Dipole Moment and Helium(I) Photoelectron Spectroscopic Studies of the Conformation of Di-2-pyridyl and Diphenyl Dichalcogenides R_2X_2 (X = S, Se, or Te)

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The dipole moments of di-2-pyridyl dichalcogenides in benzene solution at 25 and 45° and the He^I photoelectron spectra of di-2-pyridyl and diphenyl dichalcogenides R_2X_2 (X = S, Se, or Te) were investigated to obtain information about the conformation of these molecules in solution and in the gas phase. The calculated C–X–X–C dihedral angles (100—110°) for the dipyridyl dichalcogenides, for which $\mu_{calc} = \mu_{exp}$, are at least 10° larger than those for the diphenyl derivatives. These results indicate that the π-interactions between the X atoms and the pyridyl groups are more effective than between the X atoms and the phenyl rings, reducing, as a consequence, repulsion between the lone electron pairs of the chalcogen (X) atoms and lowering the torsional barriers about the X–X bonds. The variation of the dihedral angles between the phenyl derivatives and the corresponding dipyridyl dichalcogenides as derived on the basis of photoelectron spectroscopic data, is in disagreement with the results from dipole moment data. This difference between the gas phase and solution results may be caused by solvent and temperature effects or by secondary interactions between the π and σ orbitals. The dipole moment and photoelectron spectral data indicate that the diaryl dichalcogenides are conformationally flexible with a skew equilibrium conformation and very little interaction between the two aryl groups.

THE conformation of the diphenyl dichalcogenides $(C_6H_5)_2X_2$ (X = S, Se, or Te), were studied earlier by dipole moment [1,2] and n.m.r. spectroscopic methods.[3] In order to elucidate the dependence of the conformational characteristics of diaryl dichalcogenides on the aryl groups with special attention to the C–X–X–C torsion angles and the electronic structures of the dichalcogenide groups, a study of the di-2-pyridyl dichalcogenides, Py_2X_2 (Py = 2-pyridyl, X = S, Se, or Te) has been undertaken. The conformations of di-2-pyridyl disulphide in solution [4-6] and in the solid state [7] are known. Structural and conformational information about the analogous selenium and tellurium compounds is not available. In this study the electrical dipole moments of Py_2Se_2 and Py_2Te_2 were measured in benzene at 25 and 45° to elucidate the conformations of these molecules in solution.

He^I Photoelectron spectroscopy is a useful tool to probe the conformational preferences of dichalcogenides in the gas phase. Several investigations of compounds of the general formula R–X–X–R (X = As, N, O, P, S, or Se) [8-11] established that the splitting of the first photoelectron band is determined by the dihedral angle between the lone electron pairs of the X atoms. The diphenyl dichalcogenides and di-2-pyridyl dichalcogenides were studied by He^I photoelectron spectroscopy. The differences between the conformations of the gaseous and dissolved molecules are briefly discussed.

EXPERIMENTAL

Diphenyl dichalcogenides and di-2-pyridyl disulphide were available from previous studies.[1,3-6]

Di-2-pyridyl Diselenide.—Selenium (3.0 g, 0.038 mol) was suspended in ethylene glycol monomethyl ether (150 ml). Sodium borohydride (1.0 g, 0.027 mol) was added to the suspension kept under nitrogen and chilled in an ice–water bath.[12] After the initial reaction had subsided, the mixture was refluxed for 1.5 h. 2-Bromopyridine (4.1 g, 0.026 mol) was then added. The mixture was refluxed (*ca.* 7 h) until t.l.c. showed that most of the bromopyridine had reacted. The solution was cooled to room temperature and then extracted with chloroform. The separated chloroform layer was washed with water. Evaporation of chloroform produced a residue which was dissolved in hot hexane. Ethanol was added until crystallization began. On cooling yellow crystals (2.8 g) separated and these were recrystallized from hot hexane. Yellow needle-like crystals of di-2-pyridyl diselenide (1.6 g, 40% based on bromopyridine) melted at 47.5—48.5° (lit.,[13] 47.5—48.0°).

2-Pyridylmagnesium Bromide.—Magnesium (5.1 g, 0.21 mol) was added to a solution of ethyl bromide (1.2 g, 0.01 mol) in tetrahydrofuran (20 ml) kept under nitrogen. After the initial reaction had subsided, a solution of 2-bromopyridine (16.0 g, 0.10 mol) and ethyl bromide (5.0 g, 0.046 mol) in tetrahydrofuran (100 ml) was dropped on the magnesium turnings. After all the bromopyridine had been added, the mixture was refluxed for 4.5 h.

