

18-crown-6 and sodium in methanol ($\log K_s$) is 4.35 and the reported value is 4.36.¹⁰ Our $\log K_s$ value for 18-crown-6 in water is 1.80 ($K_s = 63$). This value is considerably higher than the calorimetrically determined value of 0.8 ($K_s = 6.3$)¹⁰ or the conductometric value of 0.3.⁸ The experimental error in these values determined by either method should be considerably less than an order of magnitude. Note, however, that the binding is quite weak and the sensitivity of these measurements will be lower in water than for any methanol mixture. Further note that binding constants between sodium and four other 18-crown-6 molecules have been measured. These are: cyclohexano-18-crown-6 ($K_s = 0.8$),¹¹ dicyclohexano-18-crown-6 ($K_s = 0.69$),⁹ di-*tert*-butyldicyclohexano-18-crown-6 ($K_s = 1.42$),¹¹ and dibenzo-18-crown-6 ($\log K_s = 1.16$).¹² The first two values noted above were determined calorimetrically and the latter two conductometrically and spectroscopically, respectively.

Intuitively, it seems that the binding between sodium cation and 18-crown-6 should be stronger than for 15-crown-5 just because additional solvation can be provided by the extra oxygen. The crystal structure of such a complex suggests this.¹³ Note that the two lines (Figure 1) approximately parallel each other, but binding with sodium cation is stronger for 18-crown-6 in all solvent mixtures than it is with 15-crown-5. Although size correlations have received considerable attention in the past, the relatively small and hard sodium cation does not seem to fit as well⁴ into such systematizations. In any event, we have included in Figure 1, both our (line A) and Lamb's⁹ (line B) values. Slope calculations are presented below for both.

Statistical analyses of the 18-crown-6 (A and B) and 15-crown-5 lines show that each may be approximated as linear with reasonable confidence. The slopes¹⁵ and correlation factors (r) are as follows: 15-crown-5, slope = 2.34, $r = 0.995$; 18-crown-6 (line A), slope = 2.32, $r = 0.968$; 18-crown-6 (line B), slope = 2.99, $r = 0.969$.

A visual examination corroborates that neither 18-crown-6 line fits as well as the 15-crown-5 data, although the correlation factors are not significantly different. It is interesting to note that Izatt et al.¹⁴ have reported calorimetrically determined K_s values for reaction of benzo-15-crown-5 in aqueous methanol mixtures. He reports $\log K_s$ values of 0.72, 1.17, 1.64, 1.99, and 2.26 in 20%, 40%, 60%, 70%, and 80% methanol, respectively. The calculated slope of this line is 2.57 and $r = 0.997$. This accords reasonably well with our own data for the parent system.

Although the primary purpose of this communication is to record the K_s solvent dependences for 15-crown-5 and 18-crown-6, it is interesting to note that the nitrogen lariats⁶ exhibit a similar rise in the ordinate value as polarity declines. Thus *N*-methoxyethylmonoaza-15-crown-5 binds Na^+ ($\log K_s$) as follows: 1.36, 2.13, 2.56, 3.24, 3.66, and 3.97 in water, 40%, 60%, 80%, 90%, and 100% methanol,

respectively. The slope of the best straight line is 2.63 and $r = 0.988$. The solvent trends therefore seem to be typical of a number of simple as well as more complex systems.

Experimental Section

15-Crown-5 was obtained from the Aldrich Chemical Co. and was distilled before use. 18-Crown-6 was prepared by our previously reported procedure.¹⁶ Analytical reagent grade methanol was used for all solvent compositions and mixtures were made by combining the appropriate weights of methanol and water at 25 °C. Binding constants were recorded as described in ref 7. Linear regressions were calculated with a hand calculator equipped with the appropriate program.

Acknowledgment. We warmly thank the NIH for a grant (GM 29150) which partially supported this work.

Registry No. 15-Crown-5, 33100-27-5; 18-crown-6, 17455-13-9; sodium cation, 17341-25-2.

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Carbon-13 Nuclear Magnetic Resonance Chemical Shifts of Chlorinated and Fluorinated Phthalic Anhydrides and Acids

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The theory and practice of carbon-13 NMR spectroscopy has progressed, in part, by the systematic analysis of substituent effects in classes of organic compounds.¹ Aromatic substituent effects have been extensively studied in the case of simple benzene derivatives.² However, more functionalized aromatic derivatives have received less attention.³⁻⁵ In order to partially fill this gap, we report the results of our systematic study on chlorine- and fluorine-substituted phthalic anhydrides and acids.

