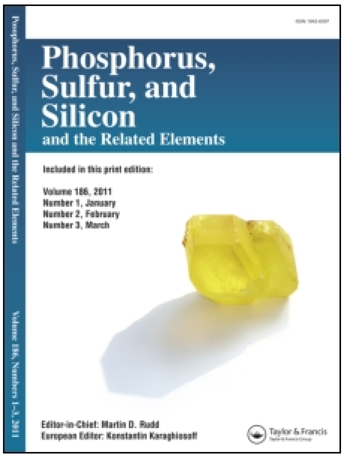

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HE I AND HE II STUDY OF THE SYMMETRICAL ISOMERS OF DIPYRIDYL DISULFIDE AND DISELENIDE

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The He I and He II photoelectron spectra of the symmetrical isomers of dipyridyl disulfide and diselenide have been measured and interpreted in terms of a composite-molecule model. The sequence of the lowest valence ionisation energies is assigned as: $(\pi_8 - n_X)^- \geq (\pi_7 - n_X)^+ > n_N \sim n_N > (\pi_6 - \delta n_X) \sim (\pi_5 - \delta n_X) > (\pi_4 + n_X)^- \geq (\pi_3 + n_X)^+$, which is consistent with He I/He II photoionisation cross-section ratios, a composite-molecule model and correlations with the assignment of the dimethyl chalcogenides and chalcogenobispyridines, but contrary to STO-3G* and extended valence basis set calculations.

Key words: Chalcogenobispyridines; conformational analysis; photionization.

INTRODUCTION

The disulfide link is commonly found in biological systems and its biochemical significance lies in the ease with which the bond is formed or broken under normal biological conditions.[1] There are an extensive number of applications of the 2,2′ and 4,4′-dipyridyl disulfides.[2–4] To date there have been no reported applications of 3,3′-dipyridyl disulfide and moreover, the dipyridyl diselenides have remained relatively untested.[5–6] Hence, there is considerable interest in the energetics and conformations of molecules containing the dichalcogenide link.

The conformations of the dipyridyl dichalcogenides are expected to be similar to those of other diaryl dichalcogenides. The crystal structures of 2,2′-dipyridyl disulfide[7] and 3,3′-dihydroxy-2,2′-dipyridyl disulfide[8] have been reported, along with a number of metal-coordinated compounds. In each of the latter cases, coordination was through the nitrogens and not the sulfur atoms. Raghavan and Seff[7] reported a C—S—S—C torsional angle of 87.1° for 2,2′-dipyridyl disulfide, along with S—S and S—C bond lengths of 2.016 and 1.785 Å, respectively. This conformation results in the S—S bond lying nearly in the plane of both pyridine rings. The corresponding values for the dihydroxy compound[8] were 93.2°, 2.018 Å and 1.782 Å, respectively. The effect of coordination was to distort the structure, although all values lay within 10° and 0.02 Å of those of 2,2′-dipyridyl disulfide. Pappalardo *et al.*[9] studied the carbon-13 relaxation times for the 2,2′-dipyridyl dichalcogenides (X = S, Se, Te) and fitted the data to a model of anisotropic reorientation of a rigid body using the extended relaxation equation. The fitting procedure was carried out for conformers with dihedral angles (C—X—X—C) of

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approximately 90°, and angles of rotation of the pyridyl rings of (0,0), (180,0) and (180,180). The calculations were best fitted by those conformers in which the pyridyl rings lie in the planes formed by the C—X—X groups. They concluded that these compounds could be present in solution as a mixture of three rigid conformers characterised by the relative position of the two nitrogen atoms (syn-syn, syn-anti, anti-anti) with respect to the dichalcogen group, although 'free rotation' was not ruled out.

Ultraviolet photoelectron spectroscopy (UPS) directly measures the valence electronic structure of most compounds and provides insight into the degree of interaction of equivalent orbitals. UPS studies have been reported only on few dichalcogens, the most notable of which are: 2,2'-dipyridyl and the diphenyl dichalcogenides,[10–12] 1,4-dithiepane,[13] 1,5-dithiocane[13] and 1,6-dithiocane.[13] When invoking Koopmans' approximation (KA), UPS has been shown to be a powerful tool in assessing the degree of lone-pair repulsion on adjacent chalcogen atoms and so aid in developing mechanisms that rationalise torsional strain.

The composite-molecule model is also a useful aid in the interpretation of UPS spectra. It is based on the premise that molecular orbitals (MOs) can be described in terms of linear combinations of orbitals that are localised on different fragments of a molecule. In the case of the disubstituted disulfides, Giordon and Bock[11] have interpreted the sequence of six lowest ionisation energies (IEs) in terms of interactions involving orbitals localised on the sulfur atoms with orbitals localised on the aryl fragment. The symmetric π MO (labelled π^S) with electron density on the substituent site resonantly interacts with sulfur 3p AOs to produce composite orbitals of anti-bonding and bonding character, whereas the symmetric π MO (labelled π^A) with a node at the substituent site remains unshifted. This interpretation is further supported by the modest splittings of first two IEs. The similarity between their average IEs and those of the corresponding IEs in the PhXMe[14–17] suggest that very little interaction takes place between the two phenyl groups through the dichalcogen bridge. The conformation with a C—X—X—C dihedral angle of ~90° between the two electron lone-pairs on the chalcogen atoms minimises repulsions between the lone-pairs. When the dihedral angle deviates of 90°, the energy separation between the first two IEs increases. The splitting of above 0.4–0.5 eV in diphenyl diselenide and ditelluride corresponds to a value of about 70° for the dihedral angle.[11–12]

Extending our earlier work on the UPS studies of the methylchalcogenopyridines,[18–19] alkyl phenyl disulfides[19] and chalcogenobispyridines,[20–24] the He I and He II spectra of the symmetrical dipyridyl disulfides and diselenides have been measured and assigned within a composite-molecule model. Single point STO-3G* and extended valence basis calculations have been performed in order to calculate IE sequences, thereby aiding spectral assignment. While these Hartree-Fock (HF) calculations are useful, it will be shown that they do not provide a definitive tool for the interpretation of these UPS spectra.