Di-2-pyridyl Ditelluride.—The ditelluride was prepared according to the procedure reported by Haller and Irgolic.[14] The Grignard reagent described above was transferred into an Erlenmeyer flask. Tellurium (7.5 g, 0.059 mol) was added. The mixture was heated gently for 20 min and then cooled in an ice–water bath. The flask was then closed with a rubber stopper into which a glass tube provided with a stopcock and connected to a balloon containing 0.5 l of oxygen was inserted. Oxygen was admitted to the flask every other minute by turning the stopcock. After all the oxygen had been consumed, the mixture was warmed to room temperature and stirred for 1.5 h. The dark red solution was poured into a large beaker kept in the hood to

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allow the solvent to evaporate. The residue was treated with a saturated, aqueous solution of ammonium chloride. The dipyridyl ditelluride was extracted with methylene chloride (3 × 70 ml). The combined extracts were evaporated to dryness. The residue was recrystallized from methanol–water (12 : 1 v/v). The dark red crystals of di-2-pyridyl ditelluride (1.4 g, 12% based on Te) melted at 50.0—51.5°. This preparation of dipyridyl ditelluride is difficult to reproduce (Found: C, 29.45; H, 1.95. $C_{10}H_8N_2Te_2$ requires C, 29.2; H, 1.95%).

Dipole Moment Measurements.—The electric dipole moments of Py_2Se_2 and Py_2Te_2 were determined in benzene at 25 and 45° (±0.01°) using apparatus and techniques described earlier.[15] Experimental dipole moment values were calculated from the total solute polarization, obtained by extrapolation to infinite dilution ($P_{2\infty}$) according to the Halverstadt–Kumler method,[16] and from the molar refraction (R_D, Na_D line), which was considered to be equal to the electronic and atomic polarizations ($P_e + P_a$). The dipole moment values μ(accuracy ±0.02 D) and the polarization data are reported in Table 1.

TABLE 1

Polarization data * for and dipole moments of di-2-pyridyl dichalcogenides, Py_2X_2 ($X = Se,Te$)† determined in benzene solution at 25 and 45°

Compound	t/°C	α	β	ε_{10}	v_{10}	$P_{2\infty}$/cm³	R_D/cm³	μ/D
Py_2Se_2	25	5.20	−0.582	2.2725	1.143 28	359.4	69.8	3.76
	45	4.69	−0.629	2.2328	1.168 70	337.6	69.8	3.74
Py_2Te_2	25	3.45	−0.619	2.2723	1.142 66	330.6	78.5	3.51
	45	3.05	−0.978	2.2325	1.168 49	268.3	78.5	3.14

* For definition of the symbols see ref. 2. † Data for Py_2S_2 are reported in ref. 4.

He^I *Photoelectron Spectra.*—The photoelectron spectra of diphenyl and di-2-pyridyl dichalcogenides were recorded on a Perkin-Elmer PS18 photoelectron spectrometer calibrated against the Xe and Ar lines. The reproducibility of the ionization energies (I.E.) was better than ±0.05 eV. The samples were sublimed inside the reaction chamber, at the lowest temperatures at which sufficiently intense signals could be obtained (Ph_2S_2 60°; Ph_2Se_2 60°; Ph_2Te_2 110°; Py_2S_2 120°; Py_2Se_2 120°; Py_2Te_2 130°). The dipyridyl dichalcogenides decomposed partially at these temperatures. The bands caused by the decomposition products occurred at energies above 12 eV and did not influence the low energy bands on which the discussion is based.

RESULTS AND DISCUSSION

Dipole Moments.—The experimental dipole moments (μ_{exp}) for Py_2Se_2 and Py_2Te_2 were analysed by the classical vector addition method of component group moments. Free rotation about the C–X bonds and a fixed skew conformation about the X–X bond characterized by a dihedral angle ϕ was assumed (Figure 1). Free rotation implies that all possible rotational conformations about the C–X bonds are equally populated on the dipole moment time scale at 25 and 45°. These assumptions are based on results of conformational studies of di-2-pyridyl disulphide.[4,6] The dihedral angles ϕ were obtained by matching calculated dipole moments, μ_{calc}, with experimental dipole moments, μ_{exp}. Relation (1) was employed[4] to find μ_{calc}. Equations (2)—(4) define

$$\mu_{calc} = (2\mu_1^2 + 2\mu_1^2 \cos\alpha \cos\omega)^{\frac{1}{2}} \qquad (1)$$

$$\mu = (\mu_{Py}^2 + \mu_{Py-X}^2 - 2\mu_{Py}\mu_{Py-X}\cos 120°)^{\frac{1}{2}} \qquad (2)$$

