8. ESR. Study of the $Ph_3\dot{A}sBr$-Radical Trapped in an X-Irradiated Single Crystal of $Ph_3As^+CH_3Br^-$

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Summary

$Ph_3\dot{A}sBr$ is trapped in an X-irradiated single crystal of $Ph_3As^+CH_3Br^-$. The g-tensor, the ^{75}As and ^{79}Br magnetic hyperfine tensors and the ^{79}Br quadrupolar interaction tensor are obtained at room temperature. They show that the structure of this arsoranyl radical is intermediate between the trigonal bipyramidal and the C_{3v}-symmetry structure. By the detection of several additional radical species, especially at 77 K, some steps of the radiation mechanism are elucidated.

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1. Introduction. – Radiolysis of As-containing organic compounds generally gives rise to a large variety of radicals, the identification of which is often difficult. This fact is due to the numerous coordination states which are available for the Group V elements. For example, the following species have been recently detected: $R_2\dot{A}s$ [1], R_3P^+ [2] [3], $R_4\dot{A}s$ [4], R_5As^- [5] [6]. The tetracoordinated species are particularly interesting since they frequently appear as intermediates in organic syntheses [7]. Two structures have been reported for phosphoranyl radicals: the trigonal bipyramid (TBP) [4] [8] and the one with C_{3v}-symmetry [9]. The energy barrier between these two extremes is, however, sufficiently low to allow an exchange process to occur in the liquid phase [10]. In the present work we report the identification of the triphenylbromoarsoranyl radical trapped in an X-irradiated single crystal of $Ph_3As^+CH_3Br^-$ and show that the conformation adopted by this radical is neither the pure C_{3v}-structure nor the pure TBP.

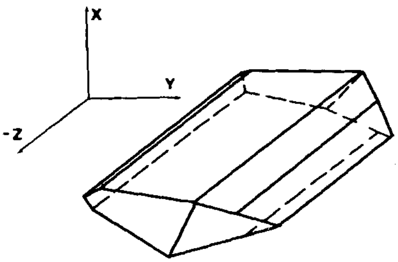

Fig. 1. *Idealized single crystal of $Ph_3As^+CH_3Br^-$*

2. Experimental. – $Ph_3As^+CH_3Br^-$ was synthesized by reaction of CH_3Br with Ph_3As at – 10° [11]. Single crystals were grown by very slow crystallization (several weeks) from a solution in THF at 4°. An idealized crystal is shown on *Figure 1* together with the reference system used for the ESR. study. The crystals were X-irradiated with a *Philips* tube having a tungsten anticathode (30 mA, 30 kV, T=77 K or 300 K). The ESR. spectra were recorded at 77 K or 300 K on a *Varian E-9* spectrometer (X-band, 100-kHz field modulation). At r.t. the angular dependance of the spectrum was studied by using a previously described goniometer [12]. The magnetic field was calibrated with an NMR. marker, and the klystron frequency was measured using a *Hewlett-Packard 540B* transfer oscillator and a *Racal 9839* frequency counter. The ESR. tensors were obtained using an optimization program which adjusts the terms of the spin Hamiltonian in order to obtain the best fitting with the experimental angular variation of the signals.

3. Results and discussion. – 3.1 *The radiation damage process.* An example of an ESR. spectrum recorded at 77 K, immediately after X-irradiation at the same temperature, is shown in *Figure 2*. The angular dependance of this spectrum shows that two radical species are trapped: *1)* Br_2^-, easily identified by its anisotropic hyperfine interaction [13] with the two isotopes $^{79/81}Br$ which give rise to the exterior signals; *2)* a C-centered radical, the signals of which appear in the central part of the spectrum (field range $\approx$ 120 G). Due to an overlap of these last signals with a component of the Br_2^--spectrum it was impossible to identify the C-radical with certainty; it is however probable that it corresponds to the trapping of $Ph_3As^+\dot{C}H_2$ [14]. On increasing the temperature the ESR. signals disappear and no spectrum remains at room temperature.