RESULTS AND CALCULATIONS

Figures 1 and 2 show the He I and He II spectra of all the symmetrical isomers of dipyridyl disulfide and diselenide, respectively. The spectra were recorded in the

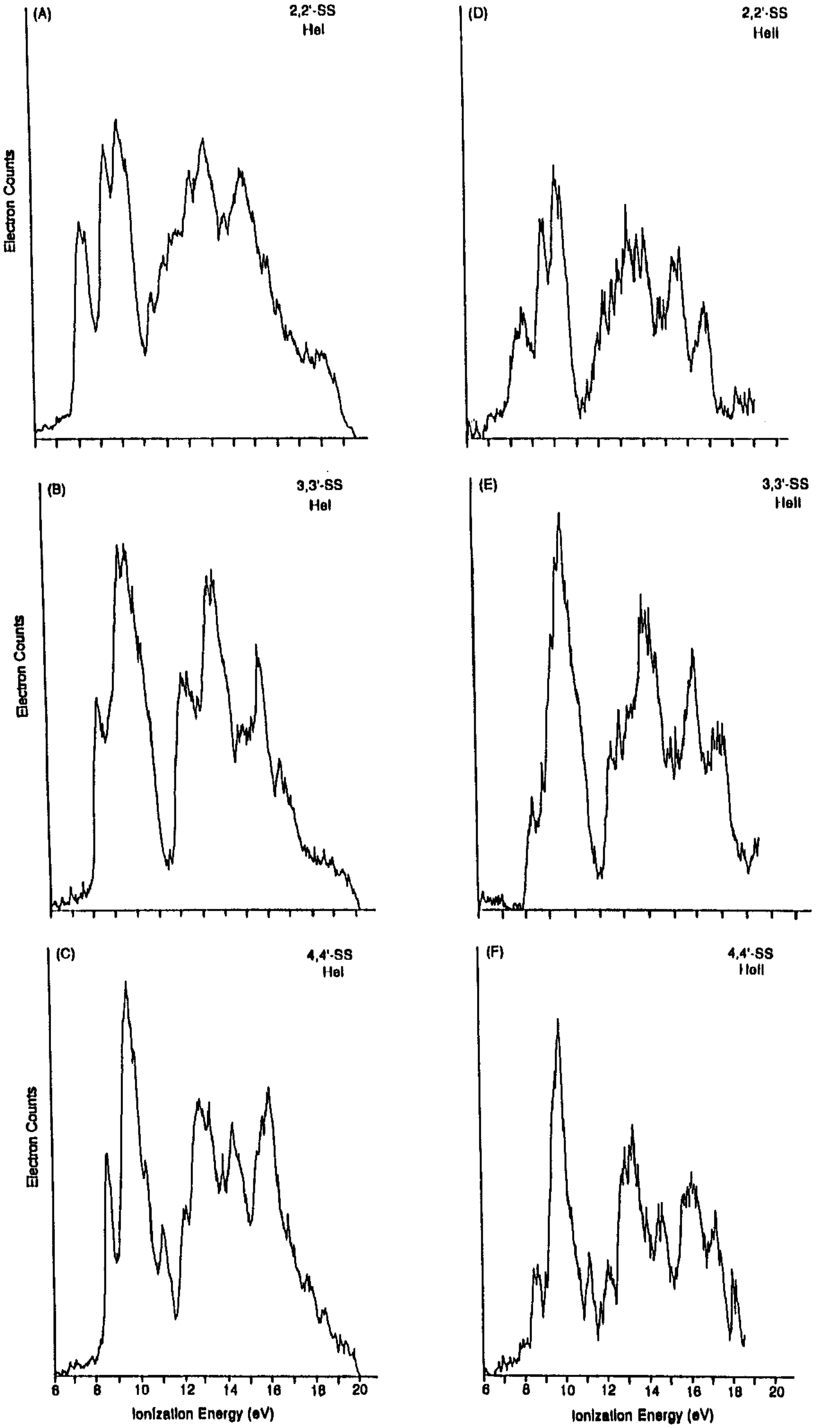

FIGURE 1 The differential: (A) He I spectrum of 2,2′-dipyridyl disulfide; (B) He I spectrum of 3,3′-dipyridyl disulfide; (C) He I spectrum of 4,4′-dipyridyl disulfide; (D) He II spectrum of 2,2′-dipyridyl disulfide; (E) He II spectrum of 3,3′-dipyridyl disulfide; (F) He II spectrum of 4,4′-dipyridyl disulfide.

