

Quantum-Mechanical PM3 Calculations and High-Field ^1H and ^{13}C NMR Studies on Chalcanthrenes, $\text{C}_{12}\text{H}_8\text{XY}$ (X, Y = O, S, Se, Te in All Combinations)

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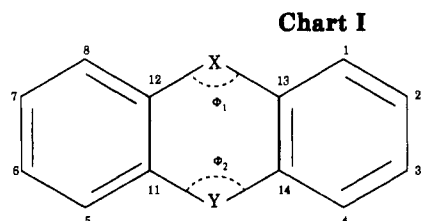
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The complete series of ten chalcanthrenes ($\text{C}_{12}\text{H}_8\text{XY}$), with X, Y = O, S, Se, Te in all combinations, was investigated using quantum mechanical PM3 calculations and two-dimensional ^1H and ^{13}C NMR spectroscopy. The former located single flat conformational minima and low interconversion energetics. The X, Y = Se, Te and Te, Te compounds had a more sharp minimum, and accordingly, this well reproduced the conformations attained in the solid state. The IPs were calculated and discussed in relation to the experimental data. The conformations in the gas were found in line with the calculated bonding situation determined by the effects of increasing, along the series, metallic character of the HOMOs. In the most folded molecules X, Y = Se, Te and Te, Te the p_z - π interactions decrease with increasing localization of the HOMO on the heavier heteroatoms. Unambiguous spectral ^1H and ^{13}C NMR assignments on correlative bases revealed combined effects of anisotropic and paramagnetic contributions by the heavy atom. The measured $^1J_{\text{Se,C}}$, $^1J_{\text{Te,C}}$, $^2J_{\text{Se,C}}$, $^2J_{\text{Te,C}}$, $^3J_{\text{Se,C}}$, and $^3J_{\text{Te,C}}$ values were interpreted and discussed in terms of possible coupling interactions.

Introduction

The chalcanthrenes are remarkable both for their thermal stability and potential use for obtaining new inorgano-organic materials. The variety of complexes that they or their derivatives form¹ makes the chalcanthrenes of interest for their applications as electroactive or magnetic materials. Molecular orbital (MO) theoretical calculations can provide a valuable tool for the exploration of the fundamental nature of these molecules. The recent extension of the semiempirical PM3 calculational method² to Se and Te made possible exploitation of quantum mechanical semiempirical calculations to treat the whole series of chalcanthrenes 1-10. Their chemical structures and atomic numbering are shown in Chart I. Here we report our complete PM3 theoretical results concerning conformations and electronic structures of 1-10. All these have been previously characterized in the solid by X-ray diffraction experiments.³⁻⁷ Some of these have been the



X, Y = O, O (1); S, S (2); Se, Se (3); Te, Te (4); O, S (5); O, Se (6); O, Te (7); S, Se (8); S, Te (9); Se, Te (10);

object of investigations in solution (dipole moments, NMR) and in the gas phase (i.e. spectroscopy).⁸⁻¹³ This provided convenient benchmarks with which to evaluate the validity of the application of the PM3 calculational method to structurally and conformationally known chalcanthrenes in the gas.

This work also reports definitive unambiguous assignment of ^1H and ^{13}C resonances of 1-10, through application of two-dimensional (2D) NMR spectroscopic techniques, together with the investigation on one-, two-, and three-bond ^{13}C -Se and ^{13}C -Te couplings.

(7) Smith, M. R.; Mangion, M. M.; Zingaro, R. A.; Meyers, E. A. *J. Heterocycl. Chem.* **1973**, *10*, 527.

(8) Colonna, F. P.; Distefano, G.; Galasso, V.; Irgolic, K. J.; King, C. E.; Pappalardo, G. C. *J. Organomet. Chem.* **1978**, *146*, 235.

(9) Distefano, G.; Galasso, V.; Irgolic, K. J.; Pappalardo, G. C. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1109.

(10) Galasso, V.; Irgolic, K. J.; Pappalardo, G. C. *J. Organomet. Chem.* **1979**, *181*, 329.

(11) Distefano, G.; Galasso, V.; Junk, T.; Irgolic, K. J.; Pappalardo, G. C. *Phosphorus Sulfur* **1988**, *36*, 281.

(12) Isbrandt, L. R.; Jensen, R. L. K.; Petrakis, L. *J. Magn. Reson.* **1973**, *12*, 143.

(13) Schaefer, T.; Sebastian, R. *J. Mol. Struct. (Theochem.)* **1990**, *204*, 41.

[†] Università di Catania.

