MAGNETIC RESONANCE STUDIES OF TRIPHENYLCARBONIUM IONS—II

CARBON-13 MAGNETIC RESONANCE STUDIES OF CHARGE DELOCALIZATION IN *para*-SUBSTITUTED TRIPHENYLCARBONIUM IONS*†

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Abstract—Carbon-13 NMR shifts of *para*-substituted triphenylcarbinols, $(p\text{-}XC_6H_4)_3COH$ and the corresponding carbonium ions, $(p\text{-}XC_6H_4)_3C^+$ where X = H, NO_2, F, Cl, Me, OMe and NMe_2) have been measured and interpreted in terms of charge densities, *via* the empirical relation between C-13 shifts and charge densities. The general features of the charge distributions given by the C-13 shifts are in accord with a simple resonance picture, with relatively large positive charges at positions alpha and *meta* to the substituent. The amount of positive charge delocalized from the central carbon is proportional to the substituent parameter, σ^+. The validity of an additivity relation for the C-13 shifts of the carbonium ion species indicates that the charge distribution in the substituted ion is, approximately, the superposition of the distributions in the unsubstituted ion and the corresponding monosubstituted benzene. However, the substituents OMe and NMe_2 bear a relatively large portion of the charge delocalized from the central carbon. The charge densities derived from C-13 shifts for triphenylcarbonium ion correlate well with those calculated by the CNDO method, even though the agreement is not quantitative.

As the first known stable carbonium ion, the triphenylmethyl cation has been the subject of numerous investigations.[1] The unusual stability of this ion has been ascribed to delocalization of the positive charge throughout the pi-electron system of the molecule. Substituents on the phenyl rings stabilize the ion insofar as they promote further delocalization of the positive charge. However, theoretical calculations are in some disagreement as to the distribution of the positive charge within the phenyl rings. This point is illustrated by the pi-electron densities, ρ_i, listed in Table 1, which have been calculated by the HMO method and by a SCFMO method. The HMO calculation agrees with the qualitative picture derived from simple resonance considerations, in that the positive charge is delocalized exclusively and equally onto the 3 and 5 positions. However, the SCFMO calculation, which should be more appropriate for the charged species, places a large portion of the positive charge at the 5 position with smaller and nearly equal charges at the 3 and 4 positions.

The latter result seems particularly anomalous since no stable resonance structure which contains a positive charge at atom 4 can be formulated.

NMR data have been used to estimate the electron density at various positions in aromatic systems.[2-8] The most straightforward approach has been to utilize the empirically demonstrated proportionality between the chemical shift of a given carbon (or proton bonded to that carbon) and the electron density at that carbon. Although electron density plays a major role in determining chemical shifts, one must account for other shielding effects also, especially for proton NMR shifts.

The difficulties and ambiguities that arise when one attempts to relate proton NMR shifts to charge densities are well illustrated in triphenylcarbonium ion: the shifts given in Table 1 show a much better apparent correlation with the SCFMO calculations than with the HMO. However, uncertainties in the magnitude of other effects, in particular ring current effects from neighboring phenyl rings, render this correlation suspect. For example, if it is assumed that in solution the twist angle of the phenyl rings (with respect to the plane of the central carbon and the three carbons bonded to it) varies within 10° of the angle in the solid,[10] the ring current contribution

TABLE 1. ESTIMATES OF PI-ELECTRON DENSITIES IN TRIPHENYLMETHYL CATION

Position[a]	Theoretical HMO	Densities[b] SCFMO[c]	Proton Shifts[d] nmr I[e]	nmr II[f,g]	nmr III[h,i]
1	0·69	0·75			
2	1·00	1·15			
3	0·92	0·95	−0·35	−0·15	−0·65
4	1·00	0·94	−0·60	−0·18	−0·59
5	0·92	0·81	−1·00	−0·70	−0·93

[a] The numbering used throughout this paper is
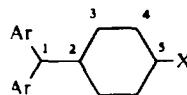
[b] In units of electron density
[c] Ref. 9
[d] In ppm from benzene
[e] Ref. 2
[f] Ref. 3
[g] Chemical shifts were corrected for neighboring ring anisotropies for an assumed angle of twist of 23° for the phenyl rings
[h] Ref. 11
[i] Chemical shifts were corrected for neighboring ring anisotropies for an assumed angle of twist of 45° for the phenyl rings.

to the shifts of the *ortho* positions will vary from −0·05 to 0·25 ppm.[11] This spread represents a large fraction of the total *ortho* proton NMR shift. For the triphenylcarbonium ion systems, the interpretation of C-13 NMR shifts in terms of charge densities would be simpler and more reliable than a similar interpretation of proton NMR shifts. While the absolute contribution to the C-13 shifts from neighboring

ring anisotropy would be, in general, smaller than that to the proton shifts, the C-13 shifts should be about 16 times more sensitive to changes in electron density. The first C-13 NMR study of triphenylcarbonium ions is that of Olah, et al. (Ref. 5f, quoted in Ref. 1).

In attempting to relate the substituent effect on C-13 NMR shifts to charge distributions in the triphenylcarbonium ion systems discussed in this work, we have used two perspectives. In one, we have assumed that the empirical relation between charge density and C-13 shift is valid; the C-13 shifts are then used to gauge the delocalizing effect of substituents and to check the qualitative validity of calculations of charge density. In the other viewpoint, C-13 shifts are correlated with calculated charge densities (which are, in this case, assumed to ve valid) and substituent parameters which reflect charge delocalization; large deviations from a smooth correlation may then indicate the effect of factors other than charge density on the C-13 shifts.

RESULTS AND DISCUSSION

Representative slow passage, absorption mode C-13 NMR spectra of the triarylcarbonium ions are shown in Figs 1 and 2. These spectra show only the aromatic region of the C-13 spectrum; the central central carbon lines (position 1) lie well outside the aromatic region. The chemical shift assignments are shown in Figs 3 and 4. The following considerations have been taken into account in making these assignments: 1. If only one-bond proton–carbon couplings are considered, the four nonequivalent phenyl carbons of these symmetrically para-substituted compounds would (except for the para-fluoro species) give a multiplet plattern consisting of two doublets (from carbons at positions 3 and 4, meta and ortho to the substituent, respectively) and two singlets (from carbons at positions 2 and 5, alpha and para to

TABLE 2. PREPARATION OF TRIARYLCARBINOLS

X	m mole Ester	m mole Grignard Reagent	yield, %	Carbinol m.p.	Carbinol lit.
Cl	5·4	26	64	oil	93–94[a]
H	14·0	50	47	161–162	161–162[b]
Me	7·3	30	30	87	93–94[c]
OMe	6·0	21	76	81–82[d]	81–82[d]
NMe$_2$	5·6	25	37	200	218[e]

