

Molecular Core Binding Energies for Some Monosubstituted Benzenes, as Determined by X-Ray Photoelectron Spectroscopy

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Summary Molecular core binding energies have been measured for some mono-substituted benzenes PhX (X = H, F, Cl, CH₃, CF₃, and CCl₃) and are interpreted in terms of CNDO-SCF-MO calculations.

As part of our study of the application of X-ray photoelectron spectroscopy to structural problems in halogeno-carbon chemistry we have investigated a large number of simple molecules. We report here molecular core binding energies for some monosubstituted benzenes PhX (X = H,

F, Cl, CH₃, CF₃ and CCl₃), and an interpretation of the results in terms of CNDO-SCF-MO calculations.

Spectra have been measured on an A.E.I. ES100 electron spectrometer using Mg-K $\alpha_{1,2}$ radiation. Samples were studied as thin films on gold and under the experimental conditions employed the gold 4f_{7/2} core level at 84 eV binding energy had a half width of 0.95 eV. Spectra were deconvoluted using a Du Pont 310 curve resolver, the line width of 1.1 eV and peak shape (almost Gaussian), for each channel being taken from our previous study of benzene.¹

Typical of the C_{1s} spectra is that of fluorobenzene shown in Figure 1. The Table shows the measured binding energies. In the absence of *ab initio* calculations assignment of C_{1s} levels has been based on CNDO-SCF-MO calculations.

It may be shown² that the binding energy of a given core level of an atom in a molecule may be related to the charge

readily be made. A full discussion of these results and measurements involving valence shell ionizations will be presented in due course. For the latter we note that the effects of differential changes in cross section in going from a low energy He to a high energy Mg- $K\alpha_{1,2}$ photon source aids considerably in the assignment of the valence shell energy levels.

TABLE. Molecular core binding energies (in eV)†

X	C_{1s} levels				X	Binding energy (eV)	
	C(1)	C(2), [C(6)]	C(3)[C(5)]	C(4)			
H	284.9	284.9	284.9	284.9			
F	287.8	285.4	285.9	285.2	F_{1s}	689.6	
Cl	287.1	286.0	285.5	285.3	Cl_{2s}	271.8	
						$Cl_{2p(1/2)}$	202.8
						$Cl_{2p(3/2)}$	201.0
CH_3	286.4	285.1	285.2	284.5	C_{1s}	284.7	
CF_3	286.9	286.5	286.0	285.5	C_{1s}	293.8	
CCl_3	286.6	285.8	285.7	285.2	C_{1s}	290.0	
						F_{1s}	690.8
						Cl_{2s}	271.7
						$Cl_{2p(1/2)}$	202.8
						$Cl_{2p(3/2)}$	201.0

† Relative binding energies for C_{1s} levels within a molecule are ± 0.2 eV. Relative binding energies between different compounds depend on sample charging effects. By studying the samples as thin films on gold these are minimized and relative binding energies between molecules are estimated to be ± 0.3 eV.

distribution by equation (1). E_0^i is a reference level and the

$$E^i = E_0^i + kq_i^i + \sum_j \frac{q_j^i}{r_{ij}} \quad (1)$$

second term represents the potential from the charge at the atom considered. The third term, an intramolecular

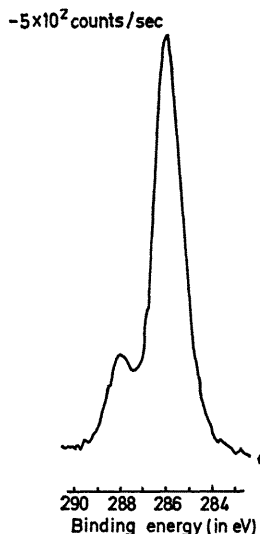


FIGURE 1. Fluorobenzene C_{1s} spectra.

