Journal of Organometallic Chemistry, 146 (1978) 235—244
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CONFORMATION, UV-ABSORPTION SPECTRA AND PHOTOELECTRON SPECTRA OF PHENOXACHALCOGENINS

FRANCESCO P. COLONNA, GIUSEPPE DISTEFANO,
Laboratorio dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni del C.N.R., Ozzano Emilia, Bologna (Italy)

VINICIO GALASSO,
Istituto di Chimica, Università di Trieste, Trieste (Italy)

KURT J. IRGOLIC, C.E. KING,
Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)

and GIUSEPPE C. PAPPALARDO *
Istituto di Chimica Generale, Università di Catania, Viale A. Doria 8, 95125 Catania (Italy)

(Received September 19th, 1977)

Summary

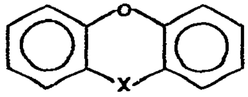
The analysis of dipole moment data obtained for dibenzo-*p*-dioxin, phenoxathiin, phenoxaselenin and phenoxatellurin in benzene at 25°C in conjunction with EHT calculations of the conformational energies show that these molecules adopt a non-planar conformation in solution. Each of the phenoxachalcogenins is folded along the axis connecting the two heteroatoms. A butterfly flapping motion about the planar conformation cannot be excluded. The uv and photoelectron spectroscopic data support the conclusions drawn from the dipole moment studies. The spectroscopic data were interpreted with the help of SCF-PPP-CI calculations.

Introduction

In continuation of an earlier study of the conformation of phenothiazin compounds [1], phenoxachalcogenins I (X = O, S, Se, Te) have now been investigated. Accurate dipole moment measurements and semiempirical MO calculations at the EHT level were carried out to elucidate the conformation of the phenoxachalcogenins in solutions. The UV and photoelectron spectra of these compounds were measured and interpreted employing perturbational MO argu-

---

* Author to whom correspondence should be addressed.



(I)

ments assisted by SCF-PPP calculations.

An inspection of the literature [2—5] revealed that there is considerable disagreement about the conformation of dibenzo-*p*-dioxin (I, X = O) as derived from dipole moment and dielectric relaxation studies. These discrepancies are probably attributable to the rather small dipole moment of dibenzodioxin. Similar studies [3—8] on phenoxathiin (I, X = S) showed that this molecule is certainly non-planar in solution.

X-Ray diffraction studies suggested the dibenzodioxin molecule to be planar in the solid state [9]. A disordered structure with slightly folded molecules [9b] cannot be excluded, however. Pheoxathiin and phenoxatellurin [11] are folded about the axis joining the two heteroatoms with angles of fold of approximately 140°. The solid state and solution conformation of phenoxaselenin (I, X = Se) seem not to have been investigated.

Experimental

Materials: Dibenzo-*p*-dioxin melting at 121°C (lit. 119°C) [12] was purchased from K & K Laboratories and used without purification. Phenoxathiin was obtained from Eastman Organic Chemicals. It was recrystallized from petroleum ether to a constant melting point of 57° C (lit. 58° C, [13]. Phenoxaselenin [14] and phenoxatellurin [15] were prepared as described in the literature. The compounds were purified by recrystallization and sublimation and had m.p.s. of 88 and 77°C, respectively.

Physical measurements. The electric dipole moment measurements were carried out at 25°C ± 0.01° with benzene as solvent using the apparatus and techniques described previously [16]. The Halverstadt-Kumler [17] and the Guggenheim methods [18] were employed for calculating the dipole moments. The sum of the electronic and atomic polarizations ($P_E + P_A$) required for the Halverstadt-Kumler calculation were assumed to be equal to the measured molar refraction (R_D, Na_D line). The estimated error in all dipole moment values is ±0.03 D.

The UV-visible absorption spectra were recorded on a Perkin—Elmer 356 spectrometer. The photoelectron spectra were obtained with a Perkin—Elmer PS 18 spectrometer using the He(I) resonance line at 584 Å (21.21 eV) as ionizing radiation. The spectra were calibrated against Ar and Xe lines. The accuracy of the ionization energies was estimated to be ±0.05 eV for values reported with two decimals or ±0.1 eV for those listed with only one decimal (Table 5) with a reproducibility of ±0.05 eV.

Results and discussion

The results of the dipole moment studies on benzene solutions of phenoxachalcogenins at 25°C are summarized in Table 1.