[a] Ref. 15
[b] Ref. 16
[c] Ref. 17
[d] Ref. 18
[e] Ref. 19

the substituent) or, in all, six lines of equal intensity. The carbon 5 line of the unsubstituted and fluorine-substituted species would be split into a doublet, giving a 7-line aromatic pattern with five lines of equal intensity and two lines one-half as intense as these five. Two lines corresponding to a doublet should be separated by 150–180 Hz, the normal range of aromatic C—H one-bond coupling constants.[7] We
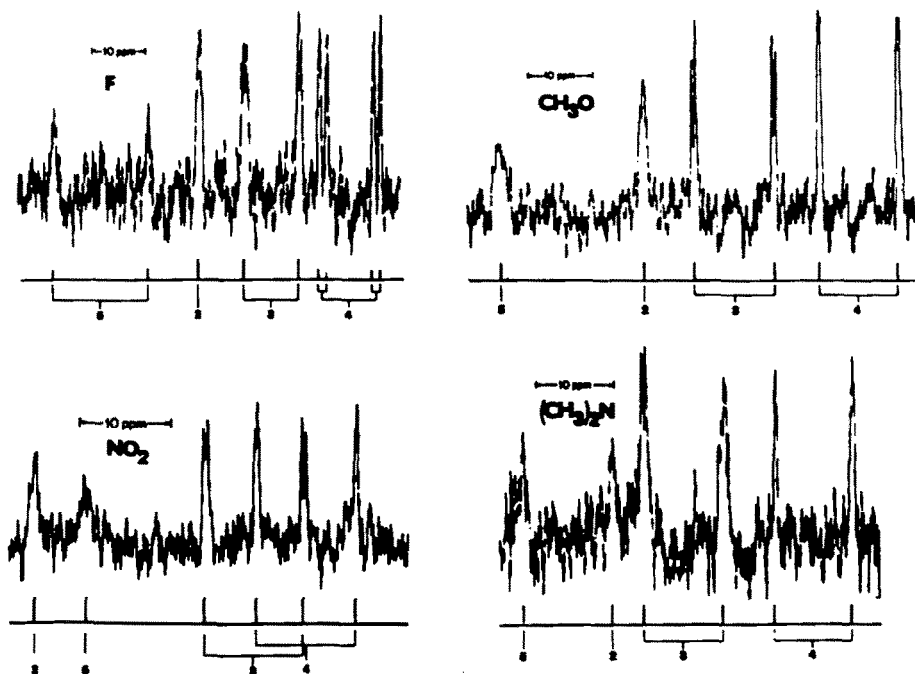
G. J. RAY, R. J. KURLAND and A. K. COLTER

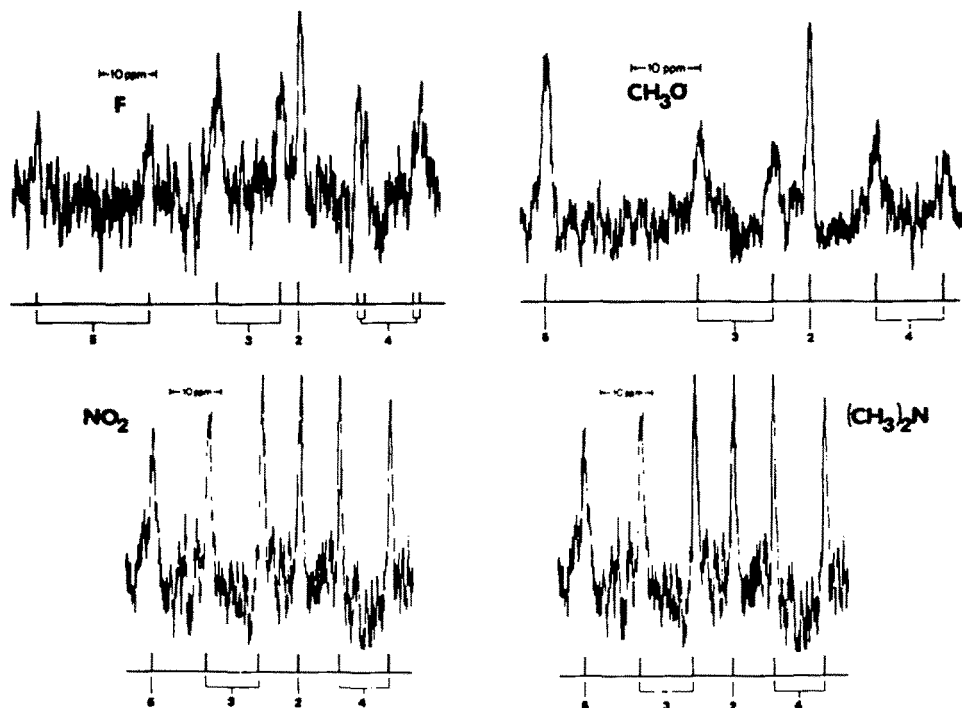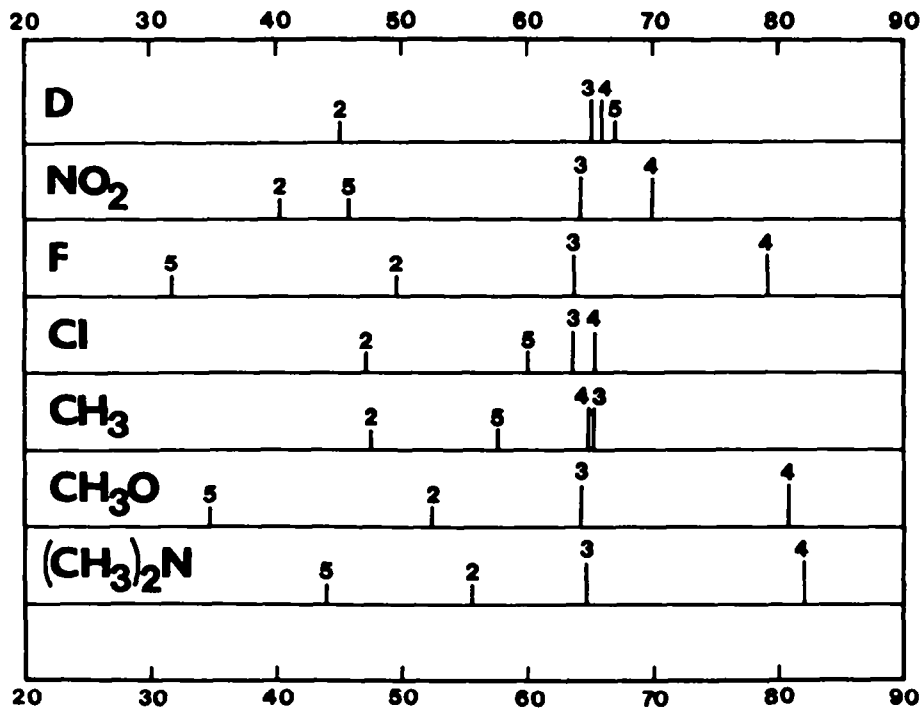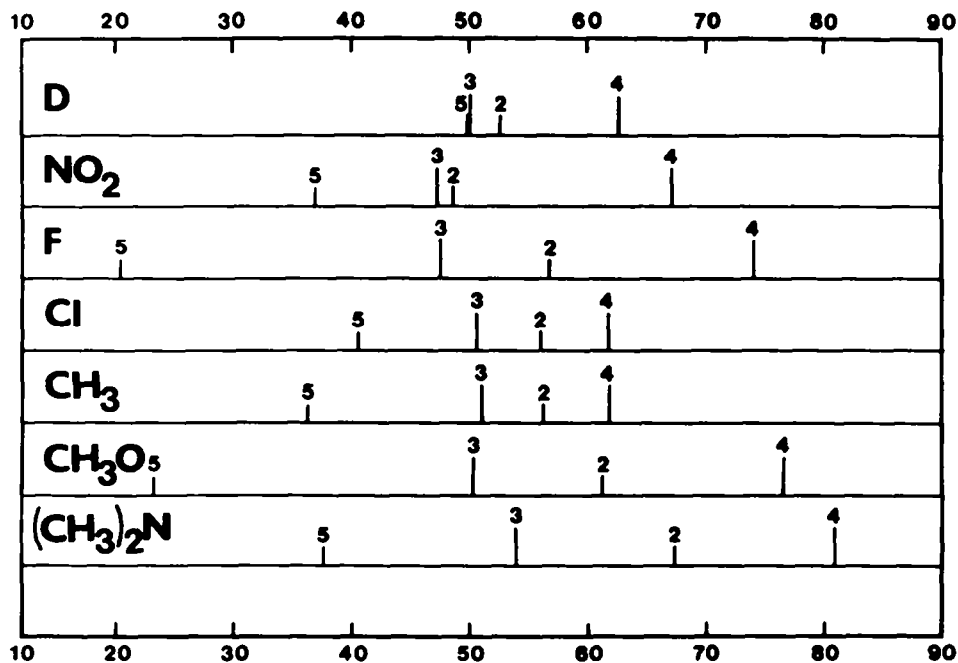FIG 1. Representative C-13 Spectra of Triarylcarbinols

