

Vibrational dynamics of the organometallic compound triarylorganoantimony (V) $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$

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Abstract. A complete normal coordinate analysis was performed for five-coordinate non-rigid triarylantimony diester $\text{SbPh}_3(\text{O}_2\text{CR})_2$, known to be a bioactive molecule, using Wilson G-F matrix method and Urey Bradley force field. The study of vibrational dynamics was performed using the concept of group frequencies and band intensities.

Keywords. FTIR spectra; triarylorganoantimony (V) complex; normal coordinate analysis; triarylantimony (V).

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1. Introduction

The preferred bonding arrangement of the five-coordinate triarylantimony dihalides R_3SbX_2 [$\text{R} = \text{Ph}$, $\text{Ph} = \text{CH}_3\text{C}_6\text{H}_4$, $\text{X} = \text{Cl}$, Br] determined via Van der Waals energy calculation is in harmony with the corresponding correlated propeller arrangement which are observed in the solid state. However, parallel calculations in the diester of the type $\text{Ph}_3\text{Sb}(\text{O}_2\text{CR})_2$ [$\text{R} = \text{C}(\text{OH})\text{Ph}_2$] are at variance with the solid state, which indicates the involvement of secondary bonding interaction between antimony and oxygen atoms of the carbonyl group of ester moiety [1]. X-ray crystallographic studies reveal that sterically disfavored conformation having trigonal bipyramidal structure around antimony is stabilized by secondary bonding interactions involving diaxially coordinated ester ligands [2]. However this feature, leading to supramolecular assembly, is not reflected in IR studies.

The coordination number of Sb is however, expanded from five to seven which is also consistent with the bonding model involving hyperconjugative $\sigma_a \leftarrow \sigma_{\text{nb}}$ non-bonding interactions [3] as revealed by X-ray crystallographic studies. However, it is not apparent by $\nu_{\text{asy}}(\text{C}=\text{O})$ frequency or by the appearance of any other IR absorption. Organic derivatives of group 15 elements of the type R_3SbX_2 have

attracted attention not only because of the structural aspects or alternate non-rigid arrangement but also from biological point of view. Apart from bactericidal and fungicidal effects of these compounds which have got considerable applications in textile industry [4,5], organoantimony carboxylates are proving to be potential candidates for antitumour activity. Our recent studies show organoantimony salicylates to be significantly potent against MCF-7 cell line [6,7], but the vibrational study of the compound have not yet been investigated and is being probed in the present work.

2. Theory

The famous Wilson's G-F matrix method [8] with Urey-Bradley [9] force field has been used to evaluate the normal modes.

These are given by the eigenvalues λ of the secular equation

$$\text{GFL} = \lambda L,$$

where $\lambda = 4\pi^2 c^2 \nu^2$.

The potential energy distribution (PED) in the j th internal coordinate for the i th normal mode is given by

$$\text{PED} = \frac{L_{ji}^* L_{ji} F_{ji}}{\lambda_i}.$$

3. Experimental

The FTIR spectra (figure 1 (please see <http://www.ias.ac.in/pramana/v68/p875/fulltext.pdf>)) of the compound $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$ have been recorded on a Perkin-Elmer Spectrum BX FTIR spectrophotometer.

4. Result and discussion

Normal coordinate calculations were performed using a program developed by Shimanouchi [10] following the G-F matrix method according to Wilson *et al* [8]. For the assignments the force constants were initially taken from the reported literature and later modified to give the 'best fit' results with the observed FTIR spectra [11–15].

The triarylantimony (V) complex $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$ has 90 atoms. However, to reduce the problem to manageable dimensions CH, CH₂, CH₃ have been treated as mass points with a mass of 13, 14 and 15 respectively. This does not in any way disturb the accuracy of the results reported here. With this approximation the problem of 90 atoms reduces to a problem of 53 atoms with 153 normal modes of vibrations [8].

