CRYSTAL STRUCTURES AND NQR SPECTRA OF MOLECULAR ADDUCTS $(\text{Et/Ph})_2\text{SnI}_2\text{L}_2$ ($\text{L} = (\text{CH}_3)_2\text{SO}$ AND $[(\text{CH}_3)_2\text{N}]_3\text{PO}$) EXHIBITING LARGE ^{127}I ASYMMETRY PARAMETERS

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A notable increase in the electric field gradient asymmetry parameter was observed at the ^{127}I sites in adducts $\text{R}_2\text{SnI}_2\text{L}_2$ when R is replaced by Et or Ph. This increase accompanied the expected elongation of Sn-I bonds *cis* to Et/Ph, hence evidencing a disturbance of the iodine valence p_π -orbitals upon the substitution. With the aim to understand the reason for this disturbance, we correlated the ^{127}I NQR and X-ray diffraction data for the title compounds. The results showed that secondary iodine-sulfur contacts may account for large η -values observed for $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$, whereas in the remaining compounds, the increased asymmetry parameters seem to be caused by an interaction of the iodine π -system with that of the phenyl (pyridine) rings.

INTRODUCTION

The adducts titled attracted our attention for their unusual ^{127}I NQR spectra. It is known that substitution of a σ -donor group R for a halo ligand in a complex $[\text{SnHal}_6]^{2-}$ or an adduct SnHal_4L_2 to give $[\text{SnHal}_5\text{R}]^{2-}$ or $\text{RSnHal}_3\text{L}_2$ results in a weakening (lengthening) of the Sn-Hal bond *cis* to R. The weakening, measured by ^{127}I NQR as a relative increase of the effective charge on the appropriate I atoms in adducts of the type $\text{AlkSnI}_3\text{L}_2$, amounted to ca. 25%, whereas the two alkyl groups in $\text{R}_2\text{SnI}_2\text{L}_2$ increased the charge almost additively (up to 49%) and gave rise to an elongation of the Sn-I bonds by up to 0.2 Å [1,2].

It was found that in most dialkyl-/diphenyl-substituted iodo adducts, in which a simultaneous determination of both quadrupole coupling constant ($\text{QCC} = e^2 Qq_{zz}/h$) and electric field gradient (EFG) asymmetry parameter [$\eta = (q_{xx} - q_{yy})/q_{zz}$] at the ^{127}I site is possible, the elongation of the *cis* Sn-I bonds mentioned above was accompanied by a dramatic increase in η . Such an increase was observed in five of six pseudo-octahedral adducts of diethyl- and diphenyltin diiodides studied by NQR [3]. This evidenced that the iodine valence p_π -orbitals were notably disturbed as a result of the substitution. In order to understand the reason for this disturbance, we correlated the ^{127}I NQR spectroscopy and X-ray diffraction data for the compounds titled.

MATERIALS AND METHODS

The organic solvents and ligands, used for the preparation of adducts, were purified and dehydrated by routine procedures [4]. The reactions proceeded in inert solvent media (benzene, hexane, dichloromethane), and all manipulations were carried out in a dry box, because the organic ligands and resulting products were highly hygroscopic. A stoichiometric amount of ligand was added to a diethyl(diphenyl)diiodostannate solution. The resulting precipitate was filtered, washed twice with benzene on a filter, and dried in vacuum.

The following abbreviations will be used through the whole text below: DMSO for dimethyl sulfoxide, and HMPT for $[(\text{CH}_3)_2\text{N}]_3\text{PO}$, hexamethylphosphotriamide.

In order to grow the $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$ single crystals, we dissolved powdered $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$ in a 1 : 1 benzene-octane mixture and added an excess of octane until the solution grew turbid. The heating of the reaction mixture gave a true solution, which was evaporated to yield the $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$ single crystals.