FIG 2. Representative C-13 Spectra of Triarylcarbonium Ions

FIG 3. Chemical Shift Assignments for Triarylcarbinols (ppm from CS_2)

FIG 4. Chemical Shift Assignments for Triarylcarbonium Ions (ppm from CS_2)

emphasize that in the above considerations the line broadenings and small splittings resulting from long-range spin-coupling (between carbon and protons) separated by two or more bonds have been neglected. 2. One would expect an additivity relation as has been demonstrated for disubstituted benzenes,[24] to hold for the aromatic C-13 shifts. The triarylcarbinols may be regarded as disubstituted benzenes bearing

the substituents X and $(p\text{-}XC_6H_4)_2\overset{|}{C}OH$. Neglecting the effect of the distant X groups (i.e., those in the diarylhydroxymethyl substituent), δ_i, the chemical shift of the ith position (for $i \neq 1$), is given by Eq (1)

$$\delta_i = \delta'_i + \delta''_{6-i} \qquad (1)$$

where δ'_i is the shift of the ith position in triphenylcarbinol and δ''_{6-i} is the shift of the corresponding position in a monosubstituted benzene (all shifts relative to benzene).* A similar additivity relation for the triphenylcarbonium ions should not hold as well as for the carbinols. Here the assumption that the distant X groups have a negligible effect is unlikely to be valid especially for cases where the X group bears a portion of the positive charge. Indeed, the deviation of the observed shift from that given by an additivity relation can be taken as a measure of the change in charge delocalization induced by the substituent (see below). 3. On the basis of the substituent effects cited by Spiesecke and Schneider[25] for monosubstituted benzenes, one would expect the smallest substituent effect on the C-13 shifts at position 3, i.e., the positions *meta* to the substituent. 4. The values for T_1, the longitudinal relaxation time, should be much less for carbons directly bonded to protons or fluorine since proton–C-13 dipolar interaction is a principal factor determining C-13 relaxation times.[26] Accordingly, lines arising from carbons 3 and 4 may be distinguished by means of progressive saturation studies, even aside from considerations of intensity. 5. The assignments for the unsubstituted species were confirmed by comparison with the spectra of 4,4′,4″-trideuterotriphenylcarbinol and 4,4′,4″-trideuterotriphenylcarbonium ion.

Spectral parameters assigned according to these considerations are given in Tables 3 and 4. Shifts calculated *via* the additivity relation, Eq (1), are also tabulated. For the carbonium ions we have used the shifts of the substituted carbinol and unsubstituted carbonium ion according to Eq (2):

$$\delta_i = \delta'_i + \delta''_i \qquad (2)$$

where δ'_i is the shift of the ith carbon in the substituted carbinol relative to triphenylcarbinol, and δ_i and δ''_i are the shifts of the ith carbon in the substituted and unsubstituted carbonium ions, respectively, relative to the same standard. Note that the shifts for the central carbon (position 1) in the carbinols and carbonium ions fall well outside the normal range for aromatic C-13 (i.e., outside the range 20 to 80 ppm upfield from the C-13 line of CS_2) and can therefore be unambiguously assigned.

The good agreement between the observed and "additivity" shifts in the triaryl-carbinol series should not be surprising, since there is no direct conjugation between

the *para* substituent, X, and the carbinol moiety, $(p\text{-}XC_6H_4)_2\overset{|}{C}\text{—OH}$. Therefore, the

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* We number the protons in the monosubstituted benzenes as follows: the carbon bearing the substituent is taken as position 1 and the remaining carbons numbered consecutively in the usual way.

same interactions giving rise to the chemical shift differences in the corresponding monosubstituted species should be present in the triarylcarbinols.

In the triarylcarbonium ions, the differences between the observed and "additivity" shifts are generally less than ca 2 ppm, except for the shifts of C-5 (the carbon to which the substituent is attached) and the shifts in the dimethylamino-substituted ion. Except for the nitro group, the substituents are of the $+R$ type[27] for which resonance structures similar to I may be formulated.

I
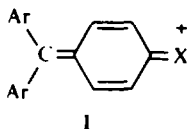
Such direct interaction is responsible for deviations from an additivity relation as shown previously with other 1,4-disubstituted benzenes bearing both a $+R$ and $-R$ substituent.[24]

Although both the carbonium ion moiety and the nitro group are $-R$ substituents, the difference between the observed and "additivity" shift of C-5 in this compound is rather large. Despite the lack of conjugation between the nitro group and the carbonium ion, nonadditivity of their substituent effects might be expected on the following basis: Delocalization of charge in nitrobenzene and triphenylcarbonium ion represented, respectively, by structures such as II and III should be less extensive in trinitrotriphenylcarbonium ion, as can be seen from the corresponding resonance structures, IV and V.

II   III   IV   V
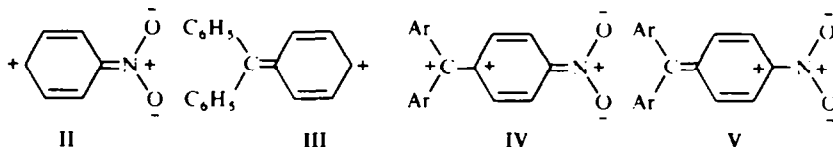
We now consider correlations of the C-13 chemical shifts with substituent parameters. Since the additivity relation holds well for the carbinol chemical shifts, we must necessarily find the same correlations as observed with the carbon-13 shifts of monosubstituted benzenes.[24] Thus, for example, δ_2 or $(\delta_2-\delta_3)$ for the carbinols correlates well with the Taft σ_R^0 value[28] of the *para* substituent.

