

of the ring π orbitals is reduced with a resulting decrease in the energy difference for this $\pi \rightarrow \pi$ transition, in agreement with the experimental observation. This picture does not, however, account for the 2.2-eV peak in the spectrum of VIII; we can offer no resolution of this question beyond suggesting that this peak may belong to an unidentified structure resulting from partial rearrangement of VIII.

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- (34) Note on terminology: in discussing π excited states of the radical cations, a useful distinction may be drawn between states obtained by promoting an electron within the set of occupied orbitals, which will be termed π excited states, and states obtained by promoting an electron from an occupied orbital into an empty orbital, which will be termed π^* states. A distinction is thus made between $\pi \rightarrow \pi$ transitions (which may be compared with neutral photoelectron spectra) and $\pi \rightarrow \pi^*$ transitions (which may be compared with neutral optical absorption spectra).

Spin-Lattice Relaxation in Triphenylphosphine, Triphenylarsine, and Triphenylstibine

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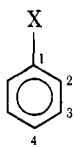
Abstract: The spin-lattice relaxation times (T_1) have been determined for all carbons in triphenylphosphine, triphenylarsine, and triphenylstibine. The ortho, meta, and para carbons all relax exclusively by the dipole-dipole mechanism. The α carbons in triphenylphosphine and triphenylarsine relax predominantly by the dipole-dipole mechanism below about 40 °C while the spin-rotation mechanism is most important above this temperature. The α carbon in triphenylstibine shows nonexponential decay since carbon bound to ^{121}Sb relaxes by the scalar coupling mechanism at all temperatures while carbon bound to ^{123}Sb relaxes by the dipole-dipole mechanism at low temperatures and spin-rotation at higher temperatures. The ^{121}Sb - ^{13}C coupling constant is calculated to be 450 Hz.

Relaxation times for carbon-13 in molecules containing a metal or metalloid have not been widely reported. A number of ^{13}C NMR studies of molecules containing phosphorus, usually in a ring, have been reported by Gray,¹ while Lambert² has recently reported on six-membered rings containing O, S, Se, and Te at the 1 position. No studies have been reported on triphenyl derivatives of the group 5 elements, P, As, and Sb. It is known that relaxation times provide information on structure, conformation, motions, and interactions.³ This work has been carried out to determine the various relaxation mechanisms for triphenylphosphine, triphenylarsine, and triphenylstibine. In order to sort out the various mechanisms, the relaxation time has been studied as a function of temperature.

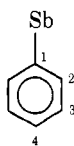
Experimental Section

Spin-lattice relaxation times were determined on a JEOL FX-60 spectrometer. The compounds were all examined as ~1 M solutions in CDCl_3 which provides the deuterium lock. The inversion-recovery technique $(180^\circ - t - 90^\circ - T)_n$ was used to obtain relaxation data. The time, t , between the 180° pulse for spin inversion and the 90° observation pulse was varied over a broad range so as to bracket the relaxation times of all carbons. The waiting time between pulses, T , was always greater than five times the longest T_1 . The 180° pulse width, 28 μs , as well as the 90° pulse width, 14 μs , was determined in the usual way.² All spectra were obtained using 8K data points over a sweep width of 1000 Hz. Chemical shifts are reported relative to Me_4Si as an internal standard.

The T_1 software for the FX-60 automatically digitizes the intensities, plots the intensities, and produces the T_1 value. In addition, for

Table I. Spin-Lattice Relaxation Times and Nuclear Overhauser Effects in Triphenylphosphine and Triphenylarsine

