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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

VII*. THE STEREOCHEMISTRY OF (ACETYLACETONATO)ORGANOANTIMONY(V) COMPOUNDS, $R_nSbCl_{(4-n)}Acac$ ($n=1$–4)

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SUMMARY

The complete series of (acetylacetonato)organoantimony(V) complexes of the type $R_nSbCl_{(4-n)}Acac$ (R = Me or Ph and $n=1$–4) has been synthesized. The influence of progressive substitution of chlorine atoms by organic groups on the spectroscopic parameters, the stability, and the stereochemistry of these compounds has been investigated. Particular attention has been given to a comparison of the merits of the electric field model of Smith and Wilkins and the inductive model of Kawasaki *et al.*, for explaining the effect of substitution at antimony on the spectra characteristics of the Acac ligand. The PMR data display an excellent linear correlation with the inductive effect of the substituents at antimony and thus strongly support the inductive model. For phenyl-substituted complexes aromatic ring current effects must be taken into account to explain the observed PMR chemical shift data.

IR and PMR data indicate that throughout the series $R_nSbCl_{(4-n)}Acac$ progressive substitution of electron-withdrawing chlorine substituents by organic groups R leads to a weakening of the Sb–Acac interaction. For $Ph_3SbClAcac$ and $Me_4SbAcac$ this is further reflected in the observed non-rigidity of these complexes in solution.

The stereochemistry of the various compounds has been unambiguously deduced from spectroscopic and molecular dipole moment data. The diphenyl derivative Ph_2SbCl_2Acac is noteworthy in that it provides an example of stereoisomerism in a hexacoordinate organometallic complex. In the isomer which shows the Acac proton PMR signals at higher field, the two phenyl groups are in *trans*-position, whereas in the "low-field isomer" the phenyl groups occupy *cis*- and the two chlorine atoms *trans*-positions.

INTRODUCTION

The chemistry of (acetylacetonato)organoantimony(V) complexes of the type $R_nSbCl_{(4-n)}Acac$ where $n=1$ (R = Me[2] and Ph[3]), $n=2$ (R = Me[2,4], Et[4] and Ph[4,5]), and

* For part VI see ref. 1.

$n=4$ (R = Me[4], Et[4] and Ph[4,6]) has been the subject of a number of recent papers. Complexes with $n=3$, *i.e.* those of the type $R_3SbClAcac$, have not yet been reported (*cf.* ref. 4).

So far the stereochemistry of these complexes has not been studied in detail. Kawasaki and Okawara[3] have shown by PMR spectroscopy that $PhSbCl_3Acac$ in solution possesses an asymmetric octahedral structure with the Ph group occupying an equatorial positon. However, for the corresponding methyl derivative, $MeSbCl_3$-Acac a symmetric structure with the methyl group occupying an axial position was recently proposed by Okawara *et al.*[7]. For the two isomeric forms observed for Ph_2SbCl_2Acac in solution[4] we proposed a *trans*-dichloro structure with a chelating and a non-chelating Acac ligand, respectively. The existence of the latter configuration has recently been questioned by Nishii *et al.*[5] who explained the PMR data in terms of the occurrence of hexacoordinate *cis*- and *trans*-diphenyl isomers (IV) and (V).

The stereochemistry of organometal complexes with bidentate ligands, in particular its dependence on the nature of the other substituents at the metal, is a subject of considerable current interest[8]. As part of a more extensive program dealing with the coordination chemistry of organoantimony(III)[9] and organoantimony(V)[4,10] complexes we have carried out a detailed structural investigation of the series R_n-$SbCl_{(4-n)}$Acac ($n=1$–4; R = Me, Et, Ph)[11]. The previously unknown $Ph_3SbClAcac$ has been included in this study. In the present paper we report on the stereochemistry of these complexes, which in every case could be unambiguously deduced from PMR, IR, Raman, and dipole moment data.

EXPERIMENTAL PART

Preparation of (acetylacetonato)organoantimony(V) compounds

The complexes were prepared as previously reported[2,3,4].

