The Vacuum-ultraviolet Photoelectron Spectra of Fluoropyridines

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The high-resolution photoelectron spectra of pyridine, 2-fluoropyridine, 3-fluoropyridine, 2,4-difluoropyridine, 2,6-difluoropyridine, 2,4,6-trifluoropyridine, and pentafluoropyridine have been measured. The shifts of the first four bands across the series have been correlated by invoking a first-order inductive perturbation by fluorine. From this correlation the order of the levels in pyridine has been deduced as $\pi_3 > n > \pi_2$ ($a_2 > 11a_1 > 2b_1$).

In an attempt to assign unambiguously the three highest molecular orbitals of pyridine we have studied the photoelectron spectra of several fluoro-substituted pyridines. The important feature of fluorine for this experiment is that it introduces no new low-energy photoelectron bands into the spectrum because of the relatively low energy of the fluorine lone-pair electrons. This property has been used to assign the bands in the spectra of benzene and the fluorobenzenes.[1] Such an analysis is simplified by the fact that the shifts are predominantly first order in an inductive perturbation by the fluorine so that they are additive for each fluorine in the molecule. From the fluorobenzene spectra inductive parameters for the fluorine atom have been deduced and from these, estimates can be made of the coefficients of the pyridine π-molecular orbitals.

Recent all-electron calculations on pyridine show that the nitrogen 'lone-pair' molecular orbital and the two highest occupied π orbitals are very close in energy. Clementi,[2] in an *ab initio* SCF calculation using an extended Gaussian basis, found the non-bonding level to be below both of the first two π levels. Dewar and Worley[3] using the MINDO/2 method found the top π and n levels to be almost degenerate. Newton and co-workers[4] using an SCF parameterised MO method found the n level to be slightly lower than the first π. Our own calculations using an approximate *ab initio* SCF method based on a minimum basis of Slater orbitals also finds the n level between the two π levels.

Experimental work has not been unambiguous in its conclusions. Yencha and El-Sayed[5] reviewed earlier work and concluded from their own photoionisation studies that the first ionisation in pyridine is likely to be from a π orbital. Turner[6] has attributed the second photoelectron band to the n level with the first band being a combination of the first two π-ionisation potentials. However he did not rule out an alternative assignment with the n level contributing to the first band. Heilbronner and his co-workers[7] examined the effect of methyl and trimethylsilyl substituents on the photoelectron spectrum of pyridine and deduced that the n level was in the first region of ionisation. It will be shown that our analysis supports this view.

EXPERIMENTAL

All spectra were recorded on a Perkin-Elmer P.S. 16 photoelectron spectrometer, and calibrated by use of rare-gases as standards. The resolution was 26 meV for the Ar doublet. 3-Fluoro-, 2,4- and 2,6-difluoro-, 2,4,6-trifluoro-, and pentafluoro-pyridines were kindly supplied by I.C.I. Mond Division and had a purity of >95%. 2-Fluoropyridine was Koch–Light pure. All compounds were distilled *in vacuo* before use.

RESULTS

The effect of successive fluorination on the spectra is shown in the Figure. The correlations we have indicated are partly based on the analysis of the π-orbital shifts which are made in the final section of the paper. The first region of ionisation in pyridine we attribute to both π- and n-

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[1] B. Narayan and J. N. Murrell, *Mol. Phys.*, 1970, **19**, 169.

[2] E. Clementi, *J. Chem. Phys.*, 1967, **46**, 4731.

[3] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, 1969, **51**, 263.

[4] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1966, **88**, 2367.

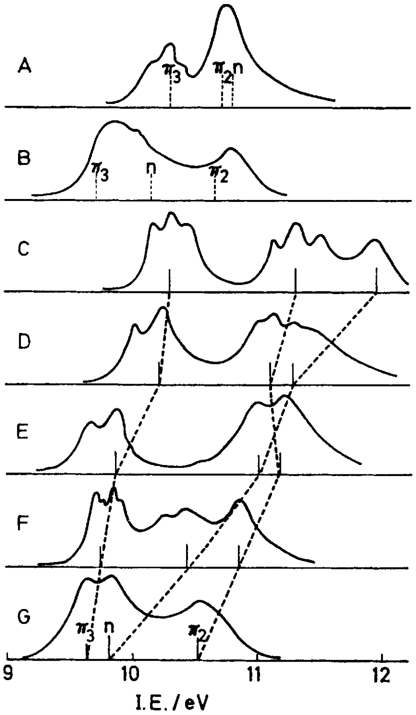
[5] A. J. Yencha and M. A. El-Sayed, *J. Chem. Phys.*, 1968, **48**, 3469.

[6] D. W. Turner, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, 1970, p. 324.

[7] E. Heilbronner, V. Hornung, H. Bock, and H. Alt, *Angew. Chem. Internat. Edn.*, 1969, **8**, 524.

ionisation, and its intensity supports the view that there are two overlapping bands. Our calculations will show that 2-substitution should increase the π-ionisation potential to a small extent, and, by comparing the spectrum of pyridine with the spectra of the 2- and 2,6-compounds, we therefore assign the first peak in pyridine to the π level (π_3).