TABLE 1

POLARIZATION DATA FOR AND DIPOLE MOMENTS OF PHENOXACHALCOGENINS I DETERMINED IN BENZENE SOLUTIONS AT 25°C

Compound I	α^a	β^b	γ^c	$P_{2\infty}$ (cm³)	R_D (cm³)	μ (D)	μ (D) literature
X = O	0.77	−0.529	0.608	60.61	54.5	0.55	0.52 [5]; 0.64 [3]
X = S	0.97	−0.258	0.227	89.35	60.6	1.18	1.09 [3]; 0.92 [4] 0.97 [6,8]; 1.31 [7]
X = Se	0.60	−0.483	0.378	76.66	65.6	0.73	
X = Te	0.42	−0.528	0.376	77.49	74.5	0.38	

[a] $\alpha = \frac{\Sigma(\epsilon_{12}-\epsilon_{10})}{\Sigma w_2}$. [b] $\beta = \frac{\Sigma(v_{12}-v_{10})}{\Sigma w_2}$. [c] $\gamma = \frac{\Sigma(n_{12}^2-n_{10}^2)}{\Sigma w_2}$.

Conformational analysis: The theoretical dipole moments (μ_{calc}) for conformations defined by the angles of fold ϕ (Fig. 1) were calculated by vector addition of the pertinent group moments (eq. 1). The angle θ, the angle between the directions of the group moments (Fig. 1), was evaluated as a function of the

$$\mu_{calc}^2 = \mu_{Ph_2O}^2 + \mu_{Ph_2X}^2 + 2\mu_{Ph_2O}\mu_{Ph_2X}\cos\theta \tag{1}$$

angle ϕ by means of eq. 2. In this equation δ represents the angle CXC, a and b stand for the sum of the bond distances (C—S + C—C) and (C—O + C—C), respectively.

$$\cos\frac{\phi}{2} = \frac{\cos(\delta/2)\sin\theta}{[a^2 + b^2\sin^2(\delta/2)]^{0.5} - b\cos(\delta/2)\cos\theta}\cdot\frac{a - b\cos 60}{\sin 60} \tag{2}$$

For dibenzodioxin, eq. 2 can be simplified to eq. 3.

$$\cos\frac{\phi}{2} = \frac{\sin\phi(1-\cos 60)}{\sin 60(1-\cos\theta)} \tag{3}$$

The group moments $\mu_{Ph_2O} = 1.16$ D [19], $\mu_{Ph_2S} = 1.55$ D [19], $\mu_{Ph_2Se} = 1.50$ D [20] and $\mu_{Ph_2Te} = 1.14$ D [21] were used in the calculations. The vectors of these moments bisect the angles δ (Fig. 1). The C—O and C—X bond distances and the angles δ were those found by X-ray structure analysis of dibenzodioxin [9], phenoxathiin [10] and phenoxatellurin [11]. Because structural data are

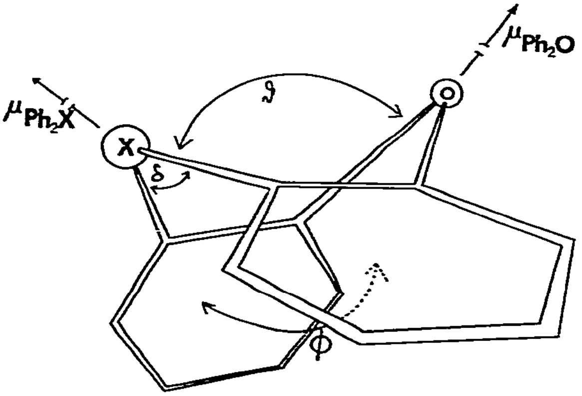


Fig. 1. The folded conformation of phenoxachalcogenins.

TABLE 2

VALUES FOR THE ANGLES θ AND ϕ(°) AS DERIVED FROM THE DIPOLE MOMENTS OF THE PHENOXACHALCOGENINS I

X	θ	ϕ	ϕ_S[a]	Ref.
O	152.6	163.8	180	9
S	135.2	163.4	141	10
Se	151.8	162.6	130[b]	—
Te	160.8	172.2	138	11

[a] Angles of fold for the molecules in the solid state. [b] Assumed geometry (see text).

not available for phenoxaselenin, an idealized geometry was assumed for this compound (C—Se 1.92 Å; CSeC 94.4°; C—O 1.39 Å; COC 118°) based on data reported for diphenyl diselenide [22] and bis(4-methylphenyl) selenide [23]. The C—C distance of 1.40 Å was used in all calculations.

