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PRELIMINARY COMMUNICATION

THE ELECTRONIC EFFECT OF MERCURY SUBSTITUENTS

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Although arylmercurials have been extensively studied[1], there appears to be no definitive evidence concerning the groundstate electronic effect of mercuri-substituents. From a study of the E_{1u} bands in the electronic spectra of certain *para*-substituted phenylmercuric halides, Gowenlock and Trotman[2] considered the chloromercury group (–HgCl) to resemble the chloro and methyl groups in its effect on the displacement of the band, but to differ from carboxyl and nitro *i.e.* the mesomeric effect of the chloromercuric group is donating electrons to the *ortho* and *para* positions*. The suggestion was also made that there may be weak interaction (perhaps involving Hg $6p_\pi$ or $6d_\pi$ bonding) between two phenyl groups attached to mercury. Subsequently, Wang[3] suggested that the failure of the phenylmercuric cation to solvolyse was due in part to conjugative stabilisation in the sense of (I) below. Neither of these suggestions appears essential to explain the data**.

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* Reactivity studies appear to indicate that mercuri-substituents have a weak orientational influence. Thus the nitration of phenylmercuric nitrate has been reported to lead to *ca.* 50% *meta*-substitution (F. CHALLENGER AND E. ROTHSTEIN, *J. Chem. Soc.*, (1934) 1258) which is not greatly different from that expected on a statistical basis, particularly considering that *ortho*-substitution may be somewhat sterically retarded. A more recent report (C. PERRIN AND F. H. WESTHEIMER, *J. Am. Chem. Soc.*, 85 (1963) 2773) indicated that σ^+ for the mercuri-substituent was about 0.1.

** (a) Since electronic spectra provide only an energy difference between ground and excited states, it is never clear that spectral changes as a result of substitution in the benzene molecule are a manifestation of ground state substituent effects only. For example, the often assumed conjugative ability of the $-NO_2$ group is based largely on interpretations of electronic spectra, but there is some evidence from reactivity and thermodynamic data that the $-NO_2$ group engages in limited conjugation in the ground state, particularly when carboxyl derivatives are studied. On the other hand, Dewar and Takeuchi[7] have recently demonstrated by ^{19}F resonance measurements that the nitro-substituent chemical shift (the substituent chemical shift is defined as the *difference* between the chemical shift of the unsubstituted fluoro-aromatic and the substituted fluoro-aromatic) for *p*-nitrofluorobenzene is -10.30 ppm while that for 3,5-dimethyl-4-nitro-fluorobenzene is -5.50 ppm, suggesting interruption of nitro-conjugation by the *ortho* methyl groups. The linear cyano substituent shows no such fluctuation.

(b) The solvolysis of organomercuric perchlorates involves C–Hg bond heterolysis in the sense below as the slow step[4], so that the

$$R\text{–}Hg^{\oplus} \longrightarrow R^{\oplus} + Hg^0$$

reluctance of the phenylmercuric cation to demercurate is probably due to the high energy of the phenyl carbonium ion.

(I)

In addition to the anticipated $+I$ effect of a metallo-substituent, two types of mesomeric interaction between mercury(II) and an aryl system are conceptually possible. Assuming essentially *sp* hybridisation for Hg^{II} in its organic compounds, mesomeric electron withdrawal may be envisaged via the vacant 6*p* mercury orbitals. On the other hand, mesomeric supply via the filled *d*-orbitals ($5d^{10}$) must be considered, although energetic mis-match of orbitals may be severe. Solvent complexation could well compete with the former process. In view of the established sensitivity of ^{19}F resonance on the nature of substituents in mono-fluoro aromatic molecules[5,6], we have synthesised a number of phenyl and benzyl mercurials with both *meta* and *para* fluoro-substituents in the expectation that ^{19}F substituent chemical shifts would provide evidence for any ground state conjugation. The *meta* orientation of fluorine and mercuric substituent would inhibit mutual conjugation. The ^{19}F data is assembled in Table 1.

