

A Dipole Moment and Helium(I) Photoelectron Spectroscopic Study of the Conformations of Chalcanthrenes

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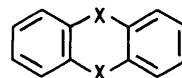
The dipole moments (μ) of thianthrene, selenanthrene, and telluranthrene in benzene solution at 25° and the He^I photoelectron spectra of all four chalcanthrenes were investigated to obtain information about the conformation of these molecules in solution and in the gas phase. The calculated angles of fold along the chalcogen–chalcogen axes, for which $\mu_{\text{calc.}} = \mu_{\text{exp.}}$, are 163.8° (O), 142.4° (S), 139.0° (Se), and 124.6° (Te). These angles are appreciably larger than the solid-state values reported for these molecules and some of their perfluoro-derivatives. These larger values are probably caused by butterfly motions of the tricyclic molecules, for which the barrier is expected to be small in solution. The photoelectron spectra show the expected six π -bands and one σ -band in the low ionization region. The empirical assignments of these bands are supported by results of π -only semi-empirical calculations (SCF-PPP). The trends in the average values of the first two ionization energies and their energy differences in this series of chalcanthrenes indicate that these molecules adopt a folded conformation in the gas phase also.

The angle of fold Φ along the O \cdots O axis in dibenzo-*p*-dioxin (1) (X = O) was determined to be 163.8° in benzene solution in an earlier study of phenoxachalcogenins¹ employing dipole moment measurements and u.v. and photoelectron spectroscopic techniques. This value is in good agreement with the angle of 165.6° found recently using the nematic liquid crystal n.m.r. method.² Our continued interest in the solution conformations and electronic structures of organic chalcogen compounds and of tricyclic systems in particular led to a systematic investigation of chalcanthrenes (1) (X = O, S, Se, Te). We report in this paper the results of dipole moment measurements and photoelectron (p.e.) spectral studies for these chalcanthrenes. The interpretation of the p.e. results is based on perturbational MO arguments and SCF-PPP calculations. Previous dipole moment studies of thianthrene (1; X = S) and selenanthrene (1; X = Se)³⁻⁵ indicated a folded conformation in solution. Thianthrene was found to be folded also in the solid state^{6,7} and in the gas phase.⁸ No information is available about the conformation of telluranthrene (1; X = Te) in solution. The crystal and molecular structures of the four octafluorochalcogenanthrenes⁹⁻¹² and of telluranthrene¹³ were published recently.

Experimental

Dibenzo-*p*-dioxin, m.p. 121°, was purchased from K and K Laboratories and used without further purification. Thianthrene was obtained from the Aldrich Chemical Company. The compound melted at 156° after recrystallization from methanol. Selenanthrene was prepared according to Cullinane *et al.*¹⁴ Three crystallizations from acetone gave a product which melted at 180–181°. Telluranthrene, m.p. 169–170°, was synthesized from *o*-phenylenemercury and finely powdered tellurium and purified as reported in the literature.¹⁵

Dipole Moment and Photoelectron Spectral Measurements.—The electric dipole moments were measured at $25.00 \pm 0.01^\circ$ in benzene solution as described earlier.¹⁶ The experimental dipole moments were calculated from the total solute polar-



(1)

izations, obtained by extrapolation to infinite dilution ($P_{2\infty}$) according to the Halverstadt–Kumler method,¹⁷ and from the molar refraction (R_D , $N_{D, \text{NaD}}$ line), which was considered to be equal to the electronic and atomic polarizations ($P_e + P_a$). The dipole moment values were estimated to have an accuracy of ± 0.02 D.

The photoelectron spectra were recorded on a Perkin-Elmer PS18 photoelectron spectrometer. The He^I resonance line at 584 Å (21.21 eV) was used for ionization. The spectra were calibrated against Ar and Xe lines. The accuracy of the ionization energies was estimated to be ± 0.05 eV.