Experimental Section

All materials were commercially available or synthesized by literature procedures. Compounds 1, 12, 14, 16, and 22 were purchased from Aldrich Chemical Co. The remaining compounds were synthesized by using the procedures in the indicated references: 2,⁶ 3,⁷ 4,⁸ 5,⁹ 6,⁷ 10,⁸ 11,⁹ 12,¹⁰ 13,¹¹ 14,¹³ 15,¹⁶ 17,¹⁷ 18,¹¹

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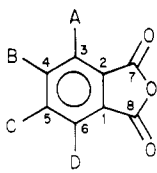
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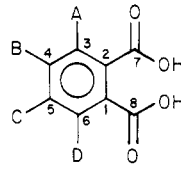
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(15) Slopes are calculated by linear regression analysis, using 0.2 = 20% by weight, etc.

Table I. ¹³C NMR Chemical Shifts of Halogenated Phthalic Anhydrides


compd	A	B	C	D	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1	H	H	H	H	131.0	131.0	125.5	136.4	136.4	125.5	163.4	163.4
2	Cl	H	H	H	133.7	131.1	128.0	137.0	137.6	124.2	160.6	162.1
3	H	Cl	H	H	130.1	133.5	125.4	141.2	136.1	127.0	162.1	162.4
4	Cl	H	H	Cl	134.0	134.0	128.9	138.2	138.2	128.9	159.4	159.4
5	H	Cl	Cl	H	131.5	131.5	127.3	139.3	139.3	127.3	161.5	161.5
6	Cl	Cl	Cl	Cl	129.4	129.4	128.9	140.0	140.0	129.4	158.4	158.4
7	F	H	H	H	133.6	118.1	157.5	123.7	139.5	122.0	159.6	162.3
8	H	F	H	H	127.7	134.5	112.9	166.7	123.7	128.3	162.1	162.3
9	F	H	H	F	119.2	119.2	153.7	126.8	126.8	153.7	158.8	158.8
10	H	F	F	H	129.0	129.0	115.2	154.7	154.7	115.2	161.5	161.5
11	F	F	F	F	114.8	114.8	a	a	a	a	157.6	157.6

^a Non-first-order complex multiplets.

Table II. ¹³C NMR Chemical Shifts of Halogenated Phthalic Acids


compd	A	B	C	D	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
12	H	H	H	H	131.4	131.4	128.6	132.9	132.9	128.6	168.8	168.8
13	Cl	H	H	H	130.1	130.1	136.2	133.5	130.4	128.8	166.0	167.3
14	H	Cl	H	H	131.1	135.5	128.2	135.9	130.8	130.8	167.7	167.7
15	Cl	H	H	Cl	129.1	129.1	134.1	132.3	132.3	134.1	165.9	165.9
16	H	Cl	Cl	H	133.0	133.0	130.4	133.8	133.8	130.4	166.6	166.6
17	Cl	Cl	Cl	Cl	134.2	134.2	129.1	133.2	133.2	129.1	164.8	164.8
18	F	H	H	H	130.8	124.8	158.4	119.9	125.8	131.3	166.1	165.9
19	H	F	H	H	128.5	136.8	115.4	163.3	117.5	131.8	168.0	167.6
20	F	H	H	F	122.7	122.7	155.1	120.1	120.1	155.1	164.4	164.4
21	H	F	F	H	130.8	130.8	118.3	150.5	150.5	118.3	166.9	166.9
22	F	F	F	F	118.1	118.1	144.9	141.4	141.4	144.9	162.7	162.7

19,¹¹ 20,¹¹ and 21.¹³ The melting points of the synthesized compounds agreed with the literature values.

