Antimony-121 Mössbauer Spectra of Some Heterocyclic *cis*-Diorganoantimony(v) Compounds

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The ^{121}Sb Mössbauer spectra are reported for a series of heterocyclic *cis*-diorganoantimony(V) compounds of general formulae $[NMe_4][SbR_2Cl_4]$ and SbR_2Cl_3. The asymmetry parameter of the electric-field-gradient (e.f.g.) tensor is large in all the tetrachloro-compounds because of distortion of the molecule by the formation of the heterocyclic ring. A point-charge model has been formulated in terms of the C–Sb–C bond angle and the partial-field-gradient contributions of the ligands; this model provides a satisfactory correlation between the e.f.g. parameters and the expected stereochemistry. Similar calculations have been carried out for the trichloro-compounds.

THE preparation, co-ordination chemistry, and spectroscopic properties of a number of diorganoantimonate(V) compounds have been reported in earlier papers.[1-3] However, little information has been published on diorganoantimonate(V) compounds having a *cis* configuration of the organic ligands. The only positive indication of a *cis* configuration comes [4] from the ^{121}Sb Mössbauer spectrum of $SbPh_2Cl_2$(quin) [quin = quinolin-8-olate (oxinate)], and it is now clear that the structure and bonding of organoantimonate(V) derivatives can be studied in detail by this technique.[1,2,5,6]

In the present work we report on the ^{121}Sb Mössbauer spectra of a number of recently synthesized [3] heterocyclic diorganoantimonate(V) compounds of formula $[NMe_4]$-$[SbR_2Cl_4]$ and SbR_2Cl_3, in which the two Sb–C bonds are obliged to take up a *cis* configuration, and provide for the first time a related series of such compounds.

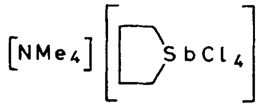
EXPERIMENTAL

The synthesis and characterization of the tetramethylammonium salts of the complex anions 1,1,1,1-tetrachlorostibolanate (1), 1,1,1,1-tetrachlorostibanate (2), 5,5,5,5-tetrachloro-5*H*-dibenzostibolate (3), 5,5,5,5-tetrachloro-5,10-dihydrodibenz[*b,e*]antimoninate (4), 10,10,10,10-tetrachlorophenoxantimoninate (5), as well as 5,5,5-trichloro-5,10-dihydrodibenz[*b,e*]antimonin (6), and 5,5,5-trichloro-10,11-dihydro-5*H*-dibenzo[*b,f*]stibepin (7), have been reported previously.[3,†]

Mössbauer data at 4.2 K

Compound	e^2qQ_g/mm s^{-1}	η	δ/mm s^{-1}
(1)	−14.14(25)	0.91(3)	−5.53(1)
(2)	15.89(21)	0.80(2)	−5.28(1)
(3)	−13.24(15)	0.48(8)	−4.19(2)
(4)	−13.03(22)	0.79(3)	−4.33(1)
(5)	−11.56(22)	0.73(3)	−3.77(2)
(6)	15.41(22)	0.74(3)	−5.25(2)
(7)	17.10(12)	0.49(2)	−5.56(1)

The ^{121}Sb Mössbauer spectra were recorded at 4.2 K using the apparatus and procedures already reported.[1] The spectra were curve-fitted using a transmission-integral method,[1] with seven variable parameters: the ground-state quadrupole coupling constant e^2qQ_g, the asymmetry parameter η, the chemical isomer shift δ relative to the $Ca^{121m}SnO_3$ source, the linewidth 2Γ, the thickness T_A, and values for the intensity scaling and baseline. The final values for e^2qQ_g, η, and δ are given in the Table, and typical spectra are shown in Figure 1.