The angles which produced agreement between calculated and experimental dipole moments are listed in Table 2. According to these results, all four compounds are in solution folded along the O—X axis. The angles of fold for the sulfur, selenium and tellurium derivatives in solution are larger than those determined for these molecules in the solid state.

Dibenzodioxin was found to be planar in solution (Kerr constant study) [5] and in the solid state [9], whereas its dipole moment of 0.55 D (Table 1) suggests a folded structure in solution similar to the conformations assumed by the other phenoxachalcogenins in the solid state and in solution.

It is well known, that, in general, conclusions derived from X-ray data of a solid cannot be used with confidence to elucidate the conformation of the same molecule in solution. A planar solid state conformation thus does not preclude a folded structure for dibenzodioxin in solution, as suggested by the present dipole moment study and supported by the earlier careful investigations of Higasi [3], who reported a moment of 0.64 D. This value demands an angle of fold of ~160° and a COC angle of ~118°.

The correct estimation of the atomic polarization, P_A, appears to be important when dipole moments smaller than 0.6 D are determined. Incorrect estimation of P_A would make it difficult to decide whether or not the molecule possesses a dipole moment. It should be noted that, in the case of dibenzodioxin, the difference of 6.1 cm^3 between R_D and $P_{2\infty}$ cannot be entirely attributed to the P_A term, since in calculating μ values the correction for atomic polarization is generally assumed to be (as a maximum) 10% of the electronic polarization. This suggests that the dibenzodioxin molecule, though symmetric, has real non-zero moment.

The folded conformation of dibenzodioxin in solution is also supported by the recent dielectric polarization studies by Davies and Swain [2]. These authors found that the molecule executes a butterfly flap of a type similar to that in thianthrene and phenoxathiin I (X = S). This process is slow on the time scale of normal dipole moment measurements, making a stable planar conformation of dibenzodioxin in solution unlikely.

Semiempirical calculations at the EHT level [24] were carried out to gain some theoretical insight into the geometry of the phenoxachalcogenins. The

TABLE 3

EHT RELATIVE ENERGIES (kcal/mole) OF THE PHENOXACHALCOGENINS I AS A FUNCTION OF FOLDING ANGLE ϕ

Compound I	180°	170°	160°	150°	140°	130°	120°
X = O	0.0	0.92	3.82	9.08	17.37	29.64	47.04
X = S	0.0	0.49	2.06	5.06	10.09	18.09	30.41
X = Se	0.0	0.85	3.50	8.26	15.67	25.56	42.15
X = Te	0.0	0.27	1.19	3.01	6.22	11.54	20.05

EHT method has been found to be well suited for the theoretical treatment of strained molecules of large size. The parametrization used was reported previously [25]. The relevant parameters for tellurium are I_s 20.8 eV, I_p 14.8 eV, ζ_{5s} 2.5076 and ζ_{5p} 2.1617. To avoid excessive calculations a systematic geometry optimization was not performed. Only the change of the molecular energy as a function of ϕ, the angle of fold, was considered. The *d* orbital of the heavy heteroatoms were not included in the calculations because the lack of pertinent spectroscopic data renders the "semiempirical" determination of the core matrix elements impossible.

The conformation of the phenoxachalcogenins can be regarded to be determined by the π-interactions between the aromatic rings and the heteroatoms, which tend to keep the molecule planar (the conjugative factor), and the strains about the chalcogen atoms (the steric factor) which is relieved when the center ring assumes a boat conformation.

The results of the calculations (Table 3) indicate that all four molecules should assume a planar conformation (ϕ = 180°) as a compromise between the two opposing factors. This prediction disagrees with X-ray structural data (with the exception of dibenzodioxin) and the evidence obtained from solution studies, and is rather surprising, because overestimation of the steric factor and a preference for non-planarity is a distinctive feature of EHT calculations. The calculations did not take into account possible changes of the C—X bond distances and CCX bond angles as a function of the angle of fold ϕ. It may be that the molecular energy is influenced by these changes. The EHT calculations show, however, that the molecular energies of the phenoxachalcogenins are rather insensitive toward significant deviations from the planar conformation, and thus allow a certain degree of butterfly flapping for all four molecules. This result is congruent with the non-rigid structure and the very low activation energy for the butterfly flapping motion of dibenzodioxin and phenoxathiin invoked by Davies and Swain [2] to explain the dielectric absorption data.