Proton-decoupled carbon-13 NMR spectra were obtained with a Varian XL-100/Nicolet TT-100 spectrometer operating at 25.15 MHz. Typically, the pulse flip angle was 45° (9 μs) and the time between pulses was 15 s. The sweep width was 5000 Hz and 8K computer points were used for time domain signal accumulation. The spectrometer was equipped with quadrature phase detection and an internal deuterium lock. Exponential multiplication was performed on free induction decays to improve the signal-to-noise ratios of the frequency domain spectra. The proton decoupler was gated off during the delay time between pulses and on during signal acquisition to eliminate the nuclear Overhauser effect. Assignments of carbon-13 chemical shifts to particular carbon atoms were based upon known substituent behavior, internal consistency, and proton and/or fluorine spin-spin couplings to carbon. In order to reduce concentration and solvent effects upon the chemical shifts, all samples were prepared by dissolving 0.2 g of material in 2.0 mL of Me₂SO-*d*₆. Me₂SO-*d*₆ was dried over molecular sieves and also provided the signal for the deuterium field-frequency lock. The probe temperature was 26 °C. Carbon-13 chemical shifts were converted to the Me₄Si scale, using the relationship:

$$\delta_{\text{Me}_4\text{Si}} = \delta_{\text{Me}_2\text{SO}-d_6} + 39.56 \text{ ppm} \quad (1)$$

The X-ray crystallographic geometry¹⁸ was used in the CNDO/2 calculations.¹⁹

Results and Discussion

Tables I and II contain the carbon-13 chemical shift assignments and structures for the halogenated phthalic anhydrides and acids, respectively. Table III contains the substituent-induced chemical shift effects at each carbon atom. These substituent effects are tabulated according to the spatial relationship between the carbon atom in question and the halogen (ipso, ortho, meta, and para). A prime was used to distinguish those carbons which are already bearing a substituent. Examination of Table III showed that the substituent effects are not strictly additive.

Aromatic Carbons. Chlorine Substituent Effects. With the exception of acids 13 and 15, the chlorine substituent effect at the ipso carbon (the carbon attached to chlorine) of both phthalic anhydrides and acids was reduced compared to that of less encumbered benzene derivatives. The chlorine substituent effects at the ortho and para carbons were small and not well-behaved. Segregation of the ortho and para effects at unsubstituted and substituted carbons did not reveal any consistent patterns. On the other hand, with the exception of acids 13 and 15, the meta chlorine substituent effect was small, positive, and well-behaved. In general, the meta effect at an unsub-

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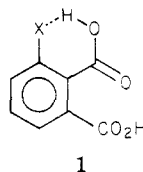
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Table III. Carbon-13 Substituent-Induced Effects

$\frac{(\text{Ar } X_m - \text{Ar } X_n)_m \text{ S}}{= n + 1}$	carbon position relative to halogen ^a								
	ipso	ortho	ortho'	meta	meta'	para	para'	C-7	C-8
2 - 1	2.5	0.6	0.1	1.2	2.7	-1.3		-2.8	-1.3
3 - 1	4.8	-0.3, -0.1		1.5	2.5		-0.9	-1.3	-1.0
4 - 2	4.7	0.6	0.3	1.2	2.9		0.9	-1.2	-2.7
5 - 3	3.2	0.3	-1.9	1.9	1.4		-2.0	-0.6	-0.9
13 - 12	7.6	0.6	-1.3	-2.5	-1.3	0.2		-2.8	-1.5
14 - 12	3.0	-0.4, -2.1		2.2	4.1		-0.3	-1.1	-1.1
15 - 13	5.3	1.9	-1.0	-1.2	-1.0		-2.1	-0.1	-1.4
16 - 14	3.0	-0.4	-2.1	2.2	1.9		-2.5	-1.1	-1.1
7 - 1	32.0	-12.7	-12.9	3.1	2.6	-3.5		-3.8	-1.1
8 - 1	30.3	-12.6, -12.7		2.8	3.5		-3.3	-1.3	-1.1
9 - 7	31.7	-12.7	-14.4	3.1	1.1		-3.8	-0.8	-3.5
10 - 8	31.0	-13.1	-12.0	2.3	1.3		-5.5	-0.6	-0.8
18 - 1	29.8	-13.0	-6.6	-7.1	-0.6	2.7		-2.7	-2.9
19 - 1	30.4	-15.4, -13.2		3.2	5.4		-2.9	-0.8	-1.2
20 - 18	23.8	-5.7	-8.1	0.2	-2.1		-3.3	-1.7	-1.5
21 - 19	33.0	-13.5	-12.8	2.9	2.3		-6.0	-1.1	-0.7

^a The carbons indicated by the primed positions are already substituted.

stituted carbon (1–2 ppm) was slightly smaller than at a substituted carbon (2–4 ppm). Interestingly, the meta effects in phthalic acids 13 and 15 are of the opposite sign. It is tempting to rationalize these unusual meta effects as well as the ipso effects noted above on the basis of structure 1 which shows intramolecular hydrogen bonding between the carboxyl moiety and adjacent chlorine atom. This interaction is, of course, not possible in the corresponding anhydride structures. The expected chlorine substituent effects are changed by this intramolecular hydrogen bonding. The chlorines ability to electronically interact with the aromatic ring must be severely compromised by the additional interaction with the carboxyl proton. Other rationales such as field effects cannot be ignored although it is difficult to visualize how they would only be operative in the acid and not the anhydride molecules.



