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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

XIII*. BENZENE SOLVENT SHIFTS IN THE PMR SPECTRA OF ISOMERIC HEXACOORDINATE DICHLORODIARYLANTIMONY(V) β-DIKETONATES

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Summary

PMR benzene solvent shifts $\Delta\delta$ [$= \delta(CCl_4) - \delta(C_6D_6)$] have been measured for β-diketonate group protons of isomeric hexacoordinate dichlorodiarylantimony(V) β-diketonates. The observed solvent shifts are interpreted on the basis of a non-specific tangential approach of the benzene molecules to the electron-deficient sites of the solute. An inductive substituent constant σ_I of 0.48 has been deduced for the 2,2′-biphenylylene group.

PMR benzene solvent shifts $\Delta\delta$ of the various protons in the two isomers of *p*-Tol_2SbCl_2Acac are not markedly different and do not allow a conclusion concerning the geometry of the isomers, which is, however, easily assigned on the basis of aromatic ring current effects.

Introduction

In an earlier paper we discussed the benzene—solute interaction for a series of organoantimony(V) and organotin(IV) acetylacetonates [2]. The results were accounted for by a model of non-specific tangential approach by the benzene molecules to the electron-deficient sites of the solute (cf. refs. 3—5) rather than by an orientation of a benzene molecule parallel to the plane of the acetylacetonate (Acac) ring as suggested by Kawasaki [6].

The observed solvent shifts were linearly correlated with the inductive effect of the substituents at the antimony or tin atoms and an explanation has been put forward, in which the solvent shift is determined by the product of an inductive and of a steric factor. The agreement between the experimental

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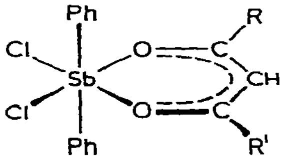
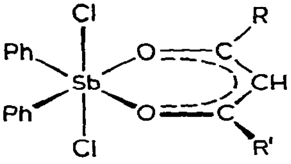
*For Part XII see ref. 1.

and calculated solvent shifts is much better for such an inductive model than for an electric field model, which is based on molecular dipole moments. This is clearly demonstrated for Ph_2SbCl_2 β-diketonates, where the β-diketonate ligand solvent shifts for both the *trans*-diphenyl (I) and the *trans*-dichloro (II) isomers (R,R′ = Me, t-Bu) appear to be much the same [2] (see Table 2). Obviously, interchange of the positions of the phenyl and chlorine groups does not markedly affect the β-diketonate—benzene interaction.



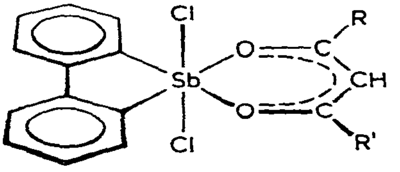
(I)



(II)

Results and discussion

We have now studied benzene solvent shifts, $\Delta\delta$, for the β-diketonate protons of a comparable series of dichloro-2,2′-biphenylyleneantimony (V) β-diketonates. Although the presence of a *trans*-diaryl configuration is precluded for steric reasons, these compounds do display geometrical isomerism. Configurations (III) and (IV) are easily assigned by PMR spectroscopy. In the asymmetric isomer (IV) the PMR signal of the alkyl substituent R′ appears at substantially higher field than expected on the basis of inductive effects alone, as a result of the diamagnetic anisotropy of the 2,2′-biphenylylene ring system (see ref. 7).



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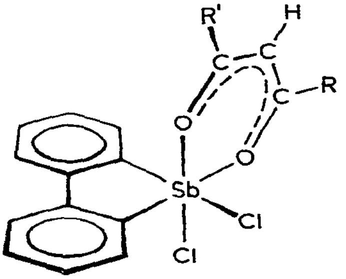


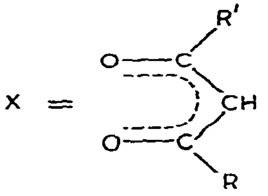
(IV)

The influence of geometry and of successive substitution of Acac-methyl groups in 2,2′-biphenylylene$SbCl_2$ Acac by tert-butyl groups on the benzene—β-diketonate ligand interaction is demonstrated by the data given in Table 1. A small but significant difference in benzene solvent shifts of the alkyl groups R′ and R in the asymmetric isomer (IV) (R = R′) is indicative of an asymmetric solvatation of the β-diketonate ligand in such a manner that benzene tends to keep away from the chlorine atoms which form the electronegative part of the molecule.

