

Bromo(triphenylarsino)gold(I)

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(Received 16 September 1974; accepted 24 October 1974)

Abstract. (AsPh₃)AuBr, $M=583.1$, orthorhombic, $P2_12_12_1$, $a=12.438$ (1), $b=13.637$ (1), $c=10.191$ (1) Å, $V=1728.6$ Å³, $\rho_o=2.22$ (4) g cm⁻³ (Berman density-balance determination in toluene), $Z=4$, $\rho_c=2.24$ g cm⁻³. Mo $K\alpha_1$ radiation, $\lambda=0.70926$ Å, $\mu(\text{Mo } K\alpha)=131$ cm⁻¹, $F(000)=1080$, $T=20 \pm 1$ °C. Final $R=0.059$ for 546 observed reflexions. The crystal structure contains discrete (AsPh₃)AuBr molecules packed together in a primitive lattice, the two-coordinate gold atom being bonded to an arsenic and a bromine atom at distances of 2.342 (5) and 2.377 (6) Å respectively. Within experimental error, the As–Au–Br bond angle is linear.

Introduction. Bright-red crystals of the title compound were kindly supplied by Dr A. D. Westland of the University of Ottawa. Precession photographs of the zones $hk0$ and $h0l$ were obtained along with photographs of the reciprocal-lattice layers $0kl-5kl$ by use of equi-inclination Weissenberg geometry. Systematically absent were reflexions in the $h00$ zone with $h=2n+1$, in the $0k0$ zone with $k=2n+1$ and in the $00l$ zone with $l=2n+1$, confirming the space group $P2_12_12_1$.

For intensity-data collection, an approximately cube-shaped crystal of dimensions $0.18 \times 0.14 \times 0.16$ mm was selected and mounted with the a axis offset with respect to ϕ by 5°. Accurate cell dimensions were determined from counter measurements and least-squares refinement of the 2θ values ($2\theta > 19^\circ$) for 19 strong reflexions centred on the Mo $K\alpha_1$ peak. Intensities and cell dimensions were measured with a Picker FACS-1 computer-controlled diffractometer. Data were collected with a symmetrical $\theta-2\theta$ scan of base width 1.6° using niobium-filtered Mo $K\alpha$ radiation at a take-off angle of 1.3° . Background counts of 10 s duration were measured at each of the scan limits. Variation in the scale factor calculated from two standard reflexions measured after every 50 reflexions was less than 1.2% during the entire data collection.

Intensity measurements were obtained for 959 reflexions of which 546 were classed as observed *i.e.* having $I/\sigma(I) > 1.8$ where $\sigma(I) = [(T) + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$ where T =total count, B_1 and B_2 are the background counts, t_s =scan time, t_b =total background count time, k is a constant set to 0.03 and I is the net

count}. Unobserved reflexions are denoted by $-F_{\text{obs}}$ in the structure-factor listing.* A spherical absorption correction using a value for the radius of 0.07 mm ($\mu R=0.92$) was applied; in addition all measured intensities were corrected for Lorentz and polarization effects.

Following solution of a three-dimensional Patterson function for the gold, arsenic and bromine atoms, a structure-factor calculation yielded an R of 0.199. Refinement of positional and isotropic thermal parameters for these items using full-matrix least-squares techniques reduced R to 0.111, where $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. Subsequent electron-density difference maps interspersed by least-squares refinement served to locate all remaining non-hydrogen atoms, and after final refinement including anomalous dispersion corrections and introduction of the weighting scheme described below, R was lowered to 0.059 ($R_w=0.068$).

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30758 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

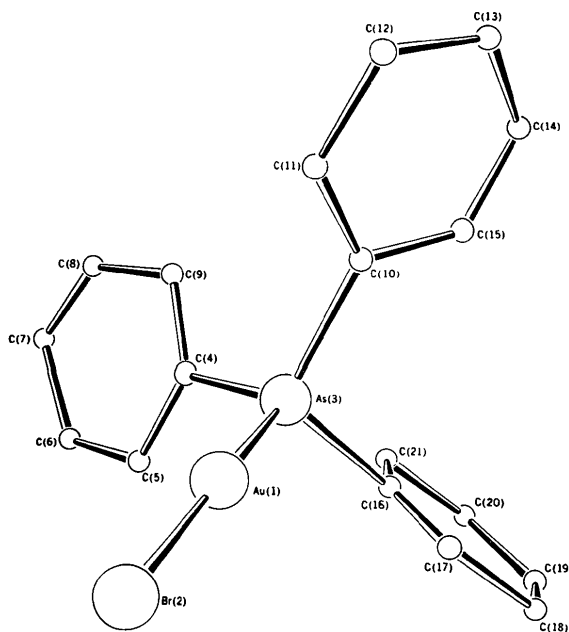


Fig. 1. The molecular structure of bromo(triphenylarsino)gold(I).