μ_1, α and ω.[17] The geometric parameter θ, the valency angle at the X atom, was taken from *X*-ray crystal structures of the diphenyl dichalcogenides Ph_2X_2 (106°

$$\sin\alpha = \mu_{Py}\sin 120°/\mu_1 \qquad (3)$$

$$\omega = 2\arcsin[\cos^2(\theta - 90)\sin^2\phi/2 + \sin^2(\theta - 90)]^{\frac{1}{2}} \qquad (4)$$

for X = Se;[18] 99° for X = Te[19]). The value of 2.20 D was used as the component group moment of pyridine, μ_{Py}.[20] The C–X bond moments, μ_{Py-Se} 1.25 D[1] and $\mu_{Py-Te} = 0.89$ D,[2] were calculated earlier.

The calculated dihedral angles ϕ for which $\mu_{calc} = \mu_{exp}$ are listed in Table 2, which also contains the corresponding angles for diphenyl dichalcogenides for comparison purposes. These results indicate that the dihedral angles for the dipyridyl dichalcogenides are considerably larger than those found for the diphenyl derivatives. If one makes the assumption, justified by the values for the C–X–X bond angles, that the C–X–X–C σ bonds are formed using *p* orbitals on the chalcogen atoms with their electron pairs in the *ns* orbitals stereo-

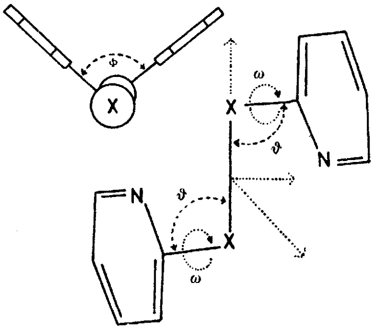

FIGURE 1 Geometrical parameters of di-(2-pyridyl) dichalcogenides

TABLE 2

Dihedral angles ϕ for diaryl dichalcogenides Py_2X_2 and Ph_2X_2 ($X = S, Se, Te$) in benzene at 25° as derived from dipole moment measurements

X	C–X–X–C Dihedral angle ϕ (°) Ph_2X_2		C–X–X–C Dihedral angle ϕ (°) Py_2X_2	
S	88.9[a]	(∼90[b]) *	100[e]	(87[g]) *
Se	74.7[a]	(97.1[c]) *	107[f]	
Te	89.7[a]	(88.5[d]) *	110[f]	

* Dihedral angles determined by *X*-ray structure analysis. [a] Ref. 1. [b] Ref. 21. [c] Ref. 18. [d] Ref. 19. [e] Calculated from data in ref. 4. [f] Present work. [g] Ref. 7.

chemically inactive, then the conformation with dihedral angles of 90° between the two lone *p* electron pairs on the chalcogen atoms and the C–X groups would minimize lone pair–lone pair repulsion. The dihedral angles ϕ in the pyridine derivatives (100—110°) could be the result of more effective π-interaction between the lone electron pairs and the pyridine rings than possible in the diphenyl dichalcogenides resulting in reduced repulsion between the lone electron pairs.[1,2,5,6] The dihedral angles for dipyridyl dichalcogenides increased in the sequence S < Se < Te pointing toward a decrease of lone electron pair repulsions with increasing X–X bond length and decreasing X–X bond strength. The torsional barriers about the X–X bonds are expected to decrease on going from the disulphide to the ditelluride. Although the dipole moments for Py_2S_2 and Py_2Se_2 are temperature-independent in the range 25—45°, the dipole moment of dipyridyl ditelluride at 45° (3.14 D) is smaller than the moment at 25° (3.51 D) (Table 1). This temperature dependence can be attributed to a low torsional barrier around the Te–Te bond permitting the population of conformers having dihedral angles larger than the one observed at 25° to increase.