Steric influences of bulky substituents in the β-diketonate ligand on the

TABLE 1

PMR CHEMICAL SHIFT AND BENZENE SOLVENT SHIFT DATA FOR DICHLORO-2,2'-BIPHENYLYLENEANTIMONY(V) β-DIKETONATES IN CCl_4 AND C_6D_6 SOLUTION AT 25°



2,2'-Biphenylylene$SbCl_2X$		Isomer	Chemical shift $\delta(CCl_4)$ (ppm)			Solvent shift $\Delta\delta^a$		
R	R'		CH	CH_3	t-Bu	CH	CH_3	t-Bu
CH_3	CH_3	(III)	5.86	2.36		0.78	0.78	
		(IV)	5.71	2.36;1.94^b		0.77	0.69;0.86^b	
CH_3	t-Bu	(III)	5.97	2.39	1.39	0.39	0.75	0.31
CH_3	t-Bu	(IV)	5.84	2.39	0.90^b	0.37	0.66	0.29^b
t-Bu	CH_3	(IV)	5.87	1.99^b	1.39	0.39	0.82^b	0.21
t-Bu	t-Bu	(III)	6.11		1.40	0.04		0.25
		(IV)	6.04		1.40;0.96^b	0.03		0.16;0.27^b

$^a\Delta\delta = \delta(CCl_4)$—$\delta(C_6D_6)$. ^{b}These data correspond to the alkyl groups, R'.

benzene—ligand interaction are clearly shown by the reduction of $\Delta\delta$(CH) to approximately half the original value upon substitution of one of the Acac-methyl groups by a tert-butyl group and to practically zero if two tert-butyl groups are introduced.

A comparison of the solvent shift data for the 2,2'-biphenylylene$SbCl_2$ β-diketonates with those observed for the corresponding Ph_2SbCl_2-derivatives points to a stronger β-diketonate—benzene interaction in the former compounds, obviously as a result of a higher electron-deficiency of the β-diketonate ligand. A linear relation, $\Delta(CH) = 0.730\ \Sigma\sigma_I - 0.10$, between Acac(CH) proton solvent shifts and $\Sigma\sigma_I$ of the substituents bound to antimony, has been observed for the compound series $R_nSbCl_{(4-n)}$Acac [2]. A σ_I value for the 2,2'-biphenylylene group has not been reported previously. Based on the observed solvent shift $\Delta\delta$-(Acac-CH) for 2,2'-biphenylylene$SbCl_2$ Acac an inductive substituent constant, σ_I, of 0.48 can be deduced for the 2,2'-biphenylylene group.

Recently Nishii and Okawara [8] have assigned the configurations of two isomers of p-Tol_2SbCl_2Acac from benzene solvent shifts interpreted on the basis of Kawasaki's model of parallel solvation. As our results clearly point to tangential approach of the solvent molecule we have reinvestigated the PMR spectra of p-Tol_2 $SbCl_2$ Acac in CCl_4, $CDCl_3$ and C_6D_6 solution. These spectra show two sets of Acac ligand proton signals, indicating the presence of two geometrical isomers in solution.