TABLE 1

SUBSTITUENT CHEMICAL SHIFTS FOR MERCURI-SUBSTITUTED FLUOROBENZENE

System	Solvent	Compound	R	scs[a]	(*para* scs–*meta* scs)
1	Dioxane	R_2Hg	*m*-FC_6H_4	+0.70	
2	Dioxane	R_2Hg	*p*-FC_6H_4	+0.80	+0.10
3	Dioxane	R_2Hg	*m*-$FC_6H_4CH_2$	+0.95	
4	Dioxane	R_2Hg	*p*-$FC_6H_4CH_2$	+7.95	+7.00
5	DMSO	R_2Hg	*m*-FC_6H_4	+1.10	
6	DMSO	R_2Hg	*p*-FC_6H_4	+1.20	+0.10
7	DMSO	R_2Hg	*m*-$FC_6H_4CH_2$	+1.35	
8	DMSO	R_2Hg	*p*-$FC_6H_4CH_2$	+9.20	+7.85
9	DMSO	RHgCl	*m*-FC_6H_4	+0.70	
10	DMSO	RHgCl	*p*-FC_6H_4	+0.65	−0.05
11	DMSO	RHgBr	*p*-FC_6H_4	+0.65	
12	DMSO	RHgCl	*m*-$FC_6H_4CH_2$	+1.80	
13	DMSO	RHgCl	*p*-$FC_6H_4CH_2$	+6.80	+5.00

[a] Substituent chemical shift, in ppm (See footnote p. P8 for definition). 1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB) was employed as internal standard. The organomercurial halides were insufficiently soluble in solvents other than DMSO. Spectra were swept at least four times in each direction and chemical shifts (which are presented to the nearest 0.05 ppm) were calculated for the center of each ^{19}F multiplet. Spectra were obtained with a Varian DP 60 instrument operating at 56.4 Mcps. The mercurials were prepared by the usual Grignard and symmetrisation procedures, and their structures verified by analyses, m.p.'s, ^1H and ^{19}F NMR spectra.

Concerning the phenyl mercurials (systems 1, 2, 5, 6, 9, 10, 11), the first point to emerge from Table 1 is that whatever effect the mercuric group has, it is extremely feeble. The quite small values of scs (1, 5, 9)[*] and scs (2, 6, 10) may be compared with scs values of +1.20 and +5.40 for the *meta* and *para* methyl substituents respectively[5]. The positive scs values also suggest that conjugative electron withdrawal in the sense

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[*] The numbers in brackets indicate the system numbers in Table 1.

of (I) is insignificant, particularly since scs (2, 6, 10) are not sensibly less than scs (1, 5, 9). This is in contrast to our, and other[5] data on *p*- and *m*-fluorophenyltrimethylsilane where the scs for *m*-$SiMe_3$ = +0.85 but scs for *p*-$SiMe_3$ = −0.50 ppm (cyclohexane solvent), consistent with electron withdrawal via silicon *d*-orbital participation. The positive scs values are expected for a $+I$ metallo-substituent, and the facts that the scs (1, 5) are not greater than scs (2, 6) are consistent with other data that inductive (field) effects seem to operate at *meta* and *para* positions in a comparable way. However, in view of the fact that the differences are so small on the ^{19}F shielding scale, we would be disinclined to make a strong case on this basis. The firm conclusion to be drawn is that in mono- and bis-phenylmercury systems, there is little net movement of π charge either in or out of the phenyl ring, *i.e.* there is no *detectable* groundstate resonance interaction between mercury and the π-system.

In systems (3, 4). (7, 8) and (12, 13) the rather large differences between *meta* and *para* scs values are consistent with conjugative stabilisation of negative charge on the benzylic carbon, resulting from C–Hg bond polarisation. Similar scs differences are found for the analogous benzyl tin and silicon systems[8]. The greater scs values for DMSO solutions may indicate greater C–Hg bond polarisation, presumably as a result of DMSO coordination.

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