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Electron spin resonance study of the radical $Ph_2\dot{Sb}$ trapped in a single crystal matrix

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A radical formed by x-irradiation of a single crystal of triphenylantimony is identified as $Ph_2\dot{Sb}$. Its ESR spectral parameters (for ^{121}Sb) $g_1 = 1.9804$, $g_2 = 2.1044$, $g_3 = 1.9959$, $T_x = 1270$ MHz, $T_y = -752$ MHz, $T_z = -699$ MHz corrected for nuclear spin–orbit interactions and decomposed into isotropic (-60.3 MHz) and anisotropic (1330.3, -691.7, -638.7 MHz) components, and the nuclear quadrupole coupling constants $e^2Qq_x = -101$ MHz, $e^2Qq_y = -205$ MHz, $e^2Qq_z = 306$ MHz, have been interpreted in terms of the radicals's electronic structure and indicate that, like the analogous $Ph_2\dot{P}$ and $Ph_2\dot{As}$ radicals, the unpaired electron is localized on the $5p_\pi$ valence orbital of the antimony atom and that the radical is strongly bent, ∠CSbC$\simeq$98°.

INTRODUCTION

In continuation of our studies of the radicals having the general formula $R_2\dot{X}$ where X is a Group V element[1,2] and which are related to the important reaction intermediates, the iminyl radicals,[3] we report here the ESR spectrum of the $Ph_2\dot{Sb}$ radical trapped in a single crystal of Ph_3Sb. The *g* tensor, the ^{121}Sb and ^{123}Sb hyperfine coupling tensors, and the corresponding nuclear quadrupole coupling tensors yield values for the valence-orbital populations and give information about the molecular geometry. These results are discussed in the light of those obtained for the related $Ph_2\dot{P}$[1] and $Ph_2\dot{As}$[2] radicals.

EXPERIMENTAL

Triphenylstibine was a recrystallized commercially available (ALFA) product. Single crystals were obtained by slow evaporation of an isopropanol solution, and they were x irradiated using a Philips x-ray tube having a tungsten anticathode. Both the irradiation and the measurement of ESR spectra took place at room temperature. The spectra were measured on a Varian E-9 ESR spectrometer using 100 kHz field modulation. For each spectrum the magnetic field sweep was calibrated with an NMR marker and the klystron frequency measured using a Hewlett-Packard transfer oscillator.

The crystal was mounted on a goniometer designed in this laboratory that allowed any mutual orientation of the crystal and the magnetic field to be obtained without any need for remounting the crystal.[4] This facility was particularly useful in that after a preliminary study to determine the principal directions of the ESR tensors the rotation pattern about these principal axes—or indeed any other desired axis—could be at once measured experimentally. This is almost essential in dealing with radicals having such large hyperfine coupling constants as $Ph_2\dot{Sb}$ and where it is desired to study the $\Delta M_I = \pm 1$ transitions in order to determine nuclear quadrupole coupling constants.

Figure 1 shows a representation of one of the single crystals studied together with the axis system used to report the direction cosines of the various principal axes. The crystal structure of triphenyl stibine reveals[5] that it is triclinic. Although this report[5] states that there are 16 molecules in the unit cell it appears that the unit cell given here is reducible and that the primitive cell only contains four molecules.[6]

Analysis of the spectra

Naturally occurring antimony contains two isotopes ^{123}Sb ($I = 7/2$, natural abundance 43.75%) and ^{121}Sb ($I = 5/2$, natural abundance 57.25%).

The results were fitted to a Hamiltonian of the form following:

$$\mathcal{H} = \beta HS \cdot \bar{g} \cdot h + g_n\beta_n HI \cdot h + I \cdot \bar{T} \cdot S + I \cdot \bar{P} \cdot I ,$$

where the terms correspond to the electronic Zeeman effect, the nuclear Zeeman effect (presumed isotropic), the nuclear hyperfine interaction, and the nuclear quadrupole interaction, respectively.

For both the antimony isotopes the hyperfine coupling constants are too big for the above Hamiltonian to be fitted even by a second order perturbation procedure. Thus, a preliminary study, analyzed by second order perturbation methods, yields approximate values for the direction cosines of the principal values of the hyperfine coupling tensor. The rotation pattern around axes corresponding to these directions was then measured. In the two planes containing the maximum value of the hyperfine coupling tensor the agreement between the experimental positions of the resonance lines and those calculated by perturbation theory is poor, deviations being as much as 20 G, while in the third plane the agreement is only a little better. Iterative complete diagonalization of the Hamiltonian for every experimen-

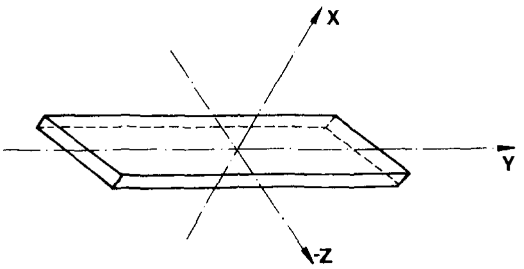

FIG. 1. Idealized single crystal and reference axes of triphenylantimony.