Immediately after irradiation at room temperature the ESR. spectrum exhibits two sets of signals *(Fig. 3a)*. The first one (A_1) is spread over a range of $\approx$250 G and exhibits a structure corresponding to a quartet of quartets. This pattern indicates a coupling with an As-nucleus (^{75}As-T $\simeq$80 G) and with a CH_3-group (^{1}H–T $\approx$20 G). Overlapping of signals A_1 with these due to an unidentified radical prevents any determination of the corresponding tensors; nevertheless these signals are consistent with the trapping of the adduct $Ph_3As\ldots\dot{C}H_3$ which was already produced by irradiation of $Ph_3As^+CH_3I^-$ [15]. The second set of signals (A_2) are more anisotropic and are spread over a range of $\approx$1000 G. Signals A_1 and A_2

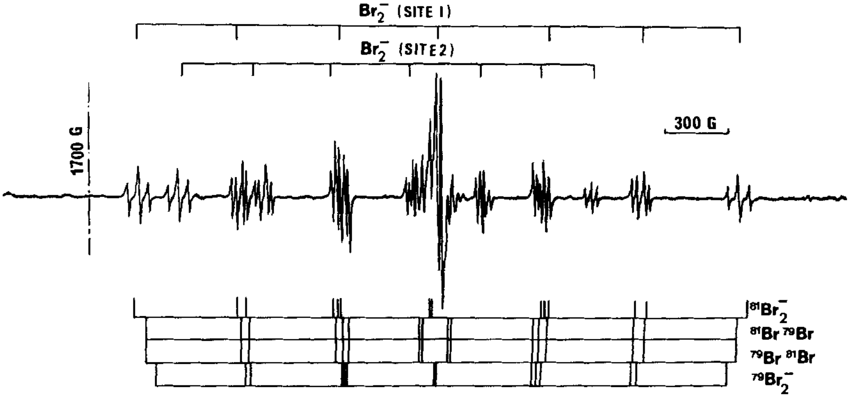

Fig. 2. *ESR. spectrum* (77 K) *obtained with a crystal of* $Ph_3As^+CH_3Br^-$ *X-irradiated at* 77 K

progressively disappear with time, A_2 more rapidly than A_1, and a new spectrum appears (signals B). The ESR. tensors show that B and A_2 correspond to the same radical trapped in two differently oriented sites. As discussed later this species is identified as being $Ph_3\dot{A}sBr$. When A_2 has become undetectable, A_1 is still present and the intensity of B continues to increase. The maximum concentration of radicals B is observed when A_1 has just disappeared, this concentration is then considerably higher than the original concentration of radicals A_2 *(Fig. 3b)*. These observations clearly show that the formation of B is related to a transformation of A_1 and that A_2 and B have a different origin. As the crystal structure of $Ph_3As^+CH_3Br^-$ is unknown the difference in the orientation of A_1 and B is hardly interpretable; however, from the preceding results we can propose the following radiation process: *1)* the first steps are the ionization of Br^- and the formation of $Ph_3\overset{+}{A}s\dot{C}H_2$ due to an homolytic scission of a methyl C,H-bond. The atomic Br, after reaction with a Br-anion gives rise to the Br_2^--anion, which is probably transformed to Br_2 with increasing temperature; *2)* during irradiation at room temperature an electron capture leads to the formation of the unstable triphenylmethylarsoranyl radical which immediately gives rise to the adduct $Ph_3As...\dot{C}H_3$ (signals A_1). Trapped Br_2-molecules can photolytically dissociate at room temperature to form $\dot{B}r$ which reacts with the adduct leading thus to the trapping of $Ph_3\dot{A}sBr$ (signals B). A second route for the formation of this radical is the homolytic scission of a $\overset{+}{\dot{A}}s,CH_3$-bond which causes