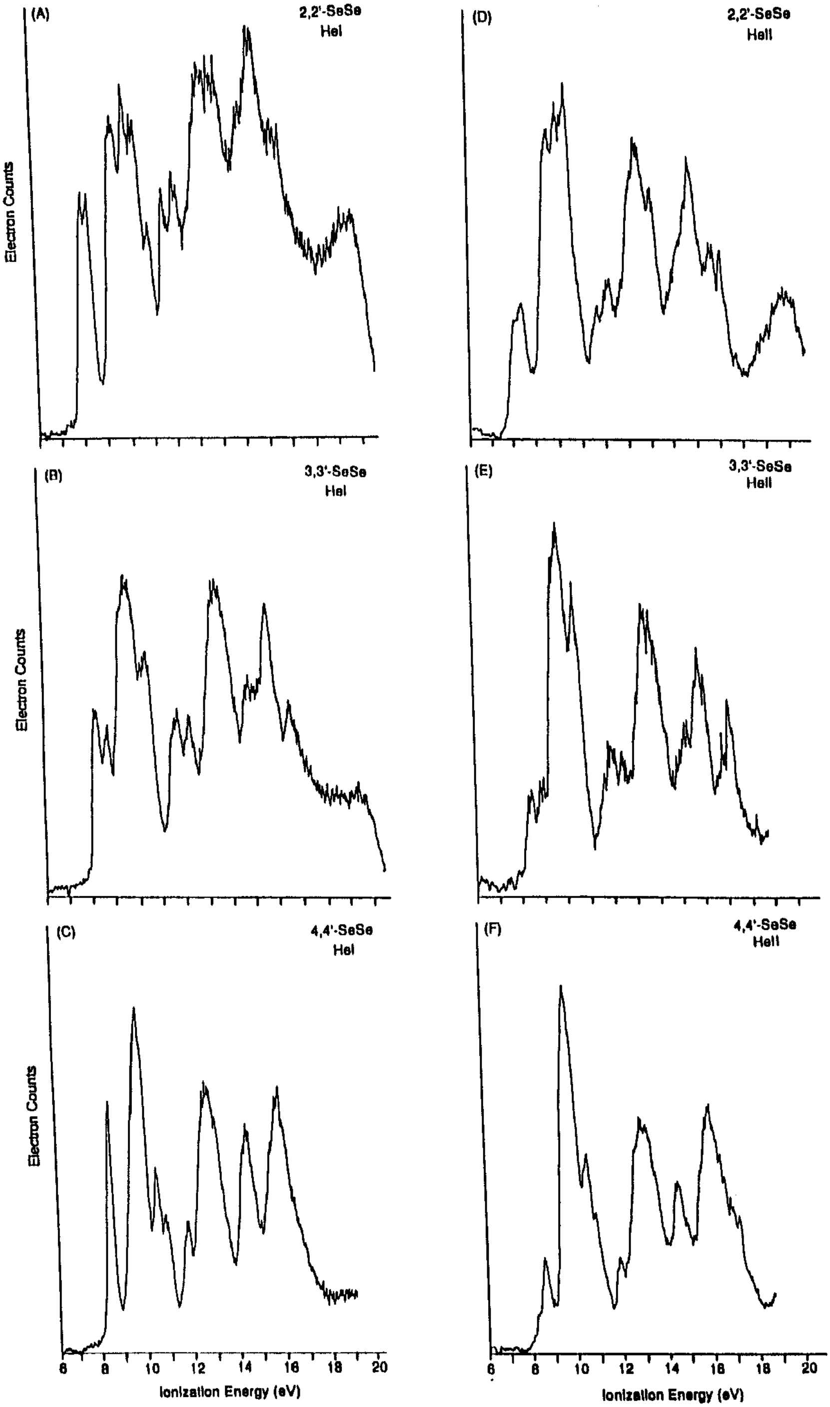

FIGURE 2 The differential: (A) He I spectrum of 2,2'-dipyridyl diselenide; (B) He I spectrum of 3,3'-dipyridyl diselenide; (C) He I spectrum of 4,4'-dipyridyl diselenide; (D) He II spectrum of 2,2'-dipyridyl diselenide; (E) He II spectrum of 3,3'-dipyridyl diselenide; (F) He II spectrum of 4,4'-dipyridyl diselenide.

temperature range between 330–355 K. For individual spectra the temperature fluctuations were kept at a minimum (i.e. below 2–3 K) in order to minimise changes in the sample pressure and therefore in the relative band intensities. Under He I and He II operating conditions, the resolution was ~35 meV and ~55 meV, respectively. Each spectrum was accumulated over 20 minutes with maximum counts in the region of 4000 cps and 1000 cps, respectively. The spectra were calibrated using butadiene/argon mixtures and digitised for use in the density-of-states analysis and in the determination of the He I/He II photoionisation cross-section ratios.

The spectra were sectioned into suitable IE ranges (representing distinct groups of bands). For the dipyridyl dichalcogenides, the *s-p* separation rule[25] predicts that the total number of *p*-based bands below 18 eV is given by,

$$N_T = N_C + 0.5N_H + 1.5N_N + 2.0N_X \qquad (1)$$

where N_C, N_H, N_C and N_X are the number of carbon, hydrogen, nitrogen and chalcogen atoms in the molecule, respectively. Equation (1) predicts a 21 *p*-based bands and with corresponding cross-overs, a total of 23 bands below 18 eV are expected in the UPS spectra of the dipyridyl dichalcogenides. Table I compares the experimental density-of-states analysis with the IE distributions calculated using HF MO models.

To determine relative He I/He II cross-section ratios, each spectrum was integrated and the total band area was normalised to 23. The percentage change in band intensity of going from He I and He II radiation is given by,[26]

$$\% \text{ change} = [(\text{He II}/\text{He I}) - 1] \times 100 \qquad (2)$$

TABLE I

Comparison of experimental band intensities and calculated IE distributions

ISOMER	IE RANGE (/eV)	BAND INT.[a] (Exp)	CALC. IE DISTRIBUTION[b] Model I	Model II	Model III
2,2'-SS	7.5 - 11.0	8.2	9	4	6
	11.0 - 18.0	14.8	14	15	13
3,3'-SS	7.0 - 11.5	9.1	9	4	6
	11.5 - 18.0	13.9	12	15	13
4,4'-SS	8.0 - 11.5	8.1	9	4	6
	11.5 - 18.0	14.9	14	14	12
2,2'-SeSe	7.0 - 11.4	6.8	9	6	8
	11.4 - 18.0	16.2	12	13	11
3,3'-SeSe	7.5 - 11.1	7.4	8	4	6
	11.1 - 18.0	15.6	13	15	13
4,4'-SeSe	8.0 - 11.4	7.7	8	4	6
	11.4 - 18.0	15.3	14	15	13

a) Based on He I band intensities, normalised to 23 bands.

b) See text for definition.

TABLE II

Relative He I and He II band intensities and percentage change for the isomers of dipyridyl disulfide and diselenide