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Unobserved reflexions were not included in the least-squares refinement at any stage. The weighting scheme was set up to approximate the condition $w=1/\sigma F^2$ where σ_F is the standard deviation of F_{obs} . Weighting functions of the type $w=1/F_{\text{obs}}$ for $F_{\text{obs}} > 135$ and $w=F_{\text{obs}}/135$ for $F_{\text{obs}} < 135$ were used. These functions were chosen to make $w\Delta^2$ constant as a function of $|F_{\text{obs}}|$, $\sin \theta/\lambda$ and reflexion index [$\Delta = (|F_o| - |F_c|)$].

With anisotropic temperature factors for the three heavy atoms, no significant improvement in the discrepancy index was apparent; hence in the final least-squares cycle, all atoms were treated isotropically. Scattering factors used for gold were those given by Cromer & Waber (1965), and for the other non-hydrogen atoms from *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections were applied for gold, arsenic and bromine and were those given by Cromer (1965). Computer programs used in the analysis were those described by Einstein & Jones (1972).

Final atomic coordinates and thermal-motion parameters are listed in Table 1 and bond lengths and angles in Table 2. Atom labelling in the molecule is illustrated in Fig. 1, drawn with the plot program ORTEP (Johnson, 1970).

Table 1. *Positional and thermal parameters with standard deviations*

The positional coordinates x , y and z are fractions of the unit-cell edges a , b and c respectively.

	x	y	z	B (\AA^2)
Au(1)	0.0660 (2)	0.2378 (1)	0.1805 (2)	3.56 (5)
Br(2)	0.0110 (5)	0.1979 (4)	0.3975 (5)	4.9 (1)
As(3)	0.1223 (4)	0.2764 (3)	-0.0326 (4)	3.3 (1)
C(4)	0.010 (4)	0.294 (3)	-0.156 (4)	4 (1)
C(5)	-0.056 (4)	0.212 (3)	-0.175 (5)	4 (1)
C(6)	-0.147 (4)	0.228 (4)	-0.271 (5)	6 (1)
C(7)	-0.173 (7)	0.323 (6)	-0.344 (8)	11 (2)
C(8)	-0.097 (4)	0.394 (3)	-0.305 (6)	5 (1)
C(9)	0.002 (5)	0.384 (4)	-0.218 (5)	6 (1)
C(10)	0.209 (5)	0.390 (4)	-0.043 (5)	4 (1)
C(11)	0.180 (5)	0.476 (4)	0.031 (5)	6 (1)
C(12)	0.252 (5)	0.560 (4)	0.041 (6)	6 (2)
C(13)	0.346 (4)	0.560 (3)	-0.027 (5)	4 (1)
C(14)	0.369 (5)	0.481 (4)	-0.115 (6)	7 (2)
C(15)	0.306 (4)	0.399 (3)	-0.107 (5)	3 (1)
C(16)	0.210 (5)	0.170 (4)	-0.120 (5)	4 (1)
C(17)	0.267 (4)	0.123 (3)	-0.037 (5)	3 (1)
C(18)	0.346 (5)	0.044 (4)	-0.090 (6)	4 (1)
C(19)	0.350 (5)	0.042 (4)	-0.221 (5)	5 (1)
C(20)	0.280 (4)	0.097 (4)	-0.316 (6)	5 (1)
C(21)	0.203 (4)	0.177 (4)	-0.250 (6)	5 (1)

Discussion. Various tertiary phosphine and arsine derivatives of gold(I) halides have been postulated to contain two-, three- and four-coordinate gold(I) (Carty & Efraty, 1969). The compound $\{(\text{Ph}_3\text{P})_2\text{Au}\}^+\{\text{Cl}\}^-$ was proposed to have linear coordination about the gold atom (Meyer & Allred, 1968). Also formulated as a linear structure with a

Table 2. *Interatomic distances (\AA) and bond angles ($^\circ$) with standard deviations*

Au(1)—Br(2)	2.377 (6)	As(3)—C(10)	1.89 (5)
Au(1)—As(3)	2.342 (5)	As(3)—C(16)	2.02 (5)
As(3)—C(4)	1.90 (5)	Average C—C distance	1.43 (9)*
As(3)—Au(1)—Br(2)	179 (1)	Au(1)—As(3)—C(16)	114 (2)
Au(1)—As(3)—C(4)	115 (1)	C(10)—As(3)—C(16)	105 (2)
Au(1)—As(3)—C(10)	114 (2)	C(4)—As(3)—C(10)	106 (2)
		C(4)—As(3)—C(16)	101 (2)

* Standard deviation for 18 C—C bonds (3 phenyl rings).

bridging diphosphine group is the compound $(\text{AuX})_2\text{DPPA}$, where $\text{X} = \text{Cl}, \text{Br}$ or I , and DPPA is the ligand bis(diphenylphosphino)acetylene; structures involving tetrahedral gold(I) are expected in the series of compounds $(\text{AuX})_2(\text{DPPA})_3$, where $\text{X} = \text{Cl}, \text{Br}$ or I (Carty & Efraty, 1969). Westland (1969) has prepared the series of compounds Ph_3EAuX where $\text{E} = \text{P}$ and As in order to study the relative importance of π -bonding with gold(I). We have undertaken the molecular and crystal structure of one of the members of this series, bromo(triphenylarsine)gold(I), with the aim of ascertaining the stereochemistry around the gold atom and contributing to existing information on the gold-arsenic linkage.