Calculations

The π -orbital energies were obtained by means of SCF-PPP calculations using the parametrization of Fabian *et al.*¹⁸ and a value of -1.2 eV for $\beta(\text{Te-C})$. The Mataga–Nishimoto formula¹⁹ was used for the two-centre electron repulsion integrals. Relevant molecular parameters were taken from the published X-ray structures of dibenzo-*p*-dioxin,²⁰ 2,7-dimethylthianthrene,²¹ octafluoroselenanthrene,¹¹ and octafluorotelluranthrene.¹² Values for the angles of fold were obtained from the present dipole moment analyses.

Results and Discussion

Dipole Moments.—The results of the dipole moment studies on benzene solutions of chalcanthrenes at 25° are summarized in Table 1. The theoretical dipole moments ($\mu_{\text{calc.}}$) of the chalcanthrenes (1; X = S, Se, Te) were calculated as a function of the angle of fold Φ by classical vector addition of the component group moments as described for dibenzo-*p*-

Table 1. Polarization data * for and dipole moments of chalcathrenes (1) determined in benzene solutions at 25 °C

Compound (1)	α	β	$P_{2\infty}/\text{cm}^3$	R_D/cm^3	μ/D	Lit. μ/D
X = O †	0.77	-0.529	60.61	54.5	0.55	1.41 ⁴
X = S	1.60	-0.410	112.30	66.0	1.50	1.51 ³
X = Se	1.06	-0.540	117.70	76.2	1.42	1.41 ⁵
X = Te	0.95	-0.622	136.02	93.8	1.43	

* For definition of the symbols see ref. 25. † Data taken from ref. 1.

Table 2. Group moment angles (θ), angles of fold (Φ), and $\widehat{\text{CXC}}$ angles for chalcathrenes

X for compound (1)	θ (°)	Φ (°)	$\widehat{\text{CXC}}$ (°)
O *	152.6	163.8	118.8 ¹
S	121.7	142.4	100.2 ⁶
Se	117.6	139.0	96.5 ¹¹
Te	102.3	124.6	92.9 ¹² 95.6 ¹³

* Data from ref. 1.

dioxin.¹ The tricyclic systems were assumed to be formed by the combination of two Ph-X-Ph moieties with θ representing the angle between the directions of the group moments of Ph₂X (X = S, 1.55 D; ²² X = Se, 1.37 D; ²³ X = Te, 1.14 D²⁴). The vector of the Ph₂X moment bisects the C-X-C angle and points toward the X atom. The results of the calculations and the angles CXC used in the calculations are given in Table 2.

The conformation of the chalcathrenes are defined by the angles of fold Φ for which the conditions $\mu_{\text{exp.}} = \mu_{\text{calc.}}$ is fulfilled. The results clearly indicate folded conformations for the chalcathrenes with the angle of fold decreasing from dibenzo-*p*-dioxin to telluranthrene. The angle of fold found by us for thianthrene in solution (142.4°) agrees well with the angle of 144° obtained by previous dipole moment studies,⁴ but is larger than the values determined for the compound in the solid state (128°)^{6,7} and in the gas phase (131°).^{8,*} Similarly selenanthrene (139°) and telluranthrene (124.6°) are more folded in solution than expected on the basis of the solid state angles of 123° for octafluoroselenanthrene,¹¹ 118.4° for octafluorotelluranthrene,¹² and 120° for telluranthrene.¹³ The smaller angles of fold in the solid state can reasonably be attributed to packing forces acting on the molecules in the crystal. In solution butterfly motions about the X...X axes, which are fast on the time scale of dipole moment measurements, have sufficient amplitudes to produce angles of fold larger (and thus *less folded* conformations) than in the solid state. The inversion barriers between the two preferred equivalent conformations of the tricyclic molecules are predicted to be small in solution. The observed trend toward a *more folded* conformation (lower Φ values) of the chalcathrenes with increasing atomic mass of the chalcogen atom is in agreement with MO arguments based on the results of the p.e. spectroscopic investigation.