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[‡] Hungarian Academy of Sciences.

(1) Kacholdt, H.; Berges, P.; Klar, G.; Hinrichs, W. *Transition Met. Chem.* **1987**, *12*, 515.

(2) Stewart, J. J. P. QCPE Program 455. Indiana University, Bloomington, IN, 1988.

(3) (a) Senma, M.; Taira, Z.; Taga, T.; Osaki, K. *Cryst. Struct. Commun.* **1973**, *2*, 311. (b) Sing, P.; McKinney, J. D. *Acta Crystallogr. Sect. B* **1978**, *34*, 2956.

(4) (a) Meyers, E. A.; Zingaro, R. A.; Rainville, D.; Irgolic, K. J.; Dereu, N. L. M.; Chakravorty, R.; Pappalardo, G. C. *Proc. Int. Conf. Org. Chem. Selenium Tellurium* **1983**, *4*, 391. (b) Larson, S. B.; Simonsen, S. H.; Martin, G. E.; Smith, K.; Puig-Torres, S. *Acta Crystallogr.* **1984**, *C40*, 103.

(5) Meyers, E. A.; Irgolic, K. J.; Zingaro, R. A.; Junk, T.; Chakravorty, R.; Dereu, N. L. M.; French, K.; Pappalardo, G. C. *Phosphorus Sulfur* **1988**, *38*, 257.

(6) Dereu, N. L. M.; Zingaro, R. A.; Meyers, E. A. *Cryst. Struct. Commun.* **1981**, *10*, 1359.

Table I

compd	X	Y	theoretical			experimental				
			θ_{\min}	$\langle\theta\rangle$	E	solid θ	solution ^g θ	C-X calc	C-Y calc	
(a) Summary of Theoretical Minimum Energy Folding Angles θ (deg), $\langle\theta\rangle$ (deg) Values, and Inversion Barriers E (kcal mol ⁻¹) ^a										
1	O	O	179	165.2	~0	~180 ^b	163.8			
2	S	S	150	156.4	0.67	128.1 ^c	142.4			
3	Se	Se	109	111.7	2.91	123.4 ^d	139.0			
4	Te	Te	120	127.3	1.7	120.1 ^e	124.6			
5	O	S	160	164.6	0.11	141.0 ^f	163.4			
6	O	Se	151.9	158.0	0.37	139.7 ^d	162.6			
7	O	Te	145.0	140.7	1.90	138.0 ^f	172.2			
8	S	Se	150.0	155.1	0.40	123.7 ^d	135.0			
9	S	Te	135.0	136.6	1.81	120.2 ^d	133.3			
10	Se	Te	120.0	121.3	3.65	119.9 ^d	134.0			
X	Y	ϕ_1		ϕ_2		$\langle C-X \rangle$	C-X	$\langle C-Y \rangle$	C-Y	
		exp	calc	exp	calc	exp	calc	exp	calc	
(b) Comparison of Calculated Bond Angles (deg) and Bond Distances (Å) at the Optimized Geometry with Measured Values in the Solid ³⁻⁷										
1	O	O	116.3	113.8	116.3	113.8	1.378	1.388	1.387	1.388
2	S	S	100.2	105.2	100.3	105.2	1.761	1.760	1.763	1.760
3	Se	Se	97.8	100.6	98.3	100.6	1.899	1.881	1.905	1.881
4	Te	Te	95.3	98.4	95.9	98.4	2.109	2.128	2.115	2.128
5	O	S	117.7	118.7	97.7	99.6	1.393	1.386	1.740	1.755
6	O	Se	119.4	118.4	93.5	96.8	1.386	1.386	1.896	1.876
7	O	Te	121.2	119.9	89.4	90.6	1.397	1.386	2.098	2.115
8	S	Se	97.5	106.9	97.5	102.7	1.843	1.758	1.866	1.880
9	S	Te	93.5	107.6	92.8	96.0	1.941	1.764	2.046	2.120
10	Se	Te	96.4	111.7	94.7	100.1	2.007	1.884	2.025	2.121

^a $\langle\theta\rangle$ denotes the mean value of θ calculated for populated conformational states at 300 K. The θ angles found in the crystal and in benzene solution, by X-ray diffraction and dipole moment analysis, respectively, are quoted for the purpose of comparison. ^b Reference 3. ^c Reference 4. ^d Reference 5. ^e Reference 6. ^f Reference 7. ^g References 8-11.

