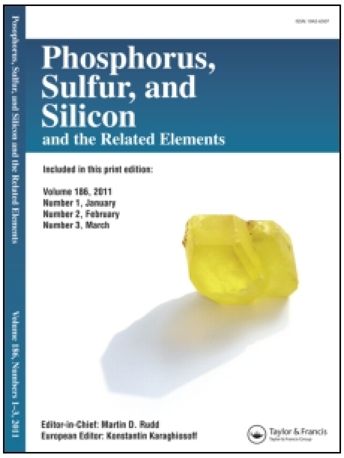

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DIPOLE MOMENTS AND HELIUM(I) PHOTOELECTRON SPECTROSCOPIC STUDIES OF THE CONFORMATIONS OF THIOSELENANTHRENE, THIOTELLURANTHRENE, AND SELENOTELLURANTHRENE

Giuseppe Distefano[a]; Vinicio Galasso[b]; T. Junk[c]; Kurtj Irgolic[c]; Giuseppe C. Pappalardo[d]
[a] Istituto Chimico, Universite di Ferrara, Ferrara, Italy [b] Dipartimento di Scienze Chimiche, Universita di Trieste, Trieste, Italy [c] Department of Chemistry, Texas A&M University, College Station, Texas, U.S.A. [d] Dipartimento, Scienze Chimiche, II Cattedra di Chimica Generale, Facolta di Farmacia, Universita di Catania, Catania, Italy

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DIPOLE MOMENTS AND HELIUM(I) PHOTOELECTRON SPECTROSCOPIC STUDIES OF THE CONFORMATIONS OF THIOSELENANTHRENE, THIOTELLURANTHRENE, AND SELENOTELLURANTHRENE

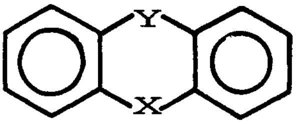
GIUSEPPE DISTEFANO, VINICIO GALASSO*, T. JUNK**, KURT J. IRGOLIC** AND GIUSEPPE C. PAPPALARDO***

Istituto Chimico, Universite di Ferrara, Via L. Borsari 46, I-44100 Ferrara, Italy; *Dipartimento di Scienze Chimiche, Universita di Trieste, I-34127 Trieste, Italy; **Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.; ***Dipartimento di Scienze Chimiche, II Cattedra di Chimica Generale, Facolta di Farmacia, Universita di Catania, Viale A. Doria 8, I-95125 Catania, Italy.

The dipole moments of thioselenanthrene (1.44 D), thiotelluranthrene (1.37 D), and selenotelluranthrene (1.25 D) were determined in benzene at 30°. The angles of fold along the chalcogen axis were calculated from the dipole moments. All three molecules adopt a butterfly conformation in solution with angles of fold of approximately 134°. The He(I) photoelectron spectra show six π-bands and one σ-band in the energy region below 11 eV. These bands were assigned with the aid of π-only semi-empirical calculations (SCF-PPP). The spectroscopic data indicate, that these molecules are folded in the gas phase.

INTRODUCTION

A systematic investigation of the conformations and electronic structures of 5,10-dihydro-5,10-dichalcogenaanthracenes **1** (chalcanthrenes) was begun in our laboratories with studies on 5,10-dihydro-5-oxa-10-chalcogenaanthracenes **1** (X = O; Y = O, S, Se, Te)[1] and homonuclear chalcanthrenes **2** (Z = 0, S, Se, Te).[2] Thioselenanthrene **1** (X = S, Y = Se), thiotelluranthrene **1** (X = S, Y = Te), and selenotelluranthrene **1** (X = Se, Y = Te), the heteroatomic chalcanthrenes containing the heavier group VI atoms, have recently become available in sufficient quantities to complete conformational and electronic studies of this type of tricyclic compounds. This paper reports the results of dipole moment measurements and photoelectron (pe) spectroscopic investigations of thioselenanthrene, thiotelluranthrene, and selenotelluranthrene.