The adducts so prepared were characterized by the results of elemental analysis (Table 1) and ^{127}I NQR spectra (Table 2). Table 1 lists also the solvents used for the preparation of the ad-

ducts. The ¹²⁷I NQR spectra were obtained using a pulse NQR spectrometer produced by SKB IRE AN SSSR.

Table 1. Results of elemental analysis for (Et₂/Ph₂)SnI₂L₂ and solvents used for their preparation

Compound	(Found/Calcd), %		N	Solvent
	H	C		
Et ₂ SnI ₂ (DMSO) ₂	3.77/3.78	16.32/16.37	-	dichloromethane
Ph ₂ SnI ₂ (DMSO) ₂	3.34/3.25	28.35/28.14	-	dichloromethane
Et ₂ SnI ₂ (HMPT) ₂	5.88/5.88	24.30/24.36	10.68/10.65	hexane
Ph ₂ SnI ₂ (HMPT) ₂	5.28/5.24	32.70/32.57	9.35/9.49	hexane
Et ₂ SnI ₂ (Py) ₂	3.43/3.42	28.61/28.56	4.69/4.76	benzene
Ph ₂ SnI ₂ (Py) ₂	2.92/2.94	38.62/38.58	4.07/4.09	benzene

Table 2. ¹²⁷I NQR spectra (MHz) of R₂SnI₂L₂ and SnI₄L₂ compounds at 77 K, the electronic characteristics of the iodine atoms^{a)}, and the appropriate Sn-I bond lengths.

Compound	e^2Qq_{zz}/h	$\eta, \%$	Np_z	Np_x-Np_y ($Np_x = 2$)	δ, e	$d, \text{\AA}$
Et ₂ SnI ₂ (DMSO) ₂	409.1	39.1	1.798	0.046	-0.752	2.941
<i>cis</i>	523.0	13.3	1.762	0.020	-0.742	2.982
			1.776 ^{b)}		-0.690 ^{b)}	
Ph ₂ SnI ₂ (DMSO) ₂	647.3	24.3	1.695	0.046	-0.649	
	707.8	8.6	1.682	0.018	-0.665	
Et ₂ SnI ₂ (HMPT) ₂	467.9	6.5	1.791	0.009	-0.782	3.016
<i>trans</i>						
Ph ₂ SnI ₂ (HMPT) ₂ (I)	495.2	41.2	1.754	0.059	-0.695	2.957
<i>trans</i> (II)	504.1	41.2	1.750	0.060	-0.689	2.938
SnI ₄ (TMU) ₂ ^{c)}						
<i>cis</i>	ax 1048.0	1.9	1.540	0.006	-0.534	
	eq 1095.3	6.0	1.512	0.019	-0.493	
SnI ₄ (TPPO) ₂ ^{d)}						
<i>cis</i>	ax					2.813
	eq					2.782
Et ₂ SnI ₂ Py ₂	504.35	25.7	1.761	0.038	-0.723	
	542.1	8.8	1.757	0.014	-0.742	
Ph ₂ SnI ₂ Py ₂	630.03	18.9	1.708	0.035	-0.673	

a) Np_i ($i=x, y, z$) - the occupancies of the iodine $5p_{\sigma,\pi}$ orbitals; δ, e - the effective charges born by the iodine atoms; b) At such values of Np_z and δ , the point 7 in Fig. 3 will lie on the correlation line, so that $Np_x = 1.979 e$ and $Np_y = 1.933 e$ (see text); c) TMU=tetramethyl urea, [(CH₃)₂N]₂CO; d) TPPO=triphenylphosphine oxide, (C₆H₅)₃PO.

