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ESR of diphenylantimony radical in a triphenylantimony single crystal

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Ultraviolet irradiation of a single crystal of triphenylantimony produces an antimony centered radical with an anisotropic ¹²¹Sb coupling having principal absolute values of 704, 352, and 352 MHz and a g tensor with the same principal axis as the hyperfine interaction and components of 1.998, 2.045, and 2.065. This radical has been assigned to the diphenyl antimony radical with approximately zero s and 0.7 p character. The linewidth of the spectra are consistent with unresolved hyperfine structure due to spin density delocalized on the phenyl rings.

INTRODUCTION

Irradiation of single crystals of triphenylphosphine or triphenylarsine with uv light^{1,2} produces the same radical as γ irradiation of triphenylphosphine oxide³ and triphenylarsine oxide⁴ single crystals. The ESR studies indicate that the unpaired electron of these free radicals resides in a nearly pure p orbital on either phosphorus or arsenic and have assigned this radical to the diphenylphosphinyl or arsinyl free radical. There is little or no delocalization of spin density into the phenyl rings. The size and relative electronegativity of the central atom with respect to the phenyl carbon may be determining factors in the amount of spin density delocalized onto the phenyl rings. An ESR study of the diphenylantimony radical is a logical extension of our previous work and the measurement of the spin distribution should give some information about the phenyl ring spin densities. This work is a report of the ESR measurements on uv irradiated single crystals of triphenylantimony.

Antimony naturally occurs in two isotopes ¹²¹Sb and ¹²³Sb of approximately equal abundance and with nuclear spins of 2.5 and 3.5, respectively. The nuclear g factors differ considerably—1.3366 for ¹²¹Sb and 0.7238 for ¹²³Sb. An antimony centered radical is expected, therefore, to exhibit an ESR consisting of the superposition of two spectra—an eight line spectra with small splitting within a six line signal of approximately twice the splitting of the other species.

EXPERIMENTAL

Reagent grade triphenylantimony obtained from Research Organic/Inorganic Chemical Corporation was recrystallized from degassed isopropanol and after drying *in vacuo* was further purified by approximately 100 passes through a zone refiner. Single crystals were grown by the Bridgmann-Stockbarger technique. A sample of the high purity triphenylantimony was sealed in an evacuated Pyrex tube. The tube was lowered slowly through two immiscible liquids. The top layer, a silicone oil, was heated 10 to 20 °C above the melting point of triphenylantimony (M.P. 51 °C) and the lower layer, propylene glycol, was at approximately room temperature because of the small heat transfer between the two liquids. The sample tube had a curved capillary drawn on the end. As the tube was lowered through the

junction of the two liquids seed crystals grew in the capillary. Most of the seed crystals ran into the walls of the capillary and by the time the main body of the melt began to crystallize the melt was often in contact with only a single seed crystal. After the melt crystallized it was annealed at a temperature about 5 °C lower than the melting point for two to three days and slowly lowered to room temperature before the crystal was removed from the tube. All subsequent operations with the crystal were performed in a nitrogen atmosphere. A portion of the single crystal was glued using Duco cement to a quartz mount with three mutually perpendicular faces. This mount was a 5 mm corner cut from a quartz fluorescence cell. A rexolite rod was glued in turn to each of the faces of the mount and held in a goniometer for each of the three rotations about the perpendicular axes. The alignment of the rod and quartz mount was determined by the reflection of a stationary laser. The rod was mounted correctly when the laser beam reflected back on itself from the two mount faces perpendicular to the rotation axes.

The sample was irradiated in the ESR cavity with a short arc 100 W high pressure mercury vapor lamp. The light was filtered with a Corning 7-54 filter cooled by a circulating nickel sulfate solution. This transmitted uv light in the range of 290 to 350 nm with a maximum at 310 nm. After 5 to 10 min of irradiation ESR signals were observed which increased in intensity with irradiation time. The ESR spectra was measured at room temperature under nitrogen for every 10° rotation about the three axes defined by the crystal mount. The ESR measurements were performed using a Varian E-4 ESR spectrometer with 100 kHz field modulation. The magnetic field was determined with the Field dial calibrated with the diphenylpicrylhydrazyl free radical.

