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Vibrational and Quantum Chemical Study of Triphenylantimony(V)-*o*-salicylate

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Abstract: A complete normal coordinate analysis was performed by two different methods: a classical Wilson G-F matrix method and the semi-empirical molecular orbital PM3 method, for a five coordinate non rigid triphenyl antimony diester $\text{SbPh}_3(\text{O}_2\text{CR})_2[\text{R}=\text{C}_6\text{H}_4\text{OH-}o]$, known to be a bioactive molecule. The study of vibrational spectra suggested that the title compound might have secondary bonding interaction between the central antimony atom and the carbonyl oxygen atoms. The atomic charge distribution, geometry optimization and thermochemistry, were also calculated by PM3 method, which help in finding the potential sites of the title compound.

Keywords: FT-IR spectra, Triphenylantimony(V)-*o*-Salicylate, Normal coordinate analysis, Semi-empirical, Organometallic compounds, Thermochemistry.

Introduction

Organic derivatives of group (15) elements have attracted attention not only because of the structural aspects but also from biological point of view. These compounds show the bactericidal and fungicidal effects¹, which have got wonderful applications in textile industry^{2,3}. Recent publications reveal a renewed interest in the antifungal, antibacterial and cytotoxic studies of organoantimony carboxylate and salicylates derivatives. The enhanced antitumour activity of diphenyl antimony(III) thiolates, both *in vitro* and *in vivo*, led to the development of other types of organoantimony(III) and antimony(V) derivatives. In phenylantimony(V) amines and dicarboxylates displayed some inhibition against a variety of human tumor cell lines. Recent studies show that organoantimony salicylates have considerable potential to be an antitumour active compound and therefore they are required to be treated in much extensive and detailed vibrational study in order to have better insight of these compounds. The title compound has been taken from the work of Barucki *et al*⁴ for its vibrational and thermodynamical study.

In this manuscript, the experimental FT-IR is compared with theoretical frequencies obtained by normal coordinate analysis using two different methods: a classical mechanics method using Wilson GF matrix method and the semi-empirical quantum chemical molecular orbital PM3 method⁵. Thus the evaluation of the advantages of both methods is useful for obtaining a reliable assignment of the vibrational spectra. Assignments are thus proposed for observed frequencies corresponding to backbone & mixed modes, side chain modes and ring modes on the basis of the potential energy distribution (PED).

The author's interest in the vibrational dynamics as well as quantum chemical study of the title compound triphenylantimony(V)-*o*-salicylate, $\text{SbPh}_3[\text{O}_2\text{CC}_6\text{H}_4(\text{OH})-\text{o}]_2$ was stimulated by the fact that the title compound exhibited the antifungal, antibacterial and antitumour activities¹ up to considerable amount.

In this work, the theoretical study for the title compound is presented, which also includes its geometrical parameters, atomic charge distribution and thermochemistry calculated by semi empirical PM3 method, using Mopac 2007 software⁶. Recent studies show that the organoantimony salicylates are significantly potent against MCF-7 cell line⁷, but the vibrational study and the quantum chemical calculations of the title compound have not been investigated yet, and are being probed in the present work.

Theory

The Wilson's G-F Matrix method⁸ with Urey Bradley¹¹ force field has been used to evaluate the normal modes. These are given by the eigen values λ of the secular Equation.

$$\begin{aligned} \text{GFL} &= \lambda L, \\ \text{as } \lambda &= 4\pi^2 c^2 v^2 \end{aligned} \quad (1)$$

The potential is represented as

$$\begin{aligned} V &= \sum_{jk} K'_{jk} r_{jk} (\Delta r_{jk}) + \frac{1}{2} K_{jk} (\Delta r_{jk})^2 + \sum_{ijk} H'_{ijk} r_{ij} r_{jk} (\Delta \phi_{ijk}) + \frac{1}{2} H_{ijk} r_{ij} r_{jk} (\Delta \phi_{ijk})^2 \\ &+ \sum_{ijk} F'_{ik} q_{ik} (\Delta q_{ik}) + \frac{1}{2} F_{ik} (\Delta q_{ik})^2 + \sum_i K_j^w (\Delta w_j)^2 + \sum_j K_j^t (\Delta t_j)^2 \end{aligned} \quad (2)$$

where, Δr_{jk} , $\Delta \phi_{ijk}$, Δw_j and Δt_j are the internal coordinate changes corresponding to bond stretch, angle bend, out of plane deformation and torsion respectively. The potential energy distribution in the j^{th} internal coordinate for the i^{th} normal mode is given by

$$\text{(PED)} = \frac{L_{ji}^* L_{ji} F_{ji}}{\lambda_i} \quad (3)$$

Experimental

X-ray data of the compound Triphenylantimony(V)-*o*-salicylate $\text{SbPh}_3[\text{O}_2\text{CC}_6\text{H}_4(\text{OH})-\text{o}]_2$ were collected from the CCDC database¹⁰. The FTIR spectra of the compound, presented in Figure 1, have been recorded on a Perkin-Elmer Spectrum BX FTIR spectrophotometer in the frequency range 4000 to 400 cm^{-1} .

Computational methods

Classical mechanics calculations

Normal coordinate calculations were performed using the program developed by Shimanouchi¹¹ following the Wilson GF matrix method⁸. This method describes the motion in terms of the internal coordinates, which are changes in bond lengths, bond angles and those out of plane bending and dihedral angles. The force constants in terms of these coordinates can easily be visualized and have a physical meaning. The Urey Bradley force

field is used in our calculations. It incorporates intra unit interactions and interactions due to the neighboring units, in addition to the bonded interactions. It also includes the interactions between non-bonded atoms. 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 FT-IR spectra (Figure 2)¹²⁻¹⁶. All force constants for the title compound are given in Table 1.