BAND	IE RANGE	BAND INT.[a]		% CHANGE
	(/eV)	HeI	HeII	[(HeII/HeI)-1]x100
		(a) 2,2'-SS		
1	7.5 - 8.8	2.411	1.907	-20.9
2	8.8 - 9.6	2.171	1.918	-11.7
3	9.6 - 11.0	3.643	3.647	0.1
4	11.0 - 12.1	1.159	1.866	61.0
5	12.1 - 18.0	13.616	13.662	0.3
		(b) 3,3'-SS		
1	8.0 - 9.0	1.686	0.989	-41.3
2	9.0 - 11.5	7.413	6.794	-8.4
3	11.5 - 18.0	13.901	15.217	9.5
		(c) 4,4'-SS		
1	8.0 - 9.0	1.482	1.219	-17.8
2	9.0 - 10.2	4.270	4.332	1.5
3	10.2 - 10.7	1.205	1.395	15.8
4	10.7 - 11.5	1.111	1.095	-1.4
5	11.5 - 18.0	14.932	14.959	0.2
		(d) 2,2'-SeSe		
1	7.0 - 8.8	1.648	1.386	-15.9
2	8.8 - 9.8	1.892	2.443	29.1
3	9.8 - 10.7	2.329	3.368	44.6
4	10.7 - 11.4	0.899	1.051	16.9
5	11.4 - 11.9	0.853	0.736	-13.7
6	11.9 - 12.5	1.256	1.120	-10.8
7	12.5 - 18.0	14.122	12.895	-8.7
		(e) 3,3'-SeSe		
1	7.5 - 8.5	1.037	0.852	-17.8
2	8.5 - 9.1	0.977	0.730	-25.3
3	9.1 - 10.2	3.494	4.157	19.0
4	10.2 - 11.1	1.891	2.575	36.2
5	11.1 - 12.0	1.556	1.625	4.4
6	12.0 - 12.6	1.185	1.261	6.4
7	12.6 - 18.0	12.861	11.799	-8.3
		(f) 4,4'-SeSe		
1	8.0 - 9.0	1.647	0.897	-45.5
2	9.0 - 10.2	3.933	4.673	18.8
3	10.2 - 10.7	1.136	1.325	16.6
4	10.7 - 11.4	1.012	1.108	9.5
5	11.4 - 12.0	1.012	0.894	-11.7
6	12.0 - 18.0	14.260	14.103	-1.1

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a) Normalised to 23 bands.

A negative (positive) percentage change indicates a decrease (increase) in band intensity on going from He I to He II radiation. Table II gives experimental He I/He II cross-section ratios.

The ab initio IEs were computed using the LCAO MO SCF restricted HF method within the GAUSSIAN 88 program[27] using two basis sets: the internal STO-3G* (C, H, N, S, Se); a more extensive 6-31G** (C, H, N, S) coupled with the selenium split valence (12s8p5d)/[5s4p2d] basis set of Lehn, Wipff and Demuynck (denoted LWD).[28] The LWD basis set is of a similar size to the 6-31G** basis set and so ensures that the bases are balanced. Comparative studies have shown[29] that due to a superposition error, unbalanced basis sets often give poorer results when compared with balanced sets.

TABLE III

Experimental and calculated IEs for the dipyridyl disulfides and diselenides[a]

	Expt. IE_{vert} (/eV)	KA IEs (/eV)[b]			MO Character (Model III)
		Model I	Model II	Model III	
			(a) 2,2'-SS		
1	8.32	6.40	8.70	8.70	$(\pi_8-n_S)^-$
2	8.60	6.43	8.95	8.95	$(\pi_7-n_S)^+$
3	9.66	8.52	10.38	9.68	$n_N+n_N'+\delta n_S$
4	9.87	8.55	10.45	9.68	$n_N+n_N'+\delta n_S$
5	10.19	8.86	11.13	10.38	$(\pi_6-\delta n_S)$
6	10.61	8.95	11.20	10.45	$(\pi_5-\delta n_S)$
7	11.71	9.57	11.94	11.13	$(\pi_4+n_S)^-$
8	12.10	9.58	11.96	11.20	$(\pi_3+n_S)^+$
			(b) 3,3'-SS		
1	8.47	6.62	8.85	8.85	$(\pi_8-n_S)^-$
2	8.99	6.66	9.01	9.01	$(\pi_7-n_S)+$
3	9.37	8.63	10.33	9.74	n_N+n_N'
4	9.72	8.64	10.44	9.74	n_N+n_N'
5	10.06	9.20	11.65	10.33	$(\pi_6-\delta n_S)$
6	10.31	9.24	11.69	10.44	$(\pi_5-\delta n_S)$
7	10.69	9.39	11.75	11.65	$(\pi_4+n_S)^-$
8	12.15	9.64	11.95	11.69	$(\pi_3+n_S)^+$
			(c) 4,4'-SS		
1	8.71	6.85	9.37	9.35	n_N+n_N'
2	9.23	6.88	9.55	9.35	n_N+n_N'
3	9.59	8.26	9.71	9.37	$(\pi_8-n_S)^-$
4	9.84	8.30	9.81	9.55	$(\pi_7-n_S)+$
5	9.99	9.09	11.56	9.71	π_6
6	10.46	9.13	11.59	9.81	π_5
7	11.14	9.56	11.97	11.56	$(\pi_4+n_S)^-$
8	12.16	9.78	12.09	11.59	$(\pi_3+n_S)^+$

TABLE III (*Continued*)

	Expt. IE_{vert} (/eV)	KA IEs (/eV)^b			MO Character (Model III)
		Model I	Model II	Model III	
			(d) 2,2'-SeSe		
1	8.09	7.28	8.55	8.55	$(\pi_8\text{-}n_{Se})^-$
2	8.34	7.32	8.71	8.71	$(\pi_7\text{-}n_{Se})^+$
3	9.39	8.85	10.28	9.71	$n_N+n_N'+\delta n_{Se}$
4	9.56	8.88	10.35	9.71	$n_N+n_N'+\delta n_{Se}$
5	9.98	9.33	10.87	10.28	$(\pi_6\text{-}\delta n_{Se})$
6	10.31	9.36	10.92	10.35	$(\pi_5\text{-}\delta n_{Se})$
7	10.89	10.03	11.81	10.87	$(\pi_4+n_{Se})^-$
8	11.53	10.04	11.82	10.92	$(\pi_3+n_{Se})^+$
			(e) 3,3'-SeSe		
1	8.18	7.49	8.72	8.72	$(\pi_8\text{-}n_{Se})^-$
2	8.70	7.54	8.83	8.83	$(\pi_7\text{-}n_{Se})^+$
3	9.40	8.90	10.29	9.75	$n_N+n_N'+\delta n_{Se}$
4	9.60	8.93	10.34	9.75	$n_N+n_N'+\delta n_{Se}$
5	9.81	9.53	11.38	10.29	$(\pi_6\text{-}\delta n_{Se})$
6	10.25	9.57	11.40	10.34	$(\pi_5\text{-}\delta n_{Se})$
7	10.40	9.99	11.64	11.38	$(\pi_4+n_{Se})^-$
8	11.61	10.11	11.76	11.40	$(\pi_3+n_{Se})^+$
			(f) 4,4'-SeSe		
1	8.45	7.74	9.18	9.18	$(\pi_8\text{-}n_{Se})^-$
2	8.45	7.79	9.29	9.29	$(\pi_7\text{-}n_{Se})^+$
3	9.48	8.52	9.68	9.37	n_N+n_N'
4	9.71	8.54	9.75	9.37	n_N+n_N'
5	9.92	9.44	11.46	9.68	π_6
6	10.43	9.46	11.51	9.75	π_5
7	10.78	10.17	11.65	11.46	$(\pi_4+n_{Se})^-$
8	11.80	10.27	11.75	11.51	$(\pi_3+n_{Se})^+$

a) All entries in eV.

b) See text for definitions of Models.

