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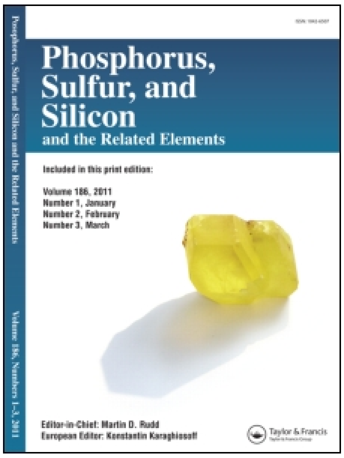

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Simon J. Dunne[a]; Lindsay A. Summers[a]; Ellak I. Von Nagy-Felsobuki[a]
[a] Department of Chemistry, The University of Newcastle, Callaghan, N.S.W., Australia

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CONFORMATIONAL AND PHOTOELECTRON ANALYSIS OF ISOMERS OF THE METHYLCHALCOGENOPYRIDINES

SIMON J. DUNNE, LINDSAY A. SUMMERS,
and ELLAK I. VON NAGY-FELSOBUKI†
Department of Chemistry, The University of Newcastle,
Callaghan, N.S.W. 2308, Australia

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The He I/He II photoelectron spectra of 2-, 3-, and 4-methylthio- and methylselenyl-pyridine are reported and interpreted in terms of a composite-molecule model based on ab initio calculations. Results from STO-3G* calculations at STO-3G* optimised geometries suggest that, for the 2- and 4-isomers, the planar conformer is more stable than the non-planar conformer, although bands due to minor conformers are evident in some of the spectra. The He I/He II band ratios are shown to be useful in locating those MOs with significant S or Se p AO contributions, thereby indicating the chalcogen content in the bonding and anti-bonding X-π orbitals. Based on spectral features, He I/He II ratios and in conjunction with ab initio calculations, the preferred sequence for the four lowest ionisation energies for all isomers of the methylchalcogenopyridines is: $\pi - n_X < n_N \sim \pi < \pi + n_X$, where X represents the chalcogen atom.

INTRODUCTION

The electronic structure of pyridine and substituted pyridines, as gleaned from ultraviolet photoelectron spectroscopy (UPS), have been the subject of a number of theoretical and experimental studies.[1–11] The relative ordering of the first three ionic states of pyridine, corresponding to ionisation from the nitrogen lone-pair and two highest π-orbitals, has been controversial. The overlapping of the first two bands in the spectrum of pyridine complicates their assignment, although the doublet nature of this band is obvious.[1] The near-degeneracy of the two highest orbitals make an unambiguous assignment of the N-and the first π orbitals impossible. The situation has not been clarified by the experimental results of Yencha and El-Sayed,[2] Dewar and Worley,[3] Jonsson *et al.*,[4] and Gleiter *et al.*[5]

Quantum mechanical calculations used in conjunction with Koopmans' approximation (KA) have been only partially successful in predicting the order of ionised states in pyridine. UPS studies on pyridine[1–8] and bispyridines[12–14] have shown that KA in conjunction with STO-3G calculations (denoted KA/STO-3G) does not ensure adequate cancellation of the relaxation errors by the correlation corrections. The KA/STO-3G assignment for pyridine gives the order of the lowest three ionisation energies (IEs) as[15]: $^2A_2(\pi_3) < {}^2B_1(\pi_2) < {}^2A_1(n)$. Both experiment[1–8] and many-body Green function calculations[10–11] yield the IE distribution as: $^2A_1(n) \sim {}^2A_2(\pi_3) < {}^2B_1(\pi_2)$. The failure of the KA model does not solely arise from basis set deficiencies, since in some cases, bases of double-zeta quality[10] have been utilised. The addition of polarisation functions and/or the use of large extended

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†Author to whom correspondence should be addressed.

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basis sets have produced changes in the ordering of the inner valence orbitals, but failed to rectify the outer valence orbitals.

Von Niessen *et al.*[10] have used many-body perturbation calculations for the interpretation of the photoelectron spectra of the azabenzenes. Many-body Green's function calculations were performed to account for electron correlation and reorganisation. They proposed that the existence of low-lying virtual orbitals led to non-uniform many-body effects, which resulted in strong shifts of the IEs of the N-electrons relative to those of the π-electrons and rendered KA models inappropriate for this class of compounds. Their calculations gave the IEs of pyridine to within 0.25 eV of the experimentally derived pattern.[6]

Semi-empirical methods have produced a variety of assignments,[16-18] with only MINDO/3[19] and HAM/3[20-23] having correctly predicted the orbital pattern in pyridine. The IEs from the MINDO calculation are shifted to higher energies by ~1 eV. On the other hand, the HAM/3 method of Åsbrink, Fridh and Lindholm[20-23] has been shown to reliably predict the distribution of ionic states for a number of problematic molecules, including pyridine. The success of the HAM/3 method is due to its inclusion of monocentric many-body effects and so directly accounts for relaxation and correlation in the calculation of IEs. Unfortunately, both MINDO/3 and HAM/3 method are not reliably parameterized for molecules containing second- and third-row atoms and so cannot be used with confidence in interpretation of UPS spectra of methylthio- and methylselenyl-pyridine.

A further possible complication in the interpretation of the UPS spectra of the methylchalcogenopyridines is the presence of several conformers. Schweig and Thon[24] recorded the UPS spectra of thioanisole over a temperature range of 20–500°C and interpreted the spectra in terms of the two conformers: a planar and a non-planar form. They found that with increasing source temperature the population of the perpendicular (or non-planar) rotamer increased significantly. The presence of non-planar forms were also reported in a study on the phenyl alkyl ethers and sulfides by Dewar *et al.*[25] They found that by increasing the size of the alkyl group the less-conjugated conformer began to dominate the spectrum, due to unfavourable steric interactions in the ring plane. A similar study was performed by Baker *et al.*[26] on some alkyl phenyl selenides. In the UPS spectrum of selenoanisole, the highest occupied molecular orbital (HOMO) was found to exhibit a doublet nature (in a 1:1 ratio). The lowest IE of this doublet (8.0 eV) corresponds to the HOMO of the planar conformer, while the higher (8.3 eV) to the rotamer with reduced conjugation. Tschmutova and Bock[27] similarly found the balance to be very much in the favour of the non-planar conformer (~2:1) for telluroanisole. It is anticipated that the UPS spectra of the more electron dense members of the methylchalcogenopyridine family will contain a significant presence of the two postulated conformers.