It is known [8] that α substitution by halogen leads to a high-energy shift in n–π^*-electronic transitions, and this is in agreement with the shift to higher ionisation potentials of the n level. If it is assumed that this shift is additive for each fluorine, we can locate the n and π_2 level under the second region of ionisation in the 2,6-compound. There are two possible assignments of the n and π_2 levels for the 2,4,6-compound but only the one shown gives a satisfactory fit to the spectrum of the 2,4-compound. It is to be noted that the band associated with the n level is not particularly sharp as it is for typical non-bonding levels of the halogens for example. This supports theoretical calculations which show that the n level is appreciably delocalised in the σ system.



He(I) Photoelectron spectra of fluoropyridine: A, 2,4-Difluoropyridine; B, 3-fluoropyridine; C, pentafluoropyridine; D, 2,4,6-trifluoropyridine; E, 2,6-difluoropyridine; F, 2-fluoropyridine; G, pyridine

Table 1 shows the shifts to low energy in the π_2, π_3, and n levels deduced from these spectra on the assumption of an additive substituent effect in all cases. We have chosen to take our data from the smoothed maxima of resolved bands where this is possible. It should however be emphasised that, as there is incomplete vibrational resolution in these photoelectron spectra, one cannot assume that the energy of a band maximum corresponds exactly to the vertical ionisation potential, which is the quantity we should be fitting in our theoretical analysis.

If the data from Table 1 are used to calculate the positions of the bands in the spectra of the 3- and 2,4-compounds one obtains the vertical lines shown in these spectra (also in the Figure). It is seen that these agree reasonably well with the observed spectra, the agreement being better for the 2,4- than for the 3-compound.

TABLE 1

Observed increases in ionisation energies (eV)

Substitution	n	π_2	π_3	Positions of F atoms in pyridine from which shifts computed
α(2)	0·62	0·33	0·10	None; 2- and 2,6-
β(3)	0·34	0·10	0·04	2,4,6- and penta-
γ(4)	0·26	−0·08	0·35	2,6- and 2,4,6-

Spectra of the compounds have also been obtained with a longer time constant, and show more vibrational details than we give in the Figure. The only feature we think relevant to quote is that we confirm a vibrational peak in the pyridine spectrum at 9·26(3) eV which is the reported [6] adiabatic ionisation potential. However we have also observed another prominent band at lower energies [9·18(6) eV] with approximately a quarter of the intensity. We attribute this to a hot band of the ground-state breathing frequency (605 cm^{-1}) which has also been observed in the u.v. spectrum of pyridine.[9] Photoelectron spectroscopy does not have a sufficiently high resolution to confirm this unambiguously, nor are variable-temperature studies readily made with our commercial spectrometer.

DISCUSSION

Analysis.—The photoelectron spectroscopic bands of the fluorobenzenes arising from π ionisation have been interpreted on the basis of a first-order inductive effect of the fluorine.[1] The increase in ionisation potential brought about by a substituent effect at position ω was found to be given by the expression (1) where $q_{\omega r}$ is the

$$\Delta I_{\omega r}\ (\text{eV}) = 0{\cdot}84 K_{\omega r} - 0{\cdot}55 q_{\omega r} \qquad (1)$$

π-electron density at position ω from an electron in the rth molecular orbital. $L_{\omega r}$ is a parameter (2) giving the interaction of a unit-point dipole $\boldsymbol{\mu}$ at the centre of the C–F bond with the π-electron charges at all positions except ω. $\mathbf{r}_\nu$ is the vector position of atom ν referred to

$$L_{\omega r} = \sum_{\nu \neq \omega} q_{\nu r} \frac{\mathbf{r}_\nu \cdot \boldsymbol{\mu}}{r^3_\nu} \qquad (2)$$

the centre of the C–F bond as origin. The parameters in (1) were deduced on the basis of the unit of r_ν being the C–C bond length in benzene (r_0).

We have calculated L_ω by taking the C–F bond length to be 1·30 Å and the pyridine ring to have the structure deduced by microwave spectroscopy.[10] Thus if the charges q_ν are known the shifts in the π-ionisation potentials are easily deduced. Alternatively we can use the observed shifts to deduce the charges. The

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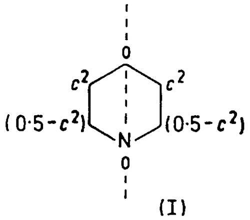
[8] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, 1963, p. 199.

[9] H. Sponer and H. Stückler, *J. Chem. Phys.*, 1936, **14**, 101.

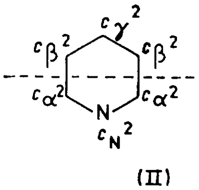
[10] B. Bak, L. Hansen-Nygaard, and J. Rastrup Anderson, *J. Mol. Spectroscopy*, 1958, **2**, 361.

following analysis for a pyridine π orbital of a_2 symmetry (π_3) will illustrate the method.