RESULTS AND DATA ANALYSIS

The ESR spectra of uv irradiated single crystals of triphenylantimony at room temperature consisted primarily of six broad lines whose separations varied with the angle of the magnetic field and the quartz mount axes. The outside lines had widths of approximately 50 G. At certain orientations an additional set of eight lines could be resolved in the region of the inner four lines: The linewidth variation of the primary six line spectrum and the additional eight lines are consistent with an antimony centered radical with hyperfine cou-

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Isotope	% Natur abundan	ral ce <i>I</i>	<i>8</i> 1	$\langle \psi_{5s}(0) \psi_{5s}(0) \rangle_{5s}^{a}$ (a.u.)	$\langle r^{-3} \rangle^{b}$ (a.u.)	$a_{5s}^{0 c}$ (MHz)	2 <i>B</i> ^{0 d} (MHz
¹²¹ Sb	57.25	2.5	1,3366	15.77	9.977114	16 868	1020
¹²³ Sb	42.75	3.5	0.7238			9 1 3 4	552
aReferen	ce 5.	^b Reference 6.	$c_{a^{0}} = (8\pi)^{-1}$	$(7/3) g_e \beta_e g_I \beta_N \langle \psi_{5s}(0) \psi_{5s}(0) \rangle$	$(0)\rangle$. $d_2B^0 =$	$=4/5n(g_e\beta_eg_I)$	β_N $\langle r^{-3} \rangle$.

TABLE I. Magnetic parameters for antimony.

pling to the antimony nucleus. The primary spectrum is due to interaction with the ¹²¹Sb with a nuclear spin of 5/2 and a nuclear g factor approximately twice that of the almost equally abundant 123 Sb with 7/2 spin. The eight lines due to the interaction with the ¹²³Sb nucleus are not always resolvable but contribute to the linewidth of the inner four lines of the ¹²¹Sb interaction. The magnetic parameters for the antimony isotopes are listed in Table I. The experimental magnetic field strengths of the primary six lines are plotted as a function of the rotation angle about the laboratory axes 1, 2, and 3 in Figs. 1, 2, and 3, respectively. The (•) are the experimental points and the continuous lines are a second order perturbation computer simulation using the principal values of the g and A tensor and their direction cosines with respect to the laboratory axes given in Table II. A description of the determination of the ESR parameters and the computer simulation is given later. All calculated line positions were within 5 G of their experimentally observed positions. Most line positions could not be determined more accurately than ± 2 G due to the linewidth and interference of lines from the other isotope.

Analysis of the data obtained in rotating the crystal about the three mutually perpendicular axes defined by the quartz mount proceeded in two steps. The spin Hamiltonian

$$\mathcal{K} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$$





was assumed appropriate and the symbols have their usual meaning. The g and A tensor coordinates are fixed by the laboratory axes in which the magnetic field **B** rotates in a plane perpendicular to the rotation axis. We analyzed only the primary six line spectrum so that the A tensor refers to interaction of the ¹²¹Sb nucleus and its coordinates are arbitrarily fixed in the laboratory axis system.

The first step was the initial estimate of the g and A tensors by standard techniques. The magnetic field B_0 at the center of the six line spectrum and the average hyperfine splitting k at each rotation angle θ was used to calculate the $g^2(\theta) = (h\nu/\beta B_0)^2$ and $k^2(\theta)$ from which the components of the g^2 and k^2 tensors were determined by least squares fit for each set of rotation equations

$$g^{2}(\theta) = g^{2}_{ii} \cos^{2}\theta + 2g^{2}_{ij} \sin\theta \cos\theta + g^{2}_{jj} \sin^{2}\theta,$$

$$k^{2}(\theta) = A^{2}_{ii} \cos^{2}\theta + 2A^{2}_{ij} \sin\theta \cos\theta + A^{2}_{ij} \sin^{2}\theta,$$

in which θ is the angle the magnetic field makes with the *i*th axis rotating about the *k* axis in the *ij* plane. The **g** and **A** tensors may be reconstructed by taking the square root of the elements of the diagonalized \mathbf{g}^2 and \mathbf{A}^2 matrices and performing a similarity transformation with the direction cosine matrix obtained in the diagonalization process.