An X-ray study of Ph₂SnI₂(HMPT)₂ was described earlier [5]. The hydrolytically unstable single crystal of Et₂SnI₂(DMSO)₂ was sealed in a capillary. Data collection was carried out on an automatic Enraf-Nonius CAD-4 diffractometer (λ MoK α , ω -scanning). The crystals are monoclinic, space group P2₁/c, $a=9.044(2)$, $b=15.111(4)$, $c=13.331(4)$ Å, $\beta=91.38(2)^\circ$, $Z=4$. 3192 Independent reflections were collected in the 2θ range 0-50°. Empirical absorption correction using ψ -scan curves for 9 reflections was applied. The coordinates of tin and two iodine atoms were determined by the Patterson method, the positions of the remaining non-hydrogen atoms were found from difference Fourier synthesis. The structure was refined on $|F|^2$ using all reflections with SHELXL93 [6] to $R_w=0.125$, $R=0.050$. Atomic coordinates for Et₂SnI₂(DMSO)₂ are given in Table 3, all crystal-

lographic data and experimental details for $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$ and $\text{Ph}_2\text{SnI}_2(\text{HMPT})_2$ are deposited at the Cambridge Crystallographic Data Centre.

Table 3. Atomic coordinates and equivalent isotropic parameters U_{eq} for $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$

Atom	X	Y	Z	U_{eq}
I1	0.45092(9)	0.28694(6)	0.64318(5)	0.0858(3)
I2	0.07082(10)	0.25884(7)	0.85845(6)	0.0938(4)
Sn	0.24666(7)	0.39759(4)	0.76280(5)	0.0555(3)
S1	0.3975(4)	0.5564(2)	0.6187(3)	0.0526(13)
S2	0.0596(4)	0.5803(2)	0.8237(3)	0.0533(13)
S11	0.4355(14)	0.5853(8)	0.6862(12)	0.054(5)
S21	0.0972(11)	0.5560(6)	0.8895(9)	0.041(4)
O1	0.3479(9)	0.5261(4)	0.7217(5)	0.084(2)
O2	0.1138(10)	0.4897(6)	0.8588(6)	0.061(3)
O21	0.1501(21)	0.5269(11)	0.7797(13)	0.024(5)
C1	0.3970(11)	0.3908(7)	0.8913(7)	0.066(3)
C2	0.5483(14)	0.4379(12)	0.8792(11)	0.121(6)
C3	0.1076(13)	0.3966(8)	0.6275(8)	0.085(4)
C4	-0.0526(17)	0.4300(15)	0.6444(16)	0.207(11)
C5	0.3333(13)	0.6677(7)	0.6119(8)	0.073(3)
C6	0.5972(11)	0.5829(8)	0.6344(9)	0.082(4)
C7	0.1667(13)	0.6609(7)	0.8953(8)	0.077(3)
C8	-0.1138(11)	0.5921(7)	0.8792(8)	0.074(3)

RESULTS AND DISCUSSION

Table 2 lists the experimentally measured ^{127}I NQR parameters for the adducts of diethyl-/diphenyltin diiodide, the estimated values of effective charges ($-\delta$) on the iodine atoms, and iodine $5p$ valence orbital occupancies Np_i ($i = x, y, z$). The appropriate Sn-I bond distances are also summarized in this table. Similar characteristics for the parent unsubstituted hexacoordinate adducts of SnI_4 are given for comparison.

As one can see from Table 2, the largest increase in η , as a result of replacement of two iodine atoms by phenyl groups, is exhibited by the adduct with HMPT. The appropriate ^{127}I NQR spectrum consists of two sets of lines corresponding to the two crystallographically nonequivalent iodine sites having closely similar spectroscopic characteristics. The introduction of the phenyl groups resulted in an elongation of the Sn-I bonds by, on average, 0.165 Å with respect to those in the unsubstituted $\text{SnI}_4(\text{TPPO})_2$ adduct. Simultaneously, the occupancy difference between the iodine valence p_π orbitals increased from 0.019 e in unsubstituted $\text{SnI}_4(\text{TMU})_2$ to 0.06 e in $\text{Ph}_2\text{SnI}_2(\text{HMPT})_2$, which gave rise to an increase of the asymmetry parameter value from 6% in $\text{SnI}_4(\text{TMU})_2$ to 41.2% in the the diphenyl-substituted adduct with HMPT.