In the carbonium ion series, the trend in charge delocalization is shown most directly by the shifts of the central carbon, δ_1. As shown in Fig 5, these shifts correlate well with the Brown–Okamoto σ^+ substituent constants[29] (slope $= -15\cdot4$, $r = 0\cdot957$). The values of σ^+ should be a measure of the substituent interaction with the Ar_2C^+ group. The correlation of the central carbon chemical shifts with the calculated charge density at this position is discussed below.

Again, to the extent that the additivity relation holds in the carbonium ion series, one should find the same correlations as observed with the monosubstituted benzenes. Thus, for example, $(\delta_2-\delta_3)$ correlates well with Taft σ_R^0 values (Fig 6, slope $= 17\cdot2$, $r = 0\cdot980$). Perhaps more relevant to the question of substituent effects on charge distribution are differences between observed and additivity shifts. The shifts of C-3
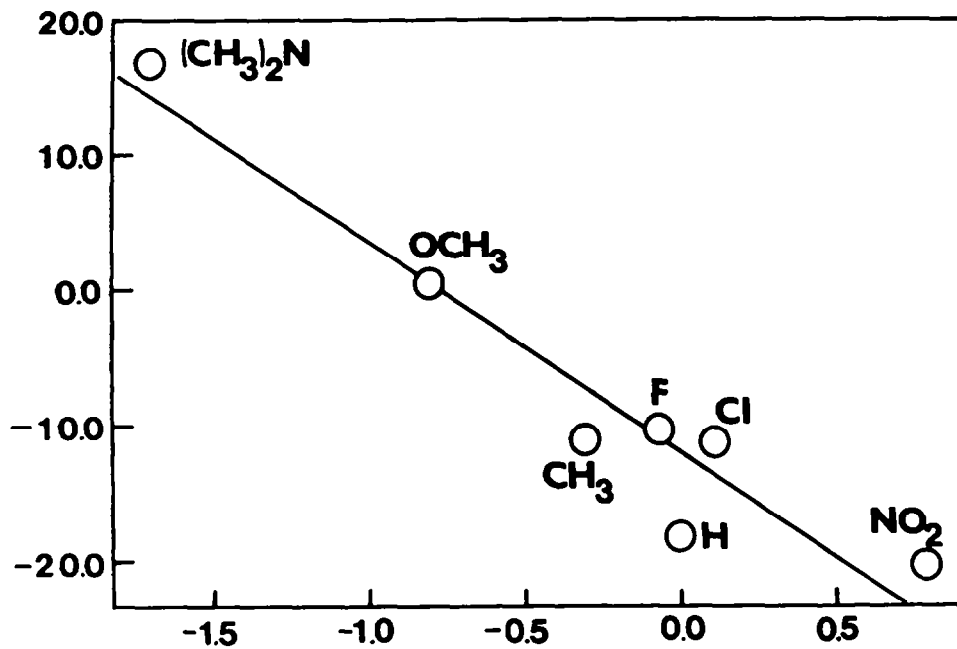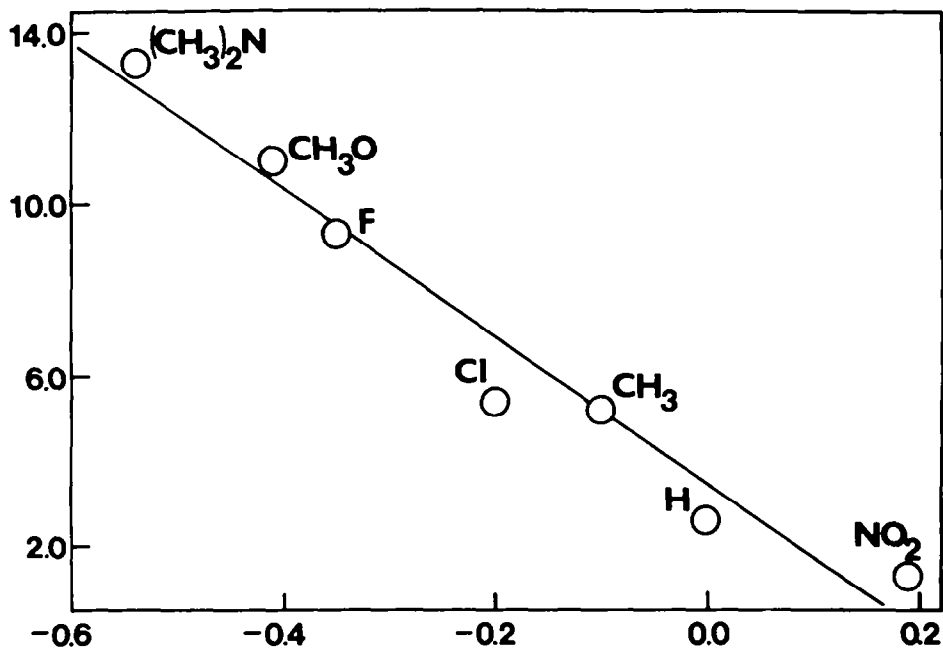
FIG 5. Plot of δ_1 for Triarylcarbonium Ions vs σ^+

FIG 6. Plot of $(\delta_2 - \delta_3)$ for Triarylcarbonium Ions vs σ_R^0

TABLE 3. C-13 NMR SPECTRAL PARAMETERS FOR para-SUBSTITUTED TRIARYLCARBINOLS, [a] $(p\text{-}XC_6H_4)_3COH$

Substituent X	Chemical shifts[b]					Coupling constants[c]			
	C-1'[c]	C-2	C-3	C-4	C-5	$J_{C,H}$	$J_{C,H}$	$J_{C,H}$	$J_{C,F}$
H[e]	113·4 ± 0·5	43·6 ± 0·5	65·1 ± 1·0	65·1 ± 1·0	65·1 ± 1·0	157	158		
D[d]	112·8 ± 0·5	45·1 ± 0·5	65·1 ± 0·2	65·9 ± 0·2	67·0 ± 1·0	166	168		
NO₂		40·6 ± 0·4 (39·1)	64·2 ± 0·3 (64·3)	69·9 ± 0·3 (71·2)	45·8 ± 0·7 (47·4)			ca 1·4 × 10²[f]	
F	113·3 ± 0·5	49·6 ± 0·4 (49·5)	63·7 ± 0·5 (64·2)	79·2 ± 0·2 (80·2)	31·8 ± 0·5 (31·9)	162	163		−247[g]
Cl	113·4 ± 0·5	47·2 ± 0·4 (47·1)	63·7 ± 0·6 (64·1)	65·4 ± 0·8 (65·7)	60·1 ± 0·8 (60·6)	164	165		
Me	112·6 ± 0·5	47·5 ± 0·5 (47·9)	65·2 ± 0·4 (64·8)	64·9 ± 0·4 (65·6)	57·6 ± 0·6 (57·9)	158	158		
Me	113·3 ± 0·5	52·4 ± 0·3 (53·2)	64·2 ± 0·2 (64·2)	80·8 ± 0·2 (80·6)	34·7 ± 0·3 (36·8)	157	158		
NMe₂	113·2 ± 0·5	55·5 ± 0·5 (56·9)	64·6 ± 0·6 (64·3)	82·0 ± 0·4 (81·6)	44·0 ± 0·4 (44·6)	158	157		

[a] At r.f. frequency ca 15·086 MHz; samples taken as approximately 1·5 M THF solutions at ambient temperature 37°.