We have previously shown that as a result of aromatic ring-current effects the *trans*-diphenyl isomer of Ph_2 $SbCl_2$Acac shows the Acac proton signals at higher field than the *trans*-dichloro-*cis*-diphenyl isomer [9]. A similar situation will apply with p-Tol_2SbCl_2Acac isomers. At 25°, freshly prepared solutions of p-Tol_2SbCl_2Acac show only the presence of the "high-field" *trans*-p-Tol_2 isomer (Fig. 1a) (cf. ref. 7). Heating the solution for 1—2 min results in the formation

TABLE 2

PMR CHEMICAL SHIFT AND BENZENE SOLVENT SHIFT DATA FOR Ph_2SbCl_2Acac AND p-Tol_2-$SbCl_2Acac$

Compound	Chemical shift δ (CCl_4) (ppm)			Solvent shift $\Delta\delta$ (ppm)		
	Acac-CH	Acac-CH_3	p-Tol-CH_3	Acac-CH	Acac-CH_3	p-Tol-CH_3
Ph_2SbCl_2Acac						
trans-Diphenyl	5.23	1.99		0.81	0.65	
trans-Dichloro	5.72	2.16		0.78	0.70	
p-Tol_2SbCl_2Acac						
trans-Di-p-tolyl	5.19	1.93	2.35	0.58	0.53	0.40
trans-Dichloro	5.66	2.10	2.35	0.61	0.60	0.37

of an equilibrium mixture of isomers, in which the *trans*-p-Tol_2 isomer predominates. In benzene solution two p-Tol methyl group signals are observed at δ 1.95 and δ 1.98 ppm, which can be assigned unambiguously on the basis of CH and CH_3 signal intensities to the *trans*-p-Tol_2 and the *trans*-Cl_2-*cis*-p-Tol_2 isomers, respectively (Fig. 1b). These results clearly show that the conclusions of Nishii et al. [8] are based on a reversed and thus false assignment of the p-Tol methyl group signals in benzene. In CCl_4 or $CDCl_3$ solutions the p-Tol group methyl signals of the two isomers accidentally coincide. In CCl_4 at 80° the isomers are present in about equimolar ratio. On rapid cooling the *trans*-p-Tol_2 isomer crystallizes and the solution is found to contain predominantly the *cis*-p-Tol_2 isomer.

PMR chemical shift and benzene solvent shift data for Ph_2SbCl_2Acac and p-Tol_2SbCl_2Acac are presented in Table 2.

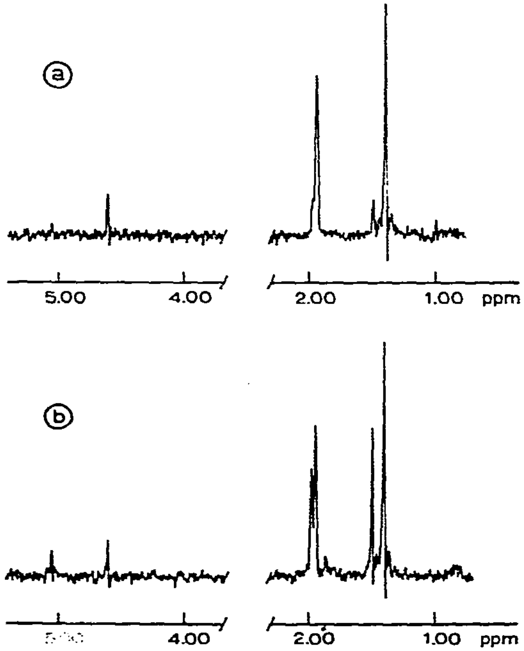


Fig. 1. Acac-PMR spectrum of p-Tol_2SbCl_2Acac in C_6D_6 solution at 25°; (a) freshly prepared solution; (b) after 2 min at 80°.

Solvent shifts $\Delta\delta$ of the various Acac protons in the two isomers of p-Tol_2SbCl_2Acac are not markedly different (0.03—0.07 ppm) and do not allow a conclusion concerning the geometry of the isomers. The results are comparable with those obtained for Ph_2SbCl_2Acac, and are in accordance with the concept of tangential approach of the benzene molecule towards the electropositive sites of the solute molecules.

Experimental

The dichlorodiarylantimony(V) β-diketonates described in this paper were synthesized by published methods [7—9].

PMR chemical shifts δ were measured with a Varian HA-100 spectrometer, in highly diluted solutions at a magnet temperature of 25°, with TMS as an internal standard.

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