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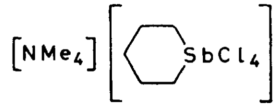

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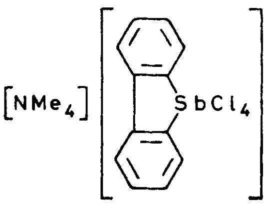

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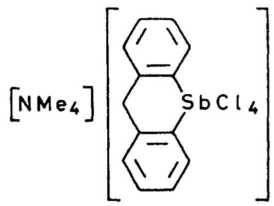

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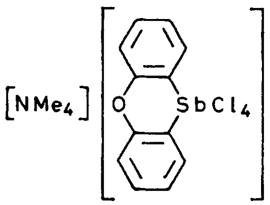

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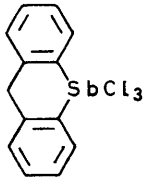

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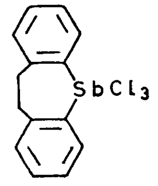


(7)

[†] More systematic names for these compounds would incorporate the symbol λ^5 before the prefix for antimony. This is necessary to indicate that the ' connecting number ' of antimony is five, not that (three) regarded as normal in the extended Hantzsch–Widman system.

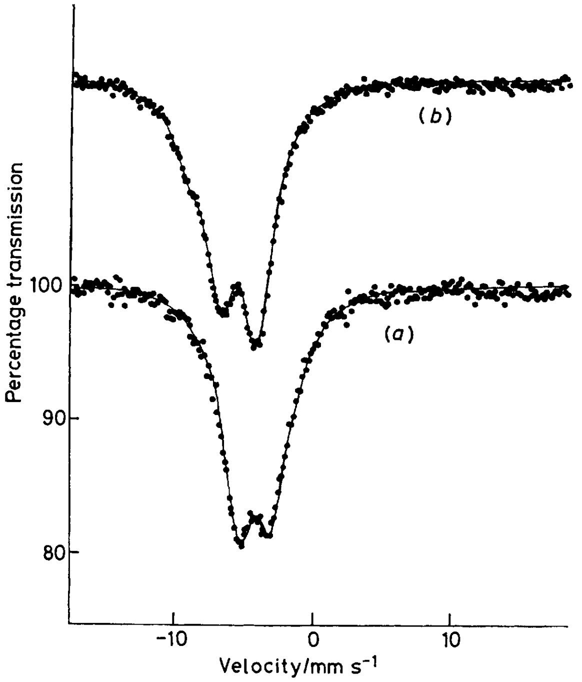


FIGURE 1 Antimony-121 spectra at 4.2 K for (*a*) compound (4) and (*b*) compound (7)

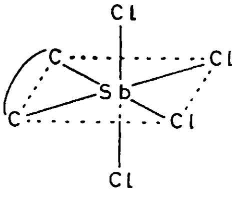
DISCUSSION

Electric Field Gradient and Structure.—A simple point-charge model for the octahedral species [*cis*-SbR_2Cl_4]$^-$ and [*trans*-SbR_2Cl_4]$^-$ predicts that the corresponding values of the quadrupole coupling constant e^2qQ_g should be in the ratio —1 : 2. Our earlier measurements [1] on [*trans*-SbR_2Cl_4]$^-$ species gave positive values for e^2qQ_g in the range 24—26 mm s^{-1}. The new data for the [*cis*-SbR_2Cl_4]$^-$ species (1)—(5) gave negative values in the range 11—16 mm s^{-1} [with the exception of (2) where the sign is positive for reasons to be explained below], and are fully consistent with the presumed geometry.

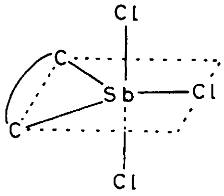
The large value of the asymmetry parameter η for all five compounds suggests that the ideal octahedral geometry about the antimony has been distorted by the formation of the heterocyclic ring. A simple point-charge model of this effect has been given by Parish and Johnson [7] in an interpretation of electric-field-gradient (e.f.g.) data for distorted diorganotin(IV) compounds. Neglecting contributions from all but the two Sn–C bonds, it was shown that η increases as the C–Sn–C bond angle deviates from 90°, eventually reaching unity at either 71 or 109° where the sign of e^2qQ changes because of an interchange of principal axes. This model has been used also to estimate the C–Sb–C bond angle in $SbPh_2Cl_2$(quin) from the expected value of η.