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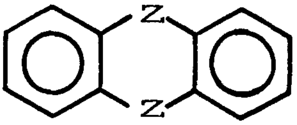

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EXPERIMENTAL

Thioselenanthrene (mp. 165°)[3], thiotelluranthrene (mp. 122°)[4], and selenotelluranthrene (mp. 138-140°)[3] were prepared according to literature procedures. The electric dipole moments were measured in benzene solutions at 30° ± 0.01° as described earlier[5]. The Halverstadt-Kumler method[6] was used to calculate dipole moments from total solute polarizations ($P_{2\infty}$, obtained by extrapolation to infinite dilution) and from molar refractions (R_D, Na_D line, taken as the sum of electronic and atomic polarization, $P_E + P_A$). The estimated error in the dipole moments is ±0.02 D.

Photoelectron spectra were recorded on a Perkin-Elmer PS18 spectrometer. The He(I) resonance line at 58.4 nm (21.21 eV) was used for ionization. The spectra were calibrated against Ar and Xe lines. The estimated error in the ionization energies is ±0.05 eV.

The π-orbital energies of the chalcanthrenes were obtained using SCF-PPP calculations and the parametrization of Fabian et al.[7] with a value of −1.2 eV for β(Te-C). The Mataga-Nishimoto formula[8] was used for the two-center electron repulsion integrals. Geometric parameters for the chalcanthrenes were taken from X-ray structures[9] and the dipole moment analyses.

RESULTS AND DISCUSSION

Dipole Moments

The results of dipole moment measurements on chalcanthrenes 1 (X,Y: Se,Se; S,Te; Se,Te) in benzene solutions are presented in Table I. The dipole moments were analyzed in terms of the angles between the component moments by vector addition of the component moments. This procedure provides estimates of the angles of fold *Φ* about the X-Y axis of the chalcanthrenes 1 (Fig 1) in the solution state. The values for the angles ϑ, the angles between the directions of the assumed component group moments [$\mu(Ph_2S) = 1.55$ D[11], $\mu(Ph_2Se) = 1.50$ D[12], $\mu(Ph_2Te) = 1.14$ D[13]] were calculated from the experimental dipole moments of the chalcanthrenes [μ(Ch)] (eqn. 1). The moments $\mu(Ph_2X)$ and $\mu(Ph_2Y)$ that lie on the bisectors of the angles C-X-C and C-Y-C (Fig. 1) act toward the

TABLE I Polarization data and dipole moments for chalcanthrenes 1 determined in benzene solutions at 30°.

Chalcanthrene 1 X	 Y	α*	β*	$P_{2\infty}$ cm3	R_D cm3	μ Debye
S	Se	1.28	-0.515	113.6	72.0	1.44
S	Te	1.07	-0.601	114.2	76.2	1.37
Se	Te	0.86	-0.667	110.1	78.8	1.25

*Symbols are defined in refs. 5,10

$$\cos\vartheta = \frac{\mu(Ch)^2 - \mu(Ph_2X)^2 - \mu(Ph_2Y)^2}{2\mu(Ph_2X)\mu(Ph_2Y)} \qquad (1)$$

heteroatoms X and Y, respectively. The angles of fold *Φ* were then obtained by solving eqns. 2, 3, and 4. The equations were derived from geometrical relationships for the molecule shown in Fig. 1, with the restriction that $\alpha + \beta = 180 - \vartheta$ in the triangle XOY. The angles ϑ, ∂ and ϵ were taken from the X-ray structures of the chalcanthrenes (refs. given in Table III). The calculated angles of fold for the chalcanthrenes **I** in solution, the experimental angles of fold in the solid state,