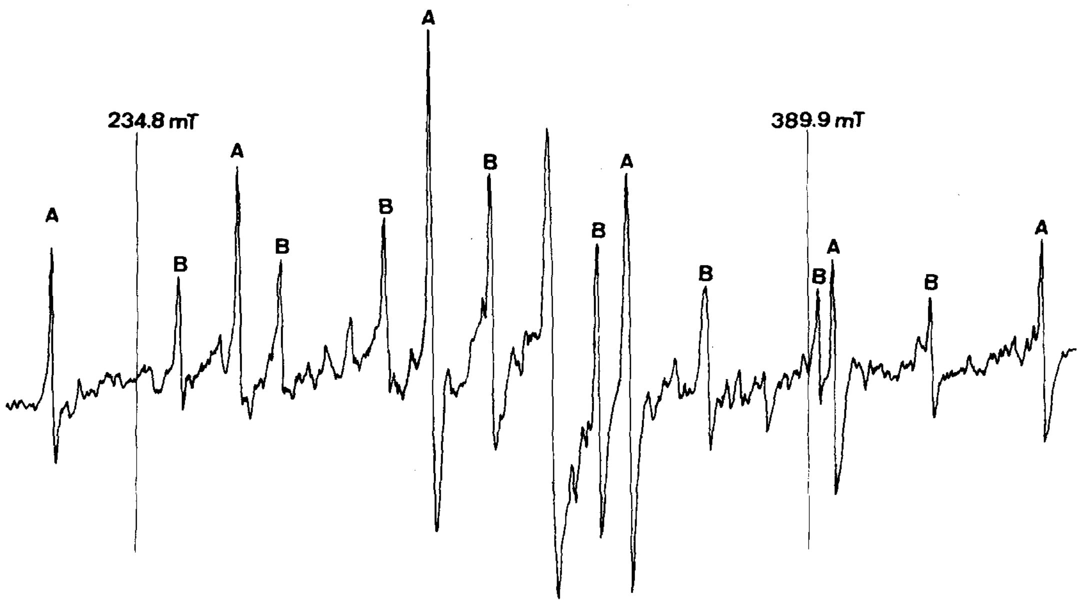

FIG. 2. Electron spin resonance spectrum of an irradiated crystal of $\mathrm{Ph_3Sb}$ (magnetic field in the direction: 0.31, 0.94, 0.13). The signals A and B are, respectively, attributed to the isotopes $^{121}\mathrm{Sb}$ and $^{123}\mathrm{Sb}$.

tal point to produce a satisfactory agreement between theory and experiment involves a prohibitively large amount of computer time; therefore, the following procedure was adopted:

For each experimental orientation, the difference between the positions of the lines calculated by perturbation theory and complete diagonalization was obtained using the approximate values of the various tensors. These corrections were then added to the results of a perturbation theory calculation and the results optimized by the least-squares procedures used previously.[2] These optimized values were used to diagonalize the Hamiltonian for each experimental orientation. The agreement between theory and experiment is now within the line width of the signals.

The above calculations were performed for $^{121}\mathrm{Sb}$. The spectrum for the $^{123}\mathrm{Sb}$ isotope calculated from these parameters was likewise in excellent agreement with experiment.

RESULTS

Spectra

Figure 2 shows a spectrum for which the direction cosines of the magnetic field vector were (0.11, 0.10, −0.98). The transitions due to $^{121}\mathrm{Sb}$ (marked A) and $^{123}\mathrm{Sb}$ (marked B) may be clearly distinguished. No other hyperfine interactions with any other magnetic nucleus are ever visible in any other orientation. On the basis of the hyperfine coupling constants reported below and by analogy with our results for $\mathrm{Ph_2\dot{P}}$[1] and $\mathrm{Ph_2\dot{A}s}$[2], we identify this radical with $\mathrm{Ph_2\dot{S}b}$.