More pertinent to this study is the UPS spectra of the isomers of methoxypyridine.[15,28] Cook *et al.*[28] have detailed the UPS spectra of 2-methoxypyridine, along with the hydroxypyridines and their corresponding tautomers. In the absence of ab initio calculations, their assignments relied upon simple correlations. However, Dunne *et al.*[15] reported the He I spectra of all the isomers (i.e. 2-, 3- and 4-methoxypyridine). Using HAM/3 and Møller-Plesset perturbation theory to second-order[29] within a ΔSCF ansatz (denoted ΔSCF/MP2) they assigned for 2-, 3- and 4 methoxypyridine the first IE of A″ symmetry arising from ionisation from a π orbital at 9.158, 9.056 and 9.583 eV, respectively, while first IE of A′ symmetry from the n_N orbital at 9.792, 9.674 and 9.259 eV, respectively.

Cook *et al.*[28] have also reported the He I study of 2- and 4-methylthiopyridine, although no He II spectra were measured for these isomers. In 2- and 4-methylthiopyridine potential tautomerism is blocked and their UPS can be used as a basis for the study of prototropic equilibria between the mercapto/thioxo forms. Their assignments were solely based upon correlations within a composite-molecule model.

As an extension of our earlier work on the electronic structure of the alkyl benzenes,[30,31] alkyl halo benzenes,[32,33] bispyridines,[12–14] alkyl phenyl disulfides[34] and moreover, on the isomers of methoxypyridine[15] we report here a thorough and systematic study on the conformational and UPS analysis of all the isomers of methylthio- and methylselenyl-pyridine, using both He I and He II radiation. Furthermore, it will be shown that ab initio assignment tools such as KA and ΔSCF/MP models are useful, but are not definitive nor exhaustive in the spectral assignment of these molecules.

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CONFORMATIONAL ANALYSIS

The calculation of accurate vertical IEs requires knowledge of the molecular geometry of the neutral molecule. One of the most widely used basis sets for geometry optimisation is the STO-3G minimal basis set developed by Pople and coworkers.[35] This basis has been formulated for first- to fourth-row main group elements and for all three rows of the transition metals. The popularity of this basis rests on its effectiveness in predicting geometries, despite its small size. Pople[36] has reported that the mean absolute deviation from experiment for SCF bond lengths in a large number of molecules containing C, H, N, O and F is 0.030Å. Nevertheless, it has been found that a large basis set superposition error which is inherent when employing the STO-3G basis, helps to correct other defects in the Hartree-Fock (HF) model, such as neglect of electron correlation, to produce reasonable structural parameters. Due to this fortuitous cancellation, HF/STO-3G calculations often yield geometries closer to experiment than those calculated using more extensive basis sets within the HF framework.

The presence of rotamers complicates the UPS spectrum. Hence in order to model the ratio of planar to non-planar conformers a series of geometry optimisations was performed on all isomers of the methylthio- and methylselenyl-pyridines. The ring geometry was fixed at the optimised alcohol form[37] and the bridge parameters (i.e., the ring-X and X-methyl bond lengths and the bridge angle) were optimised at 30° torsional angles using the Fletcher-Powell routine.[38] The optimised variables and the calculated rotational barrier heights are presented in Table I.

The bridge bond lengths are shortest for the planar form, in which the maximisation of p-π overlap is paramount compared with the relief of steric interaction by elongation of these bonds. Relief of strain energies in the planar form ($\varnothing = 0°$) is achieved by the opening of the bridge angle. The opposite trend is observed for the nonplanar forms ($\varnothing = 90°$); that is, longer bonds but a more acute bridge angle. The longer $R_{\text{Ring-X}}$ bond may arise from electronic repulsions of the sulfur

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TABLE I

STO-3G* optimised parameters and rotational barrier heights for the methylthio- and methylselenyl-pyridines

Ø (/Deg.)	ΔE(/kJmol^{-1})	$R_{Ring\text{-}X}$ (/Å)	$R_{Me\text{-}X}$ (/Å)	$A_{C\text{-}X\text{-}C}$ (/Deg.)
		(a) 2-Methylthiopyridine		
0	0.0	1.745	1.785	100.5
30	5.8	1.752	1.788	99.9
60	15.6	1.763	1.791	98.3
90	21.4	1.768	1.792	97.6
120	21.0	1.766	1.793	99.0
150	21.6	1.761	1.791	103.0
180	18.6	1.756	1.787	104.0
		(b) 2-Methylselenylpyridine		
0	0.0	1.878	1.899	98.5
30	3.8	1.882	1.902	98.1
60	11.1	1.886	1.904	96.9
90	16.2	1.888	1.905	96.6
120	17.0	1.888	1.906	97.7
150	18.8	1.888	1.902	101.2
180	17.9	1.887	1.900	102.2
		(c) 3-Methylthiopyridine		
0	0.0	1.746	1.786	103.1
30	3.7	1.752	1.789	102.3
60	6.1	1.759	1.794	99.4
90	8.1	1.762	1.794	98.1
120	8.4	1.761	1.794	99.3
150	12.1	1.757	1.789	103.1
180	10.6	1.754	1.785	104.1
		(d) 3-Methylselenylpyridine		
0	0.5	1.875	1.900	102.0
30	1.3	1.876	1.903	101.1
60	0.0	1.876	1.906	98.1
90	0.3	1.876	1.906	97.1
120	1.2	1.877	1.905	97.9
150	5.7	1.879	1.903	101.4
180	6.2	1.878	1.899	102.3
		(e) 4-Methylthiopyridine		
0	0.0	1.746	1.786	103.4
30	2.6	1.751	1.789	101.8
60	7.6	1.761	1.794	98.6
90	10.6	1.765	1.795	98.1
		(f) 4-Methylselenylpyridine		
0	0.0	1.873	1.900	101.4
30	1.2	1.875	1.903	101.0
60	3.8	1.879	1.906	98.2
90	5.5	1.881	1.907	97.0

lone-pair with the σ system of the pyridine ring, while the contraction of the bridge angle may enhance the participation of the –XMe group in a hyperconjugative interaction with the π-system of the pyridine ring. The thio-analogs show the largest differences in bond lengths between the planar and non-planar forms, whereas for methylselenylpyridines the already long $R_{C—Se}$ bonds require little adjustment on purely steric grounds and therefore show only small differences for these positional isomers.

The rotational barrier heights between the planar and non-planar forms in the 2-methylchalcogenopyridine series are 21.4 (S) and 16.2 kJmol^{-1} (Se) in favour of the planar conformer. Of all the isomers, these barriers are the largest, which highlights the removal of steric interaction by the presence of the ring-nitrogen instead of an ortho hydrogen. Assuming only two conformers exist, the planar and non-planar forms, then a Boltzmann distribution can be used to predict the relative quantities present in an equilibrium mixture. For example, at 300 K (the ambient temperature of the UPS experiment in this study) the proportion of the non-planar form would be 0.01 (S) and 0.10% (Se) and therefore undetectable.