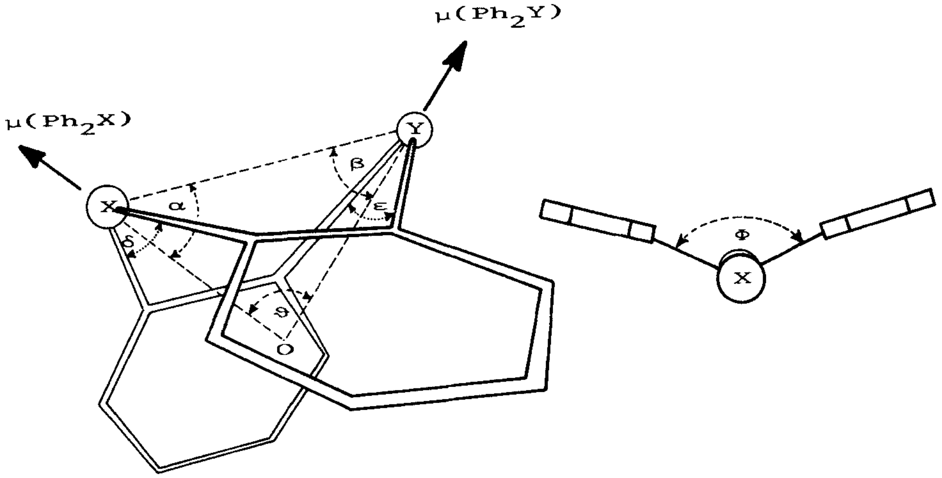

FIGURE 1: Perspective view of a molecular model for chalcanthrenes. The triangle XYO (angles α,β,ϑ) is determined by the line connecting X with Y and the bisectors of the bond angles C-Y-C(ϵ) and C-X-C(∂). The component dipole moments have the directions of the bisectors of ϵ and ∂. The plane of the triangle XYO bisects the angle of fold Φ.

and the angles ϑ between the direction of the group-moment vectors are listed in Table II. The angles were obtained from the dipole moments and also calculated from the bond lengths and bond angles determined by X-ray crystallography. The mixed chalcanthrenes **I** (X,Y: S,Se; S,Te; Se,Te) form unfortunately disordered crystals with unequal occupancies of the chalcogen sites. Because

$$\frac{\mathrm{tang}^2 \frac{\partial}{2}}{\cos^2 \frac{\varepsilon}{2}} - \frac{\mathrm{tang}^2 \frac{\varepsilon}{2}}{\cos^2 \frac{\partial}{2}} = \mathrm{tang}^2 \frac{\partial}{2} \cos^2\beta - \mathrm{tang}^2 \frac{\varepsilon}{2} \cos^2\alpha \tag{2}$$

$$\cos^2\alpha = \frac{1}{\cos^2 \frac{\partial}{2}} - \frac{\mathrm{tang}^2 \frac{\partial}{2}}{\cos^2(90 - \frac{\Phi}{2})} \tag{3}$$

$$\cos^2\beta = \frac{1}{\cos^2 \frac{\varepsilon}{2}} - \frac{\mathrm{tang}^2 \frac{\varepsilon}{2}}{\cos^2(90 - \frac{\Phi}{2})} \tag{4}$$

of this disorder only average values for the bond angles and bond distances are available for these compounds in the solid state.[9]

Table II Angles of fold Φ along the X-Y axis and angles ϑ between the directions of the group moments for thioselenanthrene, thiotelluranthrene, and selenotelluranthrene in benzene solutions at 30° (from dipole moments) and in the solid state (from X-ray data).

Compound		Angles of Fold, Φ		Angles ϑ	
X	Y	soln.	solid	soln.	solid
S	Se	135.0	123.7	123.7	104
S	Te	133.3	120.2	121.1	103.9
Se	Te	134.0	119.9	125.5	99.4

The results of the dipole moment analysis indicate, that the chalcanthrenes **1** adopt in solution a folded conformation, in which the angles of fold Φ for the center-ring are approximately 12 degrees larger than the corresponding angles in the solid state. Larger angles of fold in solution than in the solid state were also found[2] for homoatomic chalcanthrenes **2**. The smaller angles in the solid can be attributed to packing forces in the crystals. The angles of fold Φ for the heavy heteroatomic chalcanthrenes **1** in solution are very similar (S, Se 135°; S,Te 133°; Se,Te 134°), whereas the corresponding angles for the homoatomic chalcanthrenes **2** decrease with increasing atomic mass of the chalcogen atom from 164° for dioxin to 125° for telluranthrene (Table III).

TABLE III Angles of fold Φ for all possible chalcanthrenes of the formula $C_{12}H_8XY$ (X = Y, X ≠ Y) in solution and in the solid state*

X	Y	Φ(soln)	Φ(solid)	X	Y	Φ(soln)	Φ(solid)
O	O	164 [1]	180 [14]	S	O	163	141
O	S	163 [1]	141 [15]	S	S	142 [2]	128 [17]
O	Se	163 [1]	140 [9]	S	Se	135†	124 [9]
O	Te	172 [1]	138 [16]	S	Te	133†	120 [9]
Se	O	163	140	Te	O	172	138
Se	S	135	124	Te	S	133	120
Se	Se	139	123	Te	Se	134	120
Se	Te	134†	120 [9]	Te	Te	125	120 [9]
O	O	164	180				
S	S	142	128				
Se	Se	139	123 [19]				
Te	Te	125 [2]	120				

