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THE STRUCTURE AND INTRAMOLECULAR ELECTRONIC EFFECTS IN PHENAZA(OXA-, THIA-)-ELEMENTINES OF GROUP IV

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Summary

According to spectral data, the anthracene-like heterocyclic compounds containing Si, Ge or Sn atoms exhibit *p–π* or *d–π* type conjugative effects. In an attempt to confirm the presence of such conjugation, a full X-ray structure analysis has been carried out on 12 compounds of this type of phenaza (oxa-, thia-)-silines, -germines and -stannines. The geometrical features of these molecules are in a good agreement with the spectral data and testify to the presence of common π-electronic systems.

Introduction

The anthracene-like heterocyclic compounds containing two different heteroatoms in the central ring: phenaza(oxa-, thia-)-elementines, are characterized by a certain interaction between electron-donor atoms (nitrogen, sulfur, oxygen) and electron-acceptor ones (in particular silicon, germanium, tin). This interaction takes place *via* the π-system of the phenylene rings. The existence of such interaction has been shown by the investigation of a vast series of phenaza(oxa-, thia-)-silines, -germines and -stannines, in both ground and excited states, using different physico-chemical methods. In Table 1 there is a summary of experimental data on the compounds $X(C_6H_4)_2MPh_2$, where X = NEt, O, S and M = Si, Ge, Sn, obtained by IR spectroscopy [1], NMR. (^1H, ^{13}C) spectroscopy [1,2], Mössbauer spectroscopy [3], electron spectroscopy of charge transfer complexes with tetracyanoethylene [4] and with molecular O_2 [5]. The dependence of the listed data on the nature of both

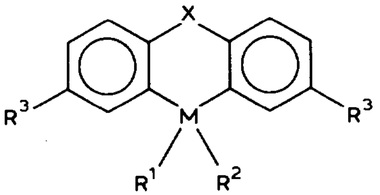

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TABLE 1

SOME CHARACTERISTIC PARAMETERS OF DIFFERENT SPECTRA OF DIPHENYLPHENAZA(OXA–, THIA–)-ELEMENTINES $X(C_6H_4)_2MPh_2$ (X = NEt, O, S; M = Si, Ge, Sn) (ref. 1–5, 9–11)

Spectrum	Parameter	M	X = NEt	X = O	X = S
IR	ν(C–M) (cm^{-1})	Si	460	435	450
		Ge	325	310	-
		Sn	265	260	-
	$\nu(C–C)_{ar}$	Si	1585	1600	1590
		Ge	1580	1585	-
		Sn	1583	1580	-
	$\nu(C–H)_{ar}$	Si	490, 500	495, 510	520, 530
		Ge	425, 462	450, 465	495, 510
		Sn	430, 445	435, 450	-
UV	λ_{max}(10 gϵ) (nm)	Si	327(3.80)	300(3.95)	290(3.90)
		Ge	320(3.83)	295(3.67)	290(3.62)
		Sn	320(3.20)	295(3.67)	290(1.88)
NMR (^1H)	$\delta(NCH_2)$	Si	4.00		
		Ge	3.96		
		Sn	3.76		
NMR (^{13}C)	$\delta(C_X, C_M)$ *endo*	Si	150.3, 122.5	160.0, 133.9	143.8, 132.7
		Ge	150.3, 125.2	160.0, 35.2	144.9, 133.9
		Sn	153.6, 127.2	-	-
Mössbauer splitting	Δ(mm/e)	Sn	1.05	0.85	-
Charge transfer complexes with $C_2(CN)_4$	$\nu \cdot 10^{-3}$ cm (c.t.)	Si	11.9	17.9	16.1
		Ge	12.1	17.9	16.4
		Sn	13.7	18.0	16.8
	$\nu_e \cdot 10^{-3}$ cm	Si	28.4	30.0	30.5
		Ge	29.0	32.6	31.5
		Sn	29.0	32.8	32.6
Emission spectra with O_2 complexes	K_q(1/mol)	Si	520	130	540
		Ge	770	190	600
		Sn	1800	530	3400

TABLE 2

THE KNOWN DATA ON THE STRUCTURES OF PHENELEMENTINES

Compound	Dihedral angle (°)	Reference
$O(C_6H_4)_2GeCl_2$	170.5	12
$EtN(C_6H_4)_2SiPh_2$	157.3	13
$S(C_6H_4)_2SiMe_2$	148.0	14
$Pyp(CH_2)_2N(C_6H_4)_2SiMe_2$	143.0, 147.4	15
$S(C_6H_4)_2GeMe_2$	143.6	16
$O_2S(C_6H_4)_2SiMe_2$	134.1, 143.0	17
$S(C_6H_4)_2Si(CH_2Cl)Me$	141.3	14
$EtN(C_6H_3Br)_2SiMe_2$	140.9	18
$EtN(C_6H_3Br)_2SiPh_2$	138.8	19
$CH_2(C_6H_4)_2SiPh_2$	136	20

heteroatoms, and also on the nature of the substituents at M and at the 2 and 8 positions of the heteroanthracene nucleus, supports the existence of the effect being discussed. The data from the EPR spectra of anion radicals [6], and the results of quantum chemical calculations [7] also confirm the internal electron interaction. Regardless of the accepted opinion that for molecules to exhibit π-conjugation it is nesessary to have planar structures, the molecules of the type under discussion, as a rule turn out to be non-planar and they are characterized by a dihedral angle between the planes of the peripheral phenyl rings (this angle is considerably smaller than 180°) and by a significant deviation of the hetero atoms from the plane of central ring carbon atoms. This is confirmed also by the variety of data in Table 2, obtained by different authors, on the crystal structures of silicon and germanium derivatives.