A similar analysis for the 3-series gives barrier heights of 8.1 (S) and −0.2 kJmol^{-1} (Se) with the corresponding populations of 3.2 (S) and 51.7% (Se), respectively, although in the case of the 3-methylselenylpyridine the predicted minimum is a gauche form (Ø = 60.0°). For the 4-series, the barrier heights are 10.6

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TABLE II

Barrier heights between planar and non-planar conformers

Congener	Ø (/Deg.)	Barrier Heights (/kJmol^{-1})^a	
		STO-3G*	6-31G**
2-SMe	0	0.00 (99.99)	0.00 (99.92)
	90	21.41 (0.01)	16.76 (0.08)
2-SeMe	0	0.00 (99.90)	0.00 (99.39)
	90	16.23 (0.10)	12.02 (0.61)
3-SMe	0	0.00 (96.82)	17.15 (0.07)
	90	8.07 (3.18)	0.00 (99.93)
3-SeMe	0	0.16 (48.31)	16.54 (0.09)
	90	0.00 (51.69)	0.00 (99.91)
4-SMe	0	0.00 (98.89)	0.08 (49.15)
	90	10.60 (1.11)	0.00 (50.85)
4-SeMe	0	0.00 (91.18)	4.29 (14.00)
	90	5.52 (8.82)	0.00 (86.00)

a) Boltzmann populations at 300K in brackets.

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(S) and 5.5 $\mathrm{kJmol^{-1}}$ (Se), which correspond to populations of 1.1 (S) and 8.8% (Se). These results show a general increase in the population of the non-planar conformer down the group and reflect experimental results on similar molecules.[24–27]

A series of single point calculations were performed at the STO-3G* optimised planar and non-planar geometries using the 6-31G** basis set (denoted 6-31G**//STO-3G*) in order to model more accurately the population balance between the two conformers. Since no 6-31G** set has been published for selenium, the split-valence set of Lehn, Wipff and Demuynck[39] was used on this heavy atom. The energy differences and populations (at 300 K) calculated at this level are shown in Table II.

The results calculated with the 6-31G**//STO-3G* model reveal a very different picture of the expected distribution of conformers. Although the barrier heights to the non-planar forms of the 2-methylchalcogenopyridines have all been reduced, the presence of this form would still be difficult to detect due to its low abundance. The situation is very different for the 3-methylchalocogenopyridines. The non-planar conformers of the sulfur and selenium analogs are predicted to be dominant. The magnitude of the barrier heights to the planar forms in these cases would suggest that the non-planar form would be the only one detected, contrary to the STO-3G*//STO-3G* results. For the 4-methylchalcogenopyridines, the 6-31G**//STO-3G* model shows a predominance of the non-planar conformer down the group, again contrary to the STO-3G*//STO-3G* results.

Hence it is anticipated that the UPS of some of these compounds will contain a significant presence of rotational contamination. The accuracy of the predictions of the 6-31G**//STO-3G* and STO-3G*//STO-3G* models can be directly tested by observation of their UPS spectra.

RESULTS AND DISCUSSION

The He I and He II UPS spectra of the methylchalcogenopyridines were recorded using a Perkin-Elmer PS 16/18 spectrometer modified with an Helectros helium source and are shown in Figures 1 and 2. Bands due to conformers other than the planar structure are shaded in Figures 1 and 2. For these compounds, the operating resolution was 25-35 meV for He I spectra and 50 meV for He II spectra. The spectra were calibrated using butadiene/argon gas mixtures. The spectra were measured with the source tip at 300 K.

The spectra in Figures 1 and 2 were digitised for use in the density-of-states analysis.[40,41] The density-of-states analysis assumes that band intensity is a measure of orbital degeneracy, so that where bands are strongly overlapped the total band area in each separable region of the spectrum is related to the number of occupied orbitals. Thus, if it is assumed that the photoionisation cross-section for each band is approximately the same, the number of bands contributing to a peak can be ascertained.

The s-p separation rule[42] allows the prediction of the number of p-based bands expected below 18 eV and is given by,

$$N_T = N_{\mathrm{C}} + 0.5N_{\mathrm{H}} + 1.5N_{\mathrm{N}} + 2.0N_{\mathrm{X}} \tag{1}$$

where N_{C}, N_{H}, N_{N} and N_{X} are the number of carbon, hydrogen, nitrogen and chalcogen atoms in the molecule. For pyridine, Equation (1) gives 9 p-based bands