Experimental Section

Samples. The source of chalcathrenes 1-10 was that given in our previous works.^{4,5,8-11}

NMR Spectroscopy. All NMR spectra were recorded on a Varian Model VXR-400 spectrometer. The solutions were ca. 5 mM in CDCl₃ (TMS). The heteronuclear 2D chemical shift experiments (¹H, ¹³C-COSY) were performed using a standard pulse sequence. The ¹H NMR spectral patterns were refined by iterative computer analyses.

Computational Methods. The semiempirical quantum mechanical PM3 calculations were performed by using the MOPAC² program package on a VAX 3500 computer. The conformational energies of 1-10 were calculated as a function of the folding angle (θ) of the heteroring with a scan of 5° in the range 90-180°, with full geometry optimization at each step. For each compound at the optimized minimum energy conformation molecular orbitals were calculated to analyze its electronic features.

Results and Discussion

Theoretical Calculations. The PM3 calculated equilibrium folding angle θ (defined as the angle made by the planes X-C-C-Y which intersect along the X---Y joining line, and thus assuming the value of $\theta = 180^\circ$ in the full-planar conformation), the averaged $\langle\theta\rangle$ values (by Boltzmann distribution calculations at 300 K), the inversion barriers, and relevant geometric parameters for 1-10 molecules are summarized in Table I. Therein are also quoted for comparison the available experimental data in the solid and in benzene solution.

All curves show a single minimum. All the minima are flat, indicating oscillations about the minimum energy conformation. Theoretical predictions for 1 agree with results coming from previous¹³ ab initio calculations. This

Table II. Comparisons (Δ) between IP_{calc} (CMO), IP_{calc} (by Eq 1), and IP_{exp} (eV) from Refs 8, 9, and 11

	IP _{exp}	IP _{calc} (CMO)	Δ	IP _{calc} (by eq 1)	Δ	
1	O, O	7.78	8.64	0.86	7.69	0.09
2	S, S	7.94	8.31	0.37	7.79	0.15
3	Se, Se	7.93	8.03	0.10	7.88	0.05
4	Te, Te	7.52	8.32	0.80	7.79	-0.27
5	O, S	7.72	8.30	0.58	7.79	-0.07
6	O, Se	7.74	8.56	0.82	7.72	0.02
7	O, Te	7.61	8.68	1.07	7.68	-0.07
8	S, Se	7.93	8.45	0.52	7.75	0.18
9	S, Te	7.70	8.53	0.83	7.72	-0.02
10	Se, Te	7.67	8.53	0.86	7.72	-0.05

is not the case for 2, in which the calculated θ value of 150° differs from that of 125° as computed by an ab initio method with the 4-31G basis set.¹³ It is noteworthy the coincidence of θ values in the gas phase and in the solid for the Te derivatives 4 (Te, Te) and 10 (Se, Te). This could be attributable to more effective geometric constraints determined by the Te atom, such as the inherent C-Te distance and C-Te-C angle, that determine a sharp minimum and thus a conformation less sensitive to medium effects. The theoretical inversion potentials, with the exception of that for 10, are low enough to determine easy "butterfly" interconversion motion, through the planar transition state ($\theta = 180^\circ$), among the two folded equivalent equilibrium conformations. Similarly, as above for the θ values, in the case of 2 the PM3-calculated barrier is smaller than that coming from ab initio results.¹⁴ The results of the two calculational methods are in agreement in the case of molecule 1.

In their optimized geometries the molecules 1, 5, 6, and 7 attained the C-O distance of 1.387 ± 0.001 Å, which does

(14) Schaefer, T.; Sebastian, R.; Beaulieu, C. *Can. J. Chem.* 1981, 69, 927.

not appreciably change along the series. This is in agreement with solid-state data. On the contrary, appreciable variations are shown by the calculated valency angle C–O–C which changes from 113.84° in 1 to 118° in 5 and 6, and to 119.98° in 7. This latter attained a value corresponding to an sp² hybrid orbital.

Inability of the oxygen atom to participate in the π delocalization effects agrees with the calculated C–O bond order very close to unity. Therefore the C–O–C angle in the planar molecule 1, which was expected to be 120° on the basis of effective p_z– π interaction like in naphthalene, takes the value of 113.84°, which can be related to the effect of the p_z lone pairs (via VSEPR) of the oxygen atoms. Stabilization at minimum energy is attained through simultaneous geometric rearrangements such as the decreased C–O–C angle and increased (by a much less extent) C–O bond distance. In the other three compounds, because of the nonplanarity of the molecule and of the greater bond distances of C–S, C–Se, and C–Te with respect to the C–O distance, the distortion of the C–O–C angle is unnecessary. In fact, the valency and the total charge of the oxygen atom do not change appreciably along the series, since they range between 2.20 and 2.21 and between –0.09 and –0.11 au, respectively. This indicates that the decreasing ortho inductive effect of an electropositive heteroatom (in the order Te > Se > S > O) does not significantly affect the charge distributions.