[b] Shifts in ppm from CS_2 external reference (positive values correspond to upfield shifts). Values in parentheses were calculated using Eq (1), C-13 shifts in monosubstituted benzenes (Ref 25), and the C-13 shifts of unsubstituted triphenylcarbinol (this work): the calculated shifts are accurate to ca ± 1 ppm, corresponding to the accuracy of the shifts in Ref 25; calculated shifts have been obtained with respect to CS_2 by adding 65 ppm to the shifts with respect to benzene.

[c] In Hz, as determined from a first order spectral analysis; precision: ± 1 Hz. Sign assumed positive, except where noted.

[d] Obtained from spectra of compounds enriched to 17·1 atom % in C-13 at position 1, except for X = F.

[e] For X = H the C-3, C-4 and C-5 absorptions overlapped and were assigned the same shift, the center of a broad doublet.

[f] Determined from the broad C–D triplet splitting ($J_{C–D} \sim 25$ Hz).

[g] Sign assumed to be negative, on the basis of values of $J_{C–F}$ calculated by G. E. Maciel, J. W. McIver, N. S. Ostlund, and J. A. Pople (private communication).

TABLE 4. C-13 NMR SPECTRAL PARAMETERS FOR *para*-SUBSTITUTED TRIARYLCARBONIUM IONS,[a] $(p\text{-}XC_6H_4)_3C^+$

Substituent X	Chemical shifts[b]					Coupling constants[c]			
	C-1[d]	C-2	C-3	C-4	C-5	J_{C_2H}	J_{C_3H}	J_{C_4H}	$J_{C,F}$
H	-18.1 ± 0.4	53.5 ± 0.6	50.1 ± 0.6	62.3 ± 0.6	50.1 ± 0.6				
H[e]		52.9 ± 0.5	49.5 ± 0.2	62.5 ± 0.3	49.7 ± 0.5				
D[e]		52.7 ± 0.2	50.1 ± 0.2	62.7 ± 0.2	49.9 ± 0.5	171	170	$ca\ 1.4 \pm 10^{2,f}$	
NO₂	-20.2 ± 2.0	48.6 ± 0.3 (48.2)	47.3 ± 0.5 (49.2)	67.2 ± 0.5 (66.7)	37.0 ± 0.5 (28.7)	172	180		
F	-10.2 ± 0.3	56.8 ± 0.4 (57.2)	47.5 ± 0.6 (48.7)	74.1 ± 0.6 (76.0)	20.5 ± 0.4 (14.7)	166	163		-276^{g}
Cl	-11.2 ± 0.3	56.0 ± 0.8 (54.8)	50.6 ± 0.6 (48.7)	61.8 ± 0.7 (62.2)	40.6 ± 0.7 (43.0)	164	168		
Me	-11.0 ± 0.4	56.2 ± 0.6 (55.1)	51.0 ± 0.6 (50.2)	61.8 ± 0.6 (61.7)	36.3 ± 0.4 (40.5)	155	160		
OMe	0.5 ± 0.3	61.3 ± 0.5 (60.0)	50.3 ± 0.2 (49.2)	76.6 ± 0.4 (77.6)	23.3 ± 0.5 (17.6)	164	165		
NMe₂[h]	16.8 ± 0.3	67.3 ± 0.5 (63.1)	54.0 ± 0.5 (49.6)	80.9 ± 0.5 (78.8)	37.6 ± 0.5 (26.9)	162	162		

[a] At r.f. frequency *ca* 15.085 MHz; samples taken as approximately 1.5 M solutions in sulfuric acid-water, except as noted, at ambient temperature 37°.

[b] Shifts in ppm from CS_2 external reference (positive values correspond to upfield shifts). Values in parentheses were calculated using Eq (2), C-13 shifts in substituted carbinols and triphenylcarbonium ion (this work); the calculated shifts are accurate to *ca* ± 0.2 ppm.

[c] In Hz, as determined from a first order spectral analysis; precision: ± 1 Hz. Sign assumed positive, except as noted.

[d] Obtained from spectra of compounds enriched to 17.1 atom % in C-13 at position 1, except for X = F.

[e] In chlorosulfonic acid solvent.

[f] Determined for the broad C-D triplet splitting $(J_{C-D} \sim 25\ Hz)$.

[g] Sign assumed to be negative, on the basis of values for J_{C-F} calculated by G. E. Maciel, G. W. McIver, N. S. Ostlund and J. A. Pople (private communication).

[h] In 100% EtOH solution.

and C-5 should be especially sensitive in this regard since these positions in the unsubstituted ion bear most of the charge delocalized into the phenyl rings. We find that for the ions bearing $+R$ substituents the deviations from the additivity relation (Eq 2) correlate best with the σ_R substituent constants,[30] which should be a measure of the positive charge taken up by the substituent *via* a resonance mechanism. In Fig 7 is displayed a plot of $(\Delta_3 + \Delta_5)$ *vs* σ_R, where Δ_i is the difference between the observed and additivity shift for position i in the triarylcarbonium ion. The correlation is reasonably good, except for the nitro-substituted ion. (For the five $+R$ groups, slope $= -22.6$, $r = 0.999$). The trend in these deviations for the $+R$ substituents is that predicted by the simple resonance picture above: the largest deviation from the additivity relation, i.e., the greatest delocalization of positive charge onto the substituent, is expected for the substituent with the largest value of $-\sigma_R$, the NMe$_2$ group. The nitro group is a $-R$ group and deviates for different reasons, as discussed above.

We should emphasize, nevertheless, that the correlation between $(\Delta_3 + \Delta_5)$ and σ_R may, in fact, be only an indirect reflection of charge delocalization. Note first that by far the largest deviations from the additivity relation occur for the C-5 shifts.
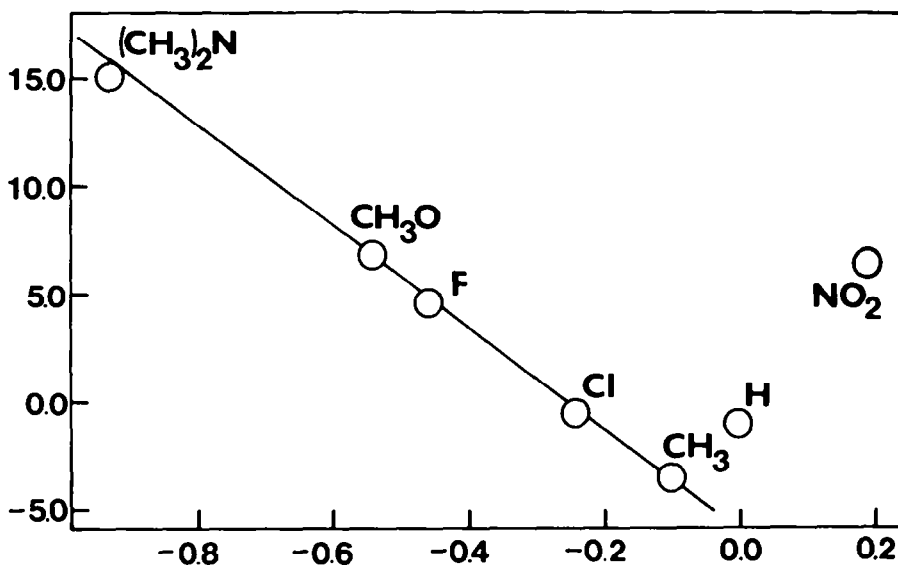

FIG 7. Plot of $(\Delta_3 + \Delta_5)$ *vs* σ_R

These differences again correlate reasonably well with σ_R, (or σ_R^0) except again, for the nitro-substituted ion. We are tempted to attribute the deviations for C-5 to changes in the double bond character of the C$_5$—X bond, as well as changes in the positive charge borne by the substituent X. Both of these factors could affect the C-5 shifts through long-range shielding effects, rather than through effects associated directly with changes in the charge at C-5. Changes in the C$_5$—X double bond character and in the positive charge at the substituent X should both correlate with the parameters σ_R or σ_R^0.