In Fig. 3 is shown a spectrum in which transitions $\Delta M_I = \pm 1$ can clearly be distinguished, as well as a few transitions which are probably due to a differently oriented $\mathrm{Ph_2\dot{S}b}$ radical. Figure 4 shows the rotation pattern around an axis which is at an angle of 2.5° to T'_x. The solid curves are calculated from the values of the tensors given in the following section.

ESR tensors

Table I shows the magnetic hyperfine coupling tensors for the $^{121}\mathrm{Sb}$ and $^{123}\mathrm{Sb}$ species while Table II shows the $\overline{g}$ tensor. These two tensors have almost the same principal directions. Thus,

$$\widehat{g_2\, T_y} = 8°; \quad \widehat{g_1\, T_x} = 6°, \quad \widehat{g_3\, T_z} = 9°.$$

The $\Delta M_I = \pm 1$ transitions are of course those most affected by the quadrupole coupling constant. Figure 5

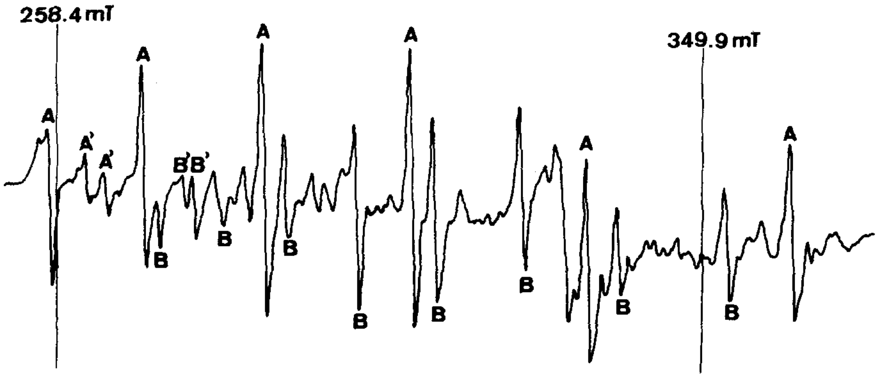

FIG. 3. Example of spectrum obtained when H_0 is near a direction perpendicular to T' maximum. A and A' are, respectively, the $\Delta M_I = 0$ and $\Delta M_I = \pm 1$ transitions for $^{121}\mathrm{Sb}$. B and B' are, respectively, the $\Delta M_I = 0$ and $\Delta M_I = \pm 1$ for $^{123}\mathrm{Sb}$.

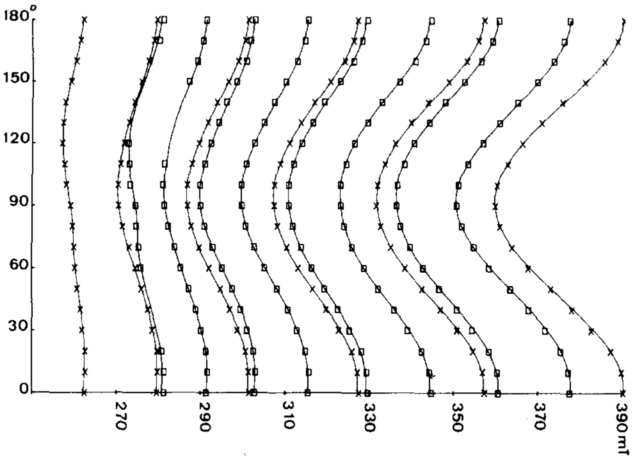

FIG. 4. Angular variation of the "allowed" ESR transitions (×: ^{121}Sb, □: ^{123}Sb) in the plane perpendicular to T' maximum.

shows the experimental rotation pattern of these lines together with the theoretical curves calculated for (i) the nuclear quadrupole coupling constants reported in Table III and (ii) no quadrupole coupling.

DISCUSSION

Magnetic hyperfine coupling

Since the g anisotropy is considerable, there is a significant orbital contribution to the coupling tensor

$$\mathcal{H} = g\beta g_n\beta_n \cdot \left\{ \frac{L\cdot I}{r^3} - \frac{S\cdot I}{r^3} + \frac{3(r\cdot I)(r\cdot S)}{r^5} \right\}.$$