In 2, 5, 8, and 9, the calculated C–S bond distance ranges about 1.76 Å, whereas a notable difference occurs in the C–S–C angle values on passing from the O, S compound 5 (99.6°) to 2, 8, and 9 (106 ± 1°).

For the selenium-containing chalcanthrenes 3, 6, 8, and 10, the C–Se–C bond angle changes from 96.8° (6) to 111.7° (10). Conversely, in the tellurium series 4, 7, 9, and 10 the C–Te–C angle shows little variation (98 ± 3°).

The ionization potentials, IPs, were calculated by using the semiempirical quantum-mechanic PM3 method. As pointed out by several authors,¹⁵ when we remove an electron from a molecule, it comes from all over the molecule and not from a particular lone pair or bond. Then, the correct values of IP could be obtained by performing a Δ SCF calculation, to take into account collective and relaxation effects. In the simple Koopman's approximation, which neglects the relaxation energy, the theoretical IPs show a satisfactory agreement with the observed IP (IP_{exp}), since the IP_{calc} differs from the experimental value by about ±1.0 eV. In Table II are compared IP_{exp} and IP_{calc}. In this table are also compared IP_{exp} and IP_{calc} calculated for the compounds 1–10 according to the relationship

$$IP_{\text{exp}} = -0.3048IP_{\text{calc}}(\text{CMO}) + 10.325 \quad (1)$$

The shapes (Figure 1) of the HOMO orbitals reflect the deviations from the planarity of the chalcanthrenes and thus the IP values. In fact, in the O, O molecule 1 the HOMO is essentially an antibonding combination between the two highest π orbitals of the rings with the two p_z oxygen orbitals. Because of the folded conformations of the molecules 5, 6, and 7, the p_z– π interactions significantly decrease with a corresponding higher localization of the HOMO on the heavier heteroatom. In the Se, Te 10 and Te, Te 4 compounds the HOMO is, at 90%, localized on

Table III. Measured and Calculated Ionization Energies (IE, eV) of the Lowest Seven Orbitals for Chalcanthrenes 1, 5, 6, and 7

1 (O, O)		5 (O, S)		6 (O, Se)		7 (O, Te)	
exp	calc	exp	calc	exp	calc	exp	calc
7.78	8.64	7.72	8.30	7.74	8.56	7.61	8.68
8.76	9.60	8.71	9.50	8.67	9.52	8.66	8.99
9.50	10.08	9.40	10.11	9.33	10.08	9.24	9.52
9.70	10.11	9.60	10.31	9.50	10.33	9.40	9.81
11.24	12.31	10.63	11.45	10.33	11.19	9.94	10.02
11.50	12.48	11.13	11.97	10.09	11.49	10.45	11.18
12.20	13.00	11.70	12.62	11.50	12.26	11.53	11.25

the p_z orbital of the tellurium atom, since the considerable high-energy differences do not allow p_z– π interactions. This trend is consistent with the values of the HOMO and thus IP_{calc} energies, since the metallic character of the HOMO increases, thus decreasing the related IP value.

Finally, in Table III are reported and compared with experimental data the values of the first seven MO orbitals for the chalcanthrenes 1, 5, 6, and 7. Table III also shows that the general trend agrees with the experimental data, since the theoretical IEs (IE_{calc}) differ by less than 1.0 eV with respect to the IE_{exp}s.