We turn now to a comparison of "empirical" charge densities (i.e., those obtained from the empirical relation between carbon-13 shifts and charge densities) with charge densities calculated at various levels of approximation. The results of this and earlier work[7, 25] reveals that by far the largest substituent effect on aromatic carbon-13 chemical shift is observed for the carbon bonded to the substituent. From the size of these changes in chemical shifts it seems likely that they are due to a combination of magnetic anisotropy and other long range shielding effects attributable to the substituent, as well as changes in charge density. Indeed, to varying degrees, this must be true for all positions. If we assume that all factors influencing chemical shift except charge distribution are the same in the carbinol and carbonium ion, then the change in *positive* charge density at position i, Δq_i, accompanying conversion of a carbinol to its carbonium ion is related to the corresponding change in chemical shift, $\Delta \delta_i$, according to Eq (3):

$$\Delta q_i = -(1/160) \Delta \delta_i \qquad (3)$$

where the factor of 1/160 unit charge per ppm shift in Eq (3) is the previously cited empirical proportionality constant between carbon-13 chemical shift and charge density.[5, 6] Due to changes in hybridization in going from the carbinol to the carbonium ion, the change in the charge density at the central carbon of the carbonium ion (Δq_1) cannot be estimated in this manner. If one assumes that the central carbon in trimethylcarbonium ion (135·4 ppm downfield from the CS_2 line[31]) carries a full positive charge (i.e., no delocalization of charge onto the Me groups) then the difference in chemical shift between the central carbons in trimethylcarbonium ion and a triarylcarbonium ion can be attributed solely to a difference in charge, since the hybridization should be essentially the same in all cases. The empirical charge density for the central carbon is therefore given by Eq (4):

$$q_1 = 1 - (\delta_1 + 135)/160 \qquad (4)$$

In Table 5 we list the empirical changes in positive charge density at the aromatic positions (Δq_i) and the empirical charge densities for the central position (q_1). The last column lists values of $\Delta q_s = (1 - q_1 - \Sigma_i \Delta q_i)/3$, where the term $\Sigma_i \Delta q_i$ is the sum of the increases in positive charge over all positions in the phenyl rings.

The quantity Δq_s accounts for the positive charge delocalized onto the substituent (or the protons) or, from another point of view, Δq_s can be regarded as a measure of the consistency of the two nonequivalent definitions given by Eq (3) and (4) for Δq_i and q_1. For substituents which should be capable of accommodating little or no positive charge (eq., H), Δq_s should be close to zero. On the other hand, values of Δq_s should be relatively large (and positive) for substituents such as OMe and NMe_2. The values of Δq_s in Table 5 are in reasonable accord with these considerations.

In Table 5 we also list values for Δq_i and q_1 calculated by a simple HMO treatment. In calculating Δq_i we have treated the substituted carbinols as monosubstituted benzenes, ignoring the effect of the diarylhydroxymethyl substituent. The parameters used were those recommended by Streitwieser[32] and used by Wu and Daily[8] in their calculations of the C-13 chemical shifts of the monosubstituted benzenes. The carbonium ion calculations are based on an assumed angle of twist of the phenyl rings of 30°. This angle, together with an assumed C_1—C_2 bond length of 1·45 Å[10]

TABLE 5. COMPARISON OF EMPIRICAL CHARGE DENSITIES WITH THOSE CALCULATED BY THE HMO METHOD FOR TRIARYLCARBINOLS

Substituent, X		q_1	Δq_2	Δq_3	Δq_4	Δq_5	$\Delta q_s{}^c$
NO$_2$	Empirical	0·280	−0·050	0·106	0·017	0·055	−0·011
	HMO	0·427	−0·021	0·062	0·008	0·046	0·026
H	Empirical	0·267	−0·048	0·094	0·020	0·107	−0·043
	HMO	0·417	0·000	0·065	0·000	0·065	0·000
Cl	Empirical	0·223	−0·055	0·082	0·022	0·099	0·007
	HMO	0·405	0·002	0·063	0·001	0·065	0·003
F	Empirical	0·217	−0·045	0·101	0·032	0·071	−0·031
	HMO	0·395	0·004	0·062	0·002	0·065	0·005
Me	Empirical	0·222	−0·054	0·089	0·019	0·133	−0·036
	HMO	0·397	0·004	0·062	0·002	0·064	0·005
OMe	Empirical	0·151	−0·056	0·087	0·026	0·071	0·042
	HMO	0·370	0·008	0·059	0·004	0·063	0·013
NMe$_2$	Empirical	0·049	−0·074	0·066	0·007	0·040	0·205
	HMO	0·349	0·011	0·056	0·006	0·060	0·022

[a] Obtained from C-13 shifts via Eq (3), (4) and (5), text.
[b] Calculated for an assumed twist angle of the phenyl rings of 30°.
[c] $\Delta q_s = (1 - q_1 - \Sigma_i \Delta q_i)/3$.

leads to a C_1—C_2 resonance integral of 0.788β, while all other C—C resonance integrals were taken as 1.0β. The HMO Δq_i values follow, qualitatively, the trend given by the empirical values: there are relatively large positive charges at the 3 and 5 positions and a small positive charge at position 4. However, the HMO calculations do not give the rather large *negative* charges at C-2 which are found in the empirical charge distribution. Despite the lack of quantitative agreement between empirical and HMO charge densities, there is a good correlation between these quantities for the central carbon, as shown in Fig 8 (slope = 0·334, $r = 0.979$). This correlation, taken with the lack of quantitative agreement, might indicate that the constants in Eq (4) relating C-13 shifts to charge densities are not correct, or, alternatively, that the HMO calculations are only qualitatively correct. Since the agreement between empirical charge densities and those obtained from (presumably) more accurate CNDO calculations is better we are inclined toward the latter view.

TABLE 6. COMPARISON OF EMPIRICAL CHARGE DENSITIES WITH THOSE CALCULATED BY THE CNDO METHOD FOR TRIPHENYLCARBONIUM ION

Position	CNDO ($\theta = 60°$)[a]	CNDO ($\theta = 30°$)[a]	Empirical[b]
1 (central)	0·317	0·249	0·267
2	−0·003	−0·013	−0·048
3	0·051	0·071	0·094
4	0·032	0·015	0·020
5	0·051	0·081	0·107

[a] θ is assumed angle of twist of the phenyl rings.
[b] Obtained from carbon-13 chemical shifts via Eq (3) and (4), text.