This procedure does not give entirely satisfactory results when applied to the heterocyclic antimony compounds, since the large values of η would imply a C–Sb–C bond angle which is considerably larger or smaller than expected. In particular, compound (2) has a positive value of e^2qQ_g which would indicate the C–Sb–C bond angle to be outside the range 71—109°. Unfortunately, there are no *X*-ray data available for these compounds; nevertheless the geometry of similar heterocyclic rings has been determined in several tellurium heterocycles such as dibenzotellurophene [8] and its di-iodide,[9] phenoxatellurin [10] and its 10,10-di-iodide derivative,[11] and 1-oxa-4-telluracyclohexane-4,4-di-iodide.[12] From inspection of these one might predict that the C–Sb–C bond angles in the five- and six-membered rings of compounds (1)—(6) would not be far from the 85—95° range. Models of the stibacyclohexane ring of compound (2) show that such a low value for the C–Sb–C angle is mainly the result of the presence of the long C–Sb bonds. (This ring is obviously non-planar, and we surmise that it is in a ' chair ' conformation in order to minimize steric interaction with the chlorine atoms bound to the antimony.)

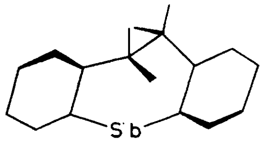
The inadequacies in the simple model of Parish and Johnson can be attributed to the assumption that the e.f.g. tensor derives exclusively from the Sb–C bonds. Using established methods,[13] we have carried out more involved calculations of the e.f.g. tensor for structures of type (A) in which all six ligands are considered. The previous studies [1,2] of octahedral organoantimony species have indicated that the partial field gradient (p.f.g.) of the organo-group R relative to Cl [p.f.g. (R) — p.f.g. (Cl)] must lie within the range —5.5 to —7.0 mm s^{-1} (expressed in units of the quadrupole coupling constant). We have considered not only distortion from the ideal geometry of (A) by changing the C–Sb–C bond angle, but also the effect of increasingly negative values of p.f.g. (R) and p.f.g. (Cl) within the above constraint.



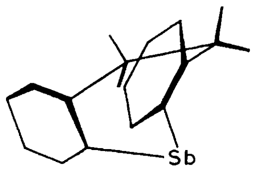
(A)



(B)



(C)



(D)

Some representative results for e^2qQ_g and η as a function of the C–Sb–C bond angle are shown in Figure 2 for a value of [p.f.g. (R) — p.f.g. (Cl)] = —6.0 mm s^{-1}. The Cl ligands are assumed to occupy regular co-ordination positions, although reasonable distortions of the $SbCl_4$ moiety produce only minor effects. It can be seen that the major effect of including the p.f.g. from the Cl ligands