(Acetylacetonato)chlorotriphenylantimony. Acetylacetone (0.7 g, 7 mmole) was added to a solution of $Ph_3SbClOMe$[12] (2.6 g, 6.8 mmole) in benzene (20 ml). Evaporation of the benzene and recrystallization of the colourless residue from benzene/-hexane gave a product with m.p. 130° (dec.). The PMR spectrum indicated that this was $Ph_3SbClAcac$ in 80% purity. (Found: Cl, 7.60; Sb, 26.22. $C_{23}H_{22}ClO_2Sb$ calcd.: Cl, 7.27; Sb, 24.97%.)

The same product was obtained by treating Ph_3SbCl_2 with NaAcac in benzene in a 1/1 molar ratio. Attempts to use methanol as a solvent resulted in the isolation of $Ph_3SbClOMe$.

Attempted preparation of (acetylacetonato)chlorotrimethylantimony. When Me_3SbCl_2 (7.2 g, 30 mmole) was added to a solution of NaAcac (30 mmole) in methanol (100 ml), NaCl (1.2 g) was precipitated. After filtration and subsequent evaporation of the methanol a colourless residue was obtained. Recrystallization from pure acetylacetone gave a colourless crystalline product, which was identified as $(Me_3SbCl)_2O$[13]. (Found: Cl, 16.94; Sb, 57.88. $C_6H_{18}Cl_2OSb_2$ calcd.: Cl, 16.88; Sb, 57.89%.)

Spectroscopic and molecular-dipole moment data

PMR spectra were taken with a Varian HA-100 spectrometer, at a magnet

temperature of 25°. Chemical shifts were measured in highly diluted solutions. Results were reproducible to ±0.2 Hz.

IR spectra were run as KBr pellets and in chloroform solutions between KBr disks in the 4000–400 cm^{-1} region, using a Grubb–Parsons Spectromaster. The spectra were also recorded in the region 500–200 cm^{-1}, using Beckman IR-7 and IR-11 spectrometers, in Nujol mulls and in some cases in benzene solution. The scales were calibrated with polystyrene and water vapour spectra. The results were found to be reproducible to ±2 cm^{-1}.

Raman spectra were obtained on a Coderg PH 1 spectrometer, provided with a Spectra-Physics 80 mW He–Ne laser. For some of the spectra a CRL model 53 MG Ar–Kr laser with 300 mW at 647.1 nm was used. Samples of R_2SbCl_2Acac (R = Me or Ph) were also run on a Jeol JRS-01 B spectrometer, equipped with a 900 mW Ar laser by courtesy of Jeol Co., Ltd. The spectra were calibrated to ±2 cm^{-1} with laser emission lines.

Dipole moments were determined in benzene with the aid of a Wissenschaftlich-Technische Werkstätten dipole meter DM 01 and a measuring cell DFL 2 in benzene at 20°, as described by Doron and Fischer[14].

RESULTS AND DISCUSSION

PMR, IR, Raman and dipole moment data

The PMR chemical shifts (CCl_4 solution) of the γ-CH and CH_3 protons of the Acac ligand together with the dipole moment data for the various $R_nSbCl_{(4-n)}Acac$ complexes are shown in Table 1. All the compounds are monomeric in benzene solution (*cf.* refs. 2 and 4). The presence of a chelated Acac ligand and, therefore of a hexacoordinate antimony atom, in each of these compounds is shown by the absence in the IR spectrum of a free carbonyl absorption and the presence of absorptions due to a coordinated carbonyl group in the region 1500–1600 cm^{-1}, generally accompanied by a C=C stretching band at slightly lower wavenumbers. The previously reported presence of a C=O absorption at 1715 cm^{-1} in the IR spectrum of Ph_2SbCl_2-Acac[4] must have been due to an impurity (*cf.* also ref. 5). IR and Raman spectroscopic data ν(C=O), ν(C=C), ν(Sb–O) and ν(Sb–Cl) for the various complexes are presented in Table 2. As shown in this Table, progressive replacement at antimony of the organic groups R by the more electron-withdrawing chlorine atoms results in a strengthening of the Sb–O [increased ν(Sb–O)] and a weakening of the C=O [decreased ν(C=O)] bond.