For the entire family of the dipyridyl dichalcogenides, the dihedral angle was held fixed at 90° (in line with structural studies[7–8]). The $R_{\mathrm{C—S}}$ and $R_{\mathrm{C—Se}}$ bond lengths were held fixed at 1.77 and 1.89 Å and the bond angles $A_{\mathrm{C—X—X}}$ were set at 101° and 99°, respectively, based on the previous studies on the chalcogenobispyridines.[20–24] Optimisations of the $R_{\mathrm{X—X}}$ bond lengths were then performed at the STO-3G* level (using the Fletcher-Powell routine[30]). Optimisations using the more extensive 6-31G** basis set were deemed too prohibitive, since for 2,2'-dipyridyl diselenide, optimising the $R_{\mathrm{Se—Se}}$ bond lengths (even within the constraints detailed above) with the STO-3G* basis set took over 400 minutes of CPU time, using the IBM 320/Risc 6000 system.

For the 2,2′-, 3,3′- and 4,4′-dipyridyl disulfides, the optimum $R_{S—S}$ bond lengths are 1.964, 1.961 and 1.962 Å, respectively, while the corresponding diselenides gave $R_{Se—Se}$ bond lengths of 2.172, 2.170 and 2.170 Å, respectively. The $R_{S—S}$ value for 2,2′-dipyridyl disulfide was within 0.05 Å of the crystallographic value, while that of 2,2′-dipyridyl diselenide was comparable with 2.29 Å in diphenyl diselenide.[31]

Table III compares the experimental IEs with the KA IEs determined by HF calculations using the STO-3G* and (6-31G**/LWD) basis sets at the optimal geometries. In Table III the STO-3G* calculations using the optimal geometries are labelled as Model I, whereas Model II employs the 6-31G** basis for the dipyridyl disulfides and (6-31G**/LWD) basis for the dipyridyl diselenides at the same geometries used for Model I. Previous work on the methylchalcogenopyridines[18–19] indicated that ΔSCF/MP2/3-21G* model correctly located the IE of the in-plane nitrogen lone-pair. However, for the isomers of the methylselenylpyridines, the CPU time for such a model is ~30 minutes on a VP 2200 supercomputer. Hence for the dipyridyl disulfides and diselenides a more tractable MO model needed to be found.

DISCUSSION

The π systems of each ring of the dipyridyl dichalcogenides are able to resonately interact exclusively with one of the chalcogen atoms, unlike their chalcogenobispyridine analogs.[20–24] Steric hindrance in the dichalcogenides is lessened due to the increased length of the bridge and thus mesomeric interactions should determine the angle between the planes of the pyridine rings—maximising overlap between the valence p AOs of the chalcogen atom with the pyridine π systems. However, low torsional barriers may permit free rotation of the rings, since concerted motion is no longer required, unlike the chalcogenobispyridines.[20–24]

The conformations of diaryl dichalcogenides are dominated by the minimisation of lone-pair/lone-pair repulsions between adjacent chalcogen valence p AOs. The minimum repulsion occurs for a C—X—X—C dihedral angle of ~90°, for which there is little resonance interaction between the valence p AOs on the two chalcogen atoms. Deviations from 90° results in the formation of bonding and anti-bonding combinations of $\pi - n_X$ MOs. The greater the deviation from 90°, the greater the interaction and the larger the separation between the bonding and anti-bonding MOs. Measurement of this splitting, from their UPS spectra, therefore provides information on the conformations of the dipyridyl dichalcogenides.

The splittings arising from ionisations of the highest occupied molecular orbitals (HOMO) for 2,2′- and 3,3′-dipyridyl disulfide were measured as 0.28 and 0.52 eV, respectively. The value for the 2,2′-isomer is comparable with the measurement of Colonna *et al.*[10] (0.25 eV), for which a dihedral angle of 100° was proposed. The splitting of 0.52 eV for the 3,3′-isomer suggests a greater interaction between MOs based on the chalcogen atoms and is similar to that displayed by diphenyl disulfide, for which a dihedral angle of 70° was proposed.[10] The splitting in the 4,4′-dipyridyl disulfide is difficult to glean from the spectra, since either a value of zero or 0.52 eV is possible from the experimental IEs. On steric considerations, the 4,4′-isomer should adopt a similar conformation to that of the 3,3′-isomer and so a value of 0.52 eV is favoured. Model II predicts that the splitting for 2,2′-, 3,3′- and 4,4′-dipyridyl disulfide is 0.25, 0.16 and 0.18 eV, respectively (agreement between absolute values of experiment and the calculations at this level of the theory should be considered fortuitous).

The splitting observed for the 2,2′-, 3,3′-dipyridyl diselenides is 0.25 and 0.52 eV, respectively, and for 4,4′-dipyridyl diselenide a splitting of either 0 or 1 eV is possible. For the first two isomers, the splitting is almost identical with those of the thio-analogs, mirroring the similarities between the conformations of the thio-[22–23] and selenobispyridines.[24] The splitting for the 4,4′-isomer is again unclear. The separation of the HOMO band for this isomer from the other valence bands makes a splitting of 1 eV unlikely and so it is proposed that the dihedral angle for this isomer is ~90°, which would yield a zero splitting. This assignment is reinforced by the He I/He II cross-section ratios, since there was no observed change to the band profile under He II conditions in the region 9.7–10.5 eV, suggesting no significant selenium contribution. Model II predicts splittings of 0.25, 0.52 and 0.11 eV, respectively, in line with the spectral assignments.

