this monomeric complex, which is consistent with the transition to the dimer on loss of water molecules, as shown by thermogravimetric studies (Borrel & Pâris, 1951; Yuchi *et al.*, 1980).

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The Structure of Acetylarsenocholine Bromide*

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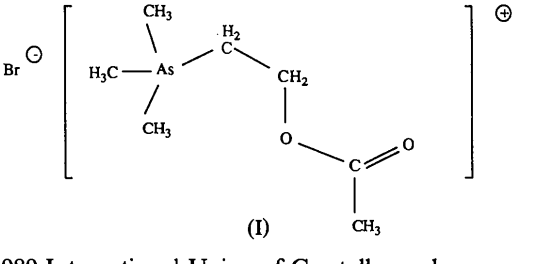
Abstract. $[C_7H_{16}AsO_2]^+.Br^-$, $M_r = 287{\cdot}03$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}121\ (3)$, $b = 11{\cdot}745\ (2)$, $c = 9{\cdot}530\ (1)$ Å, $V = 1132{\cdot}8\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}682$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6{\cdot}86$ mm^{-1}, $F(000) = 568$, $T = 296$ K, $R = 0{\cdot}034$ for 919 observed reflections. Crystalline acetylarsenocholine bromide exists in the *trans–gauche* conformation which is similar to the solution conformation of acetylcholine. The cationic structure is compared with known crystalline acetylcholine salts. In the crystal structure, each Br^- ion appears to link the arsonium ends of four cations.

Introduction. Recent innovations in nuclear medicine imaging using tomographic techniques have shown that regional brain metabolism and biochemical function can be studied *in vivo*. Therefore the structural properties of various molecules active in the neuromuscular system have been studied. Acetylcholine, the natural intercellular transmitter substance in most intercellular peripheral nervous junctions, stimulates both muscarinic and nicotinic receptor sites. The title compound (I) is an acetylcholine analog which demonstrates preferential affinity for muscarinic receptors over nicotinic receptors. The determination of the active conformation of acetylcholine in the muscarinic receptor of the parasympathetic and central nervous systems is an ongoing problem in neurochemical research. Numerous crystal structures have been completed by various researchers on acetylcholine salts, analogs and derivatives in an effort to discover which of the several stable conformers was most commonly associated with pharmacological activity and from which the active conformation could be inferred.

A crystallographic study of the title compound, (I), was undertaken in an effort to learn more about the structural features which lead to muscarinic activity of an acetylcholine-like molecule.



(I)

* Trimethyl-2-(acetoxy)ethylarsonium bromide.

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Table 1. *Final positional parameters* ($\times 10^5$ *for* Br^- *and* As, $\times 10^4$ *for* O *and* C) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
Br^-	68601 (11)	32578 (10)	19612 (10)	60
As	64535 (8)	36207 (7)	77757 (9)	35
C(10)	8309 (10)	3510 (11)	8098 (13)	54
C(9)	5723 (14)	4845 (10)	8831 (12)	48
C(8)	5620 (14)	2229 (11)	8315 (13)	60
C(6)	6189 (11)	3915 (11)	5800 (11)	52
C(5)	4870 (11)	3574 (12)	5279 (10)	52
O(4)	3903 (6)	4187 (6)	6115 (6)	50
O(3)	2322 (7)	3640 (7)	4632 (7)	64
C(2)	2623 (10)	4103 (9)	5702 (10)	48
C(1)	1724 (17)	4679 (18)	6669 (22)	75

*$U_{eq} = \frac{1}{3}$ (trace of the diagonalized anisotropic temperature-factor matrix).

Experimental. Crystals of $[C_7H_{16}AsO_2]^+.Br^-$ were grown from a benzene/acetonitrile solution. A colorless prism having approximate dimensions of 0·40 × 0·40 × 0·35 mm was mounted in a glass capillary; data collected on a Rigaku AFC6R diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a 12kW rotating-anode generator;* cell constants and an orientation matrix for data collection obtained from a least-squares refinement of the setting angles of 25 centered reflections in the range $43·95 < 2\theta < 49·62°$; space group, $P2_12_12_1$, based on the systematic absences and structure analysis; 1171 data collected using the ω–2θ scan technique to $2\theta_{max} = 50·0°$; 919 considered observed with $I \geq 2·5\sigma(I)$; scans of $(1·05 + 0·30\tan\theta)°$ made at a speed of 16·0° min^{-1} (in ω); weak reflections [$I < 10·0\sigma(I)$] rescanned (maximum of 2 rescans) and the counts accumulated to ensure good counting statistics; stationary background counts recorded on each side of the reflection with peak:background times of 2:1; reciprocal space explored $+h$(0–12), $+k$(0–13), $+l$(0–11); three standard reflections measured every 150 reflections; Lp and empirical absorption corrections applied.