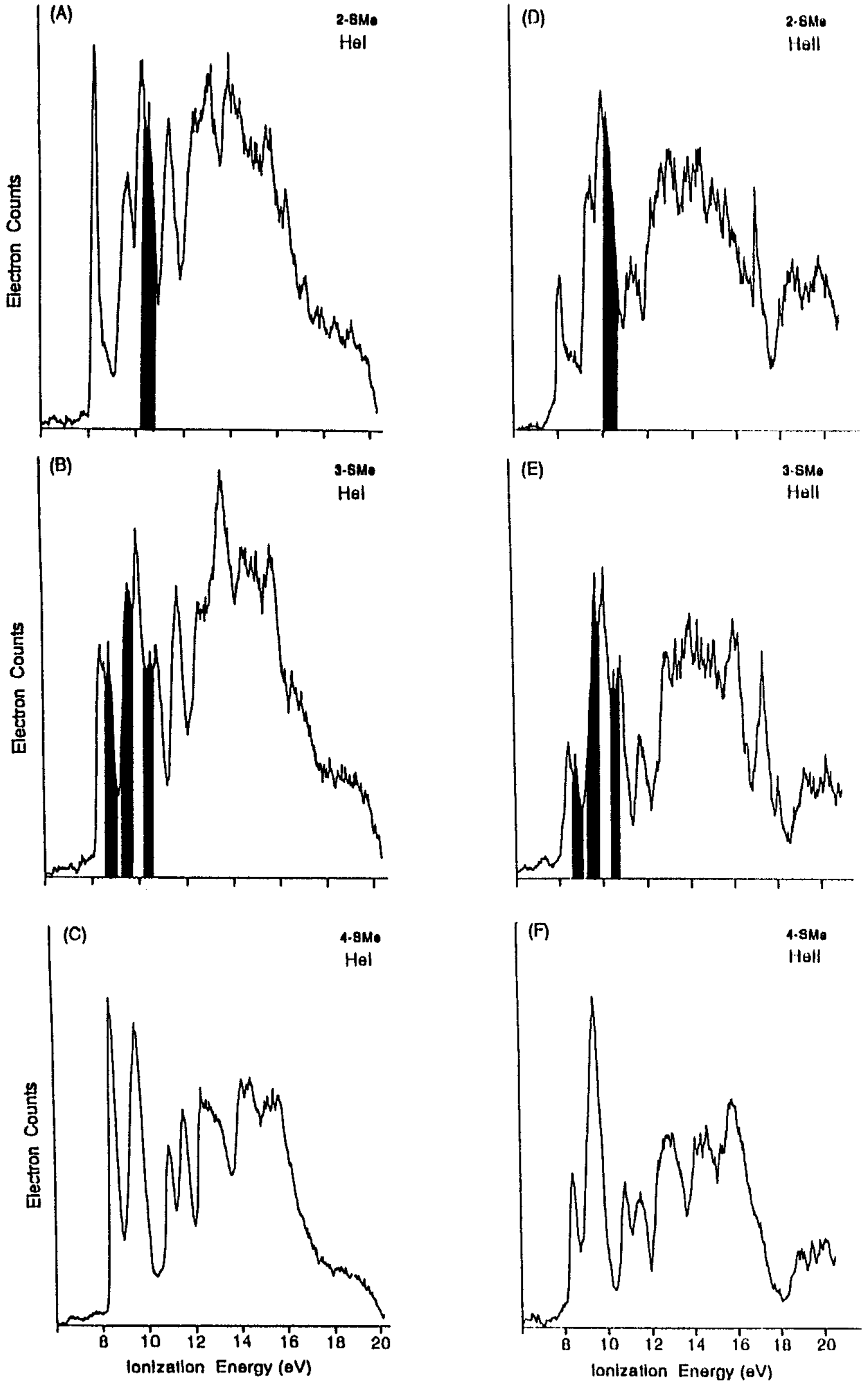

Figure 1 The He I/He II differential spectra of the methylthiopyridines: (a) He I spectrum of 2-methylthiopyridine; (b) He I spectrum of 3-methylthiopyridine; (c) He I spectrum of 4-methylthiopyridine; (d) He II spectrum of 2-methylthiopyridine; (e) He II spectrum of 3-methylthiopyridine; (f) He II spectrum of 4-methylthiopyridine. Shaded areas indicate the presence of rotamers other than the dominant planar conformer.

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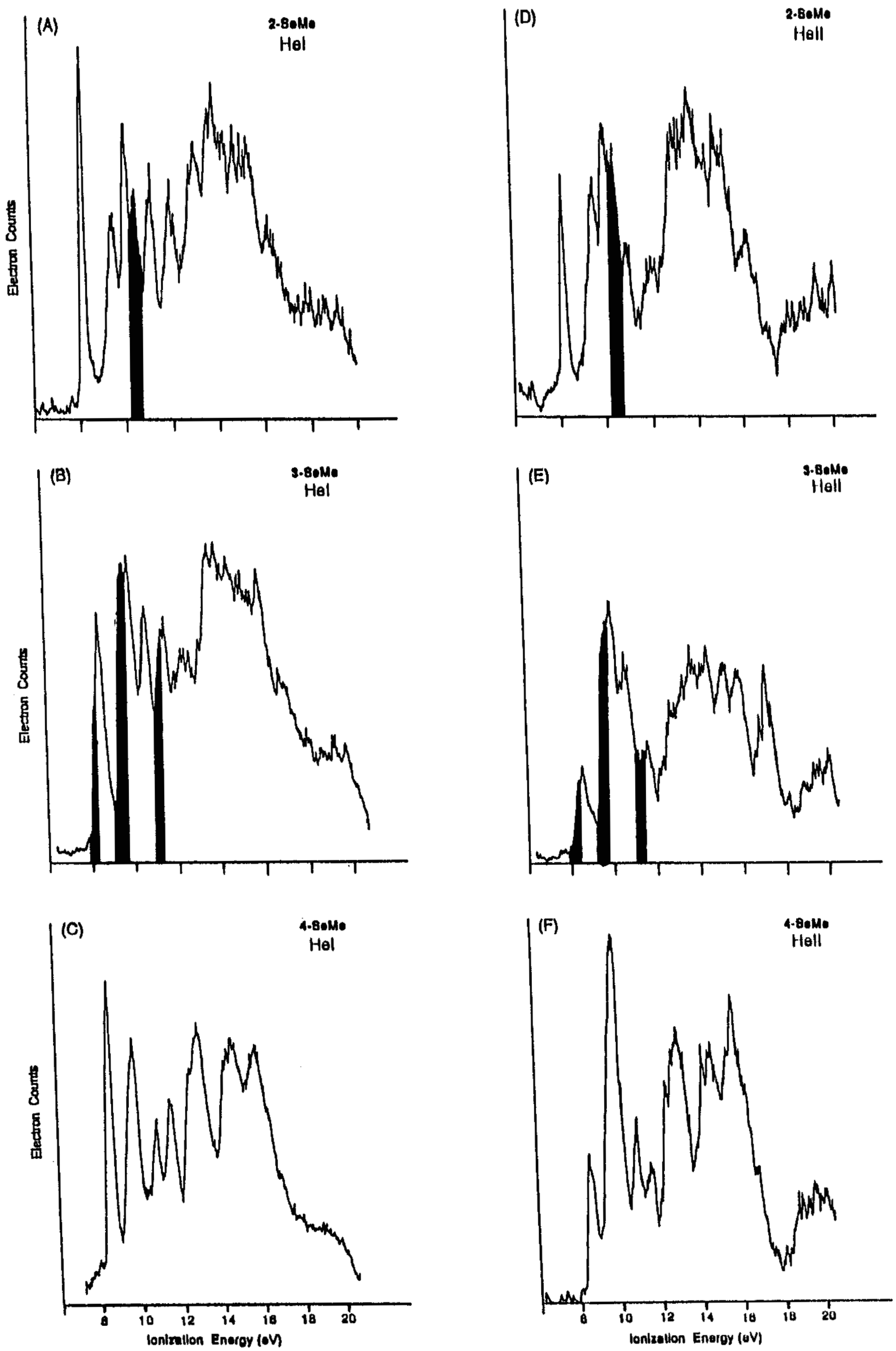

Figure 2 The He I/He II differential spectra of the methylselenylpyridines: (a) He I spectrum of 2-methylselenylpyridine; (b) He I spectrum of 3-methylselenylpyridine; (c) He I spectrum of 4-methylselenylpyridine; (d) He II spectrum of 2-methylselenylpyridine; (e) He II spectrum of 3-methylselenylpyridine; (f) He II spectrum of 4-methylselenylpyridine. Shaded areas indicate the presence of rotamers other than the dominant planar conformer.

and allowing for a cross-over of an s- and p-based band occuring in the 15-18 eV region,[43] a total of 10 bands would be predicted below 18 eV. Hence, in the case of the methylchalcogenopyridines, Equation (1) would predict 13 p-based bands and with the corresponding cross-over a total of 14 bands below 18 eV.