Compd	Temp, °C	C ₁ (η)	C ₂ (η)	C ₃ (η)	C ₄ (η)
(C ₆ H ₅) ₃ P	70	18.1 ± 0.3	4.3 ± 0.5	4.3 ± 0.5	2.4 ± 0.3
	50	26.9 ± 0.3	3.5 ± 0.1	3.7 ± 0.1	1.8 ± 0.1
	40	32.6 ± 0.2	3.3 ± 0.1	3.3 ± 0.1	1.7 ± 0.1
	30	37.3 ± 1.2 (1.0)	2.5 ± 0.1 (2)	2.7 ± 0.1 (2)	1.4 ± 0.1 (2)
	10	26.8 ± 0.9 (1.5)	1.8 ± 0.1 (2)	1.7 ± 0.1 (2)	1.2 ± 0.2 (2)
	-30	11.3 ± 0.1 (1.7)	0.74 ± 0.02 (2)	0.69 ± 0.02 (2)	0.2 ± 0.01 (2)
(C ₆ H ₅) ₃ As	70	14.75 ± 0.3 (0.8)	4.5 ± 0.1 (2)	4.5 ± 0.1 (2)	2.6 ± 0.1 (2)
	50	26.7 ± 0.2	3.8 ± 0.1	3.8 ± 0.1	2.3 ± 0.2
	40	59.3 ± 0.8	3.2 ± 0.2	3.2 ± 0.2	2.2 ± 0.2
	30	50.5 ± 9.1 (1.3)	2.7 ± 0.3 (2)	2.6 ± 0.5 (2)	1.7 ± 0.3 (2)
	10	29.5 ± 0.3	2.2 ± 0.1	2.1 ± 0.1	1.0 ± 0.1
	-20	19.2 ± 0.2	1.1 ± 0.1	1.0 ± 0.1	0.83 ± 0.3

Table II. Spin-Lattice Relaxation Times in Triphenylstibine

Temp, °C	C ₁ - ¹²¹ Sb	C ₁ - ¹²³ Sb (η)	C ₂ (η)	C ₃ (η)	C ₄ (η)
70	4.5 ± 0.9	31.9 ± 0.1	5.4 ± 0.1	5.5 ± 0.1	2.7 ± 0.1
50	3.5 ± 0.2	45.5 ± 0.4	4.1 ± 0.1	4.4 ± 0.1	2.1 ± 0.1
40	4.2 ± 0.2	46.4 ± 0.1	3.8 ± 0.1	3.9 ± 0.1	1.9 ± 0.2
30	3.7 ± 0.8	31.4 ± 1.7 (0.4)	3.0 ± 0.1 (2)	3.0 ± 0.2 (2)	1.6 ± 0.1 (2)
10	3.7 ± 0.1	27.8 ± 0.2	2.2 ± 0.3	2.2 ± 0.2	1.0 ± 0.02
-30	4.8 ± 0.6	8.0 ± 0.2	0.75 ± 0.05	0.72 ± 0.05	0.39 ± 0.03

several of these spectra the data were hand plotted and the T_1 value was obtained by a least-squares routine. All data are the average of at least two and usually three determinations on the same sample at a given temperature.

Temperature control was achieved using the JEOL FX-60 temperature controller; calibration was routinely checked by inserting a thermometer into the probe. All samples were degassed by several freeze-thaw cycles and were sealed under vacuum; 10-mm tubes were used throughout.

Nuclear Overhauser effect (NOE) measurements were obtained by comparing the peak intensity for the normal spectrum (complete proton decoupling) with that obtained using a gated decoupling mode; the decoupler was on only during data acquisition and off during the pulse delay. Pulse delay time was 300 s for all compounds. This ratio (normal/gated) gives η (NOE) + 1.

Results and Discussion

The ¹³C relaxation times and nuclear Overhauser effects for all carbons in triphenylphosphine, triphenylarsine, and triphenylstibine are reported in Tables I and II as a function of temperature. Error limits are reported as the standard deviation. The possible relaxation mechanisms³ for ¹³C are (1) dipole-dipole, (2) spin rotation, (3) scalar coupling, and (4) chemical shift anisotropy. Previous investigations have usually been of molecules in which the carbon bears a proton; in such cases a dipole-dipole mechanism has predominated. One carbon in each of the molecules studied contains no directly bonded proton and thus another mechanism may become important. Chemical shift anisotropy has not been important except in a limited number of cases.