The extent of delocalisation can be judged by comparison of the He I/He II cross-section ratios between the dipyridyl dichalcogenides and those of the symmetrical chalcogenobispyridines.[20–24] The reductions in the HOMO bands of the disulfides on changing from He I to He II radiation differ by up to 24% from their sulfide equivalents. The comparison suggests that there is greater participation of pyridine π electron density into the HOMO for the 2,2′- and 4,4′-disulfides, while the first band of the 3,3′-isomer is reduced to the same extent as that in 3,3′-thiobispyridine. The first band in 2,2′-dipyridyl diselenide shows a slightly greater reduction under He II conditions than its selenobispyridine equivalent,[24] while the 3,3′- and 4,4′-isomers show a smaller reduction.

Figure 3 shows a composite-molecule model for the valance MOs of 2,2′-dipyridyl diselenide. Similar correlation diagrams may be generated for the other dipyridyl dichalcogenides investigated in this study. The r and r' labels indicate the extent of resonance interaction between the chalcogen atom lone-pair (denoted n_X) and the fragment orbitals localised on the pyridine moiety (denoted as π^A and π^S). Since the π^A does not have correct symmetry to overlap with the chalcogen np AO perpendicular to the ring, the composite orbital remains essentially pyridine in character and so is not shifted by resonance. However, it is inductively shifted from the pyridine IE value of 9.70 eV.[32] On the other hand, the π^S MO does have the correct symmetry and so interacts wth the adjacent chalcogen np AO to form composite orbitals of anti-bonding and bonding character. The in-plane nitrogen lone-pairs (n_N) would not be resonately shifted, since they do not have π symmetry, but should be inductively shifted from the pyridine IE value of 9.70 eV.[32] The composite-molecule model suggests the following valence IE sequence for the dipyridyl dichalcogenides: $(\pi_8 - n_X)^- \geq (\pi_7 - n_X)^+ > n_N \sim n_N > (\pi_6 - \delta n_X) > (\pi_5 - \delta n_X) > (\pi_4 + n_X)^- \geq (\pi_3 + n_X)^+$. The negative and positive superscripts refer to anti-bonding and bonding combinations with respect to the dichalcogenide link. The splitting of the first two MOs may be further complicated by second-order interactions involving lower lying σ_{XX} MOs.[11]

Configuration interaction methods are necessary in order to accurately predict the IEs for the n_M MOs of pyridine[32] and the corresponding IEs of the methylchalcogenopyridines.[18–19] The n_N IEs of the chalcogenobispyridines are poorly pre-

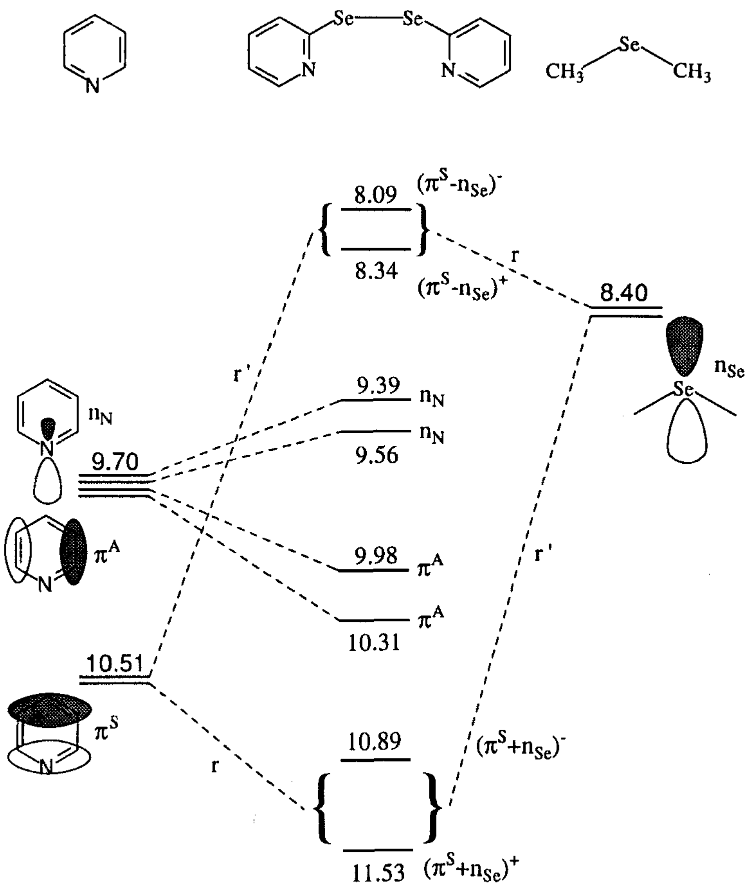

FIGURE 3 Orbital correlation diagram indicating the composite-molecule model for 2,2′-dipyridyl diselenide. The *r* and *r*′ labels indicate the extent of resonance interaction between the selenium atom lone-pair (denoted n_{Se}) and the fragment orbitals localised on the pyridine moiety (denoted as π^A and π^S).

dicted by the HF models.[21,23,24] A more useful predictor of the position of the n_N IEs in the chalcogenobispyridines is given by the correlation with the corresponding IEs in the methylchalcogenopyridines.[18–19] This can be rationalised on the grounds that the n_N MOs are localised on only one ring. The assigned n_N IEs for symmetrical isomers of oxy-,[20–21] thio-,[22–23] and seleno-[24] bispyridines were on an average within ~0.18 eV of the n_N IEs for the corresponding isomers of the methylchalogenopyridines calculated using a ΔSCF/CI model.[18–19] Substitution of the n_N IEs calculated for the corresponding methylthio- and methylselenylpyridines using the ΔSCF/MP2 model for those predicted by the 6-31G** models, giving rise to Model III. The corresponding IE distributions and MO characters based on this adjustment are given in Table II and Table III, respectively.