An a_2 orbital has a node passing through the nitrogen and *para*-carbon atoms. Thus the molecular orbital is defined by one coefficient c (because $\sum_{\omega} c_{\omega}^2 = 1$) and the resulting charge densities are shown in (I). Application



(I)



(II)

of expression (1) therefore leads to the following predictions for the increase in this ionisation energy (in eV) brought about by fluorine at the three possible positions of substitution; $\Delta I_\alpha = 0{\cdot}98c^2 - 0{\cdot}19$; $\Delta I_\beta = -0{\cdot}89c^2 + 0{\cdot}25$; and $\Delta I_\gamma = 0{\cdot}41c^2 + 0{\cdot}17$.

All theoretical calculations predict $\pi_3(a_2)$ to be the highest occupied π orbital of pyridine. The best fit between the theoretical shifts (3) and the observed shifts in Table 1 is obtained with a value $c^2 = 0{\cdot}25$, for which the calculated shifts (in eV) are 0·06, 0·04, and 0·27 for α-, β-, and γ-substitution respectively.

For the second π orbital (π_2, $2b_1$) the molecular orbital is defined by four coefficients (II), and these can be determined by three observed shifts and the normalisation condition. Application of expression (1) leads to the following results: $c_N{}^2 = 0{\cdot}33$, $c_\alpha{}^2 = -0{\cdot}08$, $c_\beta{}^2 = 0{\cdot}20$, and $c_\gamma{}^2 = 0{\cdot}44$. These coefficients have an uncertainty determined by the uncertainty in the measurement of the ionisation energies referred to above. The negative value for $c_\alpha{}^2$ has no physical significance in simple MO theory, and we will comment further on it later in the paper.

If it is assumed that the non-bonding orbital is localised on the nitrogen atom then the shifts should arise only from the first (dipolar) term in (1). This is calculated to be 0·39, 0·16, and 0·13 eV for α, β, and γ respectively. The values are smaller than those observed, which is to be expected if the n level is partly delocalised, but the ratios are in good agreement with those observed. Calculations by Clementi[2] give only 70% of the two n electrons on the nitrogen atom, the other 30% being mainly on the α-carbon atoms.

In benzene, fluoro-substitution led to the identification of the π_1 level at 12·0 eV, although this band in benzene is overlayed by σ-ionisation levels. A similar situation appears in pyridine. In all the fluoropyridines there is a band in the range 12·2—13·4 eV. For each molecule this band has a vibrational progression, one component of which has an interval of 600 ± 20 cm^{-1}, which is similar to that in the lowest-lying π level of the fluorobenzenes. By analogy with benzene we therefore tentatively identify this band with the $1b_1$ level in the fluoropyridines and by extrapolation arrive at an ionisation onset energy of 12·5 eV for pyridine.

Comparison with MO *Calculations*.—Table 2 records the LCAO coefficients of the π-molecular orbitals ofpyridine obtained by various authors. The list is by no means exhaustive. The coefficients of the two *ab initio* calculations have been renormalised to $\sum_{\mu} c_{\mu}{}^2 = 1$.

TABLE 2

Comparison of calculated MO coefficients. The Hückel results were obtained with the parameters $\alpha_N = \alpha_C + 0{\cdot}5\beta$ and $\beta_{CN} = 1{\cdot}0\beta_{CC}$. The approximate *ab initio* results come from a program developed by V. R. Saunders

$\pi_2(b_1)$	$c_N{}^2$	$c_\alpha{}^2$	$c_\beta{}^2$	$c_\gamma{}^2$
Clementi[b]	0·22	0·10	0·16	0·25
Hückel	0·33	0·04	0·12	0·36
Approximate *ab initio*	0·28	0·07	0·11	0·36
π-SCF[a]	0·28	0·05	0·12	0·37
Present study	0·33	−0·08	0·20	0·44

$\pi_3(a_2)$	$c_\alpha{}^2$	$c_\beta{}^2$
Clementi[b]	0·25	0·25
Hückel	0·25	0·25
Approximate *ab initio*	0·25	0·25
π-SCF[a]	0·24	0·26
Present study	0·25	0·25

[a] See R. D. Brown and M. L. Heffernan, *Austral. J. Chem.*, 1959, **12**, 554. [b] Ref 2.

For the π_3 level our deduction that $c_\alpha{}^2 = 0{\cdot}25$ is in reasonable agreement with all calculations; even the SCF calculations show that nitrogen has almost no effect on the benzene coefficients. For the π_2 level however there are large differences between the calculations, and the Hückel result is closest to our finding that $c_\alpha{}^2$ is negative.

The negative value is to be interpreted as a greater negative charge at the α-position in the pyridine positive ion than in the pyridine ground state. Such a finding can only arise in MO theory if configuration interaction is included. There is an analogy here with the deduction from electron spin resonance spectroscopy of negative spin densities in some positions of aromatic π radicals. The calculations of Clementi are in poor agreement with our analysis for π_2, although the coefficients are in the correct order. In addition the Clementi energy levels are in disagreement with our analysis for he finds the n level to be below both π_3 and π_2. We therefore feel that considerable scepticism must be placed on this ' best yet ' calculation of pyridine.

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