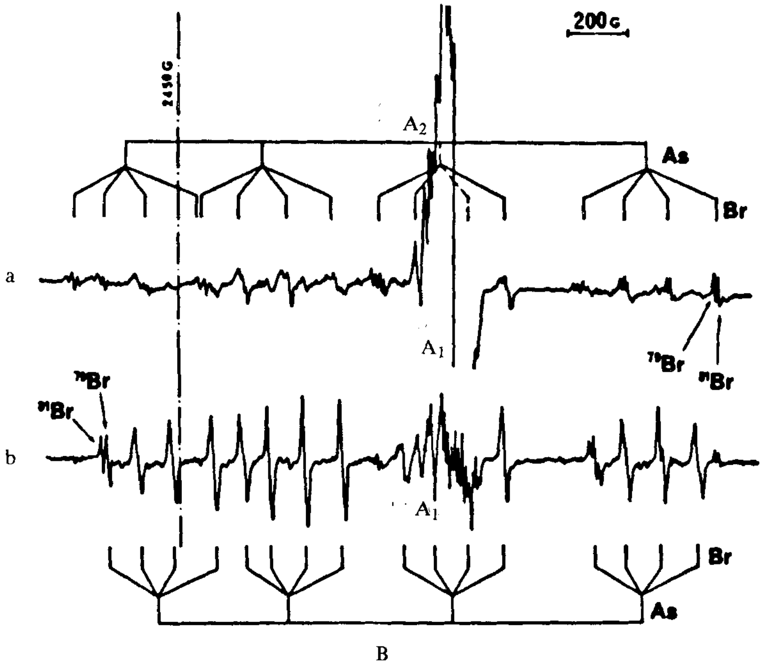

Fig. 3. *ESR. spectrum obtained with a crystal of $Ph_3As^+CH_3Br^-$ X-irradiated at room temperature:* a) immediately after irradiation; b) six days after irradiation.

the formation of the unstable $Ph_3\dot{A}s^+$ radical ion, which immediately reacts with a neighbouring Br^--ion to generate the Ph_3AsBr-radical (signals A_1).

3.2. *Structure of $Ph_3\dot{A}sBr$.* An example of a spectrum due to the radical B is shown in *Figure 3b.* It clearly appears that the hyperfine structure is due to coupling with an As-nucleus and the two Br-isotopes. The angular dependance of the spectrum is demonstrated in *Figure 4.* The small discontinuities which occur when the Br magnetic coupling is weak are attributed to the Br quadrupolar interaction. The angular variations of the B-signals have been calculated by using the following Hamiltonian:

$H = H \cdot S \cdot \bar{g} \cdot h + S \cdot ({}^{75}As - \bar{T}) \cdot I + S \cdot ({}^{79}Br - \bar{T}) \cdot I + I \cdot ({}^{79}Br - \bar{P}) \cdot I$ where $\bar{T}$ and $\bar{P}$ represent the magnetic and quadrupolar hyperfine interaction tensors, respectively. These parameters are given in *Table 1.* Assuming positive signs for all the eigenvalues the anisotropic and isotropic coupling constants listed in *Table 2* are obtained. Taking as reference values the isotropic constants compiled by *Morton & Preston* [16] together with the $\langle 1/r^3 \rangle$-values reported by *Barnes & Smith* [17], we have calculated the spin densities given in *Table 2.* These data agree with those previously reported for $Ph_3\dot{P}Br$ [18] and $Ph_3\dot{A}sCl$ [19] *(Table 2)* and are thus perfectly consistent with the identification of $Ph_3\dot{A}sBr$.

Single-crystal ESR. studies have led to two limit structures for phosphoranyl-type radicals *(Scheme):* structure **I** in which the unpaired electron is mainly localized in a $P-Y\sigma^*$-orbital and structure **II** in which the unpaired electron is in an equatorial non-bonding orbital of the trigonal bipyramid. For PCl_3O^- [8] the