$(\text{C}_6\text{H}_5)_3\text{AsAuBr}$ molecules packed together in a primitive orthogonal lattice constitute the crystal structure in this determination. The As—Au—Br angle is linear within experimental error at $179 \pm 1^\circ$. The only previous crystallographically determined Au—As distance known to us involved six-coordinate Au^{III} in the compound diiodobis- $[o$ -phenylenebis(dimethylarsine)]gold(III) where the average distance is 2.45 (3) \AA (Duckworth & Stephenson, 1969). Relative to a predicted value of 2.40 \AA based on covalent radii for an Au^{I} —As distance (Pauling, 1960) our value of 2.342 (5) \AA provides some support for Westland's proposal of $d\pi$ — $d\pi$ bonding for this bond. Shortening of metal-arsenic distances has been found in the octahedral complexes $\text{Ni}(\text{diars})_2\text{I}_2$ and $\text{Pt}(\text{diars})_2\text{X}_2$ (Stephenson, 1964).

Westland's (1969) proposal of an almost pure σ bond between the gold and bromine atoms is supported in this determination. A predicted value for this distance of 2.36 \AA (Pauling, 1960) is only three standard deviations smaller than our value of 2.377 (6) \AA .

We wish to thank Dr A. D. Westland for his gift of the crystals and Peter L. Vogel for his careful help in the preparation of both the manuscript and the diagram. We also wish to acknowledge the generous support of the National Research Council of Canada.

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Acta Cryst. (1975). B31, 626

2-Phenylbenzo-1,2,3-triaziniumbetaine 1-Oxide

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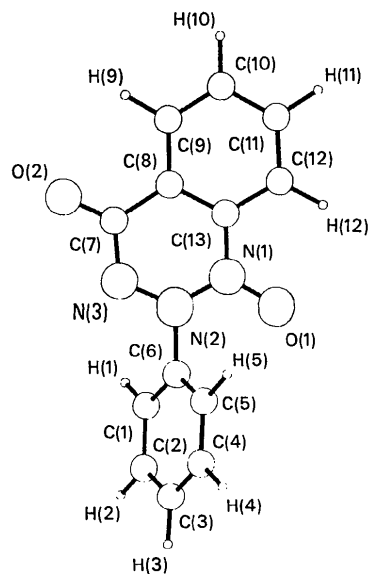
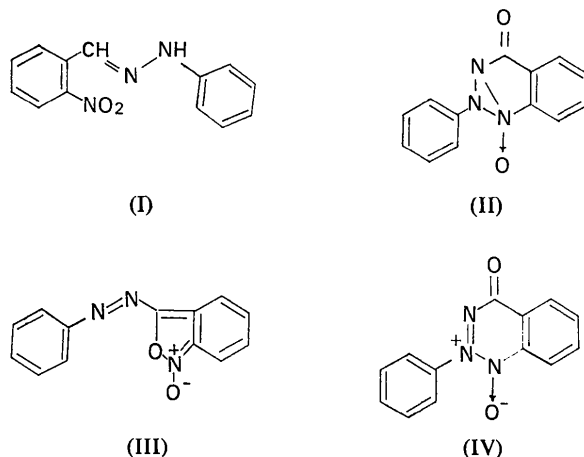
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(Received 24 October 1974; accepted 26 October 1974)

Abstract. $C_{13}N_3O_2H_9$, monoclinic, space group $P2_1/n$, $a=8.13(5)$, $b=21.02(5)$, $c=8.13(5)$ Å, $\beta=128.6(2)^\circ$, $Z=4$, $D_m=1.435(10)$, $D_x=1.463$ g cm $^{-3}$. The compound is a 1,2,3-triaziniumbetaine 1-oxide (IV) rather than a phenylazoanthranil *N*-oxide (III) or an 'isodiazomethane' (II).

Experimental. The compound was prepared by Kobylecki's (1973) method and gave bright-yellow needles m.p. 147–149° on recrystallization from $CHCl_3$. The intensities were recorded on Weissenberg photographs (1401 independent reflexions about three axes) and measured automatically by the Optronics P-100 scanner at the Atlas Computer Laboratory (S.R.C. Microdensitometer Service). No correction was made for absorption.

Finding the best set of starting phases presented the same problems as were experienced with 2,7-dimethyl-5-acetylaminopyrazolo[1,5-*a*]pyrimidine (Ballard, Nor-



Introduction. Chattaway described as an 'isodiazomethane' (II) the compound obtained by bromination and dehydrohalogenation of *o*-nitrobenzaldehyde phenylhydrazone (I) (Chattaway & Walker, 1927; Chattaway & Adamson, 1930; Chattaway & Parkes, 1935). Later (Gibson, 1962) it was suggested that the structure was that of a phenylazoanthranil *N*-oxide (III) and finally (Kerber, 1972) that it was a 1,2,3-triaziniumbetaine 1-oxide (IV). Although the chemical evidence favours (IV) the spectroscopic results were ambiguous and an X-ray study was undertaken.

Fig. 1. The molecule of 2-phenylbenzo-1,2,3-triaziniumbetaine 1-oxide.