Due to the large number of overlapping cationic states at higher energies, the assignments of the UPS spectra of the methylchalcogenopyridines, given in Table III, are restricted to the four lowest IEs. The assignments are given in terms of a composite-molecule model. This model assumes that the MOs are linear combinations of orbitals from the pyridine ring and those of the methylchalcogen group. The assignments are based on the eigenvalues and eigenvectors obtained from the STO-3G* and 6-31G**[44] methods. The geometries of the pyridine rings used were the fully optimised STO-3G* planar geometries.[37] Although the presence of non-planar conformers are obvious in the spectra of some isomers, only the IEs for the planar conformer are given in Table III.

The measured vertical IEs for 2- and 4-methythiopyridine have been previously reported by Cook *et al.*[28] The IEs quoted in their study are in reasonable agreement with the values quoted above, although the use of butadiene as a calibration gas in this study renders greater accuracy to the lower IEs quoted in this work. Their assignments were based upon simple correlations and match those presented in Table III.

The UPS of the 2-series show low-intensity bands attributable to the presence of minor conformer(s), which are not predicted by either of the models. The UPS of 3-methylthio- and 3-methylselenyl-pyridines show an even mixture of conformers (assuming that the photoionisation cross-sections for the MOs of each conformer are the same in their UPS spectra). These results are in conflict with the 6-31G**//STO-3G* model barrier heights shown in Table II, which predict a domination by the non-planar form for the S and Se analogs (>90%). On the other hand, the STO-3G*//STO-3G* results are, in general, in better agreement with the spectra. Furthermore, the STO-3G*//STO-3G* model is consistent with the UPS spectra of thioanisole,[23,24] which predicts a presence between 10–30% of the non-planar form. The UPS spectra of the 4-series show no evidence of the presence of minor conformers, which is supported by the STO-3G*//STO-3G* model.

For the non-planar methylchalcogenopyridines both the STO-3G*//STO-3G* and 6-31G**/STO-3G* models predict ionisation from a MO of significant chalcogen p-AO character. Hence, it would be anticipated that reductions of the order of 60–70% should be exhibited on going from He I to He II radiation. The peaks that are attributed to the presence of conformer(s) other than the planar conformer (see Figures 1 and 2) show no such reduction, thereby indicating the conformer(s) present may be non-planar, but not at $\emptyset = 90°$ (e.g. a gauche structure was predicted by the STO-3G*//STO-3G* model as the lowest energy conformer for 3-methylselenylpyridine). Thus, the accurate determination of the equilibrium distribution of all non-planar to planar conformers will require use of large extended basis sets with polarisation functions in conjunction with extensive geometry optimisation (which is beyond the scope of this work).

He I/He II band ratios were shown by Daamen and Oskam[1] to be useful tools not only for the differentiation between the N- and π-orbitals, but also for the assignment of the individual π-orbitals. However, in MOs comprised of purely C

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TABLE III

Comparison of experimental vertical IEs with KA IEs (/eV) for the methylchalcogenopyridines

	Exptl. IE	Assign. MO	KA/STO-3G*	KA/3-21G*	KA/6-31G**
		(a) 2-Methylthiopyridine			
IE_1	8.16	π-n_S	5.91	8.34	8.24
IE_2	9.52	n_N	8.88	11.28	11.44
IE_3	10.25	π-δn_S	8.52	10.52	10.34
IE_4	11.40	π+n_S	9.14	11.16	10.98
		(b) 3-Methylthiopyridine			
IE_1	8.47	π-n_S	6.03	8.41	8.27
IE_2	10.04	n_N	8.81	11.10	11.25
IE_3	10.89	π-δn_S	8.45	10.31	10.09
IE_4	11.72	π+n_S	9.42	11.61	11.47
		(c) 4-Methylthiopyridine			
IE_1	8.46	π-n_S	6.27	8.81	8.77
IE_2	9.58	n_N	8.92	11.18	11.35
IE_3	9.58	π-δn_S	8.10	9.85	9.54
IE_4	11.03	π+n_S	9.60	11.82	11.70
		(d) 2-Methylselenylpyridine			
IE_1	8.22	π-n_{Se}	6.72	8.12	8.07
IE_2	9.53	n_N	9.28	11.12	11.25
IE_3	10.12	π-δn_{Se}	8.79	10.46	10.27
IE_4	11.15	π+n_{Se}	9.46	10.93	10.74
		(e) 3-Methylselenylpyridine			
IE_1	8.52	π-n_{Se}	6.83	8.20	8.11
IE_2	9.89	n_N	9.18	11.02	11.13
IE_3	10.67	π-δn_{Se}	8.72	10.29	10.07
IE_4	11.43	π+n_{Se}	9.74	11.30	11.16
		(f) 4-Methylselenylpyridine			
IE_1	8.57	π-n_{Se}	7.07	8.54	8.53
IE_2	9.83	n_N	9.24	11.11	11.27
IE_3	9.83	π-δn_{Se}	8.36	9.84	9.55
IE_4	10.81	π+n_{Se}	9.93	11.53	11.40

and N contributions the changes can be quite small and thus difficult to measure if bands are even partially overlapped. The He I/He II ratios, to a first-order approximation, enable the identification of those MOs containing an atom with atomic cross-sections which are markedly reduced under He II conditions. Generally, bands showing a significant reduction under He II conditions contain a significant contribution of S (or Se) p AOs. The greater the reduction, the larger the contribution.

Whereas the He II UPS spectra of the methoxypyridines[15] show little variation relative to those recorded under He I conditions, the thio- and seleno-analogs exhibit some useful differences. Those bands showing a significant reduction under He II conditions must contain a significant contribution of S (or Se) p AOs. The greater the reduction, the larger the contribution. Table IV presents band intensities and the percentage change in those bands upon changing radiation sources.

The methylthiopyridines show significant variation in the first and fourth bands; that is, those assigned to the anti-bonding and bonding S π MOs of the planar conformer. The degree of reduction is approximately the same, suggesting that the contributions of ring and S electrons to these MOs is about the same in both cases. The predicted IE distributions for the non-planar conformers suggest that only one valence band has significant S character, thereby giving weight to the planar model. The methylselenylpyridines show a greater decrease in the HOMO but a decreased reduction of the bonding Se-π MO under He II conditions, suggesting a greater contribution of Se 4p electrons to the HOMO.