*Numbers in brackets are references

†This paper

All the chalcanthrenes are folded in solution. In the solid state they are also folded along the X-Y axis except dibenzodioxin, which was found to be planar.[14] The presence of one oxygen atom in the central ring of the chalcanthrenes flattens the molecules of the phenoxachalcogenins in solution. The angles of fold found by dipole moment analysis are in the range of 163° to 172°, whereas the corresponding angles in the solid state are approximately 140°. Although a detailed explanation of the magnitude of the angles of fold cannot be given, the angles are determined by π-interactions between the aromatic rings and the heteroatoms and geometric (steric) factors associated with the bond angles at the heteroatoms and the heteroatom-carbon bond lengths. A planar chalcanthrene ring system requires a C-X-C angle of 120°. Bond angles tend toward 90° as the atomic masses of elements in group VI increase. Angles much smaller than 120° can only be accomodated in a folded structure. Differences in C-X and C-Y bond lengths in heteroatomic chalcanthrenes will also favor a folded conformation that prevents bond-angle strains present in a planar molecule.

Overlap between π-orbitals on the aromatic rings and on the heteroatom is maximal in a planar conformation. Such overlap weakens as the orbitals in the heavier chalcogenides become diffuse. Among the ten chalcanthrenes the π-overlap dominates only in the dibenzodioxin molecule that is planar in the solid state. The energy difference between the planar and folded conformation in dioxin is probably small, because the molecule adopts a folded conformation in solution[1]. The conformations of all the other chalcanthrenes are largely determined by geometric factors. Detailed, reliable calculation for these systems with heavy atoms cannot yet be carried out.

Photoelectron Spectra

On the basis of qualitative steric and electronic arguments and assignments of bands in the pe spectra of related molecules [phenyl methyl chalcogenides[20], bis(methylchalcogeno)benzenes[20], phenoxachalcogenins[1], homoatomic chalcanthrenes[2]] six π-bands and at least one σ-band are expected to be present in the low ionization energy (IE) region (IE < 11 eV) of the pe spectra of thioselenanthrene, thiotelluranthrene, and selenotelluranthrene. All of the expected bands were found (Fig. 2). The molecular orbitals (MO) in these chalcanthrenes are formed through symmetry-allowed interactions between the in-phase Π_{XY} and Π_{XY} combinations of the p_π-lone pair orbitals of the heteroatoms with appropriate combinations of the π-ring orbitals of the aromatic groups and by the non-interacting π-ring orbitals of symmetry a_2 and b_2. For simplicity the C_{2v} point group symbols are used. Electron ejection from an outermost σ-MO of predominant chalcogen character is responsible for one σ-band (IE_7) in the energy region. The first two bands below 9 eV, IE_1 and IE_2, are mainly Π_{XY} in nature. The nearly degenerate IE_3 and IE_4 ($\sim$ 9.3 eV) are associated with π-ring MOs with no involvement of the chalcogen p_π-orbitals.

These empirical assignments are in part supported by results of π-only semi-empirical calculations. A fair linear correlation (r = 0.986) exists between the calculated SCF-PPP energies of the first highest occupied π-MOs and the experimental IEs (eqn. 5). The calculated and experimental IE values