Scalar relaxation of the first kind (chemical exchange) has not been observed in ¹³C relaxation, while scalar relaxation of the second kind (quadrupole-induced relaxation) has been

observed only for carbon bound to ⁷⁹Br.⁴ The essential requirement for scalar relaxation is that the difference in Larmor frequencies of the two nuclei be comparable to the relaxation rate of the quadrupolar nucleus. Spin-rotation can be discerned since its temperature dependence is opposite to that for the other mechanisms, i.e., the relaxation time, T_1 , decreases with an increase in temperature.

Triphenylphosphine (1). The ¹³C spectrum of triphenylphosphine consists of a doublet at 137.2 ppm ($J^{31}\text{P}-^{13}\text{C} = 10.8$ Hz, α carbon), a doublet at 133.7 ppm ($J^{31}\text{P}-^{13}\text{C} = 19.6$ Hz, ortho carbons), a doublet at 128.4 ppm ($J^{31}\text{P}-^{13}\text{C} = 6.8$ Hz, meta carbons), and a singlet at 128.6 ppm (para carbon).⁵ The para carbon overlaps with one-half of the meta doublet. The observed relaxation time is thus a composite of the para and meta relaxation time. Since the meta relaxation time is known (from the other half of the doublet) the para relaxation time may be calculated:

$$\frac{1}{T_1 \text{ obsd}} = \frac{1}{2} \left(\frac{1}{T_1 \text{ p}} + \frac{1}{T_1 \text{ m}} \right)$$

The ortho, meta, and para carbons all show a steady increase in T_1 with an increase in temperature. Since these carbons all have an attached proton, they presumably relax by the dipole-dipole mechanism.

The α carbon, i.e., that attached to phosphorus, has a maximum T_1 at about 32 °C and decreases on either side of that temperature. It is obvious then that two mechanisms are operative, one of which at high temperatures must be spin-rotation as seen from its temperature dependence. The other mechanism, operative at lower temperature, it probably the dipole-dipole mechanism. Figure 1 shows the plot of $\ln T_1$ vs.

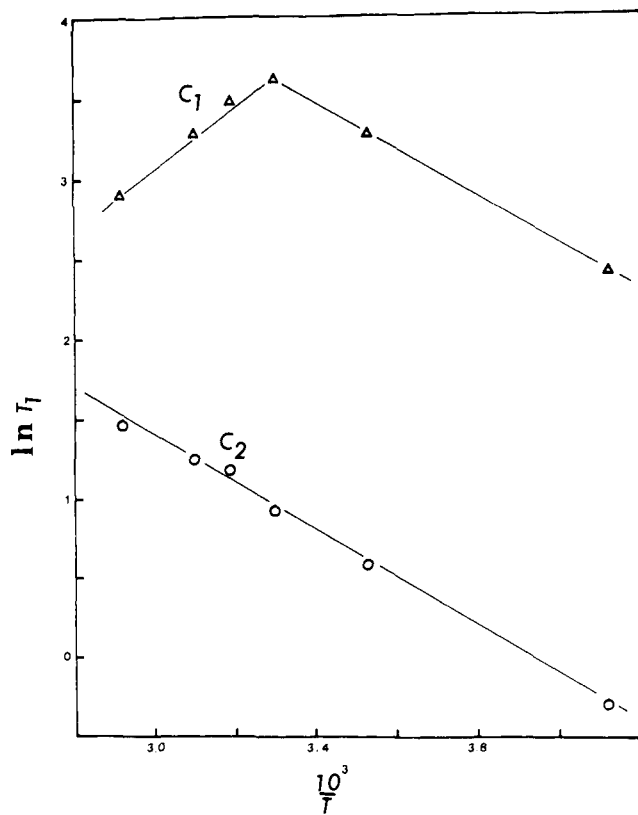


Figure 1. The logarithm of the spin-lattice relaxation time of C-1 (Δ) and C-2 (\bullet) in triphenylphosphine as a function of reciprocal temperature (K^{-1}). The line represents the best least-squares fit to the data.

