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SOLUTION STUDIES OF SOME PENTAARYLANTIMONY(V) COMPOUNDS

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Summary

A ^{1}H and ^{13}C NMR investigation of some pentaarylantimony(V) compounds indicates that they are fluxional in solution at temperatures as low as —130°C. The ^{13}C NMR data for tri- and pentaaryl Group Va compounds are discussed in terms of group trends.

Introduction

Most pentacoordinate R_5Sb compounds adopt the expected trigonal bipyramidal structure with local D_{3h} symmetry [1—8]. Considerable interest has been generated by reports that pentaphenylantimony(V), Ph_5Sb, is of approximately square pyramidal symmetry in the solid state [9,10]. It was thought that perhaps "crystal packing forces" might explain the apparently anomalous structure, and therefore a solution vibrational analysis was performed on pentaphenylantimony(V) in halocarbon solvents [11,12]. The conclusion from the vibrational study was that even in solution, pentaphenylantimony(V) is of local C_{4v} symmetry. An IR-Raman spectroscopic study on pentacyclopropylantimony(V) indicated a solution structure of C_{4v} symmetry [13] for that compound also.

Structural determinations of complex molecules such as pentaphenylantimony(V) by vibrational spectroscopy is at best fraught with considerable possibility for error or misinterpretation. We therefore decided to undertake a low temperature NMR study of penta-*p*-tolylantimony(V), which has been found to be approximately trigonal bipyramidal in the solid state [6], where the tolyl-methyl protons could be used as a "tag" for ^{1}H NMR. We herein report the results of our NMR experiments.

Results

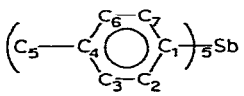
Solution structure of penta-para-tolylantimony(V), $(p\text{-tol})_5Sb$

Penta-*p*-tolylantimony(V) might seem to be a structure analog of pentaphenylantimony(V); however, the solid state structure of the former indicates that

it has the expected D_{3h} symmetry [6] while the latter has the unusual C_{4v} symmetry [9,10]. NMR experiments were performed to try to determine the solution stereochemistry of $(p\text{-tol})_5Sb$. An ^1H NMR spectrum of $(p\text{-tol})_5Sb$ at —60°C has been previously reported to yield a single absorption for the methyl protons, presumably indicating rapid intramolecular ligand exchange [14] as is common for penta-coordinate Group Va compounds [2], yielding all methyl protons magnetically equivalent on the time-scale of the experiment. We have recorded the ^1H and ^{13}C NMR spectra of $(p\text{-tol})_5Sb$ in dichloroflurormethane solvent at temperatures down to —130°C. The concurrent use of ^{13}C NMR spectroscopy with ^1H NMR virtually eliminates the possibility that the observance of a single ^1H NMR peak for the methyl protons in $(p\text{-tol})_5Sb$ could be due to accidental proton magnetic equivalence of a "static" solution structure of D_{3h} or C_{4v}, rather than to rapid intramolecular exchange. In the case of "static" solution structure without accidental magnetic equivalence of the methyl protons, two separate methyl proton resonances should occur with relative areas of 3 : 2 (equitorial : axial) or 4 : 1 (basal : apical) for D_{3h} or C_{4v} symmetry, respectively.

The width at half-height, $w_{1/2}$, for the methyl proton ^1H NMR resonance in $(p\text{-tol})_5Sb$ varied from 1.9 Hz at 30°C to 8.7 Hz at —129°C (see Fig. 1). (The ^1H NMR data for $(p\text{-tol})_5Sb$ as well as other related Group Va aryl compounds are given in Table 1.) We attribute this broadening to slowing of the rapid intramolecular exchange process, inasmuch as the $w_{1/2}$ of internal TMS broadened very little in this temperature range. Reliable ^1H NMR data could not be obtained below —130°C, at which temperatures the coalesced peak should presumably separate into two resonances. In the region of coalescence, the increased width of line i (Lorentzian) is $(w_{1/2})_i - (w_{1/2})^\circ_i = 1/\pi\tau$, where τ is the resident half-life of the nucleus at site i, $(w_{1/2})_i$ is the width at half-height for line i, and $(w_{1/2})^\circ_i$ is the width at half-height under rapid exchange conditions. Since $1/\tau$ is proportional to the first order exchange rate constant k, a plot of log k versus $1/T$ should be linear with a slope of $E_a/2.3\,R$. Such a plot for the methyl proton resonance in $(p\text{-tol})_5Sb$ from —46°C to —129°C was linear and yielded an activation energy of 1.60 kcal/mol.