In the present work we report the results of the full X-ray structure analysis of twelve silines, germines and stannines, which was undertaken in an attempt to clarify the connection between the geometry of the molecules and the presence of conjugation in them, which give a common π-electron system, as in aromatic compounds.

X–Ray experiments

For the X-ray structure analysis we selected the substances listed in Table 3.

The single crystals were obtained by solvent evaporation (octane for III, IV, X, XII; octane + CCl_4 for IX, XI; methyl ethyl ketone for V, VII; ethyl acetate + ethanol for I, II, VI, VIII).

Refinement of the unit cell parameters, and data collection were performed using a Syntex P$\bar{1}$ automatic four-circle diffractometer employing Mo radiation with a graphite monochromator in the $\theta/2\theta$ scan mode. The main crystallographic parameters are given in Table 4.

The structures were solved either by direct methods (I–IV, VII) or by the heavy atom technique (V, VI, VIII–XII). The experimental data were corrected for Lorentz and polarization effects and (for IV, VII–XII) also for absorption. The structure refinement was performed by the least-squares method using anisotropic (for non-hydrogen atoms) and isotropic (H) thermal parameters. The H atoms were localized

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TABLE 3

COMPOUNDS USED IN THE X-RAY CRYSTALLOGRAPHIC STUDY

Compound	M	X	R^1	R^2	R^3
I	Si	O	Ph	Ph	H
II	Si	S	Ph	Ph	H
III	Si	NEt	Ph	Ph	Me
IV	Si	NEt	OMe	*o*-Tol	Br
V	Ge	O	Ph	Ph	H
VI	Ge	NEt	Ph	Ph	H
VII	Ge	NEt	Ph	Ph	Br
VIII	Ge	NEt	Ph	Cl	Me
IX	Sn	NEt	Ph	Ph	Br
X	Sn	NEt	*o*-Tol	*o*-Tol	H
XI	Sn	NEt	*o*-Tol	*o*-Tol	Br
XII	Sn	NEt	*o*-Tol	*o*-Tol	Me

TABLE 4

THE MAIN CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS I–XII WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

No.	a(Å)	b(Å)	c(Å)	γ(°)	Z	SG [b]	D_c [b]	μ [b]	N [b]	R [b]
I	11.810(3)	22.380(6)	14.734(4)	103.10(2)	8	$B2/b$	1.24	1.4	1214	0.030
II	13.190(2)	8.804(1)	9.349(1)	89.99(1) [a]	2	$P\bar{1}$	1.28	2.4	1507	0.030
III	9.791(2)	23.424(4)	10.023(2)	92.19(2)	4	$P2_1/b$	1.17	1.2	1677	0.030
IV	8.880(2)	12.803(3)	18.624(4)	86.33(2)	4	$P2_1/b$	1.58	41.3	1776	0.030
V	11.891(2)	22.494(4)	14.787(3)	105.34(2)	8	$B2/b$	1.38	17.1	1851	0.032
VI	10.763(2)	22.621(5)	8.842(1)	102.43(1)	4	$P2_1/n$	1.33	15.6	2634	0.028
VII	9.901(2)	23.205(5)	10.132(2)	90.01(2)	4	$P2_1/b$	1.65	50.4	2206	0.031
VIII	8.615(2)	25.503(9)	8.943(2)	97.34(2)	4	$A2$	1.39	18.0	1504	0.031
IX	9.412(2)	16.656(4)	17.082(3)	113.89(2)	4	$P2_1/b$	1.70	45.2	2242	0.036
X	12.111(1)	18.730(2)	10.451(1)	100.05(1)	4	$P2_1/n$	1.41	11.2	2942	0.023
XI	9.958(1)	12.517(2)	21.020(3)	81.48(1)	4	$P2_1/n$	1.68	40.6	2711	0.030
XII	19.032(5)	12.731(4)	10.527(3)	93.55(2)	4	$P2_1/n$	1.37	10.2	4408	0.025

[a] α 67.10(1), β 73.56(1)° [b] SG, space group; D_c, calculated density (g/cm^3); μ, absorption coefficient (cm^{-1}); N, number of independent reflections with $I > 3\sigma(I)$; R, final R-factor.