P.e. Spectra.—On the basis of qualitative steric and electronic arguments and assignments of bands in the photo-

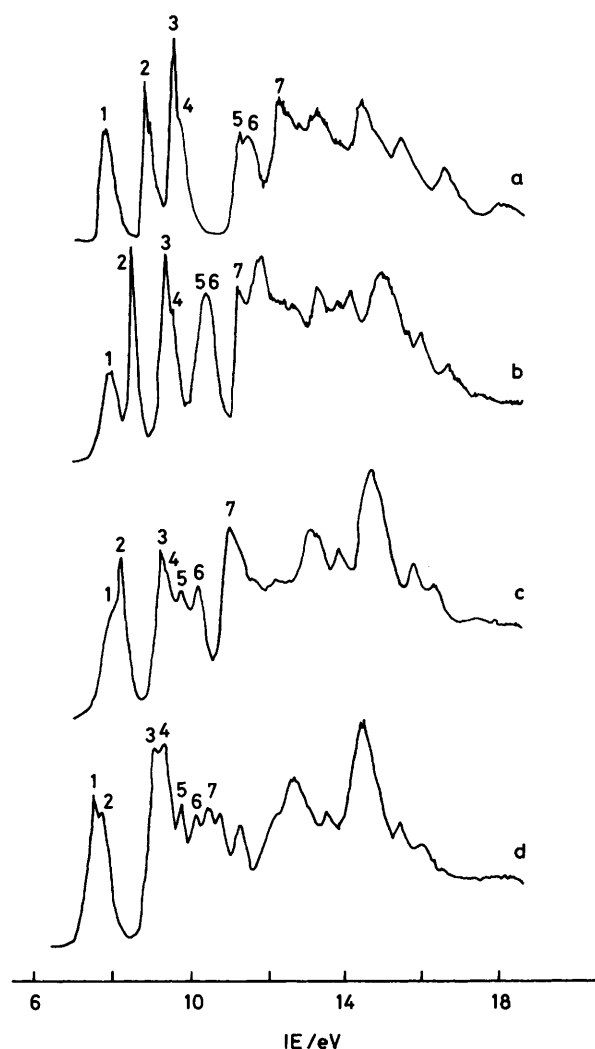


Figure. He I Photoelectron spectra of chalcathrenes: a, (1; X = O); b, (1; X = S); c, (1; X = Se); d, (1; X = Te)

electron spectra of molecules related to chalcathrenes such as phenyl methyl chalcogenides, bis(methylchalcogeno)benzenes,²⁶ and phenoxachalcogenins,¹ six π -bands and at least one σ -band are expected and found to be present in the low ionization energy (IE) region of the p.e. spectra of the chalcathrenes (Figure). The corresponding MOs are formed by symmetry-allowed interactions between the in-phase π_x^+ and out-of-phase π_x^- combinations of the $p\pi$ lone-pair orbitals of the heteroatom with appropriate combinations of the benzene π -ring orbitals, and by the non-interacting π -ring orbitals of symmetry a_2 and b_2 . Electron ejection from an outermost σ -MO of predominant chalcogen character is responsible for one σ -band in the considered energy region. In particular the first two bands, IE₁ and IE₂, are mainly π_x in nature. The nearly degenerate IE₃ and IE₄ are associated with π -ring MOs with no involvement of the chalcogen $p\pi$ -orbitals. IE₇ (IE₆ for dibenzo-*p*-dioxin) is related to the excitation of a σ_x electron. These empirical assignments are partly supported by results of π -only semi-empirical calculations.

A fair, linear correlation (r 0.98) exists between the calculated SCF-PPP energies ϵ_j of the first highest occupied π -MOs and the experimental ionization energies [equation (1)]. The theoretical and experimental IE values for the chalcathrenes are listed in Table 3.

* Very recent nematic liquid crystal n.m.r. studies (G. Fronza, E. Rugg, and G. Ronisvalle, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1209) appeared when this paper was submitted, and report an angle (140.6°) in better agreement with our present finding.