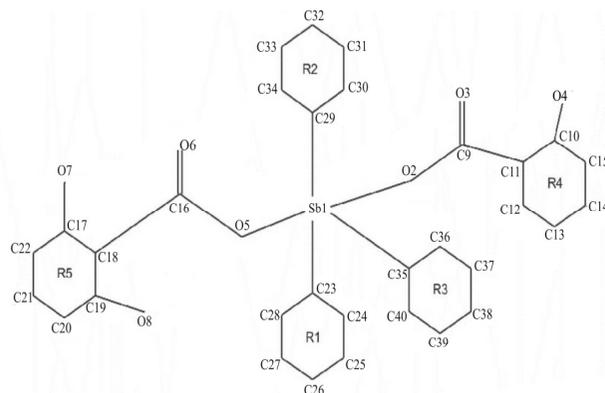


Figure 1. Model molecular structure of triphenylantimony(V)-*o*-salicylate $\text{SbPh}_3(\text{O}_2\text{CC}_6\text{H}_4(\text{OH})-o)_2$

Table 1. Internal coordinates and force constant values (mdynes/Å) of the title compound

S. No.	Internal Coordinates	Force constant values
1	$\nu(\text{C-Sb})$	2.150
2	$\nu(\text{O-Sb})$	2.350
3	$\nu(\text{C-O})_{\text{adj-Sb}}$	4.200
4	$\nu(\text{C=O})_{\text{adj-Sb}}$	7.370
5	$\nu(\text{C-O})_{\text{R1-O}}$	4.120
6	$\nu(\text{C-O})_{\text{R2-O}}$	5.300
7	$\nu(\text{C-C})_{\text{adj-C=O}}$	4.360
8	$\nu(\text{C-C})_{\text{R4-adj-O}}$	4.020
9	$\nu(\text{C-C})_{\text{R5-adj-O}}$	4.000
10	$\nu(\text{C-C})_{\text{R2-adj-Sb}}$	5.665
11	$\nu(\text{C-C})_{\text{R2-adj-Sb}}$	5.630
12	$\nu(\text{C-C})_{\text{R3-adj-Sb}}$	5.635
13	$\phi(\text{C-Sb-O})$	0.300
14	$\phi(\text{O-Sb-O})$	0.250
15	$\phi(\text{C-Sb-C})$	0.250
16	$\phi(\text{Sb-O-C})$	0.105
17	$\phi(\text{O-C=C})_{\text{adj-Sb}}$	1.125
18	$\phi(\text{O-C-C})_{\text{adj-Sb}}$	0.310
19	$\phi(\text{O=C-C})_{\text{adj-Sb}}$	1.350
20	$\phi(\text{C-C-O})_{\text{adj-R4}}$	0.790
21	$\phi(\text{C-C-C})_{\text{adj-R4}}$	0.750

Contd....

22	$\phi(\text{C-C-C})\text{R-adj-C}$	0.600
23	$\phi(\text{C-C-C})\text{R4}$	0.720
24	$\phi(\text{C-C-O})\text{adj-R4}$	0.630
25	$\phi(\text{C-C-O})\text{adj-R5}$	0.760
26	$\phi(\text{C-C-C})\text{adj-R5}$	0.770
27	$\phi(\text{C-C-C})\text{R5}$	0.600
28	$\phi(\text{C-C-C})\text{R1}$	0.760
29	$\phi(\text{Sb-C-C})$	0.300
30	$\phi(\text{C-C-C})\text{R2}$	0.660
31	$\phi(\text{C-C-C})\text{R3}$	0.745
32	$\omega(\text{C=O})\text{adj-R4}$	0.310
33	$\omega(\text{C-O})\text{R4}$	0.257
34	$\omega(\text{C-O})\text{adj-R5}$	0.450
35	$\omega(\text{C-O})\text{adj-R5}$	0.250
36	$\omega(\text{C-O})\text{R5}$	0.250
37	$\tau(\text{Sb-O})$	0.045
38	$\tau(\text{Sb-C})\text{R3}$	0.045
39	$\tau(\text{Sb-C})\text{R1}$	0.045
40	$\tau(\text{Sb-O})\text{R1}$	0.045
41	$\tau(\text{Sb-C})\text{R2}$	0.045
42	$\tau(\text{O-C})\text{R4}$	0.055
43	$\tau(\text{O-C})\text{R5}$	0.055
44	$\tau(\text{C-C})\text{R4-C=O}$	0.055
45	$\tau(\text{C-C})\text{R4}$	0.055
46	$\tau(\text{C-C})\text{R5}$	0.055
47	$\tau(\text{C-C})\text{R1}$	0.055
48	$\tau(\text{C-C})\text{R2}$	0.058
49	$\tau(\text{C-C})\text{R3}$	0.005

Note:

1. Here ν means the stretching vibration between the atoms.
2. Here ϕ means the angle inplane-bending between the three atoms.
3. Here ω means the out-of-plane bending or wagging between the atoms.
4. Here τ means the torsional vibration between the atoms.
5. R-stands for ring and adj-stands for adjacent.
6. The values in brackets denotes the non-bonded force constants values.
7. R1-O etc. stands for outside the ring R1 etc.

The computer program developed by Shimanouchi¹¹ was used for the calculation of vibrational frequencies and potential energy distribution (PED), which made it possible to obtain a detailed description of the nature of vibrational bands. Potential energy distribution provides quantification of the contribution of internal coordinate to a normal coordinate^{17,18}. For that purpose, the contribution of the diagonal force constant of internal coordinate to the vibrational eigen value is expressed as a percentage. All semi-empirical calculations were performed by Mopac 2007 package⁶. Assignment of frequency modes was performed by graphical user interface Winmostar¹⁹.

The title compound triphenylantimony(V)-*o*-Salicylate $\text{SbPh}_3[\text{O}_2\text{C}_6\text{H}_4(\text{OH})-o]_2$ has 65 atoms, however to reduce the problem to manageable dimensions CH, OH *etc.* have been treated as mass points with a mass of 13, 16 *etc.* respectively. This does not in any way disturb the accuracy of the results presented here. This is because the frequencies belonging to these can well be designated as group frequencies and many of them being in the higher range do not mix with other modes. With this approximation the triphenylantimony(V)-*o*-salicylate reduces to 40(N) atoms problem with 114 (3N-6) normal modes of vibrations⁸.