At ambient temperature, the ^1H decoupled ^{13}C NMR spectrum of $(p\text{-tol})_5Sb$ consisted of five sharp resonances due to the five non-equivalent types of carbon atoms in the p-tolyl ligand. The single resonances for all five ligands is attributed



to rapid intramolecular exchange of ligand position. (See Table 2.) As the temperature was lowered to —135°C, the C(1) resonance moved 85 Hz upfield while there was no change in the C(4) and C(5) resonances. The C(2)(C(7)) and C(3)(C(6)) peaks began to lose intensity as the temperature was lowered. At 0°C, the intensity ratio of C(2)(C(7)) or C(3)(C(6)) to C(1) was 3 : 1, at —90°C it was 2 : 1 and at —124°C, it was less than 1 : 1. The C(2)(C(7)) and C(3)(C(6)) resonances had disappeared completely in the —130°C to —135°C range, which was the low temperature limit for these experiments. The peaks reappeared upon warming and the spectrum was identical to that before cooling. A line shape analysis of the C(2)(C(7)) and C(3)(C(6)) absorbances was performed to obtain

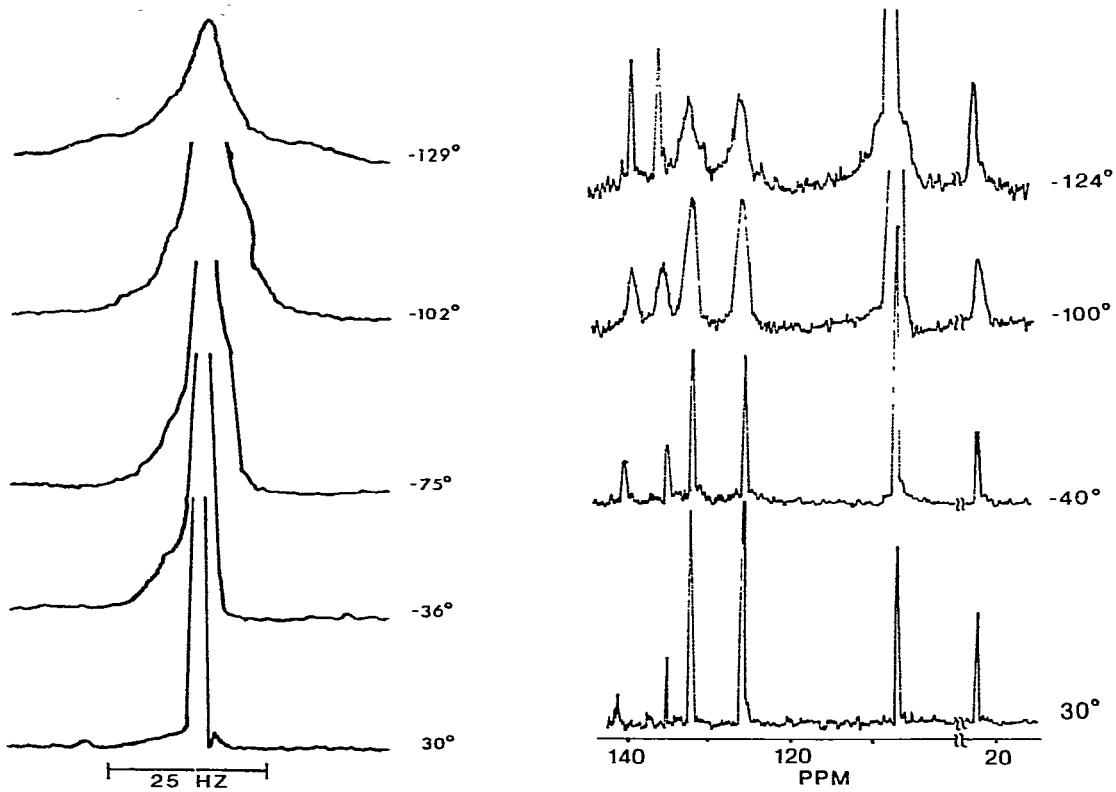


Fig. 1. Variation of $w_{1/2}$ with temperature for ^1H NMR tolyl methyl resonance in (*p*-tolyl)$_5$Sb.

Fig. 2. Variation of $w_{1/2}$ with temperature for all ^{13}C resonances in (*p*-tolyl)$_5$Sb.