Vibrational dynamics of triarylantimony diester

4.1 Structure

The crystal structure of $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$ is taken from the work of Barucki *et al* [1]. The molecular structure of triarylantimony (V) $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$ compound is given in figure 2 (please see <http://www.ias.ac.in/pramana/v68/p875/fulltext.pdf>).

4.2 Vibrational investigations

The observed frequencies agree with the calculated ones within 10 cm^{-1} . In the assignment of the normal modes given in table 1 only the dominant potential energy distributions (PED) are considered. The corresponding force constant values are given in table 2 (available on request from the corresponding author). Identification with the experimental data has been made on the basis of potential energy distribution, line profile, line intensities and the presence/absence of a given mode in similar molecules [16,17].

4.3 Backbone and mixed modes

The modes $\nu(\text{Sb-O})$, $\nu(\text{C-O})$, $\nu(\text{C-C})_{\text{out-r}}$ stretches, $\phi(\text{Sb-O-C})$ and $\phi(\text{C-C-O})$ in-plane bendings, and their wagging and torsions like $\tau(\text{O-Sb-O-C})$ etc., are termed as ‘backbone and mixed modes’. All backbone and mixed modes are given in table 1. An intense absorption peak is observed in FTIR spectra at 1280 cm^{-1} and it is calculated at 1279 cm^{-1} with vibrational modes as $\nu(\text{C-O})_{\text{adj-r}}$ (45%), $\nu(\text{C-C})_{\text{r-adj-co}}$ (34%) and $\nu(\text{C-C})_{\text{adj-r}}$ (15%). The phenolic mode $\nu(\text{C-O})$ is reported at 1280 cm^{-1} [18], which confirms the participation of oxygen in the in-plane bending (Sb-O-C) and (C-Sb-O) [19,20]. A strong peak observed at 996 cm^{-1} in FTIR spectra which is calculated at 1005 cm^{-1} is attributed to the vibrational modes $\nu(\text{C-O})_{\text{adj-r}}$ (41%) mixed with $\nu(\text{C-C})_{\text{r-adj-co}}$ (27%). A very sharp peak is observed in FTIR spectra at 761 cm^{-1} which is calculated at 761 cm^{-1} . It is attributed to the modes $\phi(\text{C-C-O})_{\text{r-adj-co}}$ (30%), $\nu(\text{Sb-O})$ (41%) and $\phi(\text{O-C=O})$ (16%). This is on a higher value of frequency as reported in [18,21–23] but is in accordance with ref. [24]. This increase in wave number may be attributed to the replacement of antimony of organic group R by more electrons withdrawing oxygen atom [25]. A weak peak is observed in far infrared region at 426 cm^{-1} which is calculated at 422 cm^{-1} with vibrational modes $\phi(\text{Sb-O-C})$ (60%) and $\nu(\text{Sb-O})$ (31%). This may be due to the participation of oxygen atom in (Sb-O-C) bonding [19,20]. This mode seems to be one of the characteristic modes of the present compound.

4.4 Side chain modes

The vibrational modes $\nu(\text{Sb-C})$, $\nu(\text{C=O})$, $\nu(\text{C-C})_{\text{adj-r}}$ stretches, $\phi(\text{Sb-C-C})$, $\phi(\text{O-C=O})$, $\phi(\text{C-C-C})_{\text{adj-r}}$ in-plane bendings, wagging $\omega(\text{O=C})$ and torsions $\tau(\text{Sb-C})$ etc., are termed as ‘side-chain modes’. A band having one highly intense peak

Table 1.

