ Further, if there is any shortcoming in the CNDO/2 method regarding the calculation of charge polarization due to inductive effects in the σ framework, the discrepancies would be most evident at the ipso position. In short, for a variety of reasons, correlations of ¹³C shifts with calculated charge densities are not expected to be as satisfactory for carbon atoms at which the substitution pattern varies as for identically substituted carbon atoms.

The ipso carbons absorb over a somewhat wider range than para and ortho carbons. Figure 4 shows the plot of the



Figure 5. Ipso carbon shift vs. ipso π charge density. Symbols are as in Figure 4. Line is correlation line for para shifts vs. para π charge density, excluding protonated substituents, and is not a correlation line for ipso carbons.

 C_1 chemical shifts against total charge densities. Overall, the correlation is very poor. It is possible to distinguish some trends by selecting related groups of substituents for separate comparison. For example, the points corresponding to C_1 atoms bound to an sp^2 hybridized carbon in the substituent generally fall below the line in Figure 4. When the substituting atom is sp hybridized or a neutral heteroatom, the corresponding points fall above the correlation line established by the para carbons. In contrast to the ortho and para positions, the pattern of point distribution in a plot of ipso carbon shieldings vs. π charge densities (Figure 5) differs greatly from the plot using total charge densities. The correlation is still very poor, and the deviations appear to have less regularity than in Figure 4. Nearly all of the points fall below the line established by the para carbons. The ipso carbon is characterized for many of the molecules in the calculations by a buildup of π electron density which is counteracted by electron withdrawal in the σ framework by an electronegative substituent.

Empirical correction factors have been used in other studies for individual substituents or types of substituents to improve the correlation of C_1 shifts with charge densities, by shifting the points in the desired direction.^{10,37} These "corrected" chemical shifts or charge densities may be useful for estimating CNDO/2 charge densities from chemical shifts or vice versa. The rough linear correlation between C1 chemical shifts in benzenes and C1 shifts in monosubstituted ethylenes³⁸ suggests that the correction factors may have some generality. However, the correction factors have not been critically examined for constancy in a variety of conditions, and as noted below, the substituent influence on chemical shifts may differ considerably when the substituent is attached to a carbon atom with electronic character significantly different from a simple phenyl or alkenyl carbon. Also, the fact that regularities are observed in the deviations of C_1 shifts from a correlation with charge does not provide information about the source of the deviations, that is, the deviations may have a physical basis, or possibly may be due to systematic failure of the CNDO/2 method in calculating the inductive effects of particular types of substituents.

Alpha Carbons. Correlations of chemical shifts for sp² hybridized α carbons with calculated charge densities are also expected to be poor because the substituent groups on C_{α} vary for each case. C_{α} shifts are plotted vs. total charge densities in Figure 6; the points are very scattered. Alkyl substituted C_{α} atoms are deshielded relative to the para carbon correlation line, and most heteroatom substituted C_{α} atoms are shielded relative to the predicted values. Fig-

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Figure 6. Alpha carbon shift vs. alpha total charge density. Line is para carbon correlation line from Figure 1, and is not a correlation line for α carbons.



Figure 7. α -Carbon shift vs. $\alpha \pi$ charge density. Line is para correlation line as in Figure 5.

ure 7 shows the plot of C_{α} shifts vs. π charge densities. Again, the alkyl substituted C_{α} atoms are deshielded relative to the C₄ correlation line, but the other points are much closer to the line than in Figure 6. It is clear that empirical correction factors which could be derived for substituents from the ipso carbon plot in Figure 4 would not be adequate to describe the deviations observed for similarly substituted α carbons in Figure 6, and likewise, correction factors for the deviations in the plot with π charges in Figure 5 could not be successfully applied to Figure 7. The calculated charge densities for $C_{\boldsymbol{\alpha}}$ are considerably more positive than at C_1 , which suggests that the deviations from the chemical shift vs. charge correlation induced by directly attached substituents may be dependent on the charge at the carbon being considered; this concept will be pursued further in a subsequent article.

Although the C_1 and C_{α} shifts are not linearly correlated with calculated charge differences, the charge densities are important factors in the chemical shifts, as shown by studies in which the substitution pattern at C_1 or C_{α} is kept constant and substituents are varied elsewhere in the systems.^{10,37,39,40} Furthermore, the range of C_{α} resonances (δ_C 168–254) is downfield of the range for phenyl carbons, which is consistent with the expectation of substantial positive charge localization at a carbenium ion center or a carbonyl carbon.

The C₄ chemical shift is probably a better indicator of electron density at C_{α} than is the C_{α} shift itself. An electron deficiency in the $2p_{\pi}$ orbital on C_{α} will be partially reduced by resonance donation of electrons from the benzene ring. This delocalization of charge into the ring is reflected in the chemical shifts, and as we have demonstrated, the para car-



Figure 8. Para π charge density vs. $\alpha \pi$ charge density.

bon chemical shifts correlate very well with charge densities at the para position. In Figure 8, the relationship between electron deficiency at C_{α} and C_4 is demonstrated by plotting the calculated π charge densities at C₄ against the C_{α} π charge densities. A fair correlation is obtained (r = 0.954, SD = 0.019), but there are some limitations to this use of the C₄ shift as a measure of charge at C_{α} , since it is a measure of all electronic interactions of the phenyl ring with the entire substituent. The resonance interaction undoubtedly dominates, but in some cases steric effects could impose restrictions on the conformational freedom of the substituent, thereby reducing $2p_{\pi}$ - $2p_{\pi}$ overlap and inhibiting resonance interaction with the ring. Inductive polarization of the electron distribution in the ring π system by the substituent without actual charge transfer to the substituent is also important,41 and may not exactly parallel the resonance polarization.