Absorption spectra. The absorption spectra of dibenzodioxin and phenoxathiin have been discussed by Lamotte and Bertier [26]. The spectrum of phenoxaselenin in heptane is very similar to that of the sulfur compound. Phenoxatellurin, in contrast to the other phenoxachalcogenins, is pale yellow. The color is caused by a low intensity band centered at 356 nm. Three other distinct absorption bands are present. Two bands of medium intensity appear at 285—305 and at 255 nm. The third, broad band has a maximum at 202 nm and a shoulder at ~230 nm.

The transition energies were obtained by means of a SCF-PPP-CI calculation

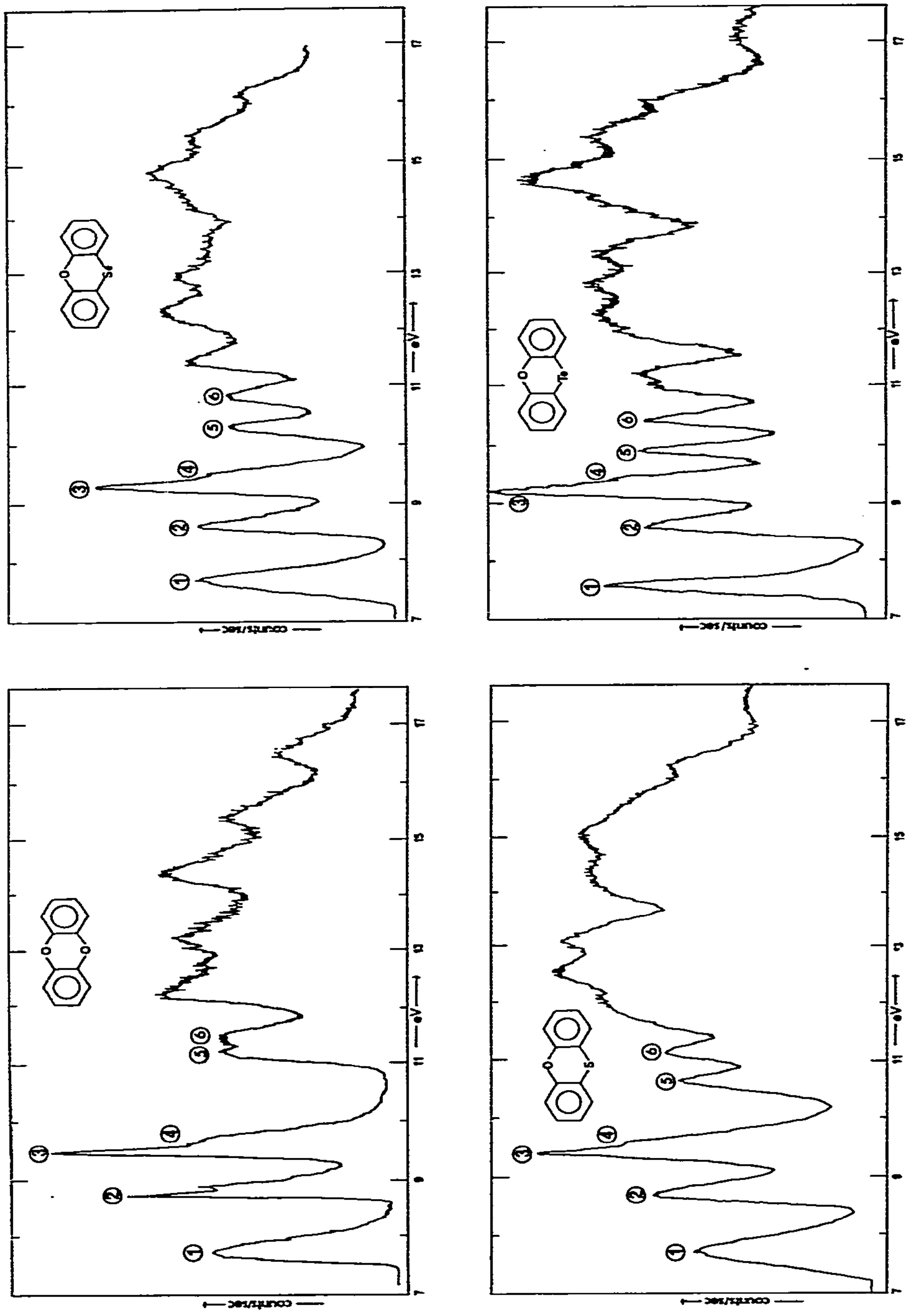


Fig. 2. The photoelectron spectra of phenoxachalcogenins.