Calculated freq. (cm ⁻¹)	Observed freq. (cm ⁻¹)	Assignment (% potential energy distribution)
1692	1692	$\nu(\text{O}=\text{C})(47)+\nu(\text{C}-\text{C})_{\text{adj-r}}(18) + \nu(\text{C}-\text{C})_{\text{adj-o}}(13)$
1667	1666	$\nu(\text{O}=\text{C})(54)+\nu(\text{C}-\text{C})_{\text{adj-r}}(15) + \nu(\text{C}-\text{C})_{\text{adj-o}}(17)$
1642	1652	$\nu(\text{C}-\text{C})_{\text{adj-r}}(67)$
1639	1629	$\nu(\text{C}-\text{C})_{\text{adj-r}}(63)+\nu(\text{C}-\text{C})_{\text{r-adj-co}}(22)$
1602	1604	$\nu(\text{C}-\text{C})_{\text{adj-r}}(24)+\nu(\text{C}=\text{O})(22)+\nu(\text{C}-\text{O})_{\text{adj-r}}(17)$
1591	1592	$\nu(\text{C}-\text{O})_{\text{adj-r}}(26)+\nu(\text{C}-\text{C})_{\text{r-ad-co}}(23) +\nu(\text{C}-\text{C})_{\text{adj-o}}(15)$
1576	1566	$\nu(\text{C}-\text{C})_{\text{r-adj-Sb}}(85)$
1557	1560	$\nu(\text{C}-\text{C})_{\text{r-adj-co}}(51)+\nu(\text{C}-\text{C})_{\text{adj-o}}(16) +\nu(\text{C}-\text{O})_{\text{adj-Sb}}(11)$
1514	1512	$\nu(\text{C}-\text{C})_{\text{r-adj-co}}(95)$
1446	1446	$\nu(\text{C}-\text{C})_{\text{r-adj-sb}}(98)$
1437	1436	$\nu(\text{C}-\text{C})_{\text{r-adj-co}}(95)$
1314	1305	$\nu(\text{C}-\text{C})_{\text{r-adj-sb}}(74)$
1292	1294	$\nu(\text{C}-\text{C})_{\text{r-adj-sb}}(57)$
1272	1279	$\nu(\text{C}-\text{O})_{\text{adj-r}}(45)+\nu(\text{C}-\text{C})_{\text{r-ad-co}}(34) +\nu(\text{C}-\text{C})(15)+\nu(\text{C}-\text{O})_{\text{ad-sb}}(10)$
1266	1267	$\nu(\text{C}-\text{O})_{\text{adj-r}}(32)+\nu(\text{C}-\text{C})_{\text{adj-r}}(12) +\nu(\text{C}-\text{O})_{\text{ad-sb}}(20)$
1176	1176	$\nu(\text{C}-\text{C})_{\text{r-ad-sb}}(88)$
1165	1162	$\nu(\text{C}-\text{C})_{\text{r-adj-co}}(88)$
1053	1054	$\nu(\text{C}-\text{C})_{\text{r-adj-sb}}(71)+\phi(\text{C}-\text{C}-\text{C})_{\text{r-ad-sb}}(18)$
1033	1032	$\nu(\text{C}-\text{C})_{\text{r-adj-sb}}(72)+\phi(\text{C}-\text{C}-\text{C})_{\text{r-ad-sb}}(10)$
1005	996	$\nu(\text{C}-\text{O})(41)+\nu(\text{C}-\text{C})_{\text{r-ad-co}}(27)$
918	918	$\nu(\text{C}-\text{C})_{\text{r-ad-sb}}(47)+\phi(\text{C}-\text{C}-\text{C})_{\text{r-ad-sb}}(43)$
897	893	$\nu(\text{C}-\text{C})_{\text{r-ad-co}}(68)$
821	815	$\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-co}}(33)+\nu(\text{C}-\text{O})_{\text{ad-sb}}(18) +\nu(\text{C}-\text{C})_{\text{r-ad-co}}(14)$
761	761	$\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-co}}(30) +\nu(\text{O}-\text{Sb})(41)+\phi(\text{O}-\text{C}=\text{O})_{\text{ad-Sb}}(16)$
743	746	$\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-c}}(30)+\nu(\text{O}-\text{Sb})(31)$
688	689	$\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-sb}}(60)+\nu(\text{C}-\text{Sb})(21)+\nu(\text{C}-\text{C})_{\text{r-ad-Sb}}(17)$
591	599	$\omega(\text{O}=\text{C})(47)+\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-c}}(24)$
583	586	$\omega(\text{O}=\text{C})(35)+\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-co}}(35)$
531	532	$\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-sb}}(85)$
474	475	$\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-co}}(30)+\nu(\text{C}-\text{Sb})(22)+\phi(\text{C}-\text{Sb}-\text{C})(16)$
458	451	$\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-co}}(88)$
435	438	$\tau(\text{C}-\text{C})_{\text{ad-sb}}(42)+\phi(\text{C}-\text{Sb}-\text{O})(21)+\tau(\text{C}-\text{C})_{\text{r-ad-co}}(12)+\tau(\text{Sb}-\text{C})(10)$
422	426	$\phi(\text{C}-\text{Sb}-\text{O})(60) +\nu(\text{O}-\text{Sb})(31)$
282	-	$\nu(\text{C}-\text{Sb})(42) + \phi(\text{C}-\text{Sb}-\text{C})(26)$