Similarly, as appears from Table 1, a considerable increase of δ(CH) and, to a smaller extent, of $\delta(CH_3)$ is observed in the PMR spectra of $R_nSbCl_{(4-n)}Acac$ upon increasing the number of electron-withdrawing chlorine atoms at antimony (*cf.* ref. 4).

Two models have recently been put forward for explaining the effect of the metal substituents on the PMR and vibrational spectra of metal acetylacetonates. Kawasaki, Tanaka and Okawara[15,16] have explained the observed shifts in δ(CH) and $\delta(CH_3)$ in the PMR and of ν(Sn–O) and ν(C=O) in the IR spectra of a number of (acetylacetonato)organotin compounds in terms of inductive effects. They established a linear relationship between the sum of the inductive substituent constants σ* of the substituents other than Acac (Σσ*) and the chemical shift δ(CH) of the Acac γ-CH proton[15] as well as between Σσ* and the IR stretching frequencies ν(Sn–O) and

TABLE 1

CHEMICAL SHIFT DATA AND MOLECULAR DIPOLE MOMENTS FOR (ACETYLACETONATO)ORGANOANTIMONY(V) COMPOUNDS, $R_nSbCl_{(4-n)}Acac$

Compound	*Chemical shifts, δ, in CCl_4*			*Dipole moment[a], μ (D)*
	Acac		*CH_3Sb*	
	CH	*CH_3*		
$Cl_4SbAcac$	5.87	2.33		7.4
$MeSbCl_3Acac$	5.76	2.23	2.61	5.1
		2.25		
$EtSbCl_3Acac$	5.75	2.22		5.2
		2.25		
Me_2SbCl_2Acac	5.50	2.11	2.27	6.4
$Me_4SbAcac$	5.01	1.79	0.99	
$PhSbCl_3Acac$	5.80	2.22		5.4
		2.31		
Ph_2SbCl_2Acac[b]	5.23	1.99		6.4[b]
	5.72	2.16		
$Ph_3SbClAcac$	5.17	1.88[c]		
$Ph_4SbAcac$	5.10	1.80		1.3

[a] Determined in benzene solution by Miss E. Ch. Th. Gevers; estimated uncertainty ±0.2 D.
[b] Two isomers are present in solution.
[c] Below +5° in $CDCl_3$ solution a doublet with 4.2 Hz separation.

TABLE 2

IR AND RAMAN SPECTROSCOPIC DATA FOR VARIOUS (ACETYLACETONATO)ORGANOANTIMONY(V) COMPOUNDS[a]

Compound	*Stretching frequencies (cm^{-1})*				
	ν(C=O), ν(C=C)[b]	*ν(Sb—O)*		*ν(Sb—Cl)*	
	IR	*IR*	*Raman*	*IR*	*Raman*
$Cl_4SbAcac$	1543 vs (br)	463 m	468 m	361 vs	362 vs
Me_2SbCl_2Acac	1563 vs, 1527 vs	435 s	423 ms	301 vs, 284 vs	278 s
$Me_4SbAcac$	1575 vs[c], 1501 vs[c]	387 ms			
$PhSbCl_3Acac$	1549 vs (br)	458 s		332 vs	
Ph_2SbCl_2Acac	1549 vs, 1529 vs	429 ms	425 m	299 vs	289 vs
$Ph_3SbClAcac$	1567 vs, 1511 vs	419 w		298 s	
$Ph_4SbAcac$	1560 vs, 1516 vs	399 m	395 vs		

[a] Spectra were run on KBr pellets or on Nujol suspensions, unless indicated otherwise. [b] *Cf.* Table 2, ref. 4.
[c] In $CDCl_3$ solution.

