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Short Communication

Charge distributions in dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene and tetradecafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene as determined by ESCA

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We have shown previously[1, 2] that, for a series of hydrocarbons and their perfluoro analogues, it is possible to assign molecular core-binding energies on the basis of all-valence electron CNDO/2 SCF MO calculations using the charge-potential model originally developed by Siegbahn and his co-workers[3]:

$$E_i = E^0 + kq_i + \sum_{j \neq i} \frac{q_j}{r_{ij}} \tag{1}$$

where E_i is the binding energy, E^0 is a reference level, q_i is the charge on atom i, k is approximately the one-centre Coulomb repulsion integral between a core and valence electron on atom i and r_{ij} is the distance between atoms i and j. Once values of E^0 and k have been determined for all the elements in a compound, it is possible, using the experimentally-determined binding energies E_i, to set up a series of simultaneous equations which may be solved uniquely to give the charge distributions within the molecule.

In a previous paper[4] we have shown the feasibility of this approach in the particular case of perfluoroindene using k and E^0 values derived independently from an analysis of core-binding energies in terms of the computed CNDO/2 SCF MO charge distributions in aromatic hydrocarbons and their perfluoro analogues. Excellent agreement was obtained between the 'experimentally'-determined charges and those obtained by direct calculation. This result does not depend on a complex deconvolution of the experimental spectra and suggests that with quite complex molecules reasonable charge distributions may be obtained from spectra at relatively poor resolution. This would then open up the possibility of obtaining charge distributions directly from experimental measurements of molecular core-binding energies for complex molecules for which molecular-orbital calculations are either tedious or impracticable.

We have measured the ESCA spectra and obtained the experimental charge distributions for dodecafluorotricyclo[5,2,2,$0^{2,6}$]undeca-2,5,8-triene (I) and tetradecafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-2,6,9-triene (II) which provide sufficiently complex examples[5].

The spectra were recorded on an A.E.I. ES100 electron spectrometer using $MgK\alpha_{1,2}$ radiation and under the conditions employed the Au $4f_{7/2}$ level at 84 eV binding energy (used as a standard) had a half-width of 1.15 eV. The samples (liquids) were introduced *via* a heated reservoir shaft, leaked through a Metrosil plug and were condensed as a thin film on gold on a cooled probe. Partially-resolved spectra were deconvoluted using a DuPont 310 curve resolver. The line shape used for deconvolution was derived from the experimental spectra from the well resolved peak at highest binding energy for both (I) and (II) and was approximately Gaussian.