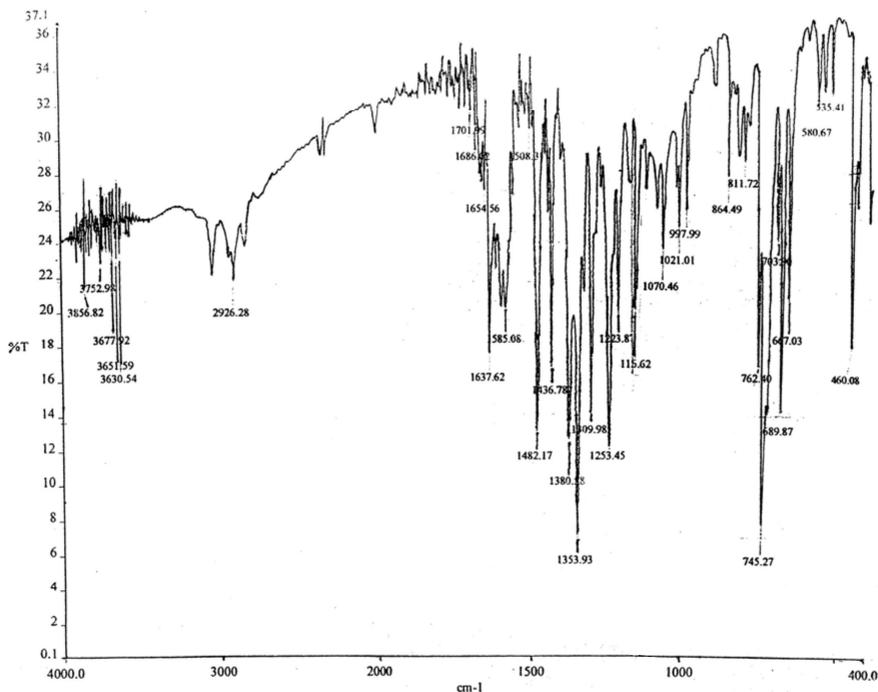


Figure 2. FT-IR spectra of Triphenylantimony(V)-*o*-salicylate.

Quantum chemical calculations

Atomic charge distribution

The knowledge of the charge distributions is essential for the interpretation of molecular properties. The atomic charges for all the atoms of the title compound calculated by PM3 method in gas phase are presented in Table 2. As seen from this table, the oxygen atoms like O1, O2, O4 and O5 have bigger negative atomic charges with values as -0.56521 , -0.55328 , -0.60315 and -0.53765 units respectively, suggesting that they may be potential sites to react with charged moieties/ions. Besides the oxygen atoms some carbon atoms like C3, C6, C7, C10, C12, C14, C15, C21 and C27 also have relatively higher negative charge values than the other carbon atoms in the molecule, and their respective values are -0.24062 , -0.0296 , -0.18295 , -0.34722 , -0.23683 , -0.2352 , -0.16773 , -0.16816 and -0.21622 units. This data of the charge distribution of atoms suggests that the oxygen atoms are relatively stronger potential sites than the carbon atoms.

Results and Discussion

In the present work the observed frequencies agree with the calculated ones within 10 cm^{-1} . In the assignment of the normal modes as given in Table 2 (a, b & c), only the dominant

potential energy distributions (PED) are considered. The corresponding force constants values are given in Table 1, which includes the force constants values for bonded as well as non-bonded interactions. The non-bonded parameters help to bring a molecule into its best spatial orientation. The physical effects represented by these parameters are Vander Waals and electrostatic forces. 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 molecules²⁰⁻²³.

Table 2(a). Calculated and observed back-bone & mixed modes

Calculated Freq cm ⁻¹		Observed Freq FTIR, cm ⁻¹	Assignment in % Potential energy distribution (PED)
Wilson GF	PM3		
1450	1459	1445, m	v(C-C)R1-O[49] +v(C-C)ad-C=O[33] + v(C-C)R3-asym[PM3]
1387	1368	1380, vs	v(C-C)R5-O[46] +v(C-O)R1-O[18]+ v(O=C)ad-Sb[13] + + v(C-O)adj-Sb[22] + v(O-C)ad-R5&Sb[PM3]
1352	1360	1353, vs	v(C-C)R2-O[53] +v(C-C)R2-O[29] + v(O-C)ad-R4&Sb[PM3]
1253	1229	1253, s	v(C-C)R2-O[43] + v(O-C)ad-Sb [22] +v(C-C)ad-O[19] + + v(O-C)adj-R4&Sb[PM3] + φ(C-C-C)R2[PM3]
1161	1164	1153, s	v(C-C)R1-O[55] + v(O-C)R1-O[32] + φ(C-C-C)R4[11] + + R2-puck[PM3] + φ(C-C-C)R1[PM3]
1061	1070, m	v(C-C)R2-O[53] + v(C-O)ad-Sb[18] +φ(C-C-C)R5[11]
1033	1034, wsh	v(C-O)ad-Sb[30] + v(C-C)R1-O[24] + φ(C-C-C)R4[21]
762	762	762, s	φ(C-C-C)R4[49] + v(Sb-O)[15] + v(C-O)R1-O[10] + + v(C-C)R2-asym[PM3] + v(C-O)ad-Sb-R4[PM3] + φ(Sb-O-C)[27]+v(Sb-O)[16]+v(C=O)adj-Sb[16]+ φ(O-C-C)ad-Sb[14] + v(C-O)ad-Sb[10] + R4-rock[PM3] + + φ(C-C-O)adj-R4[PM3]
748	736	745, vs	φ(C-C-C)R5[43] + v(Sb-O)[26] + v(C-C)ad-O[10] + + φ(C-C-O)adj-R4[PM3] + φ(Sb-O-C)adj-R5[PM3]
707	703	704, m	v(Sb-O)[31]+ v(C-C)R1-O[24] + φ(C-C-C)R4[10] + + (O=C-O)adj-R4-sciss[PM3] + φ(Sb-O-C)adj-R4[PM3]
650	642	641, wsh	φ(C-C-C)R5[35] + φ(C-C-O)R5[20] + φ(C-C-C)R5[14]+ v(C-O)R1-O[10] + R4-tors[PM3] + ω(C=O)ad-R5[PM3]
455	469	460, s	φ(C-C-O)ad-R1-O[32] + v(Sb-O)[14] + v(C-C)R1ad-O[12] + R2-rock[PM3] + φ(Sb-C-C)adj-R2[PM3]