TABLE 4

EXPERIMENTAL AND CALCULATED ELECTRONIC TRANSITIONS OF PHENOXACHALCOGENINS

Compound I	Calculated			Experiment Found	
	λ(nm)	Pol.[a]	*f*	λ(nm)	log ε
X = O	321	0	0		
	310	x	0.217	300[b]	(sh)
	286	z	0.002	289	3.87
	235	y	0.151	228	4.73
	231	x	1.471	222	4.64
	213	z	0.007		
	207		0		
	203	y	0.117	203	weak
X = S	305	x	0.024		
	302	x	0.138	295[b]	3.60
	286	yz	0.026		
	239	yz	0.177	241	4.50
	233	x	1.148	238	4.50
	217	zy	0.052	220	weak
	208	x	0.001		
	204	yz	0.156		
X = Se	303	x	0.103		
	299	x	0.055	294[c]	3.54
	287	yz	0.035		
	240	yz	0.190	241	4.30
	235	x	1.066	238	4.31
	220	zy	0.049	218	4.13
	212	x	0.010		
	204	yz	0.203	202	4.34
X = Te	312	x	0.036	356[c]	2.55
	303	x	0.117	290	3.62 (sh)
	291	yz	0.052		
	250	yz	0.190	257	3.91
	241	x	0.852		
	229	zy	0.045	230	4.07 (sh)
	220	x	0.154		
	206	yz	0.191	202	4.57

[a] Polarization (The x- and y-axes represent the long and short axis of the molecular framework, respectively). [b] In heptane solution [26]. [c] Present work, in heptane solution.

with consideration of all singlet mono-excited electronic configurations. The oscillator strengths for the various transitions were determined using the dipole length operator. The parametrization was taken from Fabian et al. [27] However, the value —1.2 eV was used for β(C—Te). The two center electron repulsion integrals were evaluated by means of the Mataga—Nishimoto formula [28]. The X-ray geometries were adopted for the phenoxachalcogenins (I, X = O *, S, Te). The structure of phenoxaselenin was assumed to be similar to that of the sulfur and tellurium derivatives.

The calculated frequencies are in fair agreement with the experimental values for all four compounds (Table 4). The interpretation of the spectra of dibenzodioxin and phenoxathiin on the basis of these calculations is quite congruent with the ones previously advanced by other authors [29—32]. The lowest energy bands are caused by transitions from the heteroatoms to the phenyl rings. The

---

* ϕ 154° assumed.

band at 289 nm in the spectrum of dibenzodioxin is correlated with the third calculated transition (286 nm). This transition is forbidden in the planar but allowed in the folded molecule. This interpretation supports a folded conformation for dibenzodioxin.

The assignments for phenoxathiin are corroborated by the fact that the theoretical band polarizations are quite consistent with those inferred from the polarized excitation spectrum [29]. The assignments for phenoxaselenin are similar to those for the sulfur derivative.

The agreement between theory and experiment is not very good in the case of phenoxatellurin probably because of a non-optimal parametrization of the Te atom. The visible band (356 nm) can be correlated with the first calculated transition (312 nm), which is an almost pure HOMO to LEMO excitation. It occurs at a lower energy than in the other chalcogenins because the HOMO electrons are more localized on the Te atom than on the other Group VI atoms. The photoelectron spectra support this argument.

Photoelectron spectra: The phenoxachalcogenins can be considered to be formed by joining two mono-substituted benzene derivatives. Based on this assumption and on qualitative perturbation MO arguments, five π bands are expected to be present in the low *IE* region of the photoelectron spectra. These bands are caused by ionization processes affecting electrons in the uppermost occupied MO's associated with two antibonding combinations and one bonding combination formed from the chalcogen p_π lone pair orbitals and the $\pi(b_1)$ phenyl orbitals and with two non-interacting $\pi(a_2)$ phenyl orbitals. The experimentally observed number of bands is in good agreement with this prediction (Fig. 2, Table 5).