The obvious suggestion accounting for such a disturbance of the iodine π -system is that in the $\text{Ph}_2\text{SnI}_2(\text{HMPT})_2$ structure, secondary non-valence intra- or intermolecular contacts exist that involve the iodine atoms. The results of the X-ray study do not, however, support this suggestion. Two crystallographically independent molecules of $\text{Ph}_2\text{SnI}_2(\text{HMPT})_2$ (I and II) occupy special positions at the centres of inversion, all the angles around the tin atom differ from octahedral only slightly (by 1.5° at largest). The phenyl rings are oriented bisectorially with respect to the O-Sn-I angles in the equatorial plane. No secondary contacts were found in this structure.

In the crystals of $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$, two crystallographically inequivalent iodine positions, characterized by essentially different spectroscopic parameters, were identified by ^{127}I NQR. According to the X-ray diffraction data, the coordination polyhedron around tin is an octahedron with *trans* ethyl groups and *cis* DMSO molecules (Fig.1). Both DMSO molecules occupy disordered positions, so that the sulphur atom of one of the DMSO molecules occupies the positions at the

opposite sides of the O1C5C6 plane, whereas in the other molecule, both sulphur and oxygen atoms are sited at disordered positions. In Table 4, the principal bond lengths and angles are summarized for the prevailing configuration of the adduct.

Fig. 1. Molecular structure of Et₂SnI₂(DMSO)₂, showing disorder in DMSO ligands (occupancies are given in parentheses)

In the DMSO ligands, the sulfur atoms are known to have a strong tendency to form secondary contacts to halogen or oxygen atoms. As is seen from Fig. 2, the intramolecular S2...O1 of 3.06 Å, S1...I1 of 4.11 Å, and intermolecular S2...I2 of 3.79 Å contacts exist in the structure of Et₂SnI₂(DMSO)₂. Therefore, in this compound, the molecular packing involving the I1 atoms in the secondary contacts with S2 seems to be the reason for the large value of η (39.1%, $Np_x - Np_y = 0.046$ e, see Table 2).

Table 4. Selected bond lengths (Å) and angles (°) in the structure of Et₂SnI₂(DMSO)₂

Sn-I1	2.982(1)	Sn-O2	2.253(6)	Sn-C1	2.164(10)
Sn-I2	2.941(1)	Sn-O21	2.16(2)	Sn-C2	2.174(10)
Sn-O1	2.220(6)				
I1-Sn-I2	100.40(4)	I2-Sn-O1	163.9(2)	O1-Sn-C1	88.9(3)
I1-Sn-O1	95.4(2)	I2-Sn-O2	83.8(2)	O1-Sn-C3	92.0(4)
I1-Sn-O2	173.9(2)	I2-Sn-C1	87.7(3)	O2-Sn-C1	85.0(4)
I1-Sn-C1	90.7(3)	I2-Sn-C3	92.7(3)	O2-Sn-C3	99.7(4)
I1-Sn-C3	84.6(3)	O1-Sn-O2	80.2(3)	C1-Sn-C3	175.3(4)

It is interesting that on the plot giving the effective charge on the iodine atom ($-\delta$) in function of the appropriate Sn-I bond length (Fig. 3), the point 7, corresponding to this site, deviates markedly from the correlation line. Note that the effective charges δ were evaluated assuming that the occupancy of one of the iodine $5p_\pi$ orbitals was equal to 2. This means that the differences $Np_x - Np_y$ between the iodine p_π orbital occupancies, calculated from the measured η -values, were taken to be equivalent to the Sn-I π -bonding character. As Fig. 3 shows, this assumption results in a good correlation between δ and the Sn-I bond length for all the points except that in question. For

this point, the relative occupancies of the iodine 5*p* orbitals (*Np_i*) are different for the same values of experimentally measured NQR parameters (*QCC* and *η*).