Fluorine Substituent Effects. The large downfield fluorine substituent effect at the ipso carbon was between 30.3 and 33.0 ppm for both phthalic anhydrides and acids (except for acids 18 and 20). The magnitude of this effect was only slightly reduced from that of more simple benzene derivatives. The effects at carbons ortho to fluorine are upfield and in the usual range of -12.0 to -15.4 ppm (except for acids 18 and 20 where the ortho effect is reduced by about one-half). The para fluorine effect is also upfield and in the range of -2.9 to -6.0 ppm. The magnitude of the ortho and para effects did not appear to consistently depend upon whether or not the ortho or para carbons were unsubstituted or substituted. The effects of meta carbons were in the range of 1–3 ppm (with the exception of compounds 18 and 20) and showed no influence upon whether the meta carbon was already bearing a substituent.

The unusual behavior of fluorine substituent effects in acids 18 and 20 can be again rationalized on the basis of structure 1 which shows the possibility of intramolecular hydrogen bonding. Alternative rationales for these effects are not as obvious.

Carbonyl Carbons. The anhydride carbonyl carbons appeared in the range 157.6–163.4 ppm, whereas the acid

carbonyl carbons appeared in the range 162.7–168.8 ppm. For anhydrides and acids with the same halogen substituents, the anhydride carbonyl carbons routinely appeared 5–6 ppm upfield from the acid carbonyl carbons. The origins of this “anhydride effect” have been previously discussed in terms of inductive, resonance, steric, and ring strain effects.²⁰ The sensitivity of carbonyl carbon chemical shifts to halogen substitution was indicated by the observation that asymmetrically halogenated compounds always gave rise to two distinct carbon-13 signals. A similar observation was made in the case of nitrogen-substituted phthalates.²¹

Halogen substituents on the aromatic ring invariably caused the carbonyl carbon chemical shifts to move upfield by 0.3–3.8 ppm. Surprisingly, the magnitude of this upfield effect was similar for both chlorine and fluorine substituents. Evidently the relative electronegativity difference between the two halogens plays only a minor role in determining the chemical shifts of the carbonyl carbons. Moreover, the upfield effect was similar for both anhydride and acid carbonyl carbons.

The magnitude of the upfield trend was dependent upon the spatial relationship to the halogen. Thus, carbonyl carbons adjacent to halogens experienced 1.5–3.8 ppm upfield shifts, whereas those more removed from halogen exhibited an 0.3–1.5 ppm upfield trend. Acids 15, 18 and 20 are exceptions to this trend presumably because of intramolecular hydrogen bonding (structure 1), although other factors may also be contributing.

Charge Density and Chemical Shifts. For assessment of the relative importance of substituent-induced charge density changes influencing carbon-13 chemical shifts, the charge densities for phthalic anhydride (1) and fluoroanhydrides 7 and 8 were calculated by the CNDO/2 method.²² Figure 1 shows the plot of total charge density vs. carbon-13 chemical shifts for all the carbons of anhydrides 1, 7, and 8. A correlation was found between total charge density and chemical shift ($p = 0.935$). We conclude that substituent-induced charge density changes play a role in determining the carbon-13 chemical shifts in these systems.

The deviations noted from strict additivity as well as the unusual behavior of halogenated carbons adjacent to

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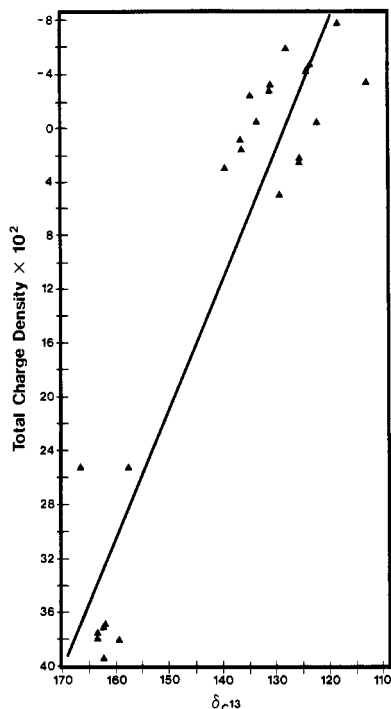