The effect of this term can be allowed for in a manner similar to that used by Knight and Weltner.[7] If it is assumed that T_x corresponds to the direction of the p orbital containing the unpaired electron then

$$T'_x = A_{\text{iso}} + 2A_{\text{dip}} - \epsilon(\Delta g_x),$$

$$T'_y = A_{\text{iso}} - A_{\text{dip}} + \epsilon(\Delta g_y),$$

$$T'_z = A_{\text{iso}} - A_{\text{dip}} + \epsilon(\Delta g_z).$$

Where

$$\epsilon = g\beta g_n\beta_n \langle 1/r^3\rangle$$

$$A_{\text{dip}} = g\beta g_n\beta_n \langle(3\cos^2\theta - 1)/r^3\rangle .$$

Various values of $\langle 1/r^3\rangle$ exist in the literature. The Hartree–Fock calculations for neutral Sb give 9.2313 a.u.,[8] and Bennett and Howard[9] have suggested that such values be corrected for relativistic effects in a manner analogous to that proposed by Mackey and Wood[10] for isotropic coupling constants. This correction would yield $\langle 1/r^3\rangle = 13.83$ a.u. Symons *et al.* have however contested this procedure[11] and in support of this the calculations of Fraga *et al*,[12] which include relativistic effects give a value (9.3457 a.u.) very little different from that given by the nonrelativistic calculation. Finally Barnes and Smith[13] have obtained semiempirical values of $\langle 1/r^3\rangle$ for various elements from atomic spectral data and propose the value 13.0 a.u. for neutral antimony. In what follows we have used this last value.

TABLE I. ^{121}Sb and ^{123}Sb magnetic hyperfine coupling tensors for the radical Ph_2Sb. (principal values in MHz).

	^{121}Sb	^{123}Sb	λ	μ	ν
T'_x	1306	707	0.36	0.05	−0.93
T'_x	−585	−317	0.89	−0.29	0.33
T'_z	−707	−383	0.25	0.95	0.15

TABLE II. g tensor for the radical Ph_2Sb.

	λ	μ	ν
$g_1 = 1.9804$	0.38	0.15	−0.91
$g_2 = 2.1044$	0.85	−0.42	0.29
$g_3 = 1.9959$	0.33	0.89	0.29

The corrected "spin only" values of the ^{121}Sb hyperfine coupling constant are

$$T_x = 1270 \text{ MHz}, \quad T_y = -752 \text{ MHz}, \quad T_z = -699 \text{ MHz}.$$

In this we have assumed (see below) the signs shown for T'_x, T'_y, and T'_z. These values may now be decomposed into isotropic and anisotropic components, but an ambiguity remains since the signs of the tensor elements are unknown. If the radical is indeed $Ph_2\dot{S}b$ then its coupling tensor must have approximate cylindrical symmetry. This can only be achieved if the correction due to the orbital contribution is applied as above (note that the only important correction is to T'_y and this must act to make T_z and T_y more nearly equal). Other possible combinations either produce a too low total density of values of the isotropic and anisotropic coupling constants that can by no means be interpreted as arising from valence orbital s and p spin densities.

To interpret these components of the coupling tensor in terms of s and p densities there remains the problem

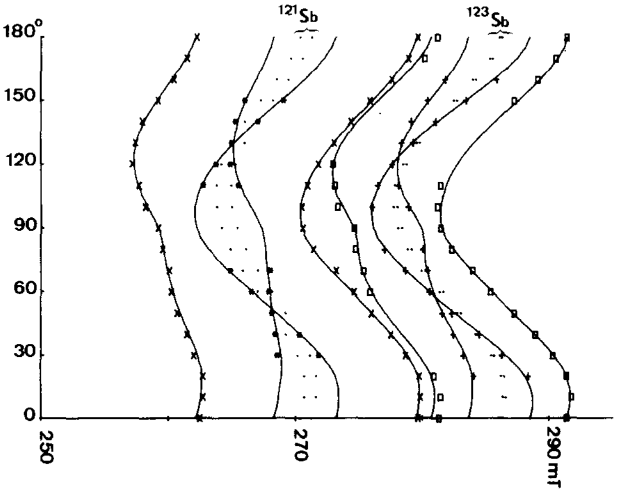

FIG. 5. Detail of the angular variation of the ESR transitions in the plane perpendicular to T' maximum. ^{121}Sb: experimental positions of the allowed transitions $M_I = 5/2$, $M_I = 3/2$: ×; $\Delta M_I = \pm 1$: *. ^{123}Sb: experimental positions of the allowed transitions $M_I = 7/2$, $M_I = 5/2$: □; $\Delta M_I = \pm 1$ transitions: +. Theoretical curves calculated (i) with the tensors of Tables I, II, III—; (ii) with no quadrupolar interaction ···.

TABLE III. Nuclear quadrupole coupling tensors for the radical $\mathrm{Ph_2Sb}$. (principal values in MHz).