Back-bone & mixed modes

The modes which includes the vibrations of v(Sb-O), v(C-O), v(C-C) out-r stretches, φ(C-C-O), φ(C-C=O), φ(Sb-O-C), φ(O-Sb-O) in plane bendings, τ(Sb-O-C-C), τ(C-Sb-O-C) torsions and their mixtures are termed as back bone modes. Steric interactions between atoms that bond distances away are accounted for with this term. All back-bone and mixed modes are given in Table 2(a).

In the FTIR spectra a medium intensity peak is observed at 1445 cm⁻¹, which is calculated at 1450 cm⁻¹ from Wilson GF method with the stretching modes v(C-C)R1-O[49%] and v(C-C)adj-C=O[33%] PED's (potential energy distributions), whereas it is

found to be at 1459 cm^{-1} due to semi-empirical PM3 method with asymmetric stretching of $\nu(\text{C-C})\text{R3}$. This peak is reported²⁴ in the range, $1616\text{--}1455\text{ cm}^{-1}$. A very intense band is obtained in the FTIR spectra with two absorption peaks one at 1380 cm^{-1} and other at 1353 cm^{-1} , and these are calculated at 1387 cm^{-1} and 1352 from Wilson GF method, with vibrational modes $\nu(\text{C-C})\text{R1-O}[46\%]$, $\nu(\text{C-O})\text{R1-O}[18\%]$ mixed with other modes in small contributions for first peak and $\nu(\text{C-C})\text{R2-O}[53\%]$ and $\nu(\text{C-C})\text{R2}[29\%]$ for the second. This band is calculated at 1368 and 1360 cm^{-1} , with modes of vibrations as $\nu(\text{C-O})\text{adj-R5\&Sb}$ and $\nu(\text{C-C})\text{adj-R4\&Sb}$, with PM3 method, respectively. This mode is reported in the range $1350\text{--}1315\text{ cm}^{-1}$ in the literature²⁴. A strong peak is observed at 1253 cm^{-1} in the spectra and is calculated at 1253 cm^{-1} from GF matrix method, having modes of vibrations as $\nu(\text{C-O})\text{out-R}[22\%]$ and $\nu(\text{C-C})\text{R2}[43\%]$, whereas from PM3 method it is obtained at 1229 cm^{-1} with vibrational modes as $\nu(\text{C-O})\text{adj-R4\&Sb}\{\text{PM3}\}$ and $\phi(\text{C-C-C})\text{R2}\{\text{PM3}\}$. The phenolic (C-O) stretching mode is reported²⁷ at 1280 cm^{-1} , which suggests the participation of oxygen in (C-O-Sb) bonding^{26,27}. A strong peak is obtained in the FTIR spectra at 1153 cm^{-1} and is calculated from GF matrix method at 1161 cm^{-1} with vibrational modes $\nu(\text{C-O})\text{R1-O}[32\%]$, $\nu(\text{C-C})\text{R1-O}[55\%]$ and $\phi(\text{C-C-C})\text{R4}[11\%]$, this peak is calculated from PM3 method at 1164 cm^{-1} attributing to the modes of vibrations as ring R2 breathing (or puckering) and in plane bending $\phi(\text{C-C-C})\text{R1}$. A medium intense peak is observed at 1070 cm^{-1} and is calculated at 1061 cm^{-1} from GF matrix method with vibrational modes $\nu(\text{C-O})\text{out-R}[18\%]$, $\nu(\text{C-C})\text{R2-O}[53\%]$ and $\phi(\text{C-C-C})\text{R2}[11\%]$, whereas this mode is absent in the PM3 method. A weak peak is observed at 1034 cm^{-1} and is calculated at 1033 cm^{-1} with modes of vibrations as $\nu(\text{C-O})\text{out-r}[30\%]$, $\nu(\text{C-C})\text{R1}[24\%]$ and $\phi(\text{C-C-C})\text{R3}[21\%]$.