The observed and calculated ionization energies and the band assignments are presented in Table 5. The first two bands are related to electrons in antibonding π-MO's with a maximum of electron density at the heavier chalcogen atom and one node along each C—X bond. The closely spaced third and fourth bands are attributed to electron removal from two nearly degenerate, non-interacting π-phenyl orbitals with no involvement of the chalcogen atoms. The fifth band is associated with the π-MO characterized by bonding interaction between the

TABLE 5

EXPERIMENTAL AND CALCULATED IONIZATION ENERGIES (eV) OF PHENOXACHALCOGENINS I

X = O		X = S		X = Se		X = Te		Assignment[a]
Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	
7.78	7.74	7.72	7.73	7.74	7.69	7.61	7.49	π_{XY}
8.76	8.94	8.71	8.85	8.67	8.80	8.66	8.68	π_{XY}
9.5	9.45	9.4	9.37	9.33	9.38	9.24	9.37	π_R
9.7	9.53	9.6	9.46	9.5	9.45	9.4	9.45	π_R
11.24	11.18	10.63	10.68	10.33	10.30	9.94	9.92	π_{XY}
11.5		11.13		10.9		10.45		σ
12.2	12.18 (π_R)	11.7	11.83	11.5	11.62	11.3	11.53	π_{XY}
						11.1		σ
	13.75		12.10		12.10		12.09	π
	15.09		14.61		14.59		14.58	π

[a] π_{XY} denotes orbitals of prevailing chalcogen character, whereas π_R denotes ring orbitals.

heavier chalcogen atom and the phenyl rings. Excitation of a σ-electron with some heteroatom character should give rise to the sixth band. This assignment is consistent with that advanced for the highest energy σ-MO of $C_6H_5XCH_3$ (X = O, S, Se, Te) [33]. A π-bonding combination between chalcogen atoms and phenyl groups should be responsible for the seventh band.

These empirical assignments (Table 5) are in excellent agreement with the results of PPP-SCFMO calculations. The theoretical energies of the first five occupied uppermost π-MO's, correlated with the experimental ionization energies via Koopmans' theorem, lead to the linear relationship expressed in eq. 4 with a correlation coefficient of 0.995. The values for IE_{obs} calculated according to eq. 4

$$IE_{obs} = 0.9244\, IE_{calc} - 0.4148 \text{ eV} \qquad (4)$$

are listed in Table 5.

The energies of the first two π-MO's in the phenoxachalcogenins are almost independent of the chalcogen atoms. If these molecules were planar, these two π-MO's would become progressively destabilized with increasing mass of the heteroatom in line with well-established evidence derived from the related series of benzo [*b*] furan [34] and its chalcogen analogs and from the compounds CH_3XR ($R = C_6H_5$) [33]. The MO energies should, therefore, decrease from dibenzodioxin to phenoxatellurin. A deviation from planarity, which reduces the π-interactions between the chalcogen atoms and the phenyl rings and releases the ring strain, is therefore very likely responsible for the near-constancy of the observed ionization energies.

Another consequence of the deviation from planarity is the increased localization of the HOMO electrons in the chalcogen p_π orbitals which explains the variations of the relative intensity and the full-width-at-half-maximum (FWHM) of the pertinent photoelectron bands observed for the phenoxachalcogenins. The FWHM of the first band (0.44 eV, O; 0.52 eV, S; 0.47 eV, Se; 0.33 eV, Te) decreases rapidly in the sequence S > Se > Te. The apparently anomalous position of dibenzodioxin in this series is caused by the predominant ring nature of its HOMO. The intensity of the first band relative to the third composite band, which has pure phenyl character, is ~0.5 (O), ~0.5 (S), ~0.65 (Se) and ~0.7 (Te). The observed, rather small destabilization of the highest occupied MO's with increasing mass of the heteroatoms, which might be caused by localization of electrons on the heteroatom and a concomitant electron shift from the ring toward the heteroatom, is in agreement with the successive NMR downfield shifts of the hydrogen atoms next to the heteroatom [35].

These results further corroborate that the near-constancy of the first band is caused by the non-planarity of the molecules. The photoelectron results are thus consistent with the conformational conclusions drawn from the dipole moment analyses.

Acknowledgements

V.G. and G.C.P. are thankful to the Consiglio Nazionale delle Ricerche of Italy for financial support. K.J.I. is grateful to the Robert A. Welch Foundation of Houston, Texas for the support of those parts of this investigation, which were carried out at Texas A & M University.