In Table 6 we compare empirical charge densities in the unsubstituted triphenyl-carbonium ion with those calculated by the CNDO method[33] for assumed values of θ, the twist angle of the phenyl rings, of 30° and 60°. The empirical and CNDO charge densities for $\theta = 30°$ are in fairly good agreement*: there is a small negative
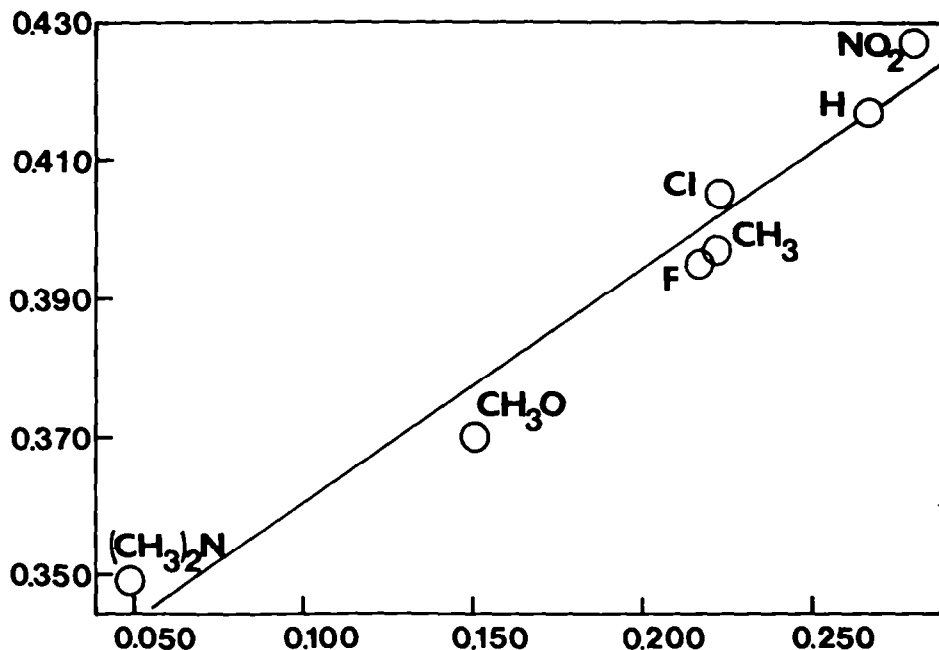

FIG 8. Plot of HMO Charge Density vs Empirical Charge Density for C_1

charge at position 2, a small positive charge at position 4, and relatively large positive charges, about equal in magnitude, at positions 3 and 5. Although the correspondence between the empirical and CNDO charge densities is not quantitative, a plot of empirical versus CNDO charge densities gives a good straight line, as shown in Fig 9 (slope = 1·14, $r = 0.985$). Theoretical justifications for the linear relation between charge density and C-13 chemical shifts in aromatic systems have, of course, been given by Karplus and Pople[34] and by Tokuhiro and Fraenkel.[35] We note finally that direct calculations of the chemical shifts[36] from the Karplus–Pople theory[34] using the parameters from CNDO calculations and, for the substituted triphenylcarbonium ions from HMO calculations, were in only rough agreement with the observed values.

In summary, we see that the C-13 shifts provide at least a qualitative measure of the charge distribution in these substituted triphenylcarbonium ions. The general features of the charge distribution to be expected from a simple resonance picture are followed in the charges obtained from the empirical relation for C-13 chemical shifts.

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* CNDO charge densities for values of θ less than 30° do not give appreciably better agreement, despite what a superficial inspection of Table 5 might indicate; that is to say, if it is assumed that the calculated charge densities follow a relation of the form $q_i = a_i + b_i \cos^2\theta$, then the values of a_i and b_i obtained from q_i at $\theta = 30°$ and 60° yield negative values of $\cos^2\theta$ for the empirical charge densities (except for position 3).

There are relatively large positive charges at the 3 and 5 positions, the amount of charge delocalized from the central carbon is proportional to substituent parameters measuring the resonance interaction of the substituent with the carbonium ion center. The empirical charge distribution in the phenyl ring of the ion is, approximately, a superposition of the distributions for the unsubstituted ion and the corresponding monosubstituted benzene; however the OMe and NMe$_2$ substituents bear a relatively large amount of the charge delocalized from the central carbon. The deviations of the C-5 shifts from an additivity relation may indicate the importance
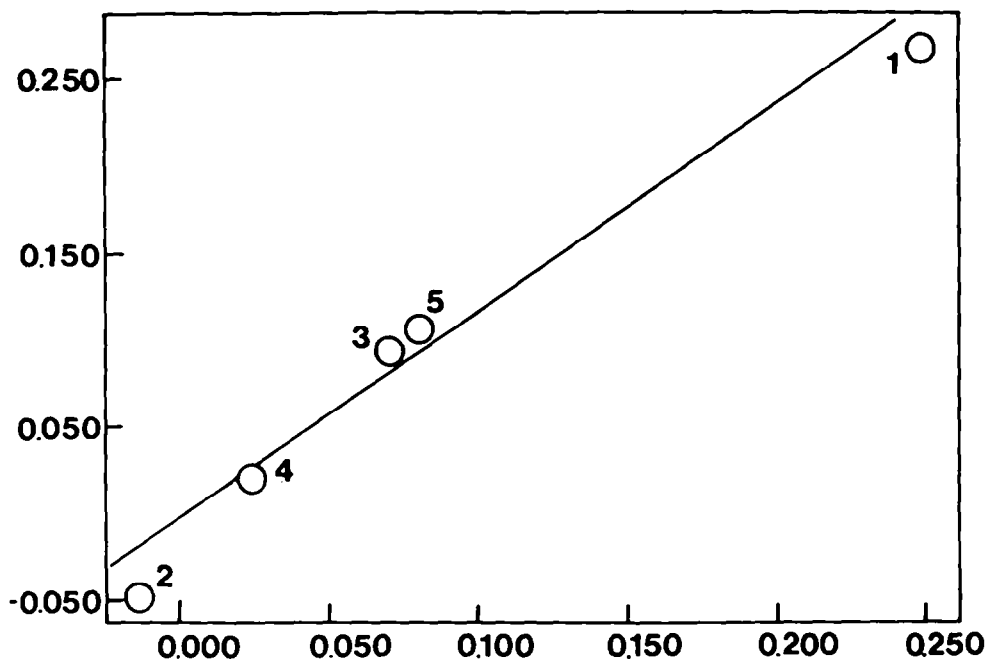
FIG 9. Plot of Empirical Charge Densities *vs* CNDO Charge Densities ($\theta = 30°$) for Triphenylcarbonium Ion

of long-range shielding effects, even though these deviations correlate with substituent parameters. The empirical charge densities in triphenylcarbonium ion are in reasonable agreement with those calculated by the CNDO method. Of particular interest is the fact that the C-13 shifts indicate that there is a small negative charge at C-2, which feature is predicted by the CNDO and an earlier SCF calculation.