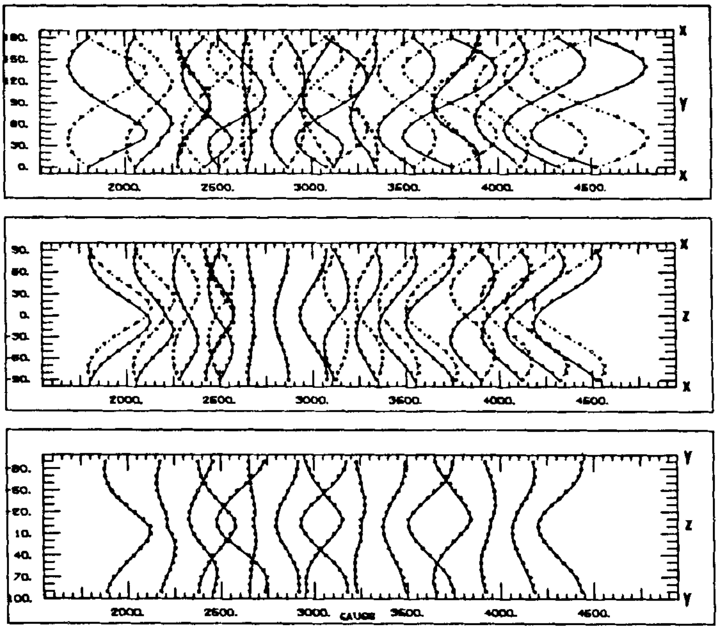

Fig. 4. *Angular variations of the B-signals in the three reference planes*

Table 1. *Experimental ESR. tensors for* $Ph_3\dot{A}sBr$

Tensor	Eigenvalues	Eigenvectors		
		/x	/y	/z
$\bar{g}$	2.048	0.63	0.58	−0.51
	2.030	0.33	0.40	0.86
	2.000	0.70	−0.71	0.06
$^{75}As-\bar{T}$ (MHz)	2044	0.86	−0.39	0.32
	1529			
	1491			
$^{79}Br-\bar{T}$ (MHz)	934	0.60	−0.80	−0.05
	346			
	324			
$^{79}Br-\bar{P}$ (MHz)	31	0.66	−0.74	−0.13
	−8			
	−23			

absence of any ^{31}P anisotropic interaction together with the equivalence of two Cl-couplings led to the TBP-structure (III).

The eigenvectors given in *Table 1* show that the $Br-P_{max}$ and $Br-T_{\parallel}$directions are almost aligned and that $As-T_{\parallel}$and $Br-T_{\parallel}$form an angle $a \approx 35°$. As it is known from single crystal NQR. studies that, for an (A, Halogen)-bond, the electric field gradient is, in general, aligned with the bond direction, we can assume that the $As-T_{\parallel}$ makes an angle $\approx 35°$ with the As, Br-bond. The present results are in discrepancy with the TBP-structure found for PF_4 [4], this last geometry would indeed imply orthogonal directions for $As-T_{\parallel}$and the As, Br-bond. Moreover the strong anisotropic character of the ^{75}As magnetic coupling is not consistent with the lack of anisotropy found for the ^{31}P hyperfine interaction in PCl_3O^- [8]. However the agreement between the present results and those predicted for C_{3v}-symmetry is far from being satisfactory. For such a $Ph_3\dot{A}sBr$ having the unpaired electron localized in a $As-Br\sigma^*$-orbital, the angle formed by $As-T_{\parallel}$and the As, Br-bond is expected to be near zero [9]. The above-mentioned value of a clearly indicates a strong distorsion from C_{3v}-symmetry. However, special care must be taken when estimating the extent of such a distorsion. As recently pointed out [20], for low-symmetry systems, non-diagonal terms in the dipolar Hamiltonian may have an appreciable contribution and must be taken into account when inter-

Scheme

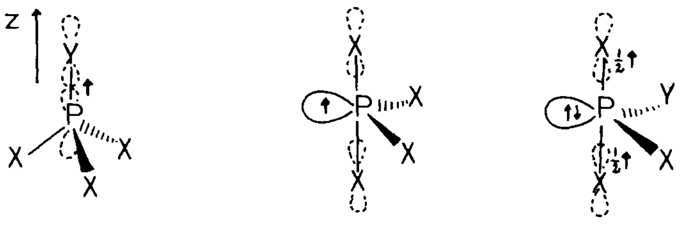

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Table 2. *Isotropic and anisotropic coupling constants and spin densities for some 'phosphoranyl'-type radicals*