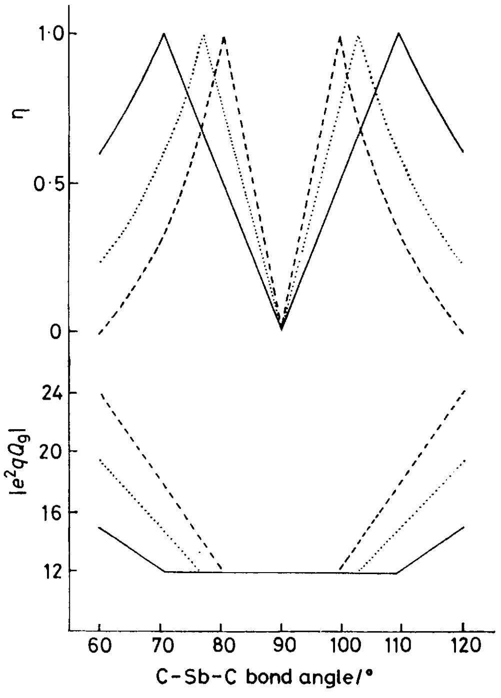


FIGURE 2 Calculated values of $|e^2qQ_g|$ and η for octahedral *cis*-$[\text{SbR}_2\text{Cl}_4]$ species [structure (A)] as a function of the C–Sb–C bond angle for different partial field gradients (in mm s^{-1}): (——) p.f.g. (R) = −6.0, p.f.g. (Cl) = 0; (· · ·) p.f.g. (R) = −9.0, p.f.g. (Cl) = −3.0; (— — —) p.f.g. (R) = −12.0, p.f.g. (Cl) = −6.0. In the central region between the cusps in η, e^2qQ_g has a constant negative value, becoming positive in sign as η exceeds unity

is to narrow substantially the range of C–Sb–C angles for which e^2qQ_g is negative.

Curves such as those in Figure 2 are probably a better description of slightly distorted *cis*-SbR_2Cl_4 structures; furthermore, they provide an acceptable interpretation of the positive value for e^2qQ_g in compound (2), since it now becomes possible to obtain this result with a C–Sb–C bond angle which is much lower than 110°. More quantitative conclusions cannot be made at present in view of the lack of estimates for the absolute partial electric field gradients, and in the absence of structural X-ray data for any of these compounds. Although the present data would indicate that the ratio p.f.g. (Cl) : p.f.g. (R) could be as high as 0.5 : 1, this is not necessarily in conflict with tin systems where the ratio has often been judged to be considerably smaller.

In the range where e^2qQ_g is negative, its calculated value is independent of the C–Sb–C angle because the principal axis lies normal to the SbC_2Cl_2 plane. The differences observed in the experimental values can therefore be attributed mainly to variations in [p.f.g. (R) − p.f.g. (Cl)] as the ligand changes, and the sequence (5) < (4) < (3) < (1) is as expected for aryl- and alkyl-type ligands. However, the e^2qQ_g value for compound (2) can also include contributions due to the bond angle.

For compounds (6) and (7), which are of the type SbR_2Cl_3, it is not known whether they are five-co-ordinated monomers in the solid state, or whether they are six-co-ordinated dimers through the formation of halogen bridges. The inability of compound (7) to give the corresponding tetrachloro-salt has been attributed [3] to a stronger steric hindrance of the seven-membered heterocycle, and it seems likely that the antimony has a co-ordination number of five in this case. The larger positive value of e^2qQ_g (17.1 mm s^{-1}) is clearly in qualitative agreement with a larger C–Sb–C bond angle in this compound. Moreover this value agrees well with the calculated value [14] (17.9 mm s^{-1}) for a hypothetical species SbPh_2Cl_3 possessing a regular trigonal-bipyramidal structure with Sb–C bonds in the equatorial plane. If this calculation is repeated using our value [1] of 3.19 : 1 for the ratio $(e^2qQ_g)_{\text{Sb}} : (e^2qQ)_{\text{Sn}}$ in isostructural antimony and tin species, then the value obtained (16.9 mm s^{-1}) is in even better agreement.

The e.f.g. tensor of SbR_2Cl_3 has been studied in an analagous way to that of $[cis\text{-SbR}_2\text{Cl}_4]^-$. The Cl ligands were assumed to be equivalent and at regular co-ordination positions, and the C–Sb–C bond angle in the equatorial plane of structure (B) was varied. Typical results are shown in Figure 3. Although the chosen value of [p.f.g. (R) − p.f.g. (Cl)] = −6.0 mm s^{-1} appears inadequate to reproduce the experimental value of e^2qQ_g, it is apparent that including the effect of the Cl ligands reduces the range of bond angles below the tetrahedral angle of 109° in which e^2qQ_g becomes negative.