$$IE_{exp} = -0.7771\ IE_{calc} + 0.8962 \quad (eV) \qquad (5)$$

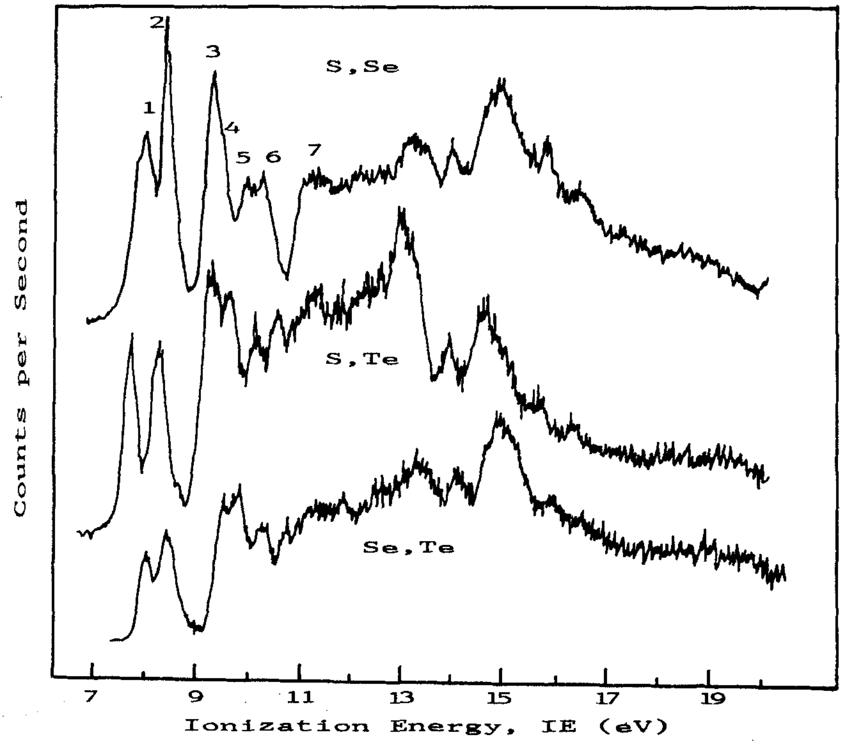

FIGURE 2: The He(I) photoelectron spectra of thioselenanthrene, thiotelluranthrene and selenotelluranthrene.

are listed in Table IV. The average values of the ionization energies, IE, for the first two π-IEs and their splittings Δ are presented in Table V for homoatomic and heteroatomic chalcanthrenes. In contrast to the homoatomic chalcanthrenes, the heteroatomic chalcanthrenes have smaller and almost equal angles of fold Φ (Table III). On the basis of literature data for chalcophenes[20] and related compounds[21], the HOMOs of the chalcanthrenes are expected to become progressively destabilized with increasing atomic mass of the heteroatom. This expected trend toward lower IEs with increasing mass is confirmed by the data in Table V.

Table IV Experimental and calculated ionization energies* (IE,eV) for heteroatomic chalcanthrenes

IE	Chalcanthrene, $C_{12}H_8XY$			Assignment**
	S, Se	S, Te	Se, Te	
1	7.93 (7.85)	7.70 (7.60)	7.67 (7.64)	π_{XY}^{+} (a_1)
2	8.32 (8.53)	8.25 (8.50)	8.07 (8.34)	π_{xy}^{-} (b_1)
3	9.27 (9.02)	9.23 (9.11)	9.21 (9.00)	π_R (b_2)
4	9.45 (9.47)	9.40 (9.31)	9.50 (9.51)	π_R (a_2)
5	9.97 (9.91)	9.60 (9.58)	9.50 (9.48)	π_{xy}^{-} (a_1)
6	10.27 (10.33)	10.15 (10.18)	9.99 (10.10)	π_{xy}^{+} (b_1)
7	11.2	10.55	10.4	

* calculated values in parentheses;

** π_{XY}: orbital of predominant chalcogen character; π_R: ring orbital

The close similarity of the HOMO energies of the chalcanthrenes to those of the corresponding methyl phenyl chalcogenides[21] is indicative of folded conformations for the heteroatomic chalcanthrenes in the gas phase. The high relative intensity and the small full-width at half-height of band 2 of the pe spectrum of thioselenanthrene (Fig. 2) suggests a limited bonding character for the parent MO, which cannot mix in a planar system with any other MO because

Table V Average ionization energies, IE, and splittings, Δ, for the first two π-IEs (eV).

Chalcanthrene X	Chalcanthrene Y	IE	Δ
S	S*	8.19	0.49
Se	Se*	8.05	0.25
Te	Te*	7.62	0.20
S	Se	8.12	0.39
S	Te	7.97	0.55
Se	Te	7.87	0.40

* from ref. 2.

of restrictions imposed by symmetry. Band 2 in the spectra of thiotelluranthrene and selenotelluranthrene do not possess the characteristics of band 2 for thioselenanthrene. This difference between heavy and lighter chalcanthrenes also observed for the homoatomic chalcanthrenes[2] may be caused by through-space destabilizing interactions between Π_X orbitals, which are more diffuse in the heavier chalcogen atoms.

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