ν(C=O)[16]. Smith and Wilkins[17,18] have recently proposed an electric field model to account for the spectral changes. A linear relation was found between δ(CH) and the electric field along the C–H bond evaluated at the H atom, which in turn is linearly

dependent on the component of the molecular dipole moment along the C–H axis, μ(CH).

The series of homologous compounds $R_nSbCl_{(4-n)}Acac$ ($n=0$–4) is especially suited for testing the inductive and electric field models, because of the presence of both substituents in the plane of the Acac ring and substituents perpendicular to this plane. As discussed below and more extensively in ref. 19, our results clearly show that the electric field model must be rejected in favour of the inductive model (*cf.* also refs. 20 and 21).

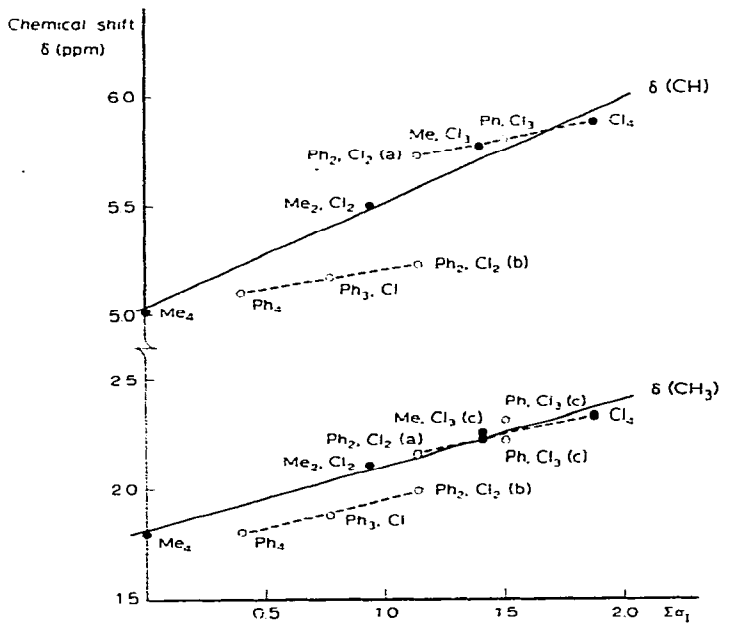


Fig. 1. Relation between proton chemical shifts, δ(CH) and $\delta(CH_3)$, and $\Sigma\sigma_I$ for Acac protons of (acetylacetonato)organoantimony(V) compounds $R_nSbCl_{(4-n)}Acac$ (R = Me, Ph; $n=0$–4) in CCl_4 solution. Substituents other than Acac are indicated: (a) absorptions due to isomer (IV), (b) absorptions due to isomer (V); (c) two absorptions are observed.

In Fig. 1 δ(CH) and $\delta(CH_3)$ in CCl_4 of the various complexes, $R_nSbCl_{(4-n)}Acac$ (R = Me, Ph; $n=0$–4) have been plotted against $\Sigma\sigma_I$, the sum of the aliphatic substituent constants σ_I of the substituents other than Acac (σ_I values are taken from ref. 22). For the methyl-substituted complexes $Me_nSbCl_{(4-n)}Acac$ ($n=0$–4) excellent linear relations are found, which are represented by the equations (calculated by the method of least-squares; correlation coefficient r between parentheses: *cf.* ref. 19):

$$\delta(CH) = 0.437\ \Sigma\sigma_I + 5.04 \quad (r=0.99) \tag{1}$$

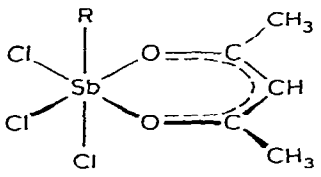
$$\delta(CH_3) = 0.295\ \Sigma\sigma_I + 1.81 \quad (r=0.99) \tag{2}$$

As appears from Fig. 1 the values of δ(CH) and $\delta(CH_3)$ observed for the phenyl-substituted complexes $Ph_nSbCl_{(4-n)}Acac$ do not fit these equations. This is not