Figure 1. Plot of total charge density vs. carbon-13 chemical shifts for compounds 1, 7, and 8.

acid carbonyls indicate that the electronic effect of the substituent is altered by proximity to other groups on the aromatic ring. The causes of such alterations are complex but must be associated with steric and resonance inhibition phenomenon. The nonadditivity of substituent effects for heavily substituted aromatics has been the subject of several reports.^{23,24} In the case of ortho halogenated phthalic acids, intramolecular hydrogen bonding is a likely cause of the observed altered substituent effect.

Acknowledgment. We thank M. P. Nancollas for performing the CNDO/2 calculations.

Registry No. 1, 85-44-9; 2, 117-21-5; 3, 118-45-6; 4, 4466-59-5; 5, 942-06-3; 6, 117-08-8; 7, 652-39-1; 8, 319-03-9; 9, 652-40-4; 10, 18959-30-3; 11, 652-12-0; 12, 88-99-3; 13, 27563-65-1; 14, 89-20-3; 15, 16110-99-9; 16, 56962-08-4; 17, 632-58-6; 18, 1583-67-1; 19, 320-97-8; 20, 651-97-8; 21, 18959-31-4; 22, 652-03-9.

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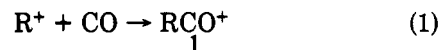
Acid-Catalyzed Carbon Monoxide Insertion in *tert*-Alkyl Aromatics and Its Use for Ring Enlargements

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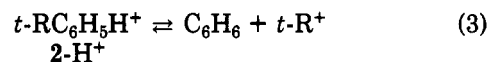
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Carbon monoxide is a weak nucleophile, which reacts with carbocations¹ or very strong acids. The first reaction (eq 1) generates acyl cations (1). The second reaction



should lead to the formyl cation. This species was never evidenced directly, but it has been implicated in the Gattermann-Koch formylation of aromatics with CO (eq 2).^{2,3} We report here on the observation that treatment of a *tert*-alkylbenzene with carbon monoxide and a superacid results in CO insertion between the ring and the tertiary alkyl group.

Previously it was shown that a dealkylation-realkylation equilibrium is established when a *tert*-alkylbenzene (2) is protonated in a superacid (eq 3).⁴ The equilibrium is

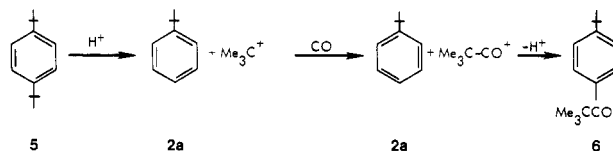


a, R = Me₃C; b, R = (Me₂CH)Me₂C

displaced toward alkylation; no alkyl cation was observed by NMR when *tert*-butylbenzene (2a) was dissolved in HF-TaF₅, although complete protonation of the alkylbenzene was indicated.⁴ Quantitative conversion of 2a to the *tert*-butyl cation was observed in HF-SbF₅,⁵ in which the other dealkylation product, benzene, is fully protonated, thus shifting the equilibrium in eq 3 to the right.⁴ A study of a *tert*-hexylbenzene (2b) indicated that the tertiary alkyl cations present at equilibrium, albeit in minute concentration, can abstract hydride ions from an appropriate donor.⁶

We reasoned that carbon monoxide¹ should also be able to react according to eq 1 with the alkyl cations present at equilibrium with 2. Indeed, *tert*-butyl cations could be trapped as pivaloyl cations (3) when 2a dissolved in HF-TaF₅ was treated with CO (0.8–2.0 MPa), between –20 and +20 °C.⁴ The acyl cations 3 reacted partially with benzene to form the conjugate acid of pivalophenone (4). Gattermann-Koch reaction took place, however, as a side-reaction, reducing the yield of 4 (Scheme I). Formation of pivalic acid from *tert*-butylarenes in the weaker acids HF^{7a} or BF₃·H₂O^{7b} was observed before, but no acylation products were formed in those experiments.⁷

The extent of ring formylation can be reduced significantly in certain cases. Thus, reaction of 1,4-di-*tert*-butylbenzene (5) with CO, catalyzed by AlCl₃-HCl, gave *p*-*tert*-butylpivalophenone (6) as the only product. This



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