Tetrahedron Letters No.35, pp. 3419-3420, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE PHOTOELECTRON SPECTRA OF BENZENE. HEXAFLUOROBENZENE AND PYRIDINE

D.W. Turner

Organic Chemistry Laboratories, Imperial College, London S.W.7.

(Received in UK 13 June 1967)

This letter is prompted by a recent comment by Dewar and Kelemen[1] upon the interpretation of the photoelectron spectra of some fluorobenzenes by Clark and Frost[2]. The main conclusion arrived at by Dewar and Kelemen is that in benzenes the second I.P. of benzene (11.49 e.v.) relates to loss of a σ electron rather than a π electron. In reaching the conclusion the interpretation placed upon their spectral data by Clark and Frost was criticized, in particular the assumption that all π orbitals level lie above the σ levels. Since our earlier study of benzene and pyridine using a retarding field energy analyser[3] we have re-examined these compounds and some fluorobenzene using an electrostatic deflexion analyser of much greater resolving power[4]. The principal new observations relate to the appearance of the 11.49 and 16.84 bands in benzene (Fig.1a) and the related ones in pyridine (Fig.1b). While in benzene both show vibrational fine structure (0.11 e.v. possibly ring breathing mode) in pyridine this only appears with the I.P. 12.3. We suggest that this implies greater delocalization and higher symmetry for the orbital with this I.P. (weakly bonding over the atoms of the ring) and no C-H bonding character and that therefore it is π_1. By analogy the similarly structured band in benzene commencing at 11.49 e.v. is also π_1. From the appearance of this region of the spectrum however, there is almost certainly a sigma (strongly bonding) orbital of about the same energy.

We support Clark and Frost's postulate that fluorine substitution should increase σ ionization potentials more than π ionization potentials for in C_6F_6 all bands in the photoelectron spectrum (Fig.1c) with I.P.> 16 e.v. show well defined vibrational fine structure. This property we have generally (though not exclusively) found to indicate π ionization. Two bands reported by Clark and Frost and counted as π (I.P.$_1$, 11.12; I.P.$_2$, 11.64 e.v.) we have not observed however, and the assignment of the remainder of the bands must therefore, be questioned.

References

1. M.J.S. Dewar and J. Kelemen, Tetrahedron Letters 25, 2341, (1967).
2. I.D. Clark and D.C. Frost, J. Amer. Chem. Soc. 89, 244, (1967)
3. M.I. Al-Joboury and D.W. Turner, J. Chem. Soc. 4434, (1964).
4. To be published. cf. Nature 213, 795, (1967).

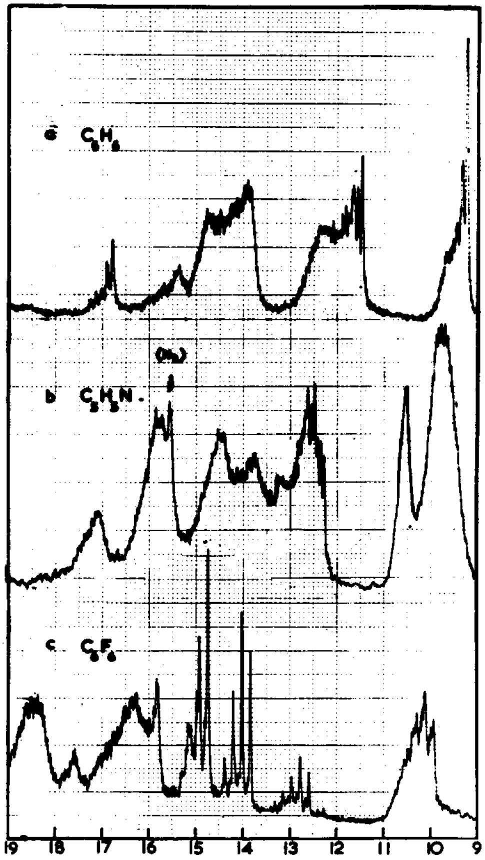

FIGURE 1

The 584 Å photoelectron spectra of (a) Benzene, (b) Pyridine, (c) Hexafluorobenzene vapours. Abscissa scale, Ionization Potential (e.v.) ordinate electron count rate (c/s).