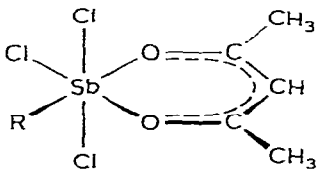
surprising, since phenyl groups give rise to aromatic ring current effects which are superimposed on the inductive effects exerted by these substituents. Therefore, the actual Acac chemical shift values must be expected to deviate considerably from those calculated from the above equations on the basis of inductive effects alone. The δ-values for the phenyl-substituted complexes and the tetrachloro complex can be fitted to two straight lines with identical slopes. The significance of this finding for the elucidation of the structure of these complexes will be discussed below.

Stereochemistry of compounds $RSbCl_3Acac$ ($R = Ph$, Me, Et)

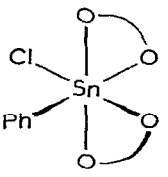
Two structures with R either in axial (I) or equatorial (II) position must be considered for octahedral compounds $RSbCl_3Acac$. Two Acac-CH_3 signals must be expected to be present in the PMR spectrum, if the asymmetric structure (II) applies



(I)



(II)



(III)

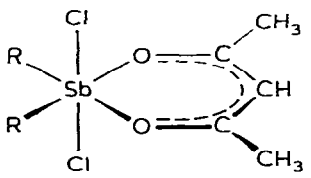
whereas only one signal is expected for structure (I). The assignment of structure (II) to $PhSbCl_3Acac$ is based on this criterion[3]. However, the suggestion by Okawara *et al.*[7] that $MeSbCl_3Acac$ has structure (I) is not borne out by our data. We have observed two distinct Acac-CH_3 signals for both $MeSbCl_3Acac$ and $EtSbCl_3Acac$ in CCl_4 (*cf.* Table 1). In benzene the two signals are separated by 1.4 Hz for $EtSbCl_3Acac$, but they fortuitously coincide for $MeSbCl_3Acac$.

Polar aromatic solvents strongly influence the magnitude of the separation of the Acac-methyl proton signals[7]. *E.g.* for $MeSbCl_3Acac$ we observed a separation of 10.7 Hz in nitrobenzene. We suggest that the already existing non-equivalence of the two Acac-methyl groups is enhanced as a result of the aromatic ring-current effect on the asymmetrically solvated solute molecule.

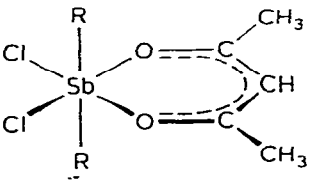
Structure (II) for each of the complexes $RSbCl_3Acac$ (R = Ph, Me, Et) is further confirmed by the values of their dipole moments, which do not differ much (5.1–5.4 D). For these complexes the contribution of the two axial chloro substituents to the molecular dipole moment is expected to be small. The observed values for μ are comparable to the μ-value of 5.15 D observed for the bis(acetylacetonato)tin complex $PhSnCl(Acac)_2$ which is known to possess structure (III)[11]. The contribution of the two Acac ligands to the dipole moment of this compound has been calculated to be equal to the contribution of one Acac ligand in plane with the Ph and Cl substituents[23].

Stereochemistry of Me_2SbCl_2Acac

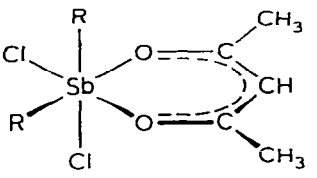
The observation of only one singlet due to the Acac-CH_3 protons in the PMR spectrum of Me_2SbCl_2Acac both at 25° in CCl_4 and at −90° in CH_2Cl_2 is consistent only with the existence of one symmetric configuration [(IV) or (V) R = Me] (*cf.* refs. 4 and 7). The asymmetric structure (VI) would give rise to two Acac-CH_3 proton signals.