Figure 4 shows a correlation diagram of the valence IEs for 2,2′-dipyridyl diselenide with those of 2-methylselenylpyridine.[19] Similar diagrams can be generated for the other symmetrical dipyridyl dichalcogenides. Those MOs with appreciable

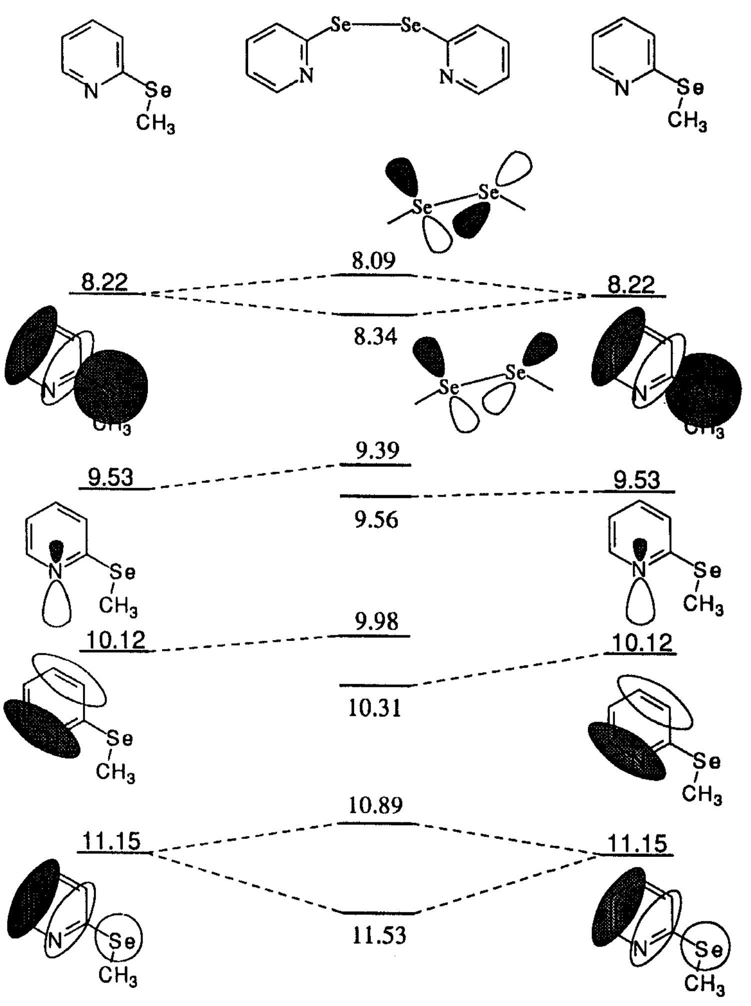

FIGURE 4 Correlation diagram of valence IEs of 2,2′-dipyridyl diselenide with those of 2-methylselenylpyridine.[19]

selenium character will interact across the Se—Se bridge when the dihedral angle deviated from 90°, giving rise to the formation of anti-bonding and bonding combinations. Therefore the anti-bonding ($\pi - n_{\mathrm{Se}}$) and bonding ($\pi + n_{\mathrm{Se}}$) MOs originating from the 2-methylselenylpyridine fragments are expected to couple in this manner. The IEs of the n_N and ring-based π MOs should be independent of this interaction and thus differ little from their 2-methylselenylpyridine values.

Adjusting the position of the n_N MOs (due to the inadequacy of the HF models) the preferred valence IE sequence for the symmetrical isomers of dipyridyl disulfide and diselenide is:

$$(\pi_8 - n_X)^- \geq (\pi_7 - n_X)^+ > n_N \sim n_N > (\pi_6 - \delta n_X) > (\pi_5 - \delta n_X) > (\pi_4 + n_X)^- \geq (\pi_3 + n_X)^+$$

This is contrary to the KA IEs calculated using HF models, but is consistent with He I/He II cross-section ratios, the composite-molecule model and correlations with the methylchalcogenopyridines[18–19] and the chalogenobispyridines.[20–24]

EXPERIMENTAL

The ^1H and ^{13}C nmr spectra were recorded in deuteriochloroform with tetramethylsilane as an internal standard and the ^{77}Se spectra were recorded in carbon tetrachloride with dimethyl selenide as an external standard. Ultraviolet absorption spectra were recorded in ethanol. While 2,2′- and 4,4′-dipyridyl disulfide were obtained as commercial products, 3,3′-dipyridyl disulfide was prepared by a facile method in which the 3-thiocyanatopyridine was warmed with hypophosphorous acid to form pyridine-3-thiol. Aerial oxidation of the thiol gave the disulfide in 79% yield. 2,2′-Dipyridyl diselenide and 4,4′-dipyridyl diselenide were prepared in good yield by the aqueous oxidation of the corresponding pyridine-selenols with hydrogen peroxide.[34,35] 3,3′-Dipyridyl diselenide was prepared by an analogous reaction with the thio analogue. 3-Selenocyanatopyridine was warmed with hypophosphorous acid for 5 hours. Aerial oxidation of pyridine-3-selenol (formed in situ) led to the formation of the diselenide in 89% yield.[33]

2,2′-Dipyridyl Disulfide. 2.2′-Dipyridyl disulfide was obtained from Aldrich and used without further purification. The uv spectrum (in ethanol) λ_{max}: 235.6 nm (log ε = 4.28) and 281.6 (4.07). The ^1H nmr spectrum consisted of δ: 8.40 – 8.46 ppm (*d*, 2H, 6.6′ protons), 7.56 – 7.61 (*m*, 4H, 3,3′,5,5′ protons) and 7.00 – 7.16 (*m*, 2H, 4,4′ protons). The ^{13}C nmr spectrum consisted of δ: 158.7 ppm (2,2′ carbons), 149.4 (6,6′ carbons), 137.3 (4,4′ carbons), 121.1 (3,3′ carbons) and 119.6 (5.5′ carbons).