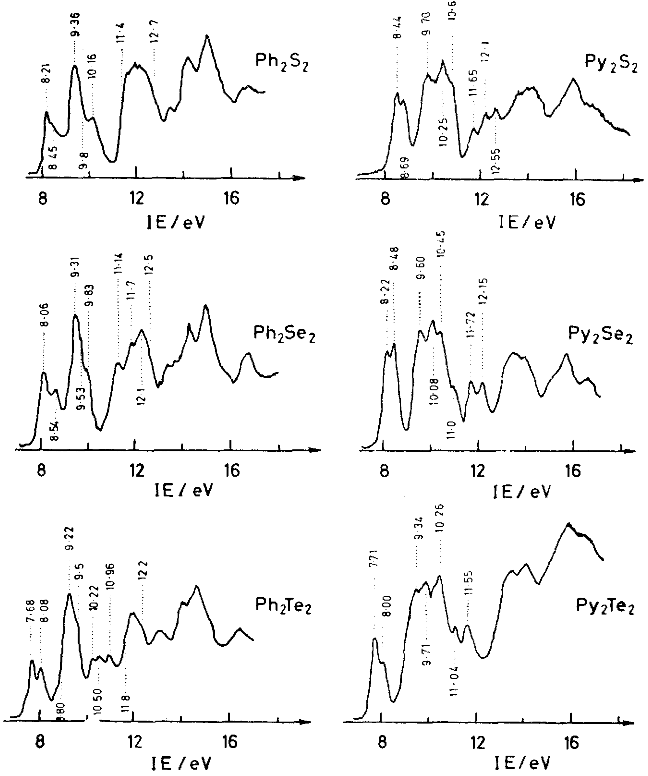

FIGURE 2 He^{I} Photoelectron spectra of diphenyl and di-2-pyridyl dichalcogenides

Photoelectron (*p.e.*) *Spectra*.—Eight bands of formal π origin are expected to be part of the low ionization energy (I.E.) region (<13 eV) of the spectra of diphenyl and di-2-pyridyl dichalcogenides. Overlap of some of these bands and an intermingling of σ-photoprocesses account for the apparent low resolution and complexity of the spectra* (Figure 2). This fact at present prevents an unambiguous assignment of the spectra of the di-2-pyridyl dichalcogenides, apart from the first partially split band.

On the basis of qualitative steric and electronic arguments, the π-ionizations are anticipated to form four pairs of nearly degenerate components associated with possible combinations between the dichalcogen π-lone pairs and the π-ring orbitals of formal b_1 symmetry and the non-interacting π-ring orbitals of a_2 symmetry. Partial assignment of the bands may be made on a correlative basis by reference to the spectra of methyl phenyl chalcogenides,[9a] dimethyl dichalcogenides,[9b] and pyridine.[22] The assignments for the σ-bands must be regarded as tentative (Table 3).

The assignments summarized in Table **3** are in part supported by results of π-only semiempirical calculations. There exists a fairly good linear correlation (*r* 0.999; s.d. 0.08 eV) between the calculated SCF-PPP orbital energies ε_j and the observed I.E. values of the $PhXCH_3$ compounds[9a] [equation (5)]. Because diphenyl dichalcogenides are closely related to methyl phenyl

$$\text{I.E.}_j = -1.010\,6\ \varepsilon_j - 1.543\,4 \qquad (5)$$

chalcogenides, equation (5) might also hold for the diphenyl derivatives. The theoretical † π-I.E. values for diphenyl dichalcogenides are reported in Table **3** together with the observed I.E. values and the proposed assignments.

Interesting features of the spectra of the diphenyl dichalcogenides are the modest splittings of the π_{XX} ionization bands (I)—(II) and (V)—(VI) (Table 3) and the similarity of their average values to the corresponding ionization energies in the $PhXCH_3$ compounds.[9a] Thus, very little interaction takes place between the two phenyl groups through the dichalcogen bridge. The splittings between the π-ring (asymmetric or non-interacting) MOs (III)—(IV) and the π_{XX} (s) MOs (V)—(VI) are good indicators of conformational preferences in the gas phase. Other factors remaining constant, the interaction and thus the energy gap between two orbitals, depend crucially on their mutual orientation and reach a maximum in a coplanar arrangement. Because both the splittings of these I.E.s [Δ 0.80 (S), 0.52 (Se), 0.28 eV (Te)] and their absolute values are very similar to those reported for the planar conformation of the $PhXCH_3$ systems[9a] [Δ 0.85 (S), 0.60 (Se), 0.25 eV (Te)], one can infer that the combination of two PhX moieties to give Ph_2X_2 will cause only a trivial alteration in the interaction between the chalcogen π-lone pair and π-ring

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* In addition to the two ionizations from the nitrogen lone electron pair in Py_2X_2 expected to occur between 9 and 10 eV, in both series some σ ionizations are expected at *ca*. 9, 9.5, and 10 eV for the Te, Se, and S derivatives, respectively.