Note: Here the abbreviation ‘adj’ means adjacent outside. ‘r’ stands for the ring 1,2,3 etc. In assigning the frequencies only dominant modes are taken in most of the cases.

observed at 1692 cm⁻¹ and calculated at 1692 cm⁻¹ is attributed to the vibrational mode $\nu(\text{C}=\text{O})$ with 47% PED mixed with $\nu(\text{C}-\text{C})_{\text{adj-r}}$ (18%) and $\nu(\text{C}-\text{C})_{\text{adj-co}}$ (13%) PED and other medium shoulder peaks are observed at 1666 cm⁻¹ and calculated at 1667 cm⁻¹ with modes of vibrations as $\nu(\text{C}=\text{O})$ (54%), $\nu(\text{C}-\text{C})_{\text{adj-r}}$ (15%) and $\nu(\text{C}-\text{C})_{\text{adj-co}}$ (17%) PED’s. A strong band is obtained at 689 cm⁻¹ which is calculated at 688 cm⁻¹, with modes of vibrations $\nu(\text{Sb}-\text{C})$ (21%) and $\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-Sb}}$ (60%). A medium peak is observed at 599 cm⁻¹ in FTIR spectra and it is calculated at 591 cm⁻¹ with out-of-plane bending $\omega(\text{O}=\text{C})$ (47%) and in-plane bending $\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-co}}$ (24%). A weak absorption peak is observed at 475 cm⁻¹ and it is calculated at 474 cm⁻¹ with vibrational modes $\phi(\text{C}-\text{C}-\text{C})_{\text{r-adj-co}}$ (30%), $\nu(\text{Sb}-\text{C})$ (22%) and $\phi(\text{C}-\text{Sb}-\text{C})$ [15]. This mode is reported in the frequency

range 449–472 cm^{-1} in ref. [24] and between 459 and 484 cm^{-1} in ref. [23], which is in good agreement.