It would be anticipated that ionisation from primarily pyridine π-based MOs should exhibit a relative intensity enhancement under He II conditions as a result of the reduction of S or Se-containing MOs. Delocalisation of lone-pair MOs should result in a decrease in the extent of reduction upon changing radiation sources. The band assigned to the lone-pair n_N MO exhibits a variety of intensity changes, highlighting its delocalised nature. The delocalisation of this MO over the σ-framework of the pyridine moiety has been reported previously by Del Bene.[45]

He I/He II ratios suggest that the STO-3G*//STO-3G* model yields relative barrier heights more consistent with the spectra compared with the 6-31G**//STO-3G* model. This is consistent with proton affinities studies of von Nagy-Felsobuki and Kimura,[46] who concluded that hybrid theories performed poorly in predicting properties associated with energy differences, where the optimised structures are extremely sensitive to the basis set employed. However, it should be noted that this does not suggest that the calculated KA IEs also follow this trend, since for this property the fortuitous cancellation of relaxation with correlation is of paramount importance.

For the non-planar form of the methylchalcogenopyridines the KA/6-31G** model predicts an IE distribution which is a composite of pyridine and chalcogen lone-pair AOs. The π and n_N MOs for the non-planar methylchalcogenopyridines are within 0.2 eV of the pyridine IEs calculated using the same model. The highest π MO of the non-planar form is more similar to the equivalent MO in pyridine (which would be anticipated on symmetry grounds, since the chalcogen lone-pair AO is orthogonal to the pyridine π-based MO). Unlike the planar conformers, the π MOs of the non-planar forms do not show a 'rotation' as a result of substitution. The experimental lowest energy IEs are in poor agreement with those predicted for the non-planar form. Hence the assignment given below will focus on the planar conformer, considered the most dominant conformer in the spectra, which is consistent with both ab initio calculations (STO-3G*//STO-3G*) and He I/He II ratios.

Substitution of a π-donating substituent into the pyridine moiety results in perturbations to its electronic structure. In a composite-molecule model the valence p AOs of the chalcogen atom will form bonding and anti-bonding combinations with the b_1 MO of the pyridine system. Depending upon the point of substitution, this will entail a 'rotation' of the pyridine-based MOs. The b_1 MO in the parent pyridine molecule has maximum electron density on the N and C_4 atoms. However,

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TABLE IV

Relative He I and He II band intensities and percentage change for the methylchalcogenopyridines

Band Area	IE Range (/eV)	Band Intensity[a]		% Change
		He I	He II	[(He II/He I)-1]x100
		(a) 2-Methylthiopyridine		
1	8.0 - 9.0	0.98	0.60	-38.8
2	9.0 - 10.1	1.04	1.59	52.9
3	10.1 - 10.9	1.49	1.61	8.1
4	10.9 - 11.9	1.32	0.99	-25.0
5	11.9 - 18.0	9.17	8.94	-2.5
		(b) 3-Methylthiopyridine		
1	8.0 - 9.1	1.09	0.91	-16.5
2	9.1 - 10.2	1.56	1.86	19.2
3	10.2 - 11.2	1.19	1.58	32.8
4	11.2 - 12.2	1.19	0.79	-33.6
5	12.2 - 18.0	8.86	8.63	-2.6
		(c) 4-Methylthiopyridine		
1	8.0 - 8.9	1.40	0.92	-34.3
2	8.9 - 10.1	1.80	2.40	33.3
3	10.1 - 11.3	0.98	1.01	3.1
4	11.3 - 12.0	1.04	0.80	-23.1
5	12.0 - 18.0	8.62	8.68	0.7
		(d) 2-Methylselenylpyridine		
1	8.0 - 8.9	1.31	0.69	-47.3
2	8.9 - 9.8	0.89	1.07	20.2
3	9.8 - 10.8	1.55	1.83	18.1
4	10.8 - 11.6	0.95	0.83	-12.6
5	11.6 - 12.5	1.20	0.90	-25.0
6	12.5 - 18.0	8.11	8.68	7.0
		(e) 3-Methylselenylpyridine		
1	8.0 - 9.0	1.08	0.63	-41.7
2	9.0 - 10.2	1.98	2.78	40.4
3	10.2 - 11.0	1.33	1.86	39.8
4	11.0 - 12.0	0.96	0.62	-35.4
5	12.0 - 18.0	8.92	8.11	-9.1
		(f) 4-Methylselenylpyridine		
1	8.0 - 9.0	1.29	0.70	-45.7
2	9.0 - 10.4	1.86	2.53	36.0
3	10.4 - 11.3	0.88	0.82	-6.8
4	11.3 - 11.9	0.99	0.62	-37.4
5	11.9 - 18.0	8.95	9.29	3.8

a) Normalised to 14 bands.

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upon interaction with a substituent in the 2 or 3 position this electron density shifts. Similarly, the a_2 MO of pyridine, which in the parent molecule has minimal electron density upon the N atom, can shift upon substitution to form a MO with substantial N character. The change in character of these MOs can produce predictable shifts in the IEs and so permit their assignment.

The lone-pair n_N MO (a_1) of pyridine cannot be significantly altered upon substitution, although it will be affected by the presence of electronegative substituents. Strong σ-acceptors will withdraw electron density, thus raising the IE of this σ-type MO. Similarly with π-donors (acceptors) addition (depletion) of electron density to the ring system will result in lower (higher) π IEs. The balance between these factors is often difficult to assess, especially for conformationally flexible systems, but the observation of a series of compounds should allow some correlations to be made.

A series of calculations at the ΔSCF/MP2/3-21G* level were performed on the methylchalcogenopyridines and the results presented in Table V. Using the assignment of pyridine as a basis, it is found that the KA/HF models gave a reasonable prediction of the IEs of the π-type MOs, but failed to position the n_N MOs correctly.[15] On the other hand, the ΔSCF/MP2 model was found to give a better description of the n_N IE and a comparable one for the lowest energy π-type IEs.[15] Therefore, the KA/6-31G** model was used to primarily assign (in a composite-

TABLE V

Comparison of experimental vertical IEs with ΔSCF/MP2/3-21G* and KA/3-21G* IEs (/eV) for the methylchalcogenopyridines[a]

Cogener	Ionic State	Expt IE	ΔSCF/MP2/3-21G*	KA/3-21G*
2-SMe	2A"	8.16	8.671	8.337
	2A'	9.52	9.679	11.276
3-SMe	2A"	8.47	8.745	8.409
	2A'	10.04	9.735	11.100
4-SMe	2A"	8.46	9.116	8.806
	2A'	9.58	9.350	11.184
2-SeMe	2A"	8.22	8.553	8.116
	2A'	9.53	9.705	11.120
3-SeMe	2A"	8.38	8.662	8.204
	2A'	9.89	9.752	11.020
4-SeMe	2A"	8.57	8.982	8.537
	2A'	9.83	9.373	11.107

a) Only the IEs of the highest occupied π MO and the n_N MO are tabled.