Radical		A_{iso} (MHz)	Anisotropic constants			ρ_s	ρ_p	Ref.
			τ_1	τ_2	τ_3			
$Ph_3\dot{A}sBr$	^{75}As	1688	356	−159	−197	0.11	0.64	[a]
	^{79}Br	535	399	−189	−211	0.02	0.27	[a]
$Ph_3\dot{A}sCl$	^{75}As	1918	341	−162	−179	0.13	0.62	[19]
	^{35}Cl	120	90	−40	−50	0.02	0.30	[19]
$Ph_3\dot{P}Br$	^{31}P	1574	301	−135	−166	0.11	0.50	[18]
	^{79}Br	544	453	−217	−235	0.01	0.31	[18]
$Ph_3\dot{P}Cl$	^{31}P	1691	325	−145	−179	0.13	0.54	[9]
	^{35}Cl	140	90	−45	−45	0.02	0.30	[9]

[a] This work.

preting the experimental eigenvectors. For $Ph_3\dot{A}sBr$ it is likely that a slight distorsion of the C_{3v}-symmetry leads to some participation of an additional As – 4p orbital – namely the $4p_x$ – to the SOMO. The angle formed by As – $T_{/\!/}$ and the z-axis is then given by $tg^2\zeta = \rho_z/\rho_x$ [20]. Thus any intermediate structure requiring similar participation of the As p_x- and p_z-orbitals is consistent with the mutual orientation of the experimental eigenvectors. It would be premature, for the moment, to attempt giving a more detailed description of the radical; *ab initio* calculations are in progress in order to determine the corresponding structure. Nevertheless it is clear that for such hypervalent radicals an additional stable structure exists which is neither the TBP nor the trigonal pyramidal structure. The fact that similar mutual orientation of the eigenvectors have been found for $Ph_3\dot{A}sCl$ [19], $Ph_3\dot{P}Br$ [18] and the isoelectronic ion Ph_3GeBr^- [21] eliminates any crystalline effect in the stabilization process of this intermediate structure.

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REFERENCES

[1] *M. Geoffroy, L. Ginet & E.A.C. Lucken,* J. Chem. Phys. *65,* 729 (1976).
[2] *T. Berclaz & M. Geoffroy,* Mol. Phys. *30,* 549 (1975).
[3] *M.C.R. Symons & J.E. Drake,* J. Chem. Res. (M) 1764 (1978).
[4] *A. Hasegawa, K. Onishi, K. Sogabe & M. Miura,* Mol. Phys. *30,* 1367 (1975).
[5] *J.R. Morton, K.F. Preston & S.J. Strach,* J. Magn. Reson. *37,* 321 (1980).
[6] *M. Geoffroy, J. Hwang & A. Llinares,* J. Chem. Phys. *76,* 5191 (1982).
[7] *W.G. Bentrude,* Acc. Chem. Res. *15,* 117 (1982).
[8] *T. Gillbro & F. Williams,* J. Am. Chem. Soc. *96,* 5032 (1974).
[9] *T. Berclaz, M. Geoffroy & E.A.C. Lucken,* Chem. Phys. Lett. *36,* 677 (1975).
[10] *J.R.M. Giles & B.P. Roberts,* J. Chem. Soc. Perkin II, *1981,* 1211.
[11] *M.C. Henry & G. Wittig,* J. Am. Chem. Soc. *82,* 563 (1960).
[12] *T. Berclaz, J. Diolot, M. Geoffroy & L. Ginet,* J. Phys. *E10,* 871 (1977).
[13] *F.W. Patten & M.J. Marrone,* Phys. Rev. *142,* 513 (1966).
[14] *M. Geoffroy, L. Ginet & E.A.C. Lucken,* Mol. Phys. *34,* 1175 (1977).
[15] *M. Geoffroy & A. Llinares,* Mol. Phys. *41,* 55 (1980).
[16] *J.R. Morton & K.F. Preston,* J. Magn. Reson. *30,* 577 (1978).
[17] *R.G. Barnes & W.V. Smith,* Phys. Rev. *93,* 95 (1954).
[18] *T. Berclaz, M. Geoffroy, L. Ginet & E.A.C. Lucken,* Chem. Phys. Lett. *62,* 515 (1979).
[19] *T. Berclaz, M. Geoffroy & E.A.C. Lucken,* J. Magn. Reson. *33,* 577 (1979).
[20] *R. Franzi, M. Geoffroy, E.A.C. Lucken & N. Leray,* J. Chem. Phys., in Press.
[21] *R. Franzi & M. Geoffroy,* Nouv. J. Chim. *12,* 731 (1980).