(IV)



(V)



(VI)

The IR spectral data suggest the presence of a *cis*-dichloro configuration (V). Two very strong $SbCl_2$ absorption bands are observed (*cf.* Table 2). The Raman spectrum confirms configuration (V). Antimony–carbon vibrations give rise to a very strong Raman band at 530 cm^{-1} [$\nu_s(SbC_2)$], whereas the IR spectrum shows very weak antimony–carbon absorptions at 585 cm^{-1} [$\nu_{as}(SbC_2)$] and 530 cm^{-1} [$\nu_s(SbC_2)$].

Structure (V), which has been tentatively proposed by Okawara *et al.*,[7] is further corroborated by the molecular dipole moment of 6.4 D observed in benzene solution. A much lower value of μ would have been expected for structure (IV) (*cf.* the dipole moment of 1.3 D for $Ph_4SbAcac$).

Stereochemistry of the two isomeric forms of Ph_2SbCl_2Acac; the influence of aromatic ring-current effects on Acac proton signals

The PMR spectrum of Ph_2SbCl_2Acac shows two sets of singlets (5/2 intensity ratio in benzene) for Acac-CH and Acac-CH_3 protons indicating the presence of two isomeric forms[4] each of which must possess a symmetric structure [(IV) or (V), R = Ph], as recently proposed by Nishii *et al.*[5], who, however did not assign the PMR data to particular isomers.

The IR solution and Nujol mull spectra of Ph_2SbCl_2Acac even under conditions of high resolution show only one C=O, C=C, and Sb–O stretching frequency (*cf.* Table 2), whereas the IR solution spectrum of Ph_2SbCl_2Acac-*d* shows only one γ-C–D stretching band. These results indicate that no marked differences exist in the bonding of the Acac ligand in the *cis*-(IV) or *trans*-(V) diphenyl isomer. Therefore, the large difference between the δ-values for the γ-CH ($\approx$0.5 ppm) and CH_3 ($\approx$0.15 ppm) proton signals for both isomers might seem surprising at first sight.

Equatorial substituents exert a much greater influence on the component of the molecular dipole moment along the C–H and C–CH_3 axes of the Acac ligand than axial substituents. Therefore, the electric field model of Smith and Wilkins predicts a greater downfield shift for the Acac proton signals, if the two electron-withdrawing chlorine atoms are in the plane of the Acac ligand [structure (V)] than if they are in the axial position [structure(IV)]. Based on this model the "low-field" isomer of Ph_2SbCl_2Acac is assumed to possess the *cis*-dichloro structure (V) (high μ) and the "high-field" isomer the *trans*-dichloro structure (IV) (low μ). However, the observed dipole moment of 6.4 D for Ph_2SbCl_2Acac in benzene solution does not seem to agree with this assignment. A much lower dipole moment would be expected for a 5/2 ratio of *trans*- and *cis*-dichloro isomers. That the electric field model may lead to erroneous conclusions[15] is further illustrated by our data for the non-aromatic compounds $MeSbCl_3Acac$ and Me_2SbCl_2Acac. $MeSbCl_3Acac$ shows the Acac proton signals at lower field than Me_2SbCl_2Acac although it has a lower dipole moment (*cf.* Table 1).

In the inductive model electron-withdrawing substituents will affect $\delta(CH)$ and $\delta(CH_3)$ in the same way irrespective of their stereochemical position, provided the bonding in axial and equatorial positions is very much the same. We find that the PMR data for the two isomers of Ph_2SbCl_2Acac can be fully explained by the inductive model if aromatic ring current effects exerted by the phenyl substituents are taken into account.

As shown in Fig. 1 the Acac γ-CH signal of $PhSbCl_3Acac$ is shifted 0.07 ppm further downfield than expected on the basis of inductive effects [eqn. (1)] alone. Apparently a phenyl group in equatorial position [structure (II)] has a deshielding effect on the Acac ligand protons. Since the γ-CH signal for the "low-field" isomer of Ph_2SbCl_2Acac is shifted 0.14 ppm to lower field one may reasonably assume that in this isomer the two phenyl groups are also in the equatorial plane. This implies that the phenyl groups of the "high-field" isomer are in the axial position and, moreover, that axial phenyl groups cause a considerable upfield shift of the Acac proton signals. The assignment of the *trans*-dichloro structure (IV) to the "low-field" isomer and the *cis*-dichloro structure (V) to the more abundant "high-field" isomer, which is the opposite of the assignment based on the electric field model, is in accordance with the observed large dipole moment of Ph_2SbCl_2Acac and is further supported by the consistency of the following description.