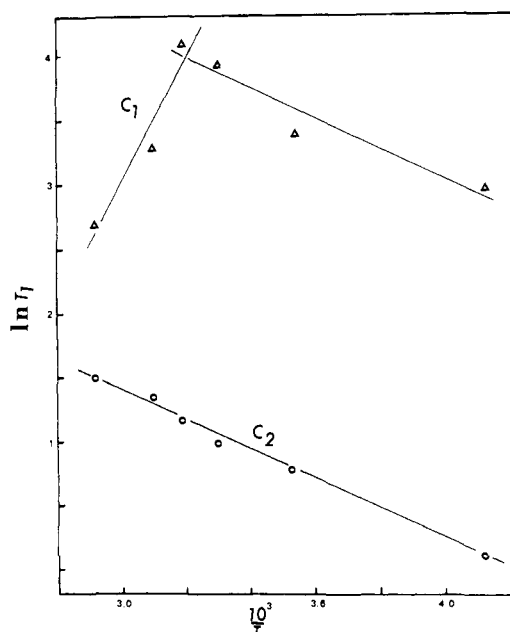


Figure 2. The logarithm of the spin-lattice relaxation time of C-1 (Δ) and C-2 (\bullet) in triphenylarsine as a function of reciprocal temperature (K^{-1}). The line represents the best least-squares fit to the data.

$1/T$ for C₁ (α carbon) and C₂ (ortho carbons). The plot for the ortho carbons is a straight line indicative of only one mechanism; since the NOE (Table I) has the maximum value for this carbon, the dipole-dipole mechanism is indicated. The meta and para carbons show a similar plot and therefore a similar mechanism. The plot for the α carbon shows two essentially straight segments. At low temperatures the slope is quite similar to that for the ortho carbon, and therefore the dipole-

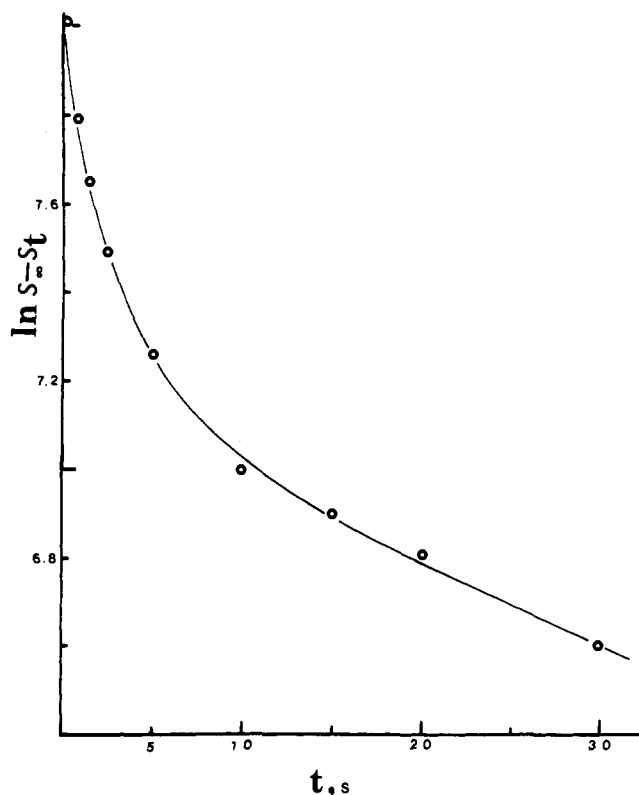


Figure 3. Plot of $\ln(S_{\infty} - S_t)$ vs. t in the inversion-recovery sequence showing nonexponential decay in C-1 in triphenylstibine. The delay time between pulse sequences was 300 s.

dipole mechanism is indicated. At higher temperatures it is likely that spin-rotation becomes the dominant mechanism. The NOE measurement on the α carbon supports this mechanism since the NOE decreases at higher temperatures. The dipole inducing relaxation of the α carbon may be either the directly attached phosphorus (1.87 Å) or the ortho hydrogens of the ring (2.02 Å).⁶ Calculations indicate that the hydrogens are far more effective (use eq 3, assume τ_c (correlation time) = 10^{-11} s, then $T_1^{C-H} = 94$ s and $T_1^{C-P} = 616$ s). Both of these will, of course, make a contribution to the observed T_1 .