Madelung type potential accounts for the potential from the rest of the molecule. The parameter k depends on the definition of atomic charge and, in an SCF-MO treatment, on the basis set employed. In studies of carbonyl compounds³ we have found a value of k of 25 eV/unit charge for C_{1s} levels using CNDO/2 charge distributions. Using this as an initial value of k an assignment of C_{1s} levels may

The results in the Table show the potential of this technique for probing the electronic structure of simple molecules. Considering the series Ph-CY₃ (Y = H, F, Cl) the C_{1s} binding energies are 284.7, 293.8, and 290.0 eV respectively. This reflects the large potential at the carbon atom due largely to the decreasing electron population in the order H > Cl > F.

Of the ring carbon atoms the highest binding energy is for C(1) the atom directly attached to the substituent. In each case there is a considerable increase in binding energy on replacing hydrogen, the 'shifts' being 2.9, 2.2, 1.5, 2.0, and 1.7 eV respectively for X = F, Cl, CH₃, CF₃, and CCl₃. It is interesting to compare these with corresponding 'shifts' we have measured⁴ in the saturated series CCl₃-X and CCl₂H-X. (2.8, 1.6, -0.6, 1.0, 0.5 eV for X = F, Cl, CH₃, CF₃, CCl₃ respectively). The different electronic effect of substituents on core levels in conjugated and saturated systems is particularly striking for the substituted methyl compounds. In the saturated compounds replacement of H by CH₃ lowers the binding energy, indicative of greater electron density about the carbon atom, whereas in the unsaturated molecule the binding energy of the attached carbon is actually increased, indicating a reduced electron density. This arises largely from π -electron drift away from C(1) to the *ortho* and *para* positions on replacing H by the π -inductive repelling CH₃ group.⁵ For CF₃ and CCl₃ the shift to higher core binding energy of the attached carbon is also enhanced compared with the saturated series. The CNDO-SCF-MO calculations indicate that there is a considerable π -electron drift towards C(1) in these molecules; however, the shifts are dominated in these cases by the large potentials due to neighbouring atoms so that overall the binding energies are somewhat increased. For fluorobenzene and toluene the calculations suggest the assignment given in the Table *i.e.* the C_{1s} binding energies are in the order *meta* > *ortho* > *para*. For the rest the order is *ortho* > *meta* > *para*. Only for toluene is the binding energy of the *para* carbon lower than that for benzene.

Having used an initial value of $k = 25$ eV/unit charge in equation (1) to make the assignment of C_{1s} binding energies,

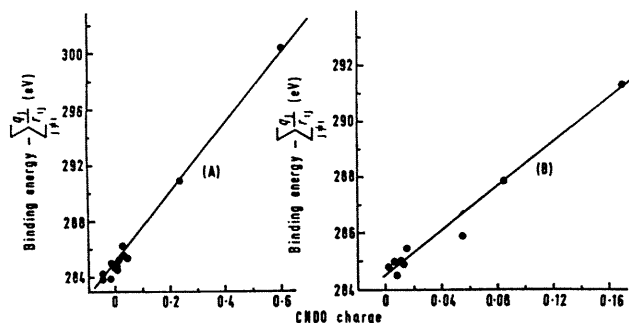


FIGURE 2

(A) Fluoro-compounds (includes all molecules containing only first row atoms), slope 24.6. (B) Chloro-compounds, slope 39.5.

we have taken the computed CNDO/2 charges and corresponding Madelung potentials, together with the experimental binding energies and Figure 2 shows a plot of Madelung corrected binding energies *vs.* charge.

Results for the chlorine containing molecules are plotted on a separate graph since it is known that the CNDO-SCF-MO treatment of bonding involving second row atoms is less adequate than for first row atoms and therefore a separate correlation might be expected. The correlations are surprisingly good, the computed value of k being 24.6 eV per unit charge and 39.5 eV per unit charge for the fluoro- (including toluene) and chloro-compounds respectively. Although the value for the charge dependence parameter k for the chloro-compound is considerably larger than that used in the assignment of core levels, this assignment is still internally self consistent.

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⁴ D. T. Clark, D. Kilcast, and W. K. R. Musgrave (in preparation).

⁵ J. N. Murrell 'The Theory of the Electronic Spectra of Organic Molecules', Methuen, London, 1963.