As shown in Fig. 1 the points for $\delta(CH)$ of the tetraphenyl, the chlorotriphenyl and the *cis*-dichloro isomer of the dichlorodiphenyl complex can be connected by a straight line with exactly the same slope as the one which connects the *trans*-dichloro isomer, the trichlorophenyl and the tetrachloro complex. Based on the PMR spectrum the chlorine atom in $Ph_3SbClAcac$ occupies an equatorial position (*cf.* following section). In Fig. 1 every transition in the two series of compounds corresponds to a replacement of an equatorial phenyl group by a chloro substituent, showing that each time the difference of the inductive effects of the phenyl and chloro groups plus the ring-current effect of an equatorial phenyl group adds up to the same amount, the influence of the axial substituents (*trans*-diphenyl in the first and *trans*-dichloro in the second series) remaining constant. Compounds with axial phenyl groups show an upfield shift from the value of $\delta(CH)$ calculated from eqn. (1). For compounds with equatorial phenyl groups only (second series), which are further removed from the Acac γ-CH, $\delta(CH)$ is close to the expected value. The shielding effect of an axial phenyl group (Δ_{ax}) on $\delta(CH)$ and the deshielding effect of an equatorial phenyl substituent (Δ_{eq}) are found by simple arithmetics. The average values of Δ_{ax} and Δ_{eq} thus calculated are -0.15 and $+0.07$ ppm. respectively. So the shielding action of an axial phenyl group on $\delta(CH)$ is about twice the deshielding effect of an equatorial phenyl substituent.

The chemical shifts $\delta(CH_3)$ in Fig. 1 follow the same trends as $\delta(CH)$, be it in reduced form. The slope of the intermittent lines are now very much the same as the slope of the drawn line for non-aromatic compounds. Also, the points for compounds with equatorial phenyl groups nearly coincide with the drawn line and thus the deshielding action of an equatorial phenyl group on $\delta(CH_3)$ is extremely small [$\Delta_{eq}(CH_3) = +0.01$ ppm]. The shielding effect of an axial phenyl group on $\delta(CH_3)$ as compared to $\delta(CH)$ is reduced with a factor 2 [$\Delta_{ax}(CH_3) = -0.08$ ppm].

The available data provide information on the position of the axial phenyl groups with respect to the plane of the Acac ligand. A freely rotating axial phenyl

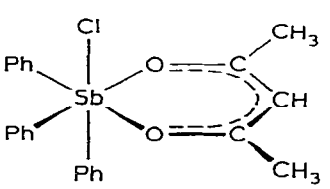
group would place the Acac hydrogens intermittently in shielding and deshielding positions. Johnson and Bovey[24] have calculated shielding and deshielding effects for hydrogen atoms in various positions with respect to a benzene nucleus. The observed overall effect is shielding, indicating that perpendicular positions are favoured. In fact, if Johnson and Bovey's data are valid for phenyl substituents, the observed magnitude of the shielding effect (0.15 ppm) on δ(CH) is very close to that calculated for a position of the phenyl rings perpendicular to the Acac ligand C–H axis. The average methyl protons are closer to the edge of the cone of shielding and a smaller shielding effect for these hydrogens results. From these data we conclude that the axial phenyl groups present in $Ph_4SbAcac$, $Ph_3SbClAcac$ and the *cis*-dichloro isomer of Ph_2SbCl_2Acac all have a preferred conformation, perpendicular to the Acac C–H axis.