Table 3. Experimental and calculated ionization energies (eV) for chalcanthrenes

Dibenzo- <i>p</i> -dioxin		Thianthrene		Selenanthrene		Telluranthrene		Assignment *
Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	
7.78	7.73	7.94	7.72	7.93	7.64	7.52	7.38	$\pi_x^+(a_1)$
8.76	8.88	8.43	8.71	8.18	8.57	7.72	8.18	$\pi_x^-(b_1)$
9.5	9.37	9.30	9.28	9.26	9.27	9.12	9.26	$\pi_R(b_2)$
9.7	9.45	9.45	9.30	9.4	9.29	9.30	9.27	$\pi_R(a_2)$
11.24	11.02	10.2	10.48	9.79	10.10	9.79	9.66	$\pi_x(a_1)$
12.20	11.98	10.36	10.68	10.2	10.22	10.22	9.91	$\pi_x(b_1)$
11.50		11.17		11.0		10.51		σ
		11.75		11.6		10.83		σ

* π_x denotes orbitals of prevailing chalcogen characters, whereas π_R denotes ring orbitals.

Table 4. Average IE values and splittings of the first two π -IEs, and angles of fold for phenoxachalcogenins and chalcanthrenes

Compound (I)	\bar{IE}	Δ	Φ (°)
XX			
OO	8.27	0.98	163.8
OS *	8.22	0.99	163.4
OSe *	8.21	0.93	162.6
OTe *	8.13	1.05	172.2
OO	8.27	0.98	163.8
SS	8.19	0.49	142.4
SeSe	8.05	0.25	139.0
TeTe	7.62	0.20	124.6

* Values taken from ref. 1.

$$IE_{\text{exp.}} = 0.8867 IE_{\text{calc.}} - 0.0954 \text{ (eV)} \quad (1)$$

The IEs related to the HOMOs of thianthrene and selenanthrene are approximately equal and larger than those for dibenzo-*p*-dioxin and telluranthrene. If the chalcanthrenes were planar or had the same angle of fold Φ , the HOMOs would become progressively destabilized with increasing mass of the heteroatom. Such a trend is well established for benzo-[*b*]furan and its chalcogen analogues²⁷⁻³¹ and for phenyl methyl chalcogenides.²⁶ The folding, inferred from dipole moment analyses to increase from dibenzo-*p*-dioxin to telluranthrene, may cause a reduction of the π -interactions between the chalcogen atoms and the phenyl rings and an increase of the chalcogen lone pair character of the first MO and thus generate the observed trend in the IE_1 values. The high relative intensity and the small full-width at half-height of band 2 in the spectrum of thianthrene are in agreement with a marked non-bonding character of the parent MO which, in a planar system, cannot mix with any other MO by symmetry. These characteristics of band 2 and its separation from band 1 decrease from thianthrene to telluranthrene (Figure). This effect may be caused by progressively increasing, through-space, destabilizing interactions between the π_x orbitals, which become more diffuse in the heavier chalcogen atoms. In addition, the corresponding MOs, π_x^- , may be destabilized by increasing interactions with σ orbitals resulting from an increasing departure of the ring systems from planarity and diminution of the $\pi - \sigma$ energy gap from oxygen to tellurium.

The average values of the ionization energies, IE, for the first two π -IEs, their splittings Δ , and the angles of fold Φ are presented in Table 4 for phenoxachalcogenins and chalcanthrenes. In contrast to the phenoxachalcogenins, the chalcanthrenes have Δ values decreasing with increasing atomic number of the chalcogen atom. This trend in Δ values and the greater similarity of the IE values to those of phenyl methyl chalcogenides²⁶ are indicative of folded conformations for chalcanthrenes as found by dipole moment studies.

The progressive destabilization along the series of the two π -ring MOs associated with IE_3 and IE_4 is clearly caused by the inductive effect of the heteroatoms. However, a through-space interaction between the two phenyl groups must also be considered in this context. A small ring-ring repulsion has indeed been considered compatible with the CSC angle of 104.1° found for thianthrene by electron diffraction.⁸

Conformational information deduced from p.e. data must be treated with caution, because secondary interactions between π and σ orbitals, which were not included in the calculations, may not be negligible.³² However, the consistency of the conclusions derived from the p.e. results and from the dipole moment analyses cannot be considered fortuitous.

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