EXPERIMENTAL

NMR *measurements*. Spectra were obtained using a Varian DP-60 spectrometer which had been extensively modified for field-frequency controlled operation at 14·1 kG.[12] All spectra were taken at an ambient temp of *ca* 37°. The spectrometer was interfaced to a Northern Scientific Model 544 signal-averager, in order to increase the effective sensitivity. The radiofrequency output of the spectrometer and the memory address of the signal averager were driven synchronously by a digital sweep unit developed in this laboratory.[12] In general, 180 scans at a sweep rate of 2 Hz/sec would give a sufficiently large signal/noise ratio for a 500 Hz scan of the aromatic region.

Samples were studied as 1·0 to 2·5 M solns in spinning 15 mm diameter tubes. Unenriched CS$_2$ was
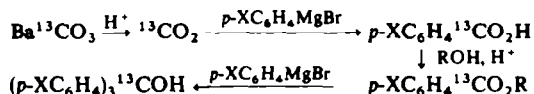
used both as an external reference for the chemical shift measurements and as a homogeneity standard. The field homogeneity was such that CS_2 samples in spinning 15 mm diameter tubes gave lines with half-height widths of 0·5 Hz or less. In the measurement of line positions, errors due to interpolation from fiducial points or to possible non-linearity of the signal-averager readout were eliminated by means of the synchronous drive of radiofrequency output and signal averager memory address. The spectrometer stability, over a 24 hr period, was such that line positions were reproducible to 0·2 Hz or better (for "narrow" lines).

Corrections to the chemical shifts to account for the differences in bulk diamagnetic susceptibility between the reference, CS_2, and the various samples were not made, since these corrections would be within the experimental error limits cited. These error limits for the chemical shifts were determined principally by the line-widths, which varied from ca 5 Hz to 50 Hz. The major contribution to the line-widths came from unresolved splittings due to long range carbon-proton spin coupling.

Sample preparation and solvent systems. The carbinol samples were run as ca 1·5 M THF solns, except for 4,4',4"-tris(dimethylamino)triphenylcarbinol. In order to inhibit formation of the carbonium ion, this compound was dissolved in THF which had been allowed to stand for several days over NaOH. The absence of the characteristic violet color associated with solns of the carbonium ion was evidence that the parent carbinol was, to better than 99%, the species present in the basic THF soln.

In most cases the carbonium ion was generated by soln of the appropriate carbinol in 96% H_2SO_4, in which all of the carbinols are >99% ionized. Exceptions were 4,4',4"-tris(dimethylamino)triphenyl-carbonium ion, 4,4',4"-trinitrotriphenylcarbonium ion, and triphenylcarbonium ion. In the case of the first of these ions, the amino nitrogens would be protonated in H_2SO_4. However, visible spectra[13] indicate that in 100% EtOH only the carbonium ion is formed. Accordingly, tris(dimethylamino)triphenylcarbonium ion was generated by solution of the chloride salt, crystal violet, in 100% EtOH. Triphenylcarbonium ion and 4,4',4"-trinitrotriphenylcarbonium ion were generated both from H_2SO_4 and chlorosulfonic acid solns of the parent carbinol. Although the unsubstituted carbinol was recovered in good yield from chlorosulfonic acid solns, the nitro-substituted carbinol was recovered in poor yield (ca 10%). The C-13 NMR spectra of the nitrosubstituted carbonium ion remained essentially unchanged for a period of 2 days after solns in chlorosulfonic or chlorosulfonic-sulfuric acid mixtures were prepared. However, after a longer period these spectra changed, indicating possible decomposition of the carbonium ion.

Compounds. Triarylcarbinols, enriched by ca 17% in C-13 at positions 1, were, with the exception of 4,4',4"-trinitrotriphenylcarbinol, prepared according to the following route:

$$Ba^{13}CO_3 \xrightarrow{H^+} {}^{13}CO_2 \xrightarrow{p\text{-}XC_6H_4MgBr} p\text{-}XC_6H_4{}^{13}CO_2H$$
$$\downarrow ROH, H^+$$
$$(p\text{-}XC_6H_4)_3{}^{13}COH \xleftarrow{p\text{-}XC_6H_4MgBr} p\text{-}XC_6H_4{}^{13}CO_2R$$

Unenriched triarylcarbinols were prepared in a similar manner starting with commercially available benzoic acids or esters.

Barium carbonate enriched to 50·02% in C-13 was purchased from Isomet Corporation.

Carbon dioxide enriched by ca 17% in C-13 was prepared in a vacuum line by adding an excess of 0·05 M HCl to a well stirred aqueous slurry of a 2:1 mixture of unenriched and enriched $BaCO_3$. The CO_2 was purified by distillation through a trap immersed in a CS_2 slurry ($-112°$) and was stored in a steel lecture cylinder. About 0·7 mole of CO_2 was prepared at a time by this method. The mass spectrum showed at 17·6% $^{13}CO_2$.

Benzoic acids were prepared by a procedure patterned after that of Murray and Williams.[14] Yields ranged from 60% (for X = $(CH_3)_2$N- to 97% (for X = Cl). The m.ps of all acids agreed with literature values. Benzoate esters were prepared by refluxing 1·0 g benzoic acid with an excess MeOH or EtOH in the presence of a small amount of conc H_2SO_4 for at least 24 hr. The mixture was poured onto an excess of water and extracted twice with 50 ml portions ether. The ether extract was washed with 25 ml sat Na_2CO_3, twice with 25 ml portions water, dried over $MgSO_4$, and the ether removed by distillation. Yields were usually better than 90%. The structures of the esters were confirmed by their IR and NMR spectra.

Triarylcarbinols were prepared by adding ca 1 g ester dissolved in a minimum amount of THF to a 2-fold excess 2 M Grignard reagent. The mixture was refluxed for at least 12 hr and then decomposed by addition of 100 ml sat NH_4Cl. The aqueous mixture was extracted 3 times with 50 ml portions ether, the extracts washed with water, and the ether removed by evaporation. The crude carbinol, which was usually

obtained as an oil, was purified by chromatography on 100 g neutral alumina. Elution with 500 ml benzene removed unreacted ester and biaryl impurities. The carbinol was then eluted in 250 ml fractions with 15:85 (v/v) ether–benzene. Crystallization was generally induced by trituration with light petroleum (30–60°). The identity of the carbinol was confirmed by its m.p. (except in the case of 4,4′,4″-trichloro-triphenylcarbinol, which resisted all attempts at crystallization) and by its IR and NMR spectra. The results relating to preparation of the triarylcarbinols are summarized in Table 2.

Enriched 4,4′,4″-trinitrotriphenylcarbinol was prepared in 3 steps from enriched triphenylcarbinol as follows. Triphenylcarbinol was converted to triphenylmethane in quantitative yield by the method of Guyot and Kovache,[20] m.p. 91·5–92° (lit.[20] 91°). Triphenylmethane was converted to 4,4′,4″-trinitro-triphenylmethane by the method of Shoesmith et al.[21] m.p. 196–205° (lit.[21] 214–215°). 4,4′,4″-Trinitro-triphenylmethane was oxidized to the corresponding carbinol by the method of Hawthorne and Hammond,[22] m.p. 189·5–190° (lit.[22] 190–191°). The overall yield based on triphenylmethane was 61%.

4,4′,4″-Trideuterotriphenylcarbinol and 4,4′,4″-trifluorotriphenylcarbinol were prepared by Dr. I. I. Schuster.[23]

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