† The calculations were carried out using the Fabian parametrization[23] with values of −1.2 and −0.3 eV for β(C–Te) and β(X–X), respectively. Experimentally determined structural parameters with the aryl groups in the C–X–X planes were used.

orbitals and hence will not change the conformation of each PhX fragment.

TABLE 3

Experimental and calculated ionization energies (eV) for diphenyl dichalcogenides Ph_2X_2

Band [a]	X = S		X = Se		X = Te		Assignment [b]
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
(I)	8.21	8.12	8.06	7.87	7.68	7.34	
							π_{XX}(a)
(II)	8.45	8.37	8.54	8.23	8.08	7.80	
					8.8		σ(Te)
(III)		9.14		9.14		9.14	
	9.36		9.31		9.22		π-ring
(IV)		9.14		9.14		9.14	
	(9.8)		9.53				σ(X)
(V)		10.13		9.76		9.46	
	10.16		9.83		9.50		π_{XX}(s)
(VI)		10.42		9.97		9.57	
	11.4 [c]		11.14		10.22		
							σ
					10.50		
			11.7		10.96		σ
			12.1				σ
					11.8 [c]		
(VII)		12.29		12.20		12.15	
	12.7		12.5		12.2		π-ring
(VIII)		12.33		12.22		12.16	

[a] The numbers refer to bands arising from π-photoprocesses. [b] π_{XX}(a) and π_{XX}(s) denote orbitals of prevailing dichalcogen character corresponding to antibonding and bonding combinations with the ring orbitals, whereas π-ring denotes ring orbitals. [c] Broad band (see Figure 2) extending from the lower to the higher figure reported.

As a supplement of conformational information the splittings of the I.E.s (I) and (II) can be considered (Table 4). The near equality of ΔI.E. (I)−(II) for Ph_2S_2 and Py_2S_2 in the gas phase can be regarded as evidence for similar C–X–X–C dihedral angles as well as for similar angles between the lone electron pairs on the two chalcogen atoms. This close similarity of the dihedral angles is at variance with the results of dipole moment measurements, which suggest a larger dihedral angle in Py_2S_2 than in Ph_2S_2. The increase of ΔI.E. (I)−(II) from Py_2Se_2 to Ph_2Se_2 is consistent with a decrease in the dihedral angles for these compounds in solution. For the tellurium derivatives the p.e. data suggest that Py_2Te_2 should have a dihedral angle closer to 90° than Ph_2Te_2. In solution the opposite trend was found.

TABLE 4

Average values of the first two I.E.'s, $\overline{\text{I.E.}}$(I) − (II) and their splittings ΔI.E.(I) − (II) (eV) for diphenyl and di-2-pyridyl dichalcogenides

Compound	Ph_2X_2		Py_2X_2	
X	$\overline{\text{I.E.}}$(I) −(II)	ΔI.E.(I) −(II)	I.E.(I) −(II)	ΔI.E.(I) −(II)
S	8.33	0.24	8.57	0.25
Se	8.30	0.48	8.35	0.26
Se	8.23 [a]	0.55 [a]		
Te	7.88	0.44	7.85	0.29

[a] Taken from ref. 9*b*.

The conclusions concerning the dihedral angles in Ph_2X_2 and Py_2X_2 drawn from p.e. data obtained in the gas phase and from dipole moment measurements on the dissolved dichalcogenides do not agree. The differences can be attributed to perturbation by the solvent and temperature effects (dipole moments 25°; p.e. spectra 60—130°). In addition, when deriving conformational information from p.e. data the possibility of secondary interactions between π- and σ-orbitals cannot be neglected.[24] Accordingly, conformational information based on p.e. data should be considered with caution. However, dipole moment analyses of the compounds in solution and p.e. data obtained in the gas phase agree that Ph_2X_2 and Py_2X_2 are conformationally flexible molecules which assume a skew equilibrium conformation. Very little information is transmitted by the X–X bridge between the two aromatic groups in a diaryl dichalcogenide molecule.

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