TABLE 1

^1H NMR CHEMICAL SHIFT DATA [a,b]

Compound	Methyl resonance δ (ppm)	AB resonance δ (ppm)	J_{om} (Hz)
(*p*-tol)$_3$Sb	2.33	7.11 7.33	8
(*p*-tol)$_3$SbF$_2$	2.38	7.32 8.02	8
(*p*-tol)$_3$SbCl$_2$	2.43	7.35 8.11	8
(*p*-tol)$_3$SbBr$_2$	2.40	7.32 8.04	8
(*p*-tol)$_3$SbI$_2$	2.42	7.32 8.02	8
(*p*-tol)$_4$SbCl	2.39	7.24 7.67	8
(*p*-tol)$_4$SbBr	2.40	7.30 7.66	8
(*p*-tol)$_5$Sb	2.29	7.00 7.23	8
(*p*-tol)$_2$	2.37	7.20 7.46	8
toluene	2.37	7.20 [c]	—
(*p*-tol)$_3$As	2.36	7.20 7.46	8
(*p*-tol)$_5$As	2.31	7.09 7.23	8

[a] All spectra obtained on a Varian Associates XL-100-15 spectrometer using $CDCl_3$ as the solvent. Chemical shift values are referenced to TMS as an internal standard. [b] The chemical shift values are concentration dependent to ±0.02 ppm. [c] The ring protons in toluene show only a singlet absorption.

TABLE 2

^{13}C NMR CHEMICAL SHIFT DATA [a]

Compound	Solvent	δC(1)	δC(2)	δC(3)(C(6))	δC(4)	δC(5)
Ph_3As	$CHCl_3$	139.3	133.3	128.1	128.3	
Ph_3Sb	$CHCl_3$	138.0	135.8	128.1	128.4	
Ph_3P [b]	$CHCl_3$	137.2	133.6	128.4	128.5	
Ph_3Bi [c]	$CHCl_3$	136.9	130.3	127.5	130.2	
Ph_5As	$CHCl_3$	131.3	134.6	131.5	132.5	
Ph_5Sb	$CHCl_3$	146.3	134.4	127.2	127.7	
Ph_5Sb [d]	CS_2		134.4	127.3	127.7	
$(p\text{-tol})_3As$	$CHCl_3$	136.2	129.1	126.4	138.0	20.9
$(p\text{-tol})_3Sb$	$CHCl_3$	134.6	135.8	129.3	137.8	21.3
$(p\text{-tol})_3P$ [b]	$CHCl_3$	134.2	133.5	129.1	138.1	21.1
$(p\text{-tol})_5As$	$CHCl_3$	136.3	133.3	129.0	137.6	21.1
$(p\text{-tol})_5Sb$	$CHCl_3$	144.6	135.6	129.1	138.5	21.4
Toluene [b]	$CHCl_3$	125.5	128.3	129.1	137.7	21.2
Benzene	$CHCl_3$	128.7	128.7	128.7	128.7	

[a] Chemical shifts are reported in ppm relative to TMS. [b] Ref. 27. [c] Ref. 28. [d] Ref. 11; the C(1) resonance was not observed in CS_2 solvent.

an alternate determination of the exchange energy barrier for geometrical interconversion. A plot of log k, obtained from corrected widths at half-height, $(w_{1/2})_i$, versus $1/T$ gave an activation energy, E_a, of 1.46 kcal/mol for the intramolecular positional exchange barrier in the $(p\text{-tol})_5Sb$ system. The $(w_{1/2})_i$ values were corrected for viscosity effects by subtracting the broadening of the solvent peak from the broadening of the C(2)(C(7)) and C(3)(C(6)) peaks. Fig. 2 shows the ^{13}C NMR low temperature spectra, including the low field half of the solvent doublet, to illustrate broadening due to non-exchange effects.

Both the ^1H and ^{13}C NMR results substantiate the conclusion that the solution stereochemistry question of Group Va pentacoordinate compounds is not readily answered. There is no static solution structure except at extremely low temperatures, and the low energy barrier suggests that ligand size is probably not a dominant factor in limiting the exchange process. We feel that it is important to note that pentaarylantimony(V) compounds undergo appreciable decomposition at room temperature in halogenated hydrocarbon solvents *.

It is interesting to note some trends in ^{13}C NMR data for tri- and pentaaryl congeners in Group Va. Bearing in mind the problems often associated with