4.5 Ring modes

In the present compound there are seven benzene rings, in which three rings R1, R2, R3 are directly attached to the central antimony atom, two rings R4, R5 are attached on the right side and the other two rings R6 and R7 are attached on the left side of the central antimony atom. The vibrations corresponding to these seven rings like $\nu(\text{C-C})_{\text{r-adj-Sb}}$, $\nu(\text{C-C})_{\text{adj-co}}$ stretches, $\phi(\text{C-C-O})_{\text{r-adj-co}}$, $\phi(\text{C-C-O})_{\text{r-adj-Sb}}$ in-plane bendings, wagging $\omega(\text{C-C})$ and torsions $\tau(\text{C-C})_{\text{r}}$ are termed as ‘ring modes’. A strong band with two peaks in the range 1436–1446 cm^{-1} is observed in FTIR spectra and it is calculated at 1436 cm^{-1} and 1446 cm^{-1} , with modes of vibration $\nu(\text{C-C})_{\text{r-adj-Sb}}$ (98%) and $\nu(\text{C-C})_{\text{r-adj-Sb}}$ (95%) PED’s respectively. Two strong peaks are again observed in band region 1032–1054 cm^{-1} and are calculated at 1033 cm^{-1} and 1053 cm^{-1} respectively with modes of vibration $\nu(\text{C-C})_{\text{r-adj-Sb}}$ (71%), $\phi(\text{C-C-C})_{\text{r-adj-Sb}}$ (18%) and $\nu(\text{C-C})_{\text{r-adj-Sb}}$ (72%), $\phi(\text{C-C-C})_{\text{r-adj-Sb}}$ (10%) respectively. A very strong peak in FTIR spectra is observed at 451 cm^{-1} and it is calculated at 458 cm^{-1} with vibrational mode $\phi(\text{C-C-C})_{\text{r-adj-co}}$ (88%) PED. This seems to be another characteristic mode of the present compound.

5. Conclusion

The structure of triarylantimony (V) compound $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$ has a slightly distorted TBPY (trigonalbipyramidal) geometry where the axial substituents adopt values close to the ideal, equatorial angles which deviate from those expected as a result of the orientation adopted by the tilted phenyl rings. The geometry of the remainder of the molecule primarily arises from the combination of the steric demands and non-bonded interactions. Normal coordinate analysis data performed on this compound show close resemblance of the calculated and observed vibrational bands. For instance a vibrational band observed at 451 cm^{-1} is calculated at 458 cm^{-1} with vibrational mode $\phi(\text{C-C-C})_{\text{r-adj-co}}$ (88%) PED. The intense band, ranging from 743 to 761 cm^{-1} , has modes $\phi(\text{C-C-C})_{\text{r-adj-co}}$ and $\nu(\text{Sb-O})$. The stretching mode $\nu(\text{Sb-O})$ seems to be due to the secondary bonding interaction between antimony and oxygen atoms and so it is one of the characteristic modes of the title compound. The calculated frequencies are well-matched with the observed frequencies along with the vibrational modes reported in literature.

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Supplementary figures

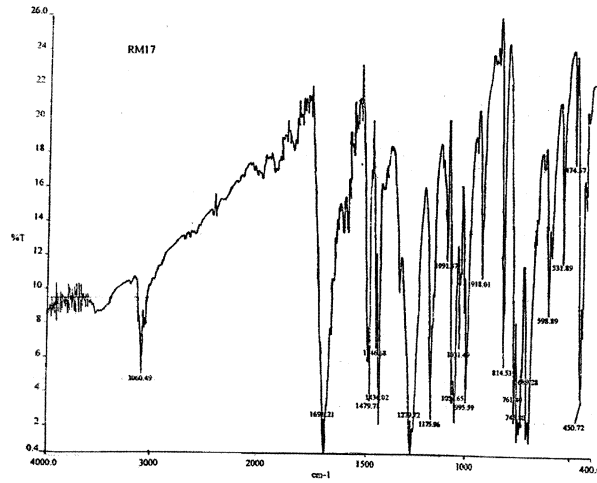


Figure 1. FTIR-spectra of triaryloroantimony (V) $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$.

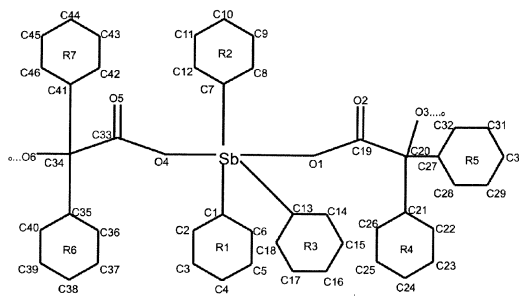


Figure 2. Model molecular structure of triaryloroantimony (V) $\text{SbPh}_3[\text{O}_2\text{CC}(\text{OH})\text{Ph}_2]_2$.