A strong peak is observed in FTIR spectra at 762 cm^{-1} and it is calculated at 762 cm^{-1} from GF matrix method, with modes of vibrations $\nu(\text{Sb-O})[15\%]$, $\phi(\text{C-C-C})\text{R4}[49\%]$ and $\nu(\text{C-O})\text{R1-O}[14\%]$, and it is also calculated at 762 cm^{-1} , from the PM3 method, attributing to the stretching modes as $\nu(\text{C-C})\text{R2-asym}$ and $\nu(\text{C-O})$. A very strong absorption peak is observed at 745 cm^{-1} and is calculated by GF matrix method at 748 cm^{-1} having vibrational modes as $\nu(\text{Sb-O})[16\%]$, $\phi(\text{Sb-O-C})[27\%]$, $\nu(\text{C=O})[16\%]$, $\phi(\text{C-C-O})[14\%]$ and $\nu(\text{C-O})\text{out-R}[10\%]$, however, it is found to be at 736 cm^{-1} with vibrational modes as ring-4(R4) rocking and in-plane bending of $\phi(\text{C-O-C})\text{adj-R4}\{\text{PM3}\}$. These two peaks obtained at 762 cm^{-1} and 745 cm^{-1} are symmetric modes, which seems to be involve in secondary bonding interactions, as suggested by low PED values (15% and 16% resp.) of $\nu(\text{Sb-O})$ mode and these are in good agreement as reported by Shanker *et al.*²⁸. A medium intense peak is observed at 704 cm^{-1} and it is calculated at 707 cm^{-1} by classical GF matrix method, having vibrational modes $\nu(\text{Sb-O})[26\%]$ and $\phi(\text{C-C-C})\text{R5}[43\%]$, and it is calculated at 703 cm^{-1} , having modes of vibrations as $\phi(\text{C-O-C})\text{adj-R4}\{\text{PM3}\}$ and $\phi(\text{Sb-O-C})\{\text{PM3}\}$. A weak shoulder absorption peak is observed at 641 cm^{-1} which is calculated at 650 cm^{-1} from Wilson GF matrix method, with modes of vibration as $\nu(\text{Sb-O})[30\%]$ and $\nu(\text{C-C})\text{R1}[23\%]$, and it is found at 642 cm^{-1} attributing to the scissoring of $(\text{O=C-O})\text{adjR4}$ and in-plane bending of $\phi(\text{Sb-O-C})\text{adj-R4}\{\text{PM3}\}$. This band is a bit lower as reported by Shanker *et al.*²⁸, and higher as compared to the reported bands by Khosa *et al.*²⁹. This band range for $\nu(\text{Sb-O})$ which is mass sensitive mode due to the heavy antimony atom, seems to be one of the characteristic mode, of the title compound, which is probably due to secondary interaction between antimony and oxygen atoms. A band in lower frequency range with one strong and one weak shoulder absorption peaks are observed in FTIR spectra. The strong peak is observed at 460 cm^{-1} and is calculated from classical method, at 455 cm^{-1} with modes of vibrations $\phi(\text{C-C-O})[20\%]$,

$\phi(\text{C-C-C})\text{R5}[48\%]$ and $\nu(\text{C-O})\text{out-R}[10\%]$ and it is calculated from quantum mechanical method at 469 cm^{-1} with torsional motion of ring R4 and out of plane wagging $\omega(\text{C=O})\text{adj-R5}$, whereas the weak shoulder peak is observed at 447 cm^{-1} and is calculated at 446 cm^{-1} and 445 from GF matrix and PM3 methods, with modes of vibrations $\phi(\text{C-C-O})[32\%]$, $\nu(\text{Sb-O})[14\%]$, $\phi(\text{C-C-C})\text{R1}[10\%]$ and rocking of ring R2, in-plane bending $\phi(\text{Sb-C-C})\text{adj-R2}$ respectively. The in-plane bending mode $\phi(\text{C-C-C})\text{R}$ is reported³⁰ at 522 cm^{-1} and 495 cm^{-1} .

Side-chain modes

The vibrational modes like $\nu(\text{Sb-C})$ and $\nu(\text{C=O})$ stretching, $\phi(\text{Sb-C-C})$, $\phi(\text{C-Sb-C})$, $\phi(\text{C-Sb-O})$ in-plane bending, $\omega(\text{C=O})$ wagging and $\tau(\text{Sb-C-C-C})$ and $\tau(\text{O=C-C-C})$ torsions are termed as "Side chain Modes". All side chain modes are presented in Table 2 (b).

Table 2 (b). Calculated and observed side chain modes

Calculated freq, cm^{-1}		Observed freq FTIR, cm^{-1}	Assignment in % potential energy distribution, PED
Wilson GF	PM3		
1632	1645	1638(m)	$\nu(\text{O=C})$ ad-Sb [51] + $\nu(\text{C-C})\text{ad-C=O}[16]$ + $\phi(\text{C-C-O})\text{adj-Sb}[14]$ + $\nu(\text{O=C})\text{ad-Sb}\&\text{R4}[\text{PM3}]$
1617	1625	$\nu(\text{O=C})$ ad-Sb [54] + $\phi(\text{C-C-O})\text{ad-Sb}[14]$ + $\nu(\text{C-C})\text{ad-C=O}[22]$
538	535	535(w)	$\omega(\text{C=O})\text{ad-R4}[65]$ + $\tau(\text{C-O})\text{R4}[15]$ + R4-twist[PM3] + $(\text{C-O})\text{-R4-sciss}[\text{PM3}]$
378	----	$\nu(\text{Sb-C})[55]$ + $\phi(\text{C-C-C})\text{R3}[22]$ + $\nu(\text{C-C})\text{R3-Sb}[12]$ + $\phi(\text{C-C-Sb})[11]$
302	$\nu(\text{Sb-C})[55]$ + $\phi(\text{C-Sb-O})[29]$ + $\phi(\text{C-C-C})[12]$ + $\phi(\text{C-C-Sb})[11]$
240	280	$\nu(\text{Sb-C})[28]$ + $\phi(\text{C-C-Sb})[16]$ + $\phi(\text{C-C-C})[13]$ + $\nu(\text{Sb-C})[\text{PM3}]$ + $\phi(\text{C-C-Sb})[\text{PM3}]$

The presence of $\nu(\text{C=O})$ double bond, makes the structure of the title compound fairly rigid and the formation of hydrogen bonds don't much disturb the charge distribution in the ring and side chains. The length of hydrogen bonds is also in support of this rigidity. In the FTIR spectra, an absorption band is obtained, with one medium intensity peak which is observed at 1638 cm^{-1} and it is calculated from classical mechanics Wilson GF matrix method at 1632 cm^{-1} comprising the vibrational modes as $\nu(\text{C=O})[51\%]$ PED, $\phi(\text{C-C-O})\text{adj-Sb}[14\%]$ and $\nu(\text{C-C})\text{adj-C=O}[16\%]$, whereas, from quantum mechanical semi-empirical PM3 method, it is calculated at 1645 cm^{-1} , with stretching $\nu(\text{C=O})\text{adj-Sb-R4}$ stretching mode. A weak shoulder absorption peak which is observed $\nu(\text{O=C})\text{ad-Sb}$ [54%], $\phi(\text{C-C-O})\text{ad-Sb}[14\%]$ and $\nu(\text{C-C})\text{adj-C=O}[22\%]$. This stretching mode $\nu(\text{C=O})$, is reported in the range $1750\text{-}1630\text{ cm}^{-1}$ in the literature²⁷, so it is in good agreement with those calculated in this work. A weak absorption peak is observed in low frequency range at 535 cm^{-1} and is calculated at 538 cm^{-1} and 535 cm^{-1} from GF matrix and PM3 methods respectively, having vibrational modes $\omega(\text{C=O})\text{adj-R4}[65\%]$, $\tau(\text{O=C-C-C})\text{R4}[15\%]$ in GF matrix method and ring R4 twisting, $(\text{C-O})\text{adj-R4}$ scissoring in PM3 method. The $\nu(\text{Sb-C})$ which is mass sensitive mode, is calculated in the lower frequency region which contains absorption peaks at 378 cm^{-1} with 56% PED from Wilson method, one absorption peak is calculated at 302 cm^{-1} with $\nu(\text{Sb-C})[31\%]$ mixed with $\phi(\text{C-Sb-O})[29\%]$. An absorption peak is also calculated at 240 cm^{-1} from Wilson GF method and 280 cm^{-1} from PM3 method, with modes of