Conclusion

Observations in earlier studies³⁻¹¹ that the ¹³C chemical shifts of para carbons in monosubstituted benzenes were linearly related to electronic charge densities have been confirmed over an additional 28 ppm range of shifts. The correlation of para carbon shifts for both electronically neutral benzenes and phenyl substituted cations by a single line indicates that organic cations generated in superacid media can be treated theoretically as isolated species, neglecting the gegenion, as successfully as neutral organic molecules. However, the para carbons in charged monosubstituted benzenes formed by protonation of a heteroatom show a small systematic deviation from the correlation line which could be explained either by hydrogen bonding to solvent or gegenion, or by a deficiency in the CNDO/2 method for that type of ion.

The para carbon chemical shift appears to be a quantitatively reliable indicator of charge density at the para position, and it is probably also the best measure of electron deficiency at a sp² hybridized carbon atom bound to the phenyl ring, provided there is no steric inhibition of resonance interaction. The ortho carbon shieldings are also responsive to differences in charge densities, but the additional shielding effect of a γ substituent is important in many instances and makes the $C_{2,6}$ shifts less reliable as indexes of charge density variations. The meta carbon shieldings may also reflect charge density variations, but the range of shifts is small and the anticipated charge pattern is not evident in CNDO/2 calculations. At carbons where the substituent pattern changes, i.e., the ipso and α carbons, the observed shieldings cannot be used as a direct measure of charge densities (even if they generally indicate the overall trend of charge distribution), although it may be possible to use cor-

¹³C chemical shifts are a powerful probe of the structure of carbocations and also provide some information about electron distributions in such structures. However, simple correlations with calculated charge densities are not precise in many cases, and therefore, quantitative interpretations of 13 C shifts should be made cautiously. It is important that the chemical shift at a particular position should not be singled out as evidence for a general trend in charge distributions without also considering the data from the rest of the molecule.

Experimental Section

Preparation of Ions. The general procedure for preparation of solutions of the ions was to add in small portions a precooled solution or suspension of the precursor in SO₂ClF to a vigorously stirred (vortex mixer) solution of superacid in SO₂ClF at -78° Details of individual ions prepared in this manner are summarized below by the information ion, precursor compound, ionizing acid, and temperature at which the ¹³C spectrum was measured: 2a, benzal fluoride, SbF5, -80°; 2b, benzal chloride, SbF5, -80°; 2f, benzaldehyde, 1:1 SbF₅-FSO₃H (MA), -80°; 2g, acetophenone, 1:1 MA, -80 and -25°; 2h, propiophenone, 1:1 MA, -80°; 2i, α, α, α -trifluoroacetophenone, 1:1 HF-SbF₅, -80°; 2j, benzotrifluoride, SbF₅, -60°; 2k, benzotrichloride, SbF₅, -80°; 2m, benzoic acid, 1:1 MA, -80°; 2n, methyl benzoate, 1:1 MA, -80°; 3b, benzonitrile, 1:1 MA, -60°; 3d, phenyltrimethylammonium chloride, SbF₅, -60°; 3e, N-methylaniline, 1:1 HF-SbF₅, -60°; 3g, nitrobenzene, 1:1 MA, -60° ; p-OCH₃-2f, 4-methoxybenzal-dehyde, FSO₃H, -60° ; p-CH₃-2f, 4-methylbenzaldehyde, 1:1 MA, -60°; p-OCH₃-2g, 4-methoxyacetophenone, FSO₃H, -60°; p-CH₃-2g, 4-methylacetophenone, 1:1 MA, -60°; p-F-2g, 4-fluoroacetophenone, 1:1 MA, -60°; p-Cl-2g, 4-chloroacetophenone, 1:1 MA. -60°

The ¹³C spectrum of phenylammonium ion, 3f, was obtained from a solution of aniline in 10 N HCl at 37°. Ion 3h was prepared by methylation of thioanisole with CH₃F-SbF₅ in SO₂ClF at -80°

The α -styryl ion, 2c, could not be prepared without the accompanying formation of the ethylenebenzenium ion and a small amount of para-protonated precursor.42 Different proportions of these products were obtained by ionizing 1-(phenyl)ethyl chloride in SbF5-SO2ClF at -80° and 2-(phenyl)ethyl chloride in SbF5-SO₂ClF at -80° . The ¹³C resonances for 2c were distinguished from the other resonances by ionizing 2-(phenyl)ethyl chloride in $(HF-SbF_5)-SO_2ClF$ at -80° , which gave the ethylenebenzenium ion and protonated 2-(phenyl)ethyl chloride without formation of 2c.

Carbon-13 Nuclear Magnetic Resonance Spectra. The ¹³C spectra were obtained on Varian Associates Model XL 100 and HA 100 spectrometers operated in the pulse-Fourier transform mode. Details of the instrumentation and methods have been described elsewhere.43

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