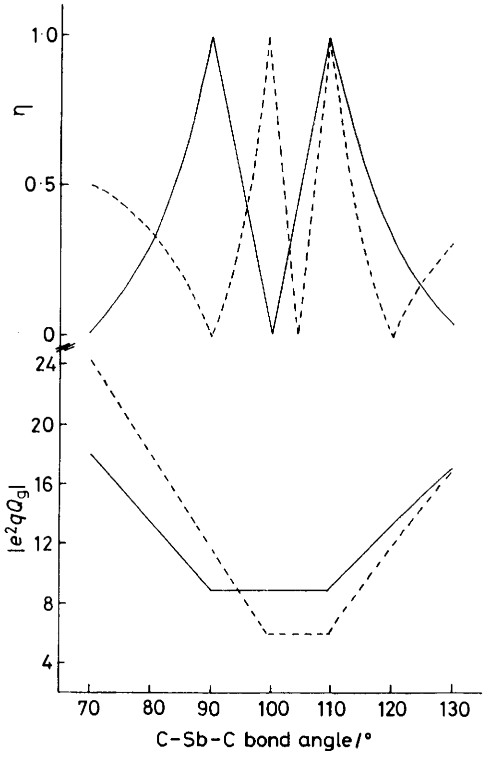


FIGURE 3 Calculated values of $|e^2qQ_g|$ and η for trigonal-bipyramidal SbR_2Cl_3 species [structure (B)] as a function of the C–Sb–C bond angle for different partial field gradients (in mm s^{-1}): (——) p.f.g. (R) = −9.0, p.f.g. (Cl) = −3.0; (— — —) p.f.g. (R) = −12.0, p.f.g. (Cl) = −6.0. e^2qQ_g has a constant negative value in the central region and is positive elsewhere

Moreover, the value of η is much more sensitive to bond angles and the p.f.g. parameters, and in consequence it is more difficult to deduce structural information.

The experimental parameters for the seven-membered heterocycle, (7), are consistent with a C–Sb–C bond angle which is larger than 109°. On these grounds we assign the conformation (C), rather than (D) which has a much smaller bond angle. The six-membered heterocycle, (6), has a much smaller value of e^2qQ_g, which could possibly be a simple consequence of a decrease in the C–Sb–C bond angle. However, the predicted behaviour as exemplified by Figure **3** is too complex to permit a more detailed discussion of the stereochemistry at the present time.

Chemical Isomer Shift.—The chemical isomer shift, δ, for the $[cis\text{-}SbR_2Cl_4]^-$ compounds is, in general, more positive than in corresponding $[trans\text{-}SbR_2Cl_4]^-$ compounds.[1] A similar situation occurs in *trans*-$SbPh_2Cl_2$ (acac) (acac = acetylacetonate) and compounds of the type *cis*-SbR_2Cl_2 (quin) where the e.f.g. tensor is again dominated by the two Sb–C bonds.[4] Here also there is a strict analogy with the corresponding tin compounds,[15] since in both cases the chemical isomer shift indicates a greater *s*-electron density at the Mössbauer nucleus of the *trans*-SbR_2L_4 octahedral species. This has been taken to indicate a greater *s* character in the M–C bonds.[15,16]

The range of values for δ shown by $[cis\text{-}SbR_2Cl_4]^-$ compounds should derive from differences in the electron-withdrawing ability of the organic residue as well as variations in the C–Sb–C bond angle. Only the first of these factors seems to be recognizable, as shown by the increasing values of δ (*s* density decreasing) along the series alkyl-, aryl-, and oxygen-substituted arylantimony derivatives.

The *cis*-SbR_2Cl_3 compounds (6) and (7) show a more negative value of δ than do the comparable $[cis\text{-}SbR_2Cl_4]^-$ species (3) and (4). This effect is similar to that observed in *trans*-$(SbR_2Cl_3)_2$ and $[trans\text{-}SbR_2Cl_4]^-$ species,[1] where it was tentatively attributed to a lower electron-withdrawing capability of the bridging ligands in the dimers.

In the present case, however, since compound (7) probably features five-co-ordination about the antimony, the larger *s* density for this SbR_2Cl_3 species seems to be due to the reduction in the number of chloride ligands. This augments our earlier observations concerning the sensitivity of δ to the type of Sb–X bonds.[1]

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