The ^{31}P relaxation time is 1.54 s at 30 °C with an NOE ($^{31}\text{P}-^1\text{H}$) of 0.04.⁷ The maximum NOE for $^{31}\text{P}-^1\text{H}$ is 1.24. Thus, at room temperature relaxation of the phosphorus is dominated by some mechanism other than the dipole-dipole mechanism.

Triphenylarsine (2). The same relaxation behavior is observed for compound **2** as was seen in compound **1**. The chemical shifts are α carbon, 139.6; ortho, 133.7; meta, 128.6; and para, 128.3 ppm.

The α carbon, bearing the arsenic, again shows a maximum at about 43 °C; spin rotation is the dominant mechanism above this temperature and dipole-dipole relaxation dominates below it. An Arrhenius plot of $\ln T_1$ vs. $1/T$ is shown in Figure 2. The ortho, meta, and para carbons relax by the dipole-dipole mechanism exclusively. The NOE for these carbons is maximum at all temperatures, while the NOE for the α carbon decreases at higher temperatures.

The relaxation time for the α carbon is greater in triphenylarsine than in triphenylphosphine. If only one dipole-dipole mechanism is important, then the relaxation time should decrease as the molecular weight increases,⁸ i.e., triphenylarsine should be less than triphenylphosphine. The larger value for compound **2** arises from the fact that there is some phosphorus dipole-dipole relaxation as well as hydrogen dipole-dipole relaxation for triphenylphosphine, allowing more efficient relaxation; calculations indicate that hydrogen dipole-dipole

relaxation is more efficient than arsenic dipolar relaxation for triphenylarsine.

Triphenylstibine (3). When first examining the relaxation of the α carbon (138.3 ppm) in compound **3**, one is struck by the nonexponential decay of magnetization (Figure 3). This was also observed for the α carbon in bromobenzene³ and is indicative of two isotopes undergoing relaxation at different rates. Antimony-121 (spin $5/2$, 57.25% abundant) has a Larmor frequency of 14.31 MHz while the ^{13}C frequency is 15.03 MHz; this difference is small enough that relaxation for this nucleus is dominated by the scalar coupling mechanism. The relaxation time of carbon bound to ^{121}Sb must be determined from the early recovery times before relaxation of the second isotope grows in, and thus is less certain than the other T_1 's. Figure 4 shows the Arrhenius plot of $\ln T_1$ vs. $1/T$ for C_1 and C_2 . The α carbon, bound to ^{123}Sb , shows the same temperature dependence as the analogous carbon in compounds **1** and **2**, i.e., spin rotation is important at high temperature, dipole-dipole relaxation at low temperature. The other three carbons (ortho, 136.1; meta, 128.8; para, 128.45 ppm) all show maximum NOE and exclusively dipole-dipole relaxation.

The equation governing relaxation by scalar coupling³ is

$$1/T_1^{\text{sc}} = \frac{8\pi^2 J^2}{3} S(S+1) \frac{T_1^{\text{Q}}}{1 + 4\pi^2(\nu_c - \nu_x)^2 T_1^{\text{Q}^2}} \quad (1)$$

where $J = \text{C-X}$ coupling constant, S is the spin of X , T_1^{Q} is the relaxation time of the quadrupolar nucleus, in this case ^{121}Sb ; ν_c and ν_x being respectively the Larmor frequency of C and X (Sb). Thus, if T_1^{Q} is known, the antimony-carbon coupling constant may be calculated. T_1^{Q} , the relaxation time of ^{121}Sb , may be calculated from³

$$1/T_1^{\text{Q}} = \frac{3}{40} \frac{(2I+3)}{I^2(2I-1)} \left(1 + \frac{\xi^2}{3}\right) \left(\frac{e^2 q Q}{\hbar}\right)^2 \tau_c \quad (2)$$

where I is the spin number, ξ is an asymmetry parameter, $e^2 q Q/\hbar$ is the quadrupole coupling constant, and τ_c is the correlation time. Thus, since the quadrupole data are available ($e^2 q Q/\hbar = 520.84, 509.00$ MHz; $\xi = 0.08, 77$ K),⁹ if τ_c is known, T_1^{Q} may be obtained. Since τ_c for antimony may not be directly measured we use the average correlation time for the ortho, meta, and para carbons as the correlation time for antimony. The equation for dipole-dipole relaxation³ is