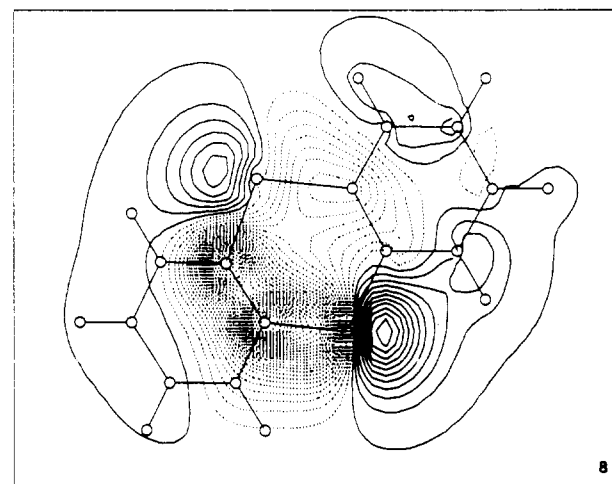
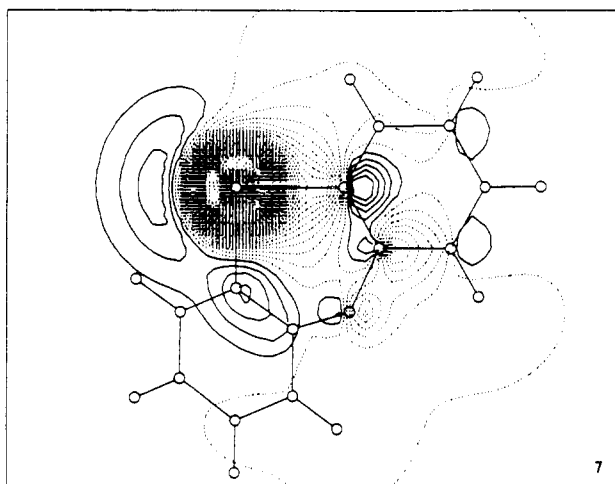
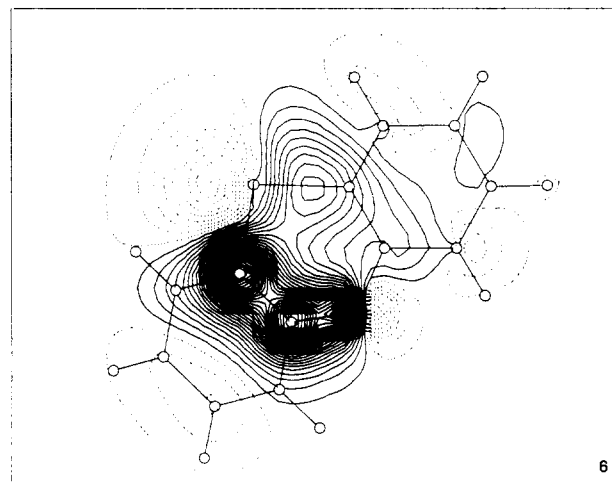
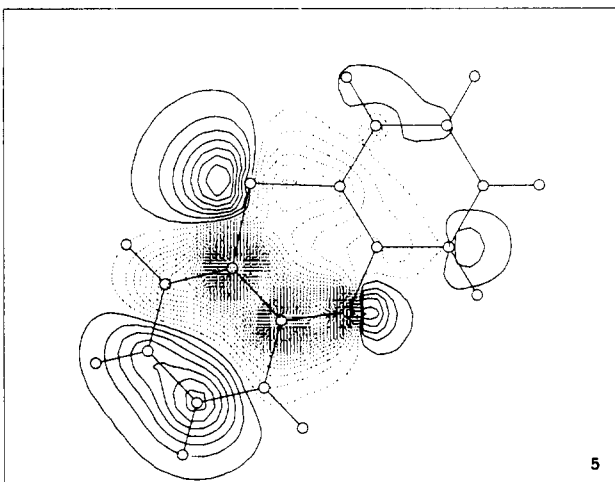
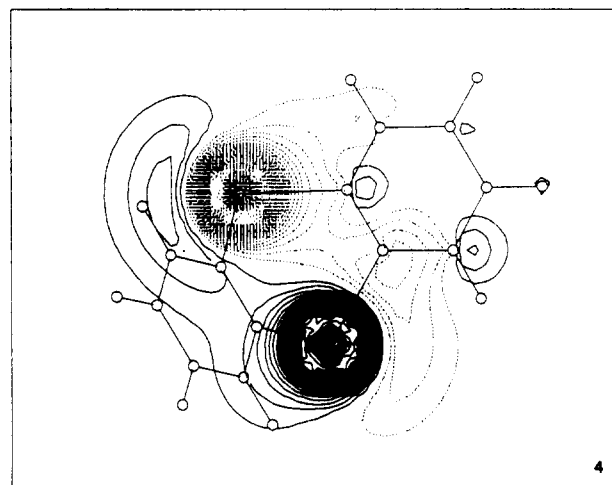
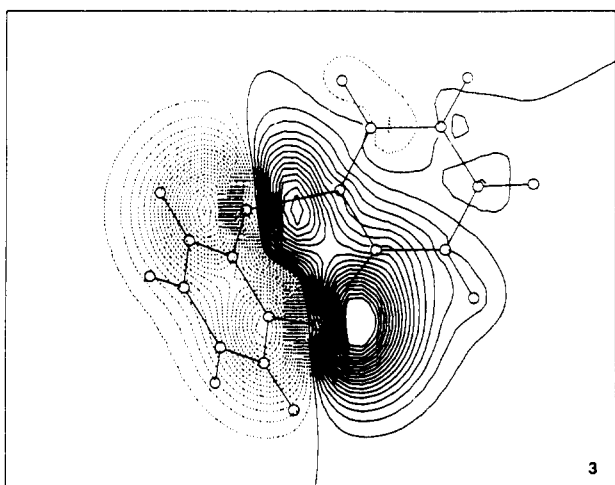
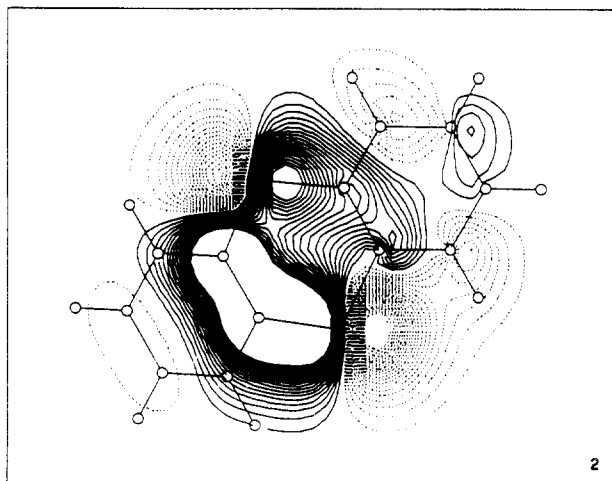
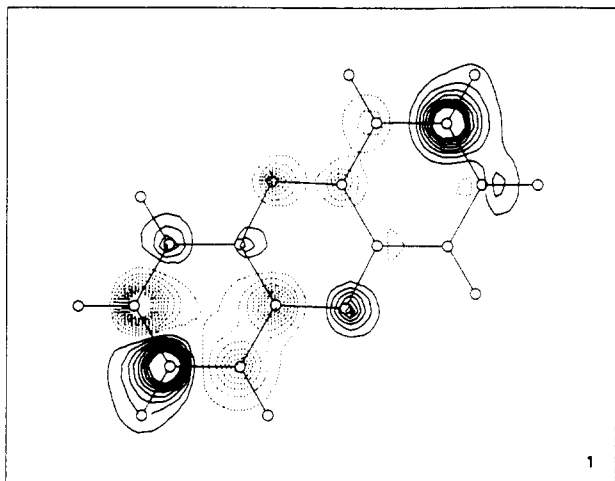
NMR Studies. The proton spectra of molecules 1–4 and 5–10 were analyzed as AA'BB' and ABXY spin-type systems, respectively. These approximated to the first-order spectra with the exception of 5 and 7. The assignment of the H-1 and H-4 resonances was possible due to the resolved long-range couplings (~0.4 Hz) in their splitting patterns. The relative assignments of H-1 and H-4 followed considerations based on the shielding effects of their adjacent heteroatoms. Inspection of Table IV shows that the shielding of the H-1 and H-4 nuclei decreases depending on the heteroatom in the sequence O, S, Se, Te, along with the same trend of the Pauling electronegativities (from 3.5 to 2.0) and the opposite trend of the diamagnetic anisotropies.