TABLE 5

THE COMPARISON OF THE MAIN STRUCTURAL FEATURES OF COMPOUNDS I–XII, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(M–C and X–C corresponding interatomic distances; CMC and CXC, corresponding valence angles; ΔM and ΔX, deviation of the corresponding atoms from the plane of carbon atoms of the central ring; ω, dihedral angle by line M…X; *h*, height of *N*-pyramid)

No.	M–C(*endo*) (Å)	M–C(*exo*) (Å)	X–C(*endo*) (Å)	X–C(*exo*) (Å)	CMC (deg.)	CXC (deg.)	ΔM (Å)	ΔX (Å)	ω (deg.)	*h* (Å)
I	1.852(3)	1.866(3)	1.385(4)	-	101.2(2)	125.2(2)	0.204(1)	0.159(3)	165.9	-
II	1.858(3)	1.870(3)	1.774(3)	-	105.9(2)	107.2(1)	0.506(1)	0.472(1)	150.4	-
III	1.849(3)	1.867(3)	1.415(4)	1.471(4)	100.4(1)	121.8(2)	0.614(1)	0.379(2)	141.4	0.105
IV	1.834(6)	1.868(6)	1.413(7)	1.474(8)	100.4(2)	125.2(5)	0.291(2)	0.188(3)	161.5	0.054
V	1.928(4)	1.939(4)	1.389(6)	-	99.1(2)	126.4(4)	0.191(1)	0.176(4)	165.8	-
VI	1.922(3)	1.940(3)	1.410(4)	1.471(4)	99.9(1)	124.9(3)	0.422(1)	0.296(3)	156.1	0.028
VII	1.927(5)	1.939(5)	1.416(7)	1.478(7)	98.1(3)	122.0(4)	0.654(1)	0.420(5)	138.2	0.143
VIII	1.920(6)	1.939(6)	1.429(8)	1.474(8)	100.1(2)	121.8(5)	0.418(1)	0.366(6)	146.6	0.054
IX	2.124(8)	2.142(7)	1.440(9)	1.470(9)	92.0(3)	118.0(7)	0.814(1)	0.596(7)	125.2	0.262
X	2.126(3)	2.140(4)	1.434(5)	1.479(5)	93.4(1)	118.2(3)	0.751(1)	0.590(3)	129.6	0.250
XI	2.132(5)	2.140(6)	1.439(7)	1.473(8)	92.6(3)	119.2(5)	0.740(1)	0.563(5)	133.3	0.211
XII	2.127(3)	2.142(3)	1.436(4)	1.472(4)	93.0(1)	116.9(3)	0.795(1)	0.610(3)	124.4	0.266

by difference syntheses. The final R-values and the number of independent reflections with $I > 3\sigma(I)$ are also given in Table 4. All calculations were made using SHELXTL (G.M. Sheldrick) programms incorporated in the Nova-3 computer in the crystallographic system Nicolet-R3.

Discussion

It can be seen first of all from the data in Table 5 that the *endo*cyclic angles CMC are significantly smaller than the usual tetrahedral values, and similarly there is a rather large deviation of the heteroatoms from the plane defined by the carbon atoms of the central ring (which has a normal or slightly flattened boat conformation). As a whole, all molecules of the investigated compounds are non-planar, being bent along the line M...X. The dihedral angle increases in the order Si < Ge < Sn, as does the height of the *N*-pyramid (i.e. the deviation of the N atom from the plane of its neighbours). The data in Tables 2 and 5 also indicate that the dihedral angle depends on the nature of the atom X (S > N > O), the nature of R1 and R2 (alkyl > aryl), and the nature of R3 (Br > CH_3 > H).

Another feature which points to the presence of conjugation is the shortening of the *endo*-bonds M-C by 0.01-0.04 Å relative to the *exo*-bonds (especially in the silines). It can also be seen that the *exo*- and *endo*-bonds at the nitrogen atom are not equivalent.

Therefore the spectral data, along with the geometrical features of the phenelementine molecules found by the X-ray structure analysis, allow us to conclude that organometallic compounds of this type exhibit p-π and d-π conjugation despite the significantly non-planar configuration of the conjugating orbitals. The possibility of conjugation diminishes with decrease in the dihedral angle (the stannines have the most non-planar conformations (Table 5) and the smallest effects of conjugation (Table 1)). Evidently this is possible because as the M and X atoms move from the plane of the central ring their *d*- and *p*-orbitals move parallel to the π-orbitals of the peripheral phenyl rings and so their mutual overlapping (conjugation) remains to a certain extent, depending on the relative displacement of M and X from the planes of these rings. The correlation between the size of the conjugation effects, the dimensions of the M atoms, and the extent of the non-planarity in the Si, Ge and Sn derivatives is probably also related to the increasing spatial capability (diffusivity) of the *d*-orbitals in this series.

The results of the present work demonstrate the fact that in the compounds discussed, phenelementines of Group IV, the conjugation effects may be retained despite the significant deviation of the conjugating elements from a planar and linear geometry, whereas conjugation in organic substances is practically impossible when the atoms are out of the plane.

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