* While the thermolysis [15,16] and photolysis [17] of pentaarylantimony(V) compounds have been reported, it has been normally assumed that solutions of these compounds in halogenated hydrocarbon solvents were stable and unreactive at ambient temperature [11]. However, we find that both pentaphenyl- and penta-*p*-tolylantimony(V) undergo decomposition reactions at 25°C in the absence of light in solutions of $CHCl_3$, CH_2Cl_2 and CH_2Br_2. This is consistent with the results by McEwen [18], et al., that pentaphenylantimony(V) reacts with CCl_4 in the dark at 52.3°C. The products of our reactions are the tetraarylstibonium halides (Ar_4SbX, 70% yield), the protonated aryl species, the α-linked aryl dimer (Ar—Ar), polymeric species in lesser amounts, and low molecular weight products from the coupling of radicals generated by the solvent. The rate of reaction of pentaphenylantimony(V) in the absence of light was monitored by ^1H NMR and found to be first order in both pentaarylantimony(V) species and in solvent, with pseudo-first order specific rate constants being obtained for reaction in $CHCl_3$ (8.1×10^{-6} sec^{-1}), CH_2Cl_2 (7.9×10^{-6} sec^{-1}) and CH_2Br_2 (7.0×10^{-6} sec^{-1}). In all solvents, exposure to light greatly accelerated the reaction, with incidental laboratory fluorescent light increasing the reaction rate four-fold [19].

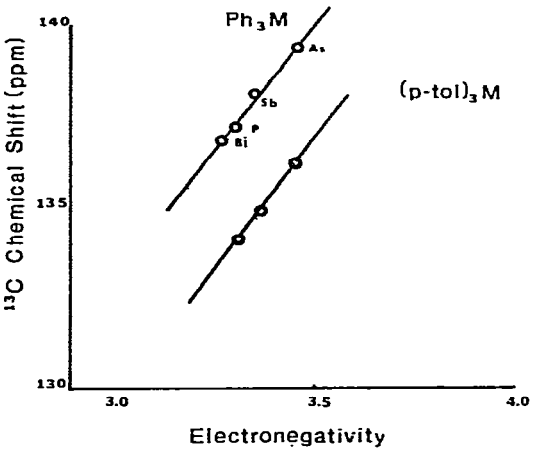


Fig. 3. Plot of ^{13}C NMR Chemical Shifts vs. Sanderson's equalized electronegativity values for the R_3M and R_5M species (M = As, Sb, P, Bi).

simple chemical shift arguments, it is generally found that ^{13}C shieldings decrease with increasing electronegativity of substituent atoms directly attached to the carbon atom [20]. The plot of the C(1) chemical shifts vs. Sanderson's equalized electronegativity [21] values is shown in Fig. 3, for both the triphenyl- and tri-*p*-tolyl-Group Va species. The fact that the slopes are parallel indicates that the shielding effects are similar for both systems. An increase in metal atom electronegativity deshields the C(1) carbon atom. The presence of a methyl group *para* to the C(1) carbon causes an increase in shielding relative to the phenyl analog, and hence the chemical shift is decreased. This is consistent with the inductive effect of the methyl group which affects the position *para* to itself most strongly. This is further supported by the chemical shift data for the C(4) position, where the ^{13}C shift values are larger by about δ 10 ppm for the *p*-tolyl series than the phenyl series, indicating increased shielding, and therefore increased electron density at the C(4) position for the triphenyl species in Group Va. This model is consonant with the resonance structures available for toluene.

For the pentacoordinate species of arsenic and antimony there are no obvious trends for the ^{13}C NMR chemical shift data. The C(1) shift values for both phenyl and *p*-tolylantimony(V) species indicate much less shielding than in the corresponding arsenic(V) compounds, and either a large change in electronegativity or a difference in orbital overlap may explain this anomaly. Evidence from the lack of decomposition of the pentaarylarsenic species (vide infra) indicates a stronger As—C sigma bond and concurrent increased electron density at the C(1) position, resulting in increased shielding.

Experimental

Preparations: (a) Tri-*p*-tolylstibine [22], (b) tri-*p*-tolylstibine dichloride [23], (c) tri-*p*-tolylstibine dibromide [23], (d) penta-*p*-tolylantimony(V) [4], (e) tetra-*p*-tolylstibonium bromide [3], (f) tetra-*p*-tolylstibonium chloride [24], (g) triphenylstibine dibromide [23], (h) pentaphenylantimony(V) [4], (i) pentaphenyl-

arsenic(V) [25], (j) tri-*p*-tolylarsine [22], (k) tri-*p*-tolylarsenic dibromide [23] and (l) penta-*p*-tolylarsenic(V) [4] were prepared by previously described methods; (m) triphenylstibine (Alfa Inorganics), (n) triphenylarsine (PCR Incorporated), and (o) tetraphenylarsonium chloride (Eastern Chemical Corporation) were obtained commercially and used following recrystallization in chloroform (m and n) and water (o). (p) Tri-*p*-tolylstibine difluoride and (q) tri-*p*-tolylstibine diiodide were prepared by treating oxybistri-*p*-tolylantimony dichloride [26] in acetone with an excess of 48% aqueous HI or HF and precipitating the product with cold water. The tri-*p*-tolylstibine difluoride has a melting point of 92°C.

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