3,3′-Dipyridyl Disulfide. 3,3′-Dipyridyl disulfide was prepared via a modification of the synthesis of 3,3′-dipyridyl diselenide.[33] 3-Thiocyanatopyridine (5 g, 0.037 moles) and hypophosphorous acid (50%; 60 cm^3) were warmed on a water bath for 5 hours. The pH of the solution was adjusted to ~8 using concentrated aqueous sodium hydroxide and then extracted with chloroform (3 × 100 cm^3). The extract was dried over magnesium sulfate and the solvent evaporated under reduced pressure to yield an orange oil. The oil was chromatographed on an alumina column using hexane as eluent. The resultant oil was vacuum-distilled to afford 3,3′-dipyridyl disulfide as a yellow oil, b.p. 155°C/1.0 mm (3.2g, 79%). The uv spectrum (in ethanol) λ_{max}: 230.8 nm (log ε = 4.15), 243.4 (sh) (4.15) and 274.4 (3.78). The ^1H nmr spectrum consisted of δ: 8.66 – 8.69 ppm (*s*, 2H, 2,2′ protons), 8.45 – 8.52 (*d*, 2H, 6,6′ protons), 7.74 – 7.87 (*m*, 2H, 4,4′ protons) and 7.16 – 7.30 (*m*, 2H, 5,5′ protons). The ^{13}C nmr spectrum consisted of δ: 149.5 ppm (2,2′ carbons), 148.9 (6,6′ carbons), 136.4 (4,4′ carbons), 133.4 (3.3′ carbons) and 123.8 (5,5′ carbons).

4,4′-Dipyridyl Disulfide. 4,4′-Dipyridyl disulfide was obtained from Aldrich and used without further purification. The uv spectrum (in ethanol) λ_{max}: 230.0 nm (log ε = 4.06), 252.0 (4.18) and 288.0 (3.88). The ^1H nmr spectrum consisted of δ: 8.50 – 8.57 ppm (*d*, 4H, 2,2′,6,6′ protons) and 7.20 – 7.27 (*d*, 4H, 3,3′,5,5′ protons). The ^{13}C nmr spectrum consisted of δ: 150.2 ppm (2,2′,6,6′ carbons), 149.7 (4,4′ carbons) and 124.6 (3,3′5,5′ carbons).

2,2′-Dipyridyl Diselenide. 2,2′-Dipyridyl diselenide was prepared using the method of Mautner *et al.*[34] Pyridine-2-selenol (2.38 g, 15 mmol) was dissolved in water (80 cm^3). An aqueous solution of hydrogen peroxide (30%, 0.3 cm^3) was added in one lot. Stirring was continued for 2 hours and then the mixture allowed to stand for 1 hour. A yellow oil separated immediately, which solidified on standing. The diselenide was removed by filtration and recrystallized from petroleum ether (b.p. 40 – 70°C) to give 2,2′-dipyridyl diselenide as long yellow needles (1.54 g, 65%), m.p. 50 – 51.5°C (Lit. 47.5 – 48.0°C[34]). The uv spectrum (in ethanol) λ_{max}: 241.6 nm (log ε = 4.17) and 282.8 (3.90). The ^1H nmr spectrum consisted of δ: 8.42 – 8.47 ppm (*d*, 2H, 6,6′ protons), 7.74 – 7.83 (*d*, 2H, 3,3′ protons), 7.41 – 7.61 (*m*, 2H, 4,4′ protons) and 6.98 – 7.12 (*m*, 2H, 5,5′ protons). The ^{13}C nmr spectrum consisted of δ: 149.5 ppm (6,6′ carbons), 137.3 (4,4′ carbons), 123.6 (3,3′ carbons) and 121.2 (5,5′ carbons). The ^{77}Se nmr spectrum consisted of δ: 439 ppm.

3,3′-Dipyridyl Diselenide. 3,3′-Dipyridyl diselenide was prepared by the method of Dunne *et al.*[33] 3-Selenocyanatopyridine (5 g, 27 mmoles) and hypophosphorous acid (50%, 60 cm^3) were warmed on a water bath. The pH of the solution was adjusted to ~8 using concentrated aqueous sodium hydroxide and then extracted with chloroform (3 × 100 cm^3). The extract was dried with magnesium sulfate and the solvent evaporated under reduced pressure to yield an orange oil. The oil was chromatographed on an alumina column using hexane as eluent. The resultant oil was vacuum-distilled to afford 3,3′-dipyridyl diselenide as an orange oil, b.p. 148°C/0.33 mm (3.76 g, 88%). The uv spectrum (in ethanol) λ_{max}: 239.6 nm (log ε = 4.17) and 275.3 (3.74). The ^1H nmr spectrum consisted of δ: 8.74 ppm (*s*, 2H, 2,2′ protons), 8.46 – 8.53 (*m*, 2H, 6,6′ protons), 7.81 – 7.95 (*m*, 2H, 4,4′ protons), 7.12 – 7.28 (*m*, 2H, 5,5′ protons). The ^{13}C nmr spectrum consisted of δ: 152.5 ppm (2,2′ carbons), 149.2 (6,6′ carbons), 140.0 (4,4′ carbons) and 124.2 (5,5′ carbons). The ^{77}Se nmr spectrum consisted of δ: 453 ppm.

4,4′-Dipyridyl Diselenide. 4,4′-Dipyridyl diselenide was prepared using the method of Wagner and Valz.[35] Pyridine-4-selenol (5.0 g, 32 mmol) was dissolved in water (100 cm^3). An aqueous solution of hydrogen peroxide (30%, 0.7 cm^3) was added in one lot. Stirring was continued for 2 hours and then allowed to stand for 3 hours. A yellow oil separated immediately. The aqueous solution was extracted with benzene (3 × 100 cm^3), the extracts dried over magnesium sulfate and evaporated under reduced pressure to yield a yellow oil. The crude oil was crystallized from petroleum ether (b.p. 40 – 70°C) to give 4,4′-dipyridyl diselenide as bright yellow crystals (3.72 g, 75%), m.p. 108 – 110.5°C (Lit. 110°C[35]). The uv spectrum (in ethanol) λ_{max}: 255.6 nm ($\log \varepsilon = 4.25$), 313.2 (3.12). The ^{1}H nmr spectrum consisted of δ: 8.40 – 8.46 ppm (*d*, 4H, 2.2′,6,6′ protons) and 7.44 – 7.53 (*d*, 4H, 3,3′,5,5′ protons). The ^{13}C nmr spectrum consisted of δ: 150.0 ppm (2,2′,6,6′ carbons) and 124.0 (3,3′,5,5′ carbons). The ^{77}Se nmr spectrum consisted of δ: 406 ppm.

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