Unambiguous assignment of the ¹³C resonances was made on correlative bases through the ¹³C–¹H COSY experiments which followed the preliminary complete ¹H spectral analyses. The data are quoted in Table IV. Therein are also reported the carbon–heteroatom one-, two-, and three-bonded couplings. The present definitive assignment of C-2 and C-4 resonances in 5, which agrees with the trend of the charge density values produced by PM3 calculation, corrects the previous uncertain assignment made on the basis of CNDO calculations.^{10,11} However it should be considered that the interpretation, at a nonempirical level, of the observed ¹³C chemical shifts in 1–10 is not possible because of not quantitatively evaluable anisotropic and paramagnetic contributions to the shielding constants.

In accord with the PM3-calculated charge density values, the position of the C-2 (C-3) signal does not appreciably change on passing from 2 to 4. The ~4 ppm upfield shift of this resonance in 1 with respect to 2–4 was not in line with the theoretical predictions of charge densities. This should indicate that the paramagnetic term is considerably modified by the oxygen atom. Such a perturbing effect is retained in the oxygen-containing 5–7.

The C-11 and C-12 nuclei reciprocally experience the inductive effect due to the directly bonded chalcogen atom, in addition to the ortho substitution effect for which the heteroatom anisotropy must be taken into account together with conformational and ring strain effects. This

(15) Peters, D. *J. Chem. Phys.* 1966, 45, 3474 and references therein.



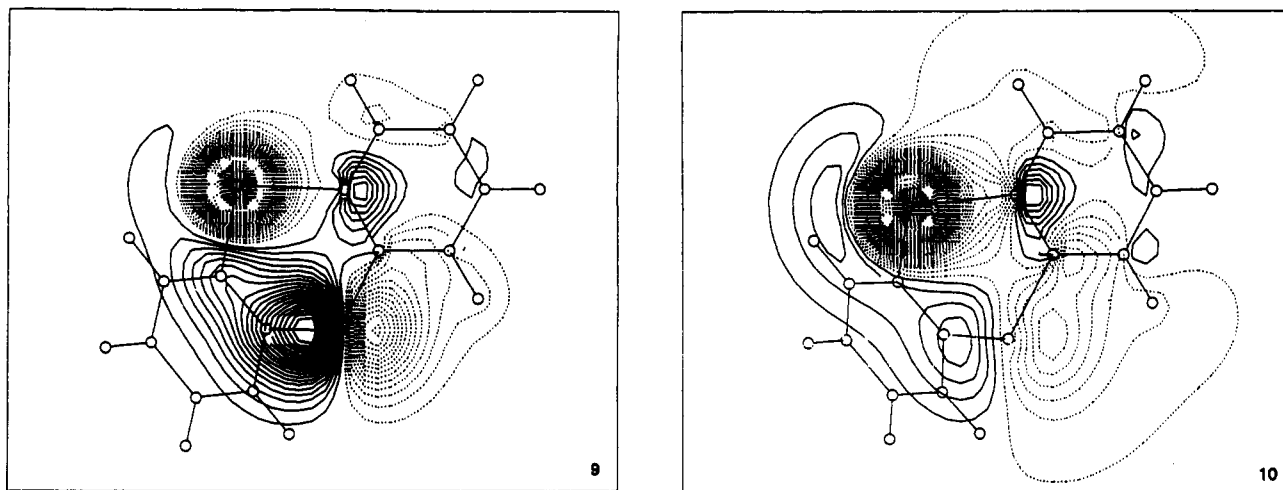


Figure 1. Contours of the real part of canonical MOs for chalcanthrenes 1-10 plotted at $z = 0$ in the C-13-C-1-C-2 plane. The negative part is given by dotted contours. The orientation of the heteroring in molecules 5-10 ($X \neq Y$) is attained by positioning the Y atom in the upper half portion of the drawing.

Table IV. Summary of NMR Spectral Parameters for Chalcanthrenes 1-10 in $CDCl_3$ Solution

compd	X	Y	chemical shifts (δ , ppm from TMS)									
			H-1	H-2	H-3	H-4	C-1	C-2	C-3	C-4	C-11	C-12
1	O	O	6.81	6.85	6.85	6.81	116.20	123.60	123.60	116.20	142.10	142.10
2	S	S	7.48	7.24	7.23	7.48	128.71	127.66	127.66	128.71	135.52	135.52
3	Se	Se	7.71	7.24	7.24	7.71	131.20	128.05	128.05	131.20	134.55	134.55
4	Te	Te	8.03	7.17	7.17	8.03	136.56	128.44	128.44	136.56	130.62	130.62
5	O	S	6.70	7.12	7.00	7.09	117.77	127.68	124.49	126.75	120.10	152.13
6	O	Se	7.11	7.19	7.03	7.29	118.71	128.24	125.00	116.29	116.29	153.02
7	O	Te	7.244	7.236	7.03	7.51	119.71	129.21	125.61	135.05	102.11	155.91
8	S	Se	7.59	7.28	7.23	7.64	129.49	127.92	127.91	130.75	133.66	136.20
9	S	Te	7.73	7.28	7.16	7.84	130.42	128.45	127.97	136.10	123.22	139.71
10	Se	Te	7.85	7.25	7.17	7.90	131.70	128.54	128.07	136.36	124.79	138.71