$$1/T_1 = n_{\text{H}} \frac{\gamma_c^2 \gamma_{\text{H}}^2 \hbar^2}{r_{\text{CH}}^6} \tau_c \quad (3)$$

where γ 's are magnetogyric ratios for carbon-13 and hydrogen, τ_c is the correlation time, and r_{CH} is the C-H distance. Using the normal aromatic C-H distance of 1.1 Å and $T_1 = 2.7$ s (30 °C) $\tau_c = 1.85 \times 10^{-11}$ s. This gives $T_1^{\text{Q}} = 8.52 \times 10^{-6}$ s and $J_{\text{Sb-C}} = 450$ Hz.

The data from the triphenylphosphine system may be used to verify the assumption that the average correlation time for the ring carbons is the same as the antimony correlation time. The dipole-dipole contribution to the relaxation of ^{31}P in compound **1** may be calculated from NOE data. The pertinent equation^{3,10} is

$$\eta = \eta_{\text{max}} \frac{T_1}{T_1^{\text{DD}}} \quad (4)$$

where T_1^{DD} is the dipole-dipole relaxation time and T_1 is the observed relaxation time. This gives $T_1^{\text{DD}} = 47.74$ s. Now the equation for dipole-dipole relaxation

$$\frac{1}{T_1^{\text{DD}}} = n_{\text{H}} \frac{\gamma_{\text{P}}^2 \gamma_{\text{H}}^2 \hbar^2}{r_{\text{PH}}^6} \tau_c \quad (5)$$

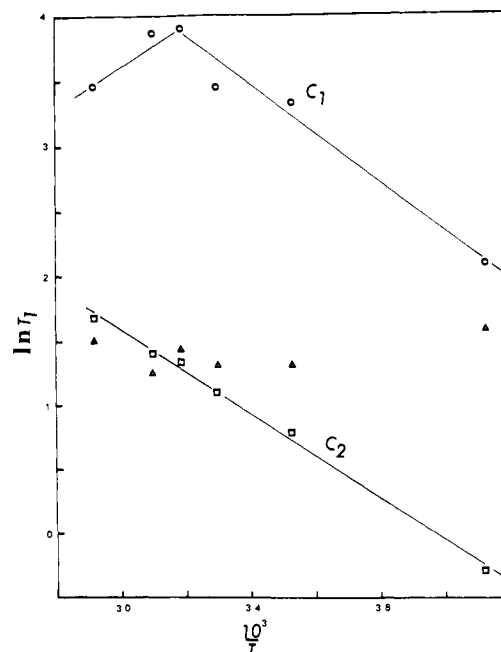


Figure 4. The logarithm of the spin-relaxation time of C-1 (bound to ^{123}Sb , O), C-1 (bound to ^{121}Sb , Δ), and C-2 (\square) in triphenylstibine as a function of reciprocal temperature (K^{-1}). The line represents the best least-squares fit to the data.

may be used to calculate τ_c , the correlation time of phosphorus. There are six ortho hydrogens in the solid state⁶ which are nearest to phosphorus at an average distance (calculated from the crystal structure) of 2.88 Å. This gives a correlation time of 2.14×10^{-11} s. The average carbon has a relaxation time of 2.3 s (30 °C) and has one hydrogen at a distance of 1.1 Å. This gives a correlation time of 2.08×10^{-11} s. Since τ_c (for phosphorus) depends on η , which is quite low and therefore somewhat uncertain, and the P-H distance, which is also somewhat uncertain, the agreement seems quite good and the assumption for triphenylantimony seems acceptable.

Summary

The ortho, meta, and para carbons in compounds **1**, **2**, and **3** all relax only by the dipole-dipole mechanism. The carbon bearing the substituted atom relaxes by spin-rotation at higher temperature and the dipole-dipole mechanism at low temperatures. For carbon bound to ^{121}Sb the scalar coupling mechanism governs relaxation and this relaxation time is temperature independent. The calculated ^{121}Sb - ^{13}C coupling constant is 450 Hz.

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