vibrations $\nu(\text{Sb-C})$ [28%], $\phi(\text{C-C-Sb})$ [16%], $\phi(\text{C-C-C})$ [13%] and $\nu(\text{Sb-C})\{\text{PM3}\}$, $\phi(\text{C-C-Sb})\{\text{PM3}\}$ respectively. These peaks are reported in the frequency range 449-472 cm^{-1} by Shanker *et al.*²⁸, in the frequency range 459-489 cm^{-1} by Khosa *et al.*²⁷ and at 234 cm^{-1} by Ludwig *et al.*³⁰ respectively.

Ring modes

In the title compound triphenylantimony(V)-*o*-Salicylate there are five benzene rings in which 3-rings R1, R2 and R3 are directly attached to the central antimony Sb atom and two rings R4 & R5 are attached on left side and right side of central Sb atom respectively. The vibrations like $\nu(\text{C-C})\text{R}$ stretching, $\phi(\text{C-C-C})\text{R}$ in-plane bending, $\omega(\text{C-O})$ wagging and $\tau(\text{C-C-C-C})\text{R}$ torsions, corresponding to these five ring atoms are termed as "ring modes". All the ring modes are given in the Table 2 (c).

Table 2 (c). Calculated and observed ring modes

Calculated freq, cm^{-1}		Observed freq FTIR, cm^{-1}	Assignment in % potential energy distribution, PED
Wilson GF PM3			
.....	4838	3905, w	$\nu(\text{O-H})\text{adj-R5}[\text{PM3}]$
.....	4805	3856, m	$\nu(\text{O-H})\text{adj-R4}[\text{PM3}]$
.....	4041	3753, w	$\nu(\text{C-H})\text{R1}[\text{PM3}]$
.....	4021	3678, m	$\nu(\text{C-H})\text{R2}[\text{PM3}]$
.....	4020	3652, m	$\nu(\text{C-H})\text{R1}[\text{PM3}]$
1586	1599	1585, m	$\nu(\text{C-C})\text{R3}[95] + \nu(\text{C-C})\text{R2-sym}[\text{PM3}] + \phi(\text{C-C-C})\text{R2}[\text{PM3}]$
1564	1554	1563, w	$\nu(\text{C-C})\text{R1-Sb}[98] + \nu(\text{C-C})\text{R4-sym}[\text{PM3}] + \nu(\text{C=O})\text{adj-R4}[\text{PM3}]$
1510	1523	1508, w	$\nu(\text{C-C})\text{R1-Sb}[98] + \nu(\text{C-C})\text{R4-asym}[\text{PM3}] + \phi(\text{O=C-O})\text{adj--R4}[\text{PM3}]$
1485	1486	1482, vs	$\nu(\text{C-C})\text{R2-Sb}[71] + \nu(\text{C-C})\text{R1-Sb}[24] + \nu(\text{C-C})\text{R5-sym}[\text{PM3}] ++ \nu(\text{C-C})\text{adj-R5}[\text{PM3}]$
1434	1431	1437, s	$\nu(\text{C-C})\text{R2-O}[42] + \nu(\text{C-O})\text{R2-O}[24] + \nu(\text{O=C})\text{ad-Sb}[14] ++ \nu(\text{C-C})\text{R5-sym}[\text{PM3}] + \nu(\text{C-C})\text{adj-R5}[\text{PM3}]$
1331	1319	1326, msh	$\nu(\text{C-C})\text{R2-O}[98] + \nu(\text{C-C})\text{R2-asym}[\text{PM3}] + \phi(\text{C-C-C})\text{R2}[\text{PM3}]$
1310	1291	1310, s	$\nu(\text{C-C})\text{R1-O}[96] + \nu(\text{C-C})\text{R5-asym}[\text{PM3}] + \phi(\text{C-C-C})\text{R5}[\text{PM3}]$
1265	1278	1270, wsh	$\nu(\text{C-C})\text{R1-O}[59] + \nu(\text{C-C})\text{ad-O}[16] + \nu(\text{O-C})\text{ad-Sb}[14] + \nu(\text{C-C})\text{R1-asym}[\text{PM3}] + \phi(\text{C-C-C})\text{R1}[\text{PM3}]$
1227	1223	1224, m	$\nu(\text{C-C})\text{R1-Sb}[90] + \text{R1-puck}[\text{PM3}] + \nu(\text{C-C})\text{R1-asym}[\text{PM3}]$
1193	...	1185, m	$\nu(\text{C-C})\text{R3-Sb} [86]$
1181	...	1175, w	$\nu(\text{C-C})\text{R2-Sb} [86]$
1092	...	1197, w	$\nu(\text{C-C})\text{R1-O}[70] + \phi(\text{C-C-C})\text{R4}[10]$
1024	...	1021, w	$\nu(\text{C-C})\text{R1-Sb} [78]$

Contd...