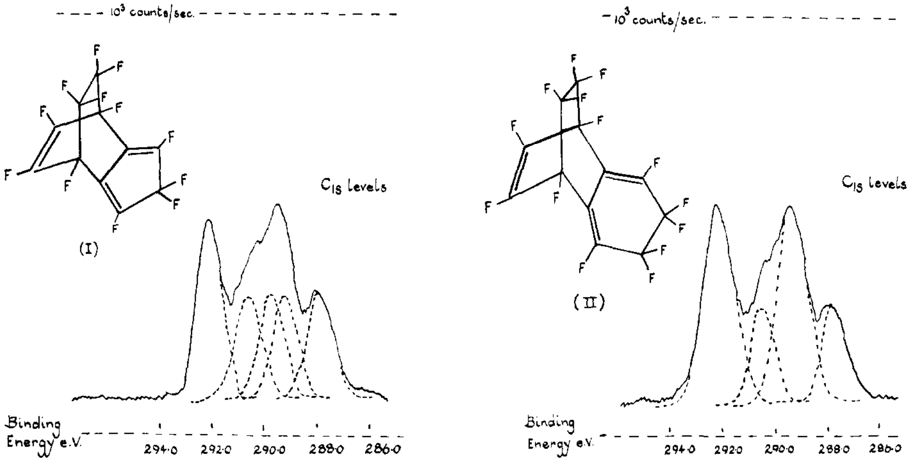


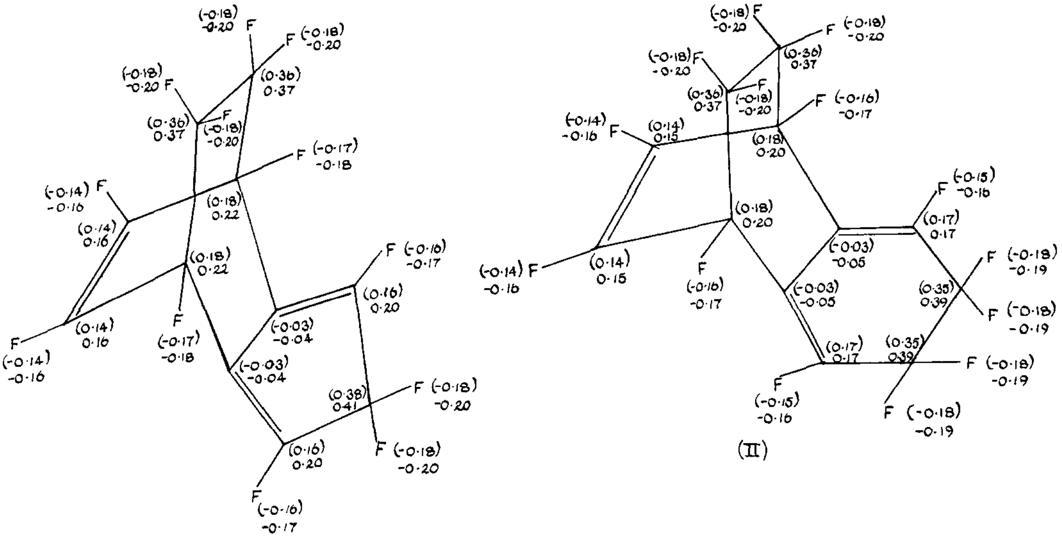
Fig. 1. The C_{1s} spectra and their deconvolutions for compounds (I) and (II).

The C_{1s} spectra are quite well resolved and are shown in Fig. 1 together with the deconvolution into their component peaks. Compound (II) has four component peaks with area ratios, in order of decreasing binding energy, (4:2:4:2) and these are assigned to the ($>CF_2$) carbons, the tertiary ($\geqslant CF$) carbons, the vinylic ($\geqslant CF$) carbons and the bridgehead ($\underset{|}{\diagdown C \diagup}$) carbons respectively. Compound (I) has five component peaks in the area ratio 3:2:2:2:2. The two types of vinylic CF carbons have slightly different binding energies (289.9 and 289.4 eV) but are still readily distinguished from the tertiary CF (290.9 eV). The experimental binding energies and assignments are listed in Table 1. Using these binding energies and assignments together with the previously determined[4] parameters $E^0{}_C = 284.6$ eV, $E^0{}_F = 693.2$ eV, $k_C = 25.0$ eV/unit charge and $k_F = 30.0$ eV/unit charge, the experimental charge distributions were determined and are shown in Fig. 2. In order to obtain a direct comparison between experimental and theoretical charge distributions in these molecules CNDO/2 SCF MO calculations were carried out, and these are shown in Fig. 2. However, for molecules of this size ($\sim$ 100 basis functions) the calculations are rather lengthy (~ 12 min cpu time on an IBM 360/67 using a convergence limit of 0.0002 a.u.).

TABLE 1

BINDING ENERGIES AND THEIR ASSIGNMENTS

Environment of atom	Compound (I) Binding energy (eV)	Compound (I) Area ratio	Compound (II) Binding energy (eV)	Compound (II) Area ratio
	C_{1s}		C_{1s}	
CF_2	292.3	3	292.3	4
—CF	290.9	2	290.6	2
=CF	289.9 } 289.65 (av.)	2	289.4	4
	289.4 }	2		
=C	288.0	2	287.8	2
	F_{1s}		F_{1s}	
All F atoms	690.9		691.0	



(I) (II)

Fig. 2. Experimental and CNDO/2 charge distributions in compounds (I) and (II). ( ) CNDO/2 SCF MO charges.

A least-squares fit between experimental and CNDO/2 charges gives the following relationships:

$$q_{\text{exp.}} = 0.00 + \underset{(\pm 0.01)}{1.10}\, q_{\text{CNDO}} \quad \text{(for compound (I))}$$

$$q_{\text{exp.}} = 0.00 + \underset{(\pm 0.01)}{1.08}\, q_{\text{CNDO}} \quad \text{(for compound (II))}$$

This is remarkably good, the correlation coefficient in both cases being better than 0.99.

The above discussion considered charge distributions obtained from CNDO/2 calculations but in an SCF MO treatment the values of E^0 and k depend on the basis set used and the definition of atomic charge. Hence, if our initial correlations between charge and binding energy for aromatic hydrocarbons and their perfluoro analogues had referred to a given basis-set *ab initio* treatment, then the derived values of E^0 and k could have been used to obtain the corresponding *ab initio* charge distributions in the more complex molecules.

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