The second step in the analysis is to fit the simulated field positions at resonance to the observed data. The resonance field positions are simulated using ini-



FIG. 2. Magnetic field strength versus angle of rotation about laboratory axis 2. Points are experimental. Lines are computer simulated using parameters in Table II.



FIG. 3. Magnetic field strength versus angle of rotation about laboratory axis 3. Points are experimental. Lines are computer simulated using parameters in Table II.

tial principal \mathbf{g} and \mathbf{A} values and three Euler angles defining the orientation of the magnetic field and rotation axis with respect to the principal \mathbf{g} and \mathbf{A} axis. A nonlinear least squares program fits the observed data using the initial estimates from the first step and determining corrections to these estimates which are added to the initial values and are used in turn as initial estimates until a self-consistent set of parameters is obtained.

The simulation of the magnetic fields at resonance follows the "effective fields" approach in which the electron spin **S** is quantized in the direction $\mathbf{g} \cdot \mathbf{B}$ and the nuclear spin interacts with the field $\mathbf{A} \cdot \mathbf{S}$. The transformation matrices which relate the magnetic field direction and rotation axis with the principal axis system of the radical are defined in the papers of Lin⁷ and McClung.⁸ The energies are determined by second order perturbation theory and the magnetic fields for which the energy differences are the microwave energy $h\nu$ are computed by solving the quadratic equation.

The nonlinear least squares program is standard.⁹ The square of the sum of the differences of the calculated and observed magnetic fields for resonance is minimized by expanding the calculated magnetic field in a Taylor expansion about the initial estimates of the spin parameters. The resulting matrix equation for the corrections is solved and added to the original estimates. These new parameters are used to calculate corrected values of the resonant magnetic fields and the cycle continues until the corrections are very small and there is no further improvement in the parameters. These parameters are listed in Table II. The direction cosines listed in Table II refer to the orientations of the crystal for which the computer simulations are illustrated in Figs. 1-3. Unfortunately, they refer the principal axes to neither the macroscopic crystalline faces nor to the unit cell axes, but to the laboratory axes defined by the quartz holder to which the crystal was arbitrarily glued. This data is from one of four crystals investigated and in each case an unsuccessful attempt was made to determine the unit cell directions by x-ray precession photographs. A large crystal (~25 mm³) was necessary to observe the ESR spectra. This meant that the diffracted x-ray beam was as large as the incident beam. The unit cell is quite large (6029.6 Å³)¹⁰ so that the diffracted pattern of the reciprocal lattice merged into an unresolved blur. Attempts to observe radical ESR in well-formed crystals of triphenylantimony grown from solution were unsuccessful.

DISCUSSION

The relatively small value of the ¹²¹Sb splitting indicates that the unpaired electron is predominately in a 5p orbital with very little *s* character. The calculated Fermi contact interactions for an antimony 5*s* electron is given in Table I and for ¹²¹Sb is 16867 MHz. Our experimental isotropic coupling is either 469 MHz or approximately zero depending on the relative signs of the principal elements of the hyperfine interaction. If the elements have the same sign, the 5*s* spin density is about 0.03. The 5*p* electron density for this case is only 0.23 since the anisotropic coupling components are -117, 234, and -117 MHz.