Very recently the crystal structure of Ph_2SbCl_2Acac has been elucidated by Kroon, Hulscher and Peerdeman[25]. In contrast with the presence of both a *cis*- and a *trans*-diphenyl isomer in solution, crystalline Ph_2SbCl_2Acac possesses the *trans*-diphenyl configuration. The crystal structure of the molecule is nearly ideally octahedral. The axial phenyl groups are bent towards the Acac ligand ($\angle$C–Sb–C 172°). The phenyl groups are twisted from a position perpendicular to the Sb–Acac γ-CH axis by 12° and 25°, respectively, the dihedral angle being 37°.

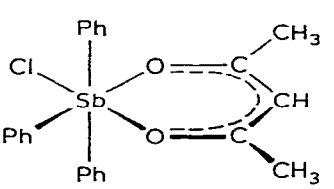
Preparation and stereochemistry of compounds $R_3SbClAcac$

So far compounds $R_3SbClAcac$ have not been reported (*cf.* ref. 4). In our present study we have succeeded in obtaining the triphenyl derivative via the 1/1 reaction of $Ph_3SbClOMe$ with HAcac or of Ph_3SbCl_2 with NaAcac in benzene. As appears from the IR spectrum both in Nujol and in $CHCl_3$ solution $Ph_3SbClAcac$ contains a chelating Acac ligand. The presence of additional absorptions due to free acetylacetone points out the relative instability of this compound, which also follows from the occurrence of rapid methanolysis. Whereas Ph_2SbCl_2Acac may be recrystallized from methanol, the same procedure for $Ph_3SbClAcac$ results in the isolation of $Ph_3SbClOMe$.

The PMR spectrum of $Ph_3SbClAcac$ displays only one Acac γ-CH signal suggesting the presence of only one configuration in solution. The chloro substituent in $Ph_3SbClAcac$ may occupy either an axial (VII) or equatorial (VIII) position. The PMR spectra in C_6D_6, CCl_4 and $CDCl_3$ solution at first sight point to the presence of configuration (VII) rather than (VIII) as only one Acac-CH_3 signal is observed. However, as discussed in the previous section (*cf.* Fig. 1) the chemical shift data unequivocally point to configuration (VIII), as the observed δ-values can be accounted for in terms of aromatic ring-current effects exerted by two axial and one equatorial phenyl group. Since the observed magnetic equivalence of the Acac-methyl groups



(VII)



(VIII)

might be the result of the molecule having a non-rigid structure, the PMR spectrum was recorded at lower temperatures. Upon cooling a $CDCl_3$ solution below $+5°$ the CH_3 singlet transforms into a doublet with 4.2 Hz separation confirming that $Ph_3SbClAcac$ indeed exists in the asymmetric configuration (VIII). At room temperature $Ph_3SbClAcac$ does not exchange the Acac ligand with acetylacetone as separate signals are observed for the HAcac and the SbAcac proton resonances.

Attempts to prepare $Me_3SbClAcac$ by the reaction of Me_3SbCl_2 with NaAcac led to the isolation of $(Me_3SbCl)_2O$. This compound appears to be inert towards acetylacetone and can even be recrystallized from it.

Stereochemistry of compounds $R_4SbAcac$

The metal–Acac ligand bonds in compounds $R_4SbAcac$ are relatively weak, as is apparent from the low (Sb–O) and high (C=O) stretching wavenumbers (*cf.* Table 2). As already observed for $Ph_3SbClAcac$, the presence of a weakly bonded Acac ligand may result in the structure being non-rigid. For $Me_4SbAcac$ this is clearly demonstrated by the results of low-temperature PMR spectroscopy in toluene-d_8[10]. Whereas at 27° only one sharp $SbCH_3$ proton resonance signal is observed, this singlet is transformed at $-100°$ into a broad doublet with 29 Hz separation. The observed chemical shift data for $Ph_4SbAcac$ can be accounted for in terms of two axial and two equatorial phenyl groups in the molecule (*cf.* Fig. 1). At room temperature the PMR spectra of a mixture of acetylacetone and $Me_4SbAcac$ and $Ph_4SbAcac$ display separate signals for the HAcac and SbAcac proton resonances.

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