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molecule sense) the higher energy π IEs, whereas the ΔSCF/MP2/3-21G* model is the most reliable model in this work and so is used to assign the n_N IEs (as shown in Table V).

The first band in each spectrum is assigned to an anti-bonding combination of the valence p AOs of the chalcogen atom and the b_1 MO of pyridine. In the 2- and 4-series, this band gets sharper down the group. The change in band shape is a reflection of the changing band character—becoming more lone-pair in character due to the reduction in overlap of the pyridine-based π orbitals and the chalcogen valence AOs. For example, the b_1 MO in pyridine has an IE of ~10.5 eV,[1-5] while the first IEs of the dimethyl chalcogenides are 10.04 (O), 8.71 (S) and 8.40 eV (Se).[47] Thus, the HOMO in the methoxypyridine case[15] will have substantial ring character, leading to a broader band profile, whereas for the more electron dense methylthio- and methylselenylpyridines the band shape should appear much sharper (which is in agreement with the observed spectra).

The second bands seen in the UPS spectra arise from the a_1-and a_2-based MOs of pyridine. There is much conjecture over the relative ordering of these two bands. There is little difference in their band shapes and their behaviour under He II conditions does not give a conclusive resolution of their nature. The fourth band is assigned to the bonding combination of the p AOs of the chalcogen and the pyridine b_1 MO, while the fifth can be assigned in some cases as having substantial chalcogen p character. Like the HOMO, the bonding MO also shifts with atomic number in a predictable manner.

Of the KA/HF models used in this study, only the 3-21G* and 6-31G**(LWD) sets produce reasonable IEs for the π MOs. The STO-3G* results are typically shifted by several eV to lower IE values. The 3-21G* values are comparable with and in some cases better than the more extensive 6-31G** results. This suggests that the KA model may not be capable of producing better results even when employing more extensive basis sets.

As shown earlier for pyridine, the effect of electronic relaxation can have a dramatic effect on specific IEs (shifts of up to 2.5 eV), rendering KA models inappropriate. However, the ΔSCF process is limited in its use by symmetry constraints. The ΔSCF/MP2 method has been used to calculate the IEs for the HOMO and the lone-pair n_N MO and the results show good correspondence with the experimental values. The IEs of the n_N MOs show vast improvement, while the HOMO is comparable to the KA/6-31G** result—revealing the difference in the effect of relaxation upon these two MOs. The similarity between these values decreases down the group—suggesting that the interplay between correlation and relaxation is changing for these molecules containing second- and third-row atoms.

The σ-nature of the n_N MO means that it is directly influenced by the electronegativity of the substituent. Substitution in the 2-position will have the greatest effect. The methylthio (SMe) group has an assigned group electronegativity of 2.65.[48] It is anticipated that the methylseleno (SeMe) group will possess a similar group electronegativity value as its sulfur analog, due to the similarity of the atomic electronegatives of S and Se.[49] The similarity between the electronegativity of the pyridine ring and the $-$SMe and $-$SeMe groups may lead to a donation of electron density into the ring system and a resultant destabilisation of the n_N MO (ie. to lower IE).

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The former a_2 pyridine MO is stabilised by 0.40–0.65 eV in the 2-series and this can be directly related to increase in the π-electron density upon the ring nitrogen, since it is a strong π acceptor. This results in a higher IE for the second π-band. The trends in the IEs of these two MOs are reflected in all of the molecules reported here, although overlapping of peaks and rotational contamination can make unambiguous assignment difficult.

Consistent with spectral and ab initio analyses the preferred sequence for all isomers of the dominant planar methylchalcogenopyridines is,

$$\pi - n_X < n_N \sim \pi < \pi + n_X$$

where X represents the chalcogen element.

In conclusion, the UPS of the methylthio- and methylselenyl-pyridines can be confidently assigned using a combination of techniques; the He I/He II band ratios readily locate these MOs with significant S or Se p orbital contributions and can indicate the chalcogen content in the bonding and anti-bonding X π orbitals, KA assignments for π-based MOs (if bases of split-valence quality are used), ΔSCF/MP assignments for the σ-type n_N MOs, and electronegativity correlations.

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EXPERIMENTAL

The nmr spectra refer to ^1H and ^{13}C spectra (90 MHz) with tetramethylsilane as an internal standard. Ultraviolent absorption spectra were recorded in ethanol solution. The syntheses of all compounds used in this study, except 3-methylselenylpyridine, were based upon adaptations of the methods of Albert and Barlin[50] and Mautner *et al.*[51] 3-methylselenylpyridine was prepared by the procedure reported by Dunne *et al.*[52]

2-Methylthiopyridine. 2-Mercaptopyridine (2.78 g, 0.025 moles) was dissolved in an aqueous sodium hydroxide solution (25 ml, 1 M). Methyl iodide (3.55 g, 0.025 moles) was added over a 2 minute period and the solution stirred for 2 hours at room temperature. After 5 minutes, a second phase separated from the aqueous layer. The mixture was extracted with benzene (4 × 50 ml), the extracts combined, dried over magnesium sulfate then evaporated under reduced pressure to yield a pale yellow liquid. This produce was vacuum-distilled to give 2-methylthiopyridine as a colourless liquid (2.6 g, 83%), bp 93-4°C/4 mm (Lit. b.p. 100-4°C/33 mm[50]). The uv spectrum showed λ_{max}: 241.0, 253.9 and 290.7 nm (log ε: 3.68, 3.67 and 3.59). The ^1H nmr (deuteriochloroform) consisted of δ: 2.50 (s, 3H, methyl protons), 6.81–6.94 (m, 1H, 5 proton), 7.05–7.15 (d, 1H, 3 proton), 7.31–7.48 (m, 1H, 4 proton) and 8.37–8.41 ppm (d, 1H, 6 proton). The ^{13}C nmr consisted of δ: 12.97 (methyl carbon), 118.82 (5 carbon), 121.31 (3 carbon), 135.45 (4 carbon), 149.22 (6 carbon) and 159.78 ppm (2 carbon).