If on the other hand the experimental values of the hyperfine components have the values and signs of -352, +704, and -352 MHz, the 5p electron spin density is about 0.7 and the 5s density is very close to zero. This choice of signs leads to a 5p spin density more consistent with the values observed for ${}^{31}P(0.82)$ and $^{75}As(0.98)$ in similar radicals.¹⁻⁴ The remainder of the spin density may be distributed in the phenyl rings and the unresolved coupling to the protons could contribute to the large linewidth. This interpretation of the data suggests a planar diphenyl antimony radical with the unpaired electron in a nearly pure p orbital which is perpendicular to the C-Sb bonds and the nonbonding antimony electron pair. The phenyl rings could be oriented to allow partial delocalization of the unpaired electron into their π system.

The preparation of this radical by the absorption of uv light suggests that one of the Sb-C bonds cleave homolytically, producing phenyl radicals as well as the observed radical. Our failure to observe distinct

TABLE II. Electron spin resonance parameters for the ¹²¹Sb centered radical produced in a uv irradiated single crystal of triphenylantimony.

ğ	A (MHz)	Direction cosines ^a			
2.061±0.005	352 ± 20	0.761	0.589	0.272	
1.988 ± 0.005	704 ± 20	0.649	-0.692	-0.316	
2.033 ± 0.005	352 ± 10	0.002	0.417	- 0.909	

^aBoth g and A are diagonal in the same axis system. The direction cosines relate the principal g and A axes to the arbitrary laboratory axes about which the rotations in the magnetic field and the computer simulations portrayed in Figs. 1-3 were performed.

phenyl radicals could result from either of the following reasons: (a) The phenyl radicals migrate rapidly and react with each other or with other radical or impurity traps. (b) The phenyl radical signal is obscured by the overlap of the antimony signal in the central region of the spectrum. The postulate of phenyl radical production is strengthened by the observations of Shen, Mc-Ewen, and Wolf.¹¹ These investigators irradiated pentaphenyl antimony with uv and found triphenylantimony, biphenyl, and p-quarterphenyl among the products. They proposed that the latter two products resulted from phenyl radical production of the photolysis. Thermolysis of pentaphenylantimony, on the other hand, only yielded triphenylantimony and biphenyl and ¹⁴C tracer studies indicated that this was an intramolecular process, not involving free phenyl radicals.

The g factor anisotropy is sensitive to the energies of those electronic levels which correspond to the excitation of a bonding or a nonbonding electron into the p_s orbital originally containing the unpaired electron. Estimates of these energy levels may be obtained by assuming a reasonable bond angle and the applicability of the first order correction of the g factor by the spin orbit interaction. These corrections are

$$g_{yy} - g_{zz} = -2\zeta \eta \left[\frac{\cot^2 \theta/2}{\Delta E_{\sigma-z} *} + \frac{(1 - \cot^2 \theta/2)}{\Delta E_{\eta-z} *} \right]$$
$$g_{xx} - g_{zz} = -2\zeta \eta / \Delta E_{\sigma-z} *,$$

in which $\zeta = -2604 \text{ cm}^{-1}$ is the spin orbit interaction¹² for a single 5p antimony hole, η is the occupation number of the p_z orbital, θ is the C-Sb-C bond angle, and x is the direction of the lone pair and the unpaired electron is in the p_z orbital. A reasonable bond angle θ lies between 95° and 100°—a range of values consistent with that of the diphenylarsinyl radical. For $\eta = 0.7$ (determined from the anisotropic hyperfine interaction) the $\sigma - \pi^*$ level lies approximately 81 000 cm⁻¹ above the ground state. The $n - \pi^*$ state then lies between 10 000 and 25 000 cm⁻¹.

The radical investigated in a uv irradiated single crystal of triphenylantimony has been assigned to the diphenylantimony radical in which the unpaired electron primarily resides in a pure antimony p orbital perpendicular to the plane of the phenyl-antimony bonds and the lone pair. The C-Sb-C bond angle is bent and delocalization of the unpaired electron into the phenyl rings occurs.

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