Fig. 2. Crystal structure of $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$ (only prevailing conformation retained), showing non-valence contacts.

The effective charge value for the point 7 to be on the correlation line is $\delta = -0.69$ e, which gives the following iodine valence orbital occupancies: $Np_z = 1.778$ e, instead of 1.798 e for this point deviating from the correlation line; $Np_x = 1.979$ e, instead of 2; and $Np_y = 1.933$ e, instead of 1.954 e. Therefore, the deviation of the point 7 from the correlation line serves an indirect evidence that the assumption $Np_x = 2$, used for plotting the correlation, notably underestimates the Sn-I π -bonding character for the iodine atom involved in secondary contacts to sulfur. As Fig. 3 allows to estimate, this contact is associated with the transfer of 0.045 e from the iodine valence p_π -orbitals.

Coming back to the $\text{Ph}_2\text{SnI}_2(\text{HMPT})_2$ adduct, note that its asymmetry parameters ($\eta = 41.2\%$, Table 2), although close in value to the larger one in $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$, correspond to a relatively stronger, than in the latter adduct, disturbance of the iodine π -orbitals: $Np_x - Np_y = 0.06$ e as compared to 0.046 e. As one can see from Table 2, the introduction of the alkyl substituents results in a stronger, than due to the phenyl groups, weakening of the appropriate Sn-I bonds. The effective charges on the iodine atoms in the alkyl-substituted adducts exceed those in the phenyl-substituted analogs by, on average, 0.08 e. But it is seen from Fig. 4 that a rapid increase in the experimentally measured η -values occurs, at a fixed $Np_x - Np_y$ difference, as the σ -electron density at the iodine atom (Np_z) increases, i.e., the weaker the Sn-I bond as a result of substitution, the higher the measured η -value at the given $Np_x - Np_y$ difference and the larger the contribution of the iodine valence p_σ -orbital to η . This accounts for the fact that the closely similar values of η in $\text{Et}_2\text{SnI}_2(\text{DMSO})_2$ and $\text{Ph}_2\text{SnI}_2(\text{HMPT})_2$ (points ■ and ▲, respectively, Fig. 4) are associated with a smaller difference $Np_x - Np_y$ in the former adduct, in which the ethyl substituents weaken the Sn-I bond to a larger extent than the phenyl groups do, hence producing a higher occupancy of the iodine 5*p_σ*-orbital.

Fig. 3. Correlation between the effective charges on the iodine atom ($-\delta$, e) and interatomic Sn-I distances (d , Å) [3]: EtSnI₃(HMPT)₂ (1); Et₂SnI₂(HMPT)₂ (2); SnI₄(Ph₂SO)₂ (3); EtSnI₃(Ph₂SO)₂ (4); Ph₂SnI₂(HMPT)₂ (5, 6); Et₂SnI₂(DMSO)₂ (7, 8); SnI₄(TMU)₂ (9, 10).

Fig. 4. Measured value of the EFG asymmetry parameter (η) as a function of valence π -orbital occupancy difference $Np_x - Np_y$ for various σ -orbital occupancies Np_z ; ■ is the point corresponding to the point 7 and ▲, to the points 5 and 6 on the plot of Fig. 3.

As to the disturbance of the iodine π -system in Ph₂SnI₂(HMPT)₂, resulting in the increased $Np_x - Np_y$ difference, this is most probably produced, in the absence of prominent secondary contacts, by an interaction of the iodine π -system with that of the phenyl rings. Such a suggestion is supported by the data of Table 2, showing that Et₂SnI₂(HMPT)₂, in which the substitution was not accompanied by an increase in η , is the only adduct comprising no cyclic fragments in the ligands and substituents. The π - π interactions between I atoms and phenyl rings, which gave here no structural evidence, although changed considerably the spectroscopic parameters (η), were earlier clearly revealed by X-ray studies in several salts of imidazopyridinium [7].

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