997	955	998, m	$\nu(\text{C-C})\text{R2-Sb}[73] + \phi(\text{C-C-C})\text{R3}[10] + \text{R1}\&\text{R3-deform}[\text{PM3}]$
919	908	916, w	$\nu(\text{C-C})\text{R1-O}[67] + \nu(\text{C-O})\text{R1-O}[10] + \text{R4-puck}[\text{PM3}] + \nu(\text{C-O}) \text{adj-R4} [\text{PM3}]$
866	871	864, m	$\phi(\text{C-C-C})\text{R3} [85] + \phi(\text{C-C-Sb}) [10] + \nu(\text{C-O}) \text{adj-R5} [\text{PM3}]$
695	689	690, s	$\tau (\text{C-C})\text{R1} [62] + \tau (\text{C-C}) \text{R3} [18] + \tau (\text{C-C})\text{R5}[17] + \text{R2-puck}$
665	669	667, m	$\omega(\text{C-O})\text{R4}[64] + \tau (\text{C-C})\text{R4}[15] + \phi(\text{C-C-C})\text{R2}\&\text{R3}[\text{PM3}]$
621	619	615, w	$\phi(\text{C-C-C})\text{R2} [56] + \nu(\text{Sb-C})[18] + \nu(\text{C-C})\text{R2-Sb}[10] + \text{R4-twis}$
571	580	581, w	$\phi(\text{C-C-C})\text{R3} [74] + \phi(\text{C-C-Sb})[10] + \text{R1-twis} + \tau (\text{C-C}) \text{R2} [\text{PM3}]$
559	554	554, w	$\phi(\text{C-C-C})\text{R1}[84] + \nu(\text{O=C-O})\text{R5-rock}[\text{PM3}] + \nu(\text{Sb-O})[\text{PM3}] + \omega(\text{C=O})\text{adj=R5}[\text{PM3}]$
393	397	400, m	$\tau (\text{C-C})\text{R2} [91] + \text{R5-rock} [\text{PM3}] + \phi(\text{C-C=O})[\text{PM3}]$

Note:

1. Here the abbreviation ad means adjacent outside.
2. R-stands for the ring one ,two etc.
3. Only the dominant modes are taken in most of the cases.
4. R-Sb etc. means attached both ring and Sb etc.

The vibrations above 500 cm^{-1} , were assigned for mono-substituted benzene derivatives. In literature^{31,32} the observed frequencies of 1327 cm^{-1} was assigned as in-plane $\nu(\text{C-C})$ stretching. The out of plane vibrations according to Whiffen³³ are well known, although it is more difficult to find a good force field for these vibrations.

In this region, moderately intense bands due to (O-H) and (C-H) stretching vibrations are observed in FT-IR spectra. The calculated values from PM3 method, of $\nu(\text{O-H})$ and $\nu(\text{C-H})$ vibrations at 4838, 4805, 4041, 4021 and 4020 cm^{-1} can be assigned with the observed frequencies at 3905, 3856, 3753, 3678 and 3652 cm^{-1} respectively. The $\nu(\text{O-H})$ stretching vibrations is reported in the region $3580\text{-}3500 \text{ cm}^{-1}$ in the literature [26-p260], whereas, the $\nu(\text{C-H})$ vibration is reported in the range $3100\text{-}3000 \text{ cm}^{-1}$ in the literature [26-p226]. So these modes are found at higher values as reported earlier. An absorption band is observed in the FTIR spectra at 1585 cm^{-1} and it is calculated at 1586 cm^{-1} from Wilson GF matrix method with vibrational modes $\nu(\text{C-C})\text{R3}$ [95%] PED, it is calculated at 1599 cm^{-1} with vibrations $\nu(\text{C-C})\text{R2-symm}$ and $\phi(\text{C-C-C})\text{R2}$ from semi-empirical PM3 method. A weak band is observed having two peaks observed at 1563 and 1508 cm^{-1} & these are calculated at 1564 and 1510 cm^{-1} respectively with Wilson method, with vibrational modes $\nu(\text{C-C})\text{R1}$ [98%] and $\nu(\text{C-C})\text{R1}$ [98%] in both cases. In the PM3 method only one peak in this band at frequency 1523 cm^{-1} is obtained, with $\nu(\text{C-C})\text{R4-asymmetric stretch}$ and in-plane bending of $\phi(\text{O=C-O})\text{adj-R4}$. This band is reported in the range $1515\text{-}1646 \text{ cm}^{-1}$ by Ludwig *et al*³⁰, which is in good harmony. A highly intense absorption band, with two peaks one at 1482 cm^{-1} and other at 1437 cm^{-1} is obtained in the FTIR spectra, which are calculated in GF matrix method at 1485 cm^{-1} and 1434 cm^{-1} with modes of vibrations as $\nu(\text{C-C})\text{R2}$ [70%], $\nu(\text{C-C})\text{R1}$ [24%] and $\nu(\text{C-C})\text{R2}$ [42%], $\nu(\text{C-O})$ [24%], $\nu(\text{C=O})$ [14%] for the second peak, respectively. In the PM3 method these absorption peaks are calculated at 1486 and 1431 cm^{-1}

respectively, attributing to the symmetric stretching of $\nu(\text{C-C})\text{R5}$ and $\nu(\text{C-C})\text{adj-R5}$. The stretching mode $\nu(\text{C-C})$ ring is reported in the frequency range, 1616-1455 cm^{-1} in the literature²⁴. In the FTIR spectra an absorption band with two peaks, one at 1326(msh) and the other at 1310(s) cm^{-1} , are observed and these are calculated from Wilson method at frequencies 1331 and 1310 cm^{-1} respectively, with modes of vibrations as $\nu(\text{C-C})\text{R2-O}[98\%]$ and $\nu(\text{C-C})\text{R1}[96\%]$ respectively. This band is calculated at 1319 and 1291 cm^{-1} from second method having vibrational modes as $\nu(\text{C-C})\text{R2}$ asymmetric stretch, in-plane bending $\phi(\text{C-C-C})\text{R2}$ and $\nu(\text{C-C})\text{R5}$ asymmetric stretch, in-plane bending $\phi(\text{C-C-C})\text{R5}$, respectively.