3-Methylthiopyridine. 3-Mercaptopyridine (10.5 g, 0.095 moles) was dissolved in an aqueous sodium hydroxide solution (100 ml, 1 M). Methyl iodide (13.5 g, 0.095 moles) was added over a 2 minute period and a dark oil separated immediately from the aqueous layer. The solution was stirred for 2 hours at room temperature. The mixture was extracted with ether (3 × 100 ml), the extracts combined, dried over magnesium sulfate then evaporated under reduced pressure to yield a dark yellow liquid (8.5 g). This produce was vacuum-distilled to give 3-methylthiopyridine as a pale yellow liquid (4.7 g, 40%), bp 54-6°C/0.4 mm (Lit. b.p. 102°C/17 mm[50]). The uv spectrum (ethanol) λ_{max}: 254.0 (sh) and 294.1 nm (log ε: 3.89 and 3.44). The ^1H nmr (deuteriochloroform) consisted of δ: 2.44 (s, 3H, methyl protons), 7.06–7.21 (m, 1H, 5 proton), 7.44–7.58 (m, 1H, 4 proton), 8.31–8.38 (d, 1H, 6 proton) and 8.50 ppm (s, 1H, 2 proton). The ^{13}C nmr consisted of δ: 15.60 (methyl carbon), 123.26 (5 carbon), 133.98 (4 carbon), 135.35 (3 carbon), 146.00 (6 carbon) and 147.86 ppm (2 carbon).

4-Methylthiopyridine. 4-Mercaptopyridine (5.56 g, 0.05 moles) was dissolved in an aqueous sodium hydroxide solution (50 ml, 1 M). Methyl iodide (7.1 g, 0.05 moles) was added over a 2 minute period and the solution stirred for 2 hours at room temperature. After 5 minutes, a second phase separated from the aqueous layer. The mixture was extracted with benzene (4 × 50 ml), the extracts combined, dried over magnesium sulfate then evaporated under reduced pressure to yield a pale yellow liquid, which solidified upon standing. The crude solid was recrystallised from hexane to give 4-methylthiopyridine as colourless crystals (5.1 g, 82%), m.p. 48°C (Lit. m.p. 47°C[50]). The uv spectrum (ethanol)

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λ_{max}: 254.4, 219.5 (sh) and 271.5 nm (sh) (log ε: 3.77, 3.74 and 3.73). The ^{1}H nmr (deuteriochloroform) consisted of δ: 2.44 (s, 3H, methyl protons), 7.02–7.09 (d, 2H, 3,5 protons) and 8.33–8.40 ppm (d, 2H, 2,6 protons). The ^{13}C nmr consisted of δ: 13.55 (methyl carbon), 119.80 (3,5 carbons), 148.98 (2,6 carbons) and 150.29 ppm (4 carbon).

2-Methylselenylpyridine. Under an atmosphere of nitrogen, 2-selenopyridine (2.0 g, 0.0126 moles) was dissolved in an aqueous sodium hydroxide solution (13 ml, 1 M). Methyl iodide (1.7 g, 0.0126 moles) was added over a 2 minute period and the solution stirred for 3 hours at room temperature. After 5 minutes, a second phase separated from the aqueous layer. The mixture was extracted with benzene (5 × 100 ml), the extracts combined, dried over magnesium sulfate then evaporated under reduced pressure to yield a pale yellow liquid. This produce was vacuum-distilled to give 2-methylselenylpyridine as a pale yellow liquid of unpleasant odour (1.8 g, 83%), bp 47.5°C/0.55 mm (Lit. b.p. 43-5°C/0.25 mm[51]). The uv spectrum (ethanol) λ_{max}: 215.4 (sh), 249.7, 262.5 (sh) and 297.8 nm (log ε: 3.67, 3.86, 3.82 and 3.64). The ^{1}H nmr (deuteriochloroform) consisted of λ: 2.41 (s, 3H, methyl protons), 6.87–7.02 (m, 1H, 5 proton), 7.26–7.40 (m, 2H, 3,4 protons) and 8.37–8.43 ppm (d, 1H, 6 proton). The ^{13}C nmr consisted of δ: 5.41 (methyl carbon), 119.84 (5 carbon), 124.48 (3 carbon), 135.64 (4 carbon), 149.88 (6 carbon) and 155.93 ppm (2 carbon).

3-Methylselenylpyridine. 3-Selenocyanatopyridine (10 g, 0.055 moles) was dissolved in aqueous hydrochloric acid (50 ml, 6 M) in an atmosphere of nitrogen. Hypophosphorous acid (50%, 30 ml) was added dropwise over a 20 minute period and the mixture stirred at ambient temperature for 3 hours. The pH of the solution was adjusted to ~12 with a concentrated sodium hydroxide solution. After cooling, methyl iodide (7.8 g, 0.055 moles) was added dropwise and after five minutes a dark liquid phase separated. Stiring was continued for 2 hours and the mixture allowed to stand overnight. It was then extracted with chloroform (5 × 100 ml). The chloroform extract was dried over magnesium sulfate and the solvent removed. The brown liquid residue was distilled to afford a light yellow liquid of unpleasant odour (7.9 g, 84%), bp 64°C/0.46 mm[52] (Lit. oil[53]). The uv spectrum (ethanol) λ_{max}: 251.2, 266.8 and 295.2 nm (log ε: 3.65, 3.65 and 3.42). The ^{1}H nmr (deuteriochloroform) consisted of δ: 2.31 (s, 3H, methyl protons), 7.10–7.23 (m, 1H, 5 proton), 7.65–7.76 (m, 1H, 4 proton), 8.38–8.42 (d, 1H, 6 proton) and 8.61 ppm (s, 1H, 2 proton). The ^{13}C nmr consisted of δ: 7.31 (methyl carbon), 123.75 (5 carbon), 128.86 (3 carbon), 137.91 (4 carbon), 147.20 (6 carbon) and 151.05 ppm (2 carbon).

4-Methylselenylpyridine. Under an atmosphere of nitrogen, 4-selenopyridine (6.0 g, 0.038 moles) was dissolved in an aqueous sodium hydroxide solution (40 ml, 1 M). Methyl iodide (5.1 g, 0.038 moles) was added over a 2 minute period and the solution stirred for 16 hours at room temperature. After 5 minutes, a second phase separated from the aqueous layer. The mixture was extracted with chloroform (5 × 100 ml), the extracts combined, dried over magnesium sulfate then evaporated under reduced pressure to yield a pale brown liquid. This product was vacuum-distilled to give 4-methylselenylpyridine as a pale yellow liquid of unpleasant odour, which solidified on cooling (4.8 g, 73%), bp 70-4°C/0.58 mm, m.p. 38°C (Lit. oil[53]). The uv spectrum (ethanol) λ_{max}: 224.1, 250.7 (sh) and 279.7 nm (log ε: 3.84, 3.59 and 4.01). The ^{1}H nmr (deuteriochloroform) consisted of δ: 2.35 ppm (s, 3H, methyl protons), 7.19–7.25 (d, 2H, 3,5 protons) and 8.30–8.37 (d, 2H, 2,6 protons). The ^{13}C nmr consisted of δ: 5.41 ppm (methyl carbon), 123.50 (3,5 carbons) and 149.20 (2,6 carbons).

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