References

1 G.C. Pappalardo and G. Ronsisvalle, J. Mol. Struct., 22 (1974) 361.
2 M. Davies and J. Swain, Trans. Faraday Soc., 67 (1971) 1637.
3 K. Higasi, Sci. Papers Inst. Phys. Chem. Res. (Tokyo), 38 (1941) 331; K. Higasi and S. Uyeo, J. Chem. Soc. Jap, 63 (1941) 400.
4 N.J. Leonard and L.E. Sutton, J. Amer. Chem. Soc., 70 (1948) 1564.
5 M.J. Aroney, G.M. Hoskins, R.J.W. LeFevre, R.K. Pierens and D.V. Radford, Aust. J. Chem., 22 (1969) 2243.
6 F. Hufnagel, G. Klages and P. Knoblock, Z. Naturforsch. A, 17 (1962) 96.
7 H. Lumbroso and G. Montaudo, Bull. Soc. Chim. France, 9 (1964) 2119.
8 M.J. Aroney, G.M. Hoskins and R.J.W. LeFèvre, J. Chem. Soc. B, (1969) 980.
9 (a) R.G. Wood, C.H. McCale and G. Williams, Phil. Mag., 31 (1941) 71; (b) N. Senma, Z. Taira, T. Taga and K. Osaki, Cryst. Struct. Comm., 2 (1973) 311.
10 S. Hosoya, Acta Crystallogr., 20 (1966) 429.
11 M.R. Smith, M.M. Mangion, R.A. Zingaro and E.A. Meyers, J. Het. Chem., 10 (1973) 527.
12 F. Ullmann and A. Stein, Chem. Ber., 39 (1966) 624.
13 B. Hetnarsky and A. Grabowska, Rocz. Chem., 44 (1976) 1713.
14 H.D.K. Drew, J. Chem. Soc., (1928) 511.
15 H.D.K. Drew, J. Chem. Soc., (1926) 223.
16 G.C. Pappalardo and S. Pistarà, J. Chem. Eng. Data, 17 (1972) 2.
17 D.F. Halverstadt and W.D. Kumler, J. Amer. Chem. Soc., 64 (1942) 2988.
18 E.A. Guggenheim, Trans. Faraday Soc., 45 (1949) 714.
19 A.L. McClellan, Tables of Experimental Dipole Moments, Rahara Enterprises, 1973, New York.
20 L. Chierici, H. Lumbroso and R. Passerini, Bull. Soc. Chim. France, (1955) 686.
21 E. Bergman, L. Engel and S. Sandor, Z. Phys. Chem. B, 10 (1930) 397.
22 R.E. Marsh, Acta Crystallogr., 5 (1952) 458.
23 W.R. Blackmore and S.C. Abrahams, Acta Crystallogr., 8 (1955) 323.
24 R. Hoffman, J. Chem. Phys., 39 (1963) 1397.
25 V. Galasso, G. De Alti and A. Bigotto, Tetrahedron, 27 (1971) 6151.
26 B. Lamotte and G. Bertier, J. Chim. Phys., 63 (1966) 369.
27 J. Fabian, A. Mehlorn and R. Zaradnik, Theor. Chim. Acta, 12 (1968) 247.
28 N. Mataga and K. Nishimoto, Z. Physik. Chem. N.F., 13 (1957) 140.
29 M. Hillebrand, O. Maior, V.E. Sahini and E. Volanski, J. Chem. Soc. B, (1969) 755.
30 R.J. Wratten and M.A. Ali, Mol. Phys., 13 (1967) 233.
31 H.H. Mantsch and J. Dehler, Can. J. Chem., 47 (1969) 3173.
32 M. Kamiya, Bull. Chem. Soc. Japan, 43 (1970) 3929; 45 (1972) 1589.
33 G. Tshmutowa and H. Bock, Z. Naturforsch. B, 31 (1976) 1611.
34 J.H.D. Eland, J. Mass Spectrometry Ion Phys., 2 (1969) 471. P.A. Clark, R. Gleiter and E. Heilbronner, Tetrahedron, 29 (1973) 3085. J.P. Maier and D.W. Turner, J. Chem. Soc. Faraday II, 69 (1973) 196. M.H. Palmer and S.M.F. Kennedy, J. Chem. Soc. Perkin II, (1974) 1893. J.F. Muller, Helv. Chim. Acta, 58 (1975) 2646.
35 I.C. Calder, R.B. Johns and J.M. Desmarchelier, Aust. J. Chem., 24 (1971) 325.