An absorption band with peaks at 1270, 1224, 1185, 1175 and 1163 cm^{-1} are observed in the FTIR spectra, which are calculated from Wilson method at 1265, 1227, 1193, 1181 and 1164 cm^{-1} respectively with vibrational modes as $\nu(\text{C-C})\text{R1-O}[59\%]$ + $\nu(\text{C-O})\text{adj-Sb}[14\%]$, $\nu(\text{C-C})\text{R1-Sb}[90\%]$, $\nu(\text{C-O})\text{R3-Sb}[86\%]$, $\nu(\text{C-C})\text{R2}[86\%]$ and $\nu(\text{C-C})\text{R3-Sb}[92\%]$ respectively. From the PM3 method only three absorption peaks in this band region are found which are calculated at 1278, 1223 and 1164 cm^{-1} with modes as $\nu(\text{C-C})\text{R1}$ asymmetric stretch + in-plane bending $\phi(\text{C-C-C})\text{R1}$, ring R1-breathing (or puckering) + $\nu(\text{C-C})\text{R1}$ asymmetric stretch. This band is reported in the range of 1110 to 1069 cm^{-1} in the literature²⁴.

A weak absorption band is observed containing four peaks found at 1097(w), 1021(w), 998(w) and 916(w) cm^{-1} , these are calculated from Wilson GF matrix method, at 1092, 1024, 997 and 919 cm^{-1} with vibrational modes as $\nu(\text{C-C})\text{R1-O}[70\%]$ + $\phi(\text{C-C-C})\text{R4}[10\%]$, $\nu(\text{C-C})\text{R1-Sb}[78\%]$, $\nu(\text{C-C})\text{R2-Sb}[73\%]$ + $\phi(\text{C-C-C})\text{R3}[10\%]$ and $\nu(\text{C-C})\text{R1-O}[67\%]$ + $\nu(\text{C-O})\text{R1-O}[10\%]$ respectively. This absorption band is calculated from PM3 method at only two peaks *viz.* 955 & 908 cm^{-1} respectively, with modes of vibration as, rings R1&R3 deformations and ring R4 breathing + $\nu(\text{C-O})\text{adj-R4}$ stretching.

A medium intense peak is observed at 864 cm^{-1} in the FTIR spectra and it is calculated at 866 cm^{-1} from Wilson method having vibrational modes as $\phi(\text{C-C-C})\text{R3}[85\%]$ & $\phi(\text{Sb-C-C})[10\%]$, whereas, from PM3 method it is calculated at 871 cm^{-1} with stretching mode $\nu(\text{C-O})\text{adj-R5}$. In the FTIR spectra a strong band is obtained comprising three absorption peaks at frequencies 690(s), 667(s) and 615(wsh) cm^{-1} , this band is calculated from Wilson GF method at frequencies 695, 665 and 621 cm^{-1} respectively, having modes of vibrations as $\tau(\text{C-C})\text{R1}[62\%]$ + $\tau(\text{C-C})\text{R3}[18\%]$ + $\tau(\text{C-C})\text{R2}[17\%]$, $\omega(\text{C-O})\text{R4}[64\%]$ + $\tau(\text{C-C})\text{R4}[12\%]$ and $\phi(\text{C-C-C})\text{R2}[56\%]$ + $\nu(\text{Sb-C})[18\%]$ + $\nu(\text{C-C})\text{R2}[10\%]$, respectively, whereas this band is calculated from PM3 method at frequency peaks 689, 669 and 619 cm^{-1} , attributing to the vibrational modes as ring R2-breathing, in-plane bending $\phi(\text{C-C-C})\text{R2}\&\text{R3}$ and ring R4-twisting. This band seems to be one of the characteristic modes of the title compound. In the lower part of the FTIR spectra a weak absorption band is obtained comprising three peaks observed at frequencies 581(w), 554(w) and 400(m) cm^{-1} , these are calculated from Wilson method at frequencies 571, 559 and 393 cm^{-1} respectively, attributing to the vibrational modes as, $\phi(\text{C-C-C})\text{R3}[74\%]$ + $\phi(\text{Sb-C-C})[10\%]$, $\phi(\text{C-C-C})\text{R1}[84\%]$ and $\tau(\text{C-C})\text{R2}[91\%]$. From semi-empirical PM3 method, this band is calculated with absorption peaks at 580, 554 and 397 cm^{-1} respectively, with vibrational modes as ring R1-twisting + $\tau(\text{C-C})\text{R2}$, (O=C-O)R5-R5-rocking + in-plane bending $\phi(\text{C-C=O})$, respectively. Torsional mode $\tau(\text{C-C})\text{R2}[91\%]$, also seems to be a characteristic mode of the title compound, and it is reported in the frequency range of 251-412 cm^{-1} in the literature³⁰.

Conclusions

Normal coordinate analysis data performed for the title compound from both Wilson G F matrix method and Semi-empirical PM3 method shows close resemblance of the calculated & observed vibrational bands. The value of frequency difference for asymmetric and symmetric stretching $\Delta\nu$ for $\nu(\text{CO}_2)_{\text{asym}}$ and $\nu(\text{CO}_2)_{\text{sym}}$ is calculated as $1638-1253=385\text{ cm}^{-1}$ from Table 2(a) and 2(c), which is greater than 300 cm^{-1} , this suggests that the coordination number of antimony is five confirming the trigonal bipyramidal(TBPY) structure of the title compound. Further the high value of $\Delta\nu$ also indicates that the secondary bonding interactions between central antimony atom and carbonyl oxygen atoms is on weaker side for this molecule³⁴.

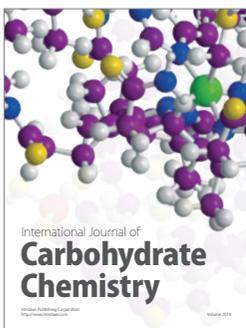
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