	^{121}Sb	^{123}Sb	λ	μ	ν
$e^2Qq_x = 2I(2I-1)P_x$	−101	−129	0.13	0.00	−0.99
$e^2Qq_y = 2I(2I-1)P_y$	−205	−261	0.93	−0.34	0.12
$e^2Qq_z = 2I(2I-1)P_z$	306	390	0.34	0.93	0.04

of the valence state contact term. For ^{121}Sb the atomic parameter estimated from the Hartree–Fock wavefunctions is 17 005 MHz.[8] We have included relativistic corrections using the method of Mackey and Wood[10] and found for the atomic isotropic coupling constant the value $A_{\mathrm{iso}}(^{121}\mathrm{Sb}) = 25\,474$ MHz. This, together with the value of $\langle 1/r^3\rangle$ used above, corresponding to a p-orbital coupling of 1333 MHz, yields the values of 0.002 and 0.998 for the 5s and 5p spin densities, respectively. Such values are those expected for a radical in which the unpaired electron is essentially localized on a pure p orbital.

g value

As mentioned above the T and g tensors are essentially parallel and, as to be expected for $\mathrm{Ph_2\dot{S}b}$ and as previously observed for $\mathrm{Ph_2\dot{P}}$ and $\mathrm{Ph_2\dot{A}s}$, the directions of g_{max} and $T_{\parallel}$ are perpendicular. The much larger value of g_{max} compared with those measured for $\mathrm{Ph_2\dot{P}}$ and $\mathrm{Ph_2\dot{A}s}$ is in agreement with the much higher value of the spin orbit coupling for antimony.

In the $T_{\parallel}$ direction it is noteworthy that, whereas a value close to the free-electron g value of 2.0023 would have been expected, the value observed is noticeably less than this. Following a suggestion of Atkins *et al.*[14] for the analogous $\mathrm{\dot{S}eO_2}$ radical, this could be due to a participation of the d_{xz} orbital, of b_1 symmetry in the bonding. It is moreover likely that d_{yz} orbitals—of b_2 symmetry—have affected the third principal value of the g tensor.

Nuclear quadrupole coupling constants

The absolute signs of the elements of the coupling tensor are unknown but the value of maximum absolute magnitude lies along T_z ($\widehat{P_z\ T_z} = 8°$). The Townes and Dailey theory of the coupling constants of a Group V $\mathrm{R_2M}$ fragment[15] together with the experimental values for pyridine[16] and arsabenzene[17] indicates that, since the valence p electron coupling constant of atomic ^{121}Sb is positive, P_z should also be positive. The Townes and Dailey theory yields the following equations relating the coupling tensor to the valence orbital populations of the $\mathrm{R_2Sb}$ fragment:

$$2 - b = (1 - \cot^2\gamma)^{-1}(1 + \eta/3)\, e^2Qq_z/e^2Qq_0$$

$$a - b = \tfrac{2}{3}\,\eta e^2Qq_z/e^2Qq_0 \, .$$

Here a is the population of the 5p_π orbital while b is the population of each of the two equivalent R–Sb 5s 5p hybrid orbitals. The $\widehat{\mathrm{RSbR}}$ angle is 2γ. These equations differ slightly from those used for pyridine[16] since the P_x and P_y axes are interchanged in pyridine compared to $\mathrm{Ph_2\dot{S}b}$.

The use of the above equations may well be inappropriate in the present case since no account is taken of possible 5d orbital contributions to the bonding. A further difficulty arises from using an s–p hybrid model for elements other than those belonging to the first short period, and finally of course there is the question of the appropriate value of e^2Qq_0. To be consistent we use the value of 13.0 a.u. for $\langle 1/r^3\rangle$ together with the value $-0.531\ 10^{-24}$ cm^{-2} for the nuclear quadrupole moment, Q, given by Smith[18] to obtain $e^2Qq_0 = 1298$ MHz for ^{121}Sb.

If it is now assumed that the *total* 5p electron density, a, corresponds to the *unpaired* electron density estimated from the magnetic hyperfine coupling constant then substitution in the above equations yields the values $b = 0.94$ and $2\gamma = 98°$. This is in most satisfactory agreement with the value obtained in a analogous manner for $\mathrm{Ph_2\dot{A}s}$ (97°) and with the general tendency for interbond angles in compounds of Group V elements other than nitrogen to have values in the range 90°–100°.

Finally, in all respects the structures of the $\mathrm{Ph_2\dot{P}}$, $\mathrm{Ph_2\dot{A}s}$, and $\mathrm{Ph_2\dot{S}b}$ are very similar and the *electronic* structure is well represented by a strongly bent $\mathrm{R_2M}$ fragment where the unpaired electron is essentially localized on the pure p_π valence orbital of the heteroatom.

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