compd	X	Y	coupling constants (Hz)											
			J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	$^1J_{X,C-12}$	$^1J_{Y,C-11}$	$^2J_{X,C-1}$	$^2J_{Y,C-4}$	$^3J_{X,C-2}$	$^3J_{Y,C-3}$
1	O	O	7.97	1.50	0.36	7.53	1.50	7.97						
2	S	S	7.68	1.45	0.42	7.48	1.45	7.68						
3	Se	Se	7.70	1.44	0.38	7.35	1.44	7.70	104.4	104.4	23.9	23.9	6.24	6.24
4	Te	Te	7.54	1.53	0.39	7.47	1.53	7.54	281.9	281.9	54.8	54.8	12.80	12.80
5	O	S	8.12	1.29	0.37	7.41	1.58	7.74						
6	O	Se	8.11	1.32	0.34	7.38	1.58	7.69		94.8		21.3		5.7
7	O	Te	7.98	1.37	0.33	7.33	1.62	7.57		250.6		38.9		9.8
8	S	Se	7.75	1.36	0.46	7.45	1.33	7.71		103.4	22.7		6.3	
9	S	Te	7.78	1.40	0.46	7.50	1.38	7.60		274.66	45.48		12.6	
10	Se	Te	7.76	1.37	0.46	7.40	1.41	7.60	105.2	282.0	25.2	49.7	6.29	12.82

"heavy atom" effect, reported for anisoles and chalcogen derivatives,¹⁶⁻¹⁹ could therefore account for the abnormally high shielding of the carbon bonded to Te in 4, 7, 9, and 10. Such a shielding effect of the Te atom on C-11 was also observed in 2, 8, and 9 accordingly to a trend previously observed for 1,3-diheteroles.²⁰

In the case of compounds 5-10 the trends of chemical shifts of corresponding carbons along the series can be interpreted in terms of simple combinations of the effects of the substituents.

Carbon-heteroatom (Se, Te) coupling constants were detected in the broadband $^{13}C\{^1H\}$ spectra. The $^1J_{Se,C-11}$ values approximate the range of those observed in com-

pounds having the heteroatom bonded to an sp^2 carbon²¹ and are in fair agreement with the 1J constant in dihydrobenzoselenophene²² and organoselenium compounds.²³ The $^1J_{Te,C-11}$ were of the same order of magnitude as those reported in diaryltellurium compounds²⁴ and in 1,3-ditellurole.²⁵ The magnitudes of the evidenced $^2J_{Se,C-4}$ in 3, 6, and 8 and $^2J_{Te,C-4}$ in 4, 7, and 9 were larger than those previously measured for selenium and tellurium derivatives,^{21,22} respectively. Surprisingly, the $^2J_{Se,C-12}$ and $^2J_{Te,C-12}$ were undetectable in compounds 3, 6, and 8 and 4, 7, and 9 respectively. These near-zero coupling values could be resulting from the algebraic sum of two simultaneous couplings (positive and negative) to the C-12 carbon through two different pathways. One of them can be the two-bond route Y,C-11,C-12 (positive J) and the

(16) Llabres, G.; Baiwir, M.; Christiaens, L.; Denoel, J.; Laitem, L.; Piette, J.-L. *Can. J. Chem.* 1978, 56, 2008 and references therein.

(17) Piette, J.-L.; Debergh, D.; Baiwir, M.; Llabres, G. *Spectrochim. Acta* 1980, 36A, 769.

(18) Laitem, L.; Christiaens, L.; Renson, M. *Org. Magn. Reson.* 1980, 13, 319.

(19) Barwir, M.; Llabres, G.; Luxen, A.; Christiaens, L.; Piette, J.-L. *Org. Magn. Reson.* 1984, 22, 312.

(20) Sukai, R. S.; Verboom, W.; Mejer, J.; Schoufs, M. J. M.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* 1981, 100, 10.

(21) Meese, C. O.; Walter, W. *Magn. Reson. Chem.* 1985, 23, 327.

(22) Reich, H. J.; Trend, J. E. *J. Chem. Soc., Chem. Commun.* 1976, 310.

(23) Laitalainen, T.; Rahkamaa, E. *Org. Magn. Reson.* 1982, 20, 102.

(24) Fazakerley, G. V.; Celotti, M. *J. Magn. Reson.* 1979, 33, 219.

(25) Dettly, M. R.; Henrichs, P. M.; Whitefield, J. A. *Organometallics* 1986, 5, 1544.

other the Y,C-14,C-13,X,C-12 one (negative J) as hypothesized for 9,10-dihydroanthracene.²⁶ An alternative explanation can consist of a through-space interaction of the back lobes of the heteroatoms which determines, owing

to their impinging effect, a negative sign contribution to the coupling.²⁶

(26) Marshall, J. L.; *Carbon-Carbon and Carbon-Proton NMR Couplings: Applications to Organic Stereochemistry and Conformational Analysis*; Verlag Chemie International: Deerfield Beach, FL, 1983; Chapter 3-4.

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