Coordinates for the As and Br atoms were obtained from a Patterson map and refined by full-matrix least-squares techniques; remaining non-H atoms located in subsequent difference Fourier maps and refined; H-atom positions determined by locating at least one positive electron density peak in the vicinity of H-atom-bearing C atoms, then calculating ideal positions for remaining H atoms not discernible from difference Fourier maps; all H-atom positional and isotropic thermal parameters refined [except for temperature factors of H atoms on C(8)]; anisotropic temperature factors included for heavy atoms; convergence reached at $R = 0·032$ and $wR = 0·038$. For the complete data set $R = 0·060$ and $wR = 0·041$; function minimized throughout refinement was $w(|F_o| - k|F_c|)^2$ with $w = 1/\sigma^2(F_o)$; weighting analyses confirmed the suitability of the chosen weights by showing uniform average values of $w(|F_o| - k|F_c|)^2$ over ranges of F_o; GOF = 1·025 for 161 variables; Δ/σ on final cycle 0·432; highest peak on difference map 0·411 e $Å^{-3}$ at 1·5 Å from H(51); lowest trough −0·495 e $Å^{-3}$ at 1·4 Å from As; atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Final atomic positional parameters and equivalent isotropic thermal parameters are given in Table 1.*† Fig. 1 shows the structure of (I) with atomic labeling commonly used for acetylcholine and its derivatives.

Discussion. Despite the variety of structures of muscarinic agonists known, there is yet to be established a firm basis for any inference about the active conformation of the muscarinic pharmacophore. Acetylcholine itself adopts two distinct types of conformations in the solid state depending on the counterion present and these conformations are commonly described by the torsion angles τ_1 [C(2)—O(4)—C(5)—C(6)] and τ_2 [O(4)—C(5)—C(6)—N] which determine the conformer to be of the

* Data collection and reduction were carried out by Molecular Structure Corporation, 3304 Longmire Drive, College Station,TX, USA.

* Computation was carried out on the University of Manitoba Computer Services Department's Amdahl 580/5850 mainframe computer using locally written programs for processing and modified versions of the following programs for structure solution, refinement and calculations: *FORDAP* (Zalkin, unpublished); *ORFLS* (Busing, Martin & Levy, 1962); *ORFFE* (Busing, Martin & Levy, 1964); *ORTEP*II (Johnson, 1976).

† Lists of structure factors, anisotropic thermal parameters, H-atom positional and thermal parameters, bond distances and angles involving H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51873 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

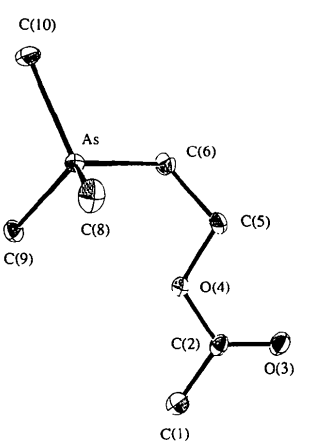

Fig. 1. *ORTEP* plot (Johnson, 1976) of the acetylarsenocholine cation; ellipsoids at 50% probability level.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(10)—As	1·907 (10)	C(5)—O(4)	1·453 (12)
C(9)—As	1·904 (11)	O(4)—C(2)	1·357 (11)
C(8)—As	1·910 (12)	O(3)—C(2)	1·195 (11)
As—C(6)	1·933 (10)	C(2)—C(1)	1·46 (2)
C(6)—C(5)	1·479 (15)		

C(10)—As—C(9)	110·4 (5)	As—C(6)—C(5)	113·8 (8)
C(10)—As—C(8)	109·5 (6)	C(6)—C(5)—O(4)	106·9 (9)
C(10)—As—C(6)	107·8 (5)	C(5)—O(4)—C(2)	116·7 (8)
C(9)—As—C(8)	109·4 (6)	O(4)—C(2)—O(3)	121·6 (10)
C(9)—As—C(6)	109·0 (5)	O(4)—C(2)—C(1)	112·2 (10)
C(8)—As—C(6)	110·7 (5)	O(3)—C(2)—C(1)	126·2 (12)

trans–gauche or *gauche–gauche* type. A comparison of several structures of choline esters substituted at C(5) and C(6) shows a clustering of torsion angles, τ_1 and τ_2, about 180, 90° (*trans–gauche*) and 90, 90° (*gauche–gauche*) indicating the stability of these conformations relative to those less frequently observed, but suggesting nothing about which more closely approximates the active conformation. Chothia, Baker & Pauling (1976) showed that for 5-methylfurmethide, a semi-rigid analog of, and equal in pharmacological activity to acetylcholine, the conformation in the solid state was *trans–gauche* with $\tau_1 \sim 180°$ and $\tau_2 \sim 80°$; steric hindrance in the molecule prevents τ_2 from achieving values very different from 80°. Since this is also the conformation of acetylcholine found in solution (Partington, Feeney & Burgen, 1972) one may reasonably expect this to be close to the active conformation. More recently, Schulman, Sabio & Disch (1983) developed a theoretical model which was used to deduce the pharmacologically active conformations of acetylcholine and other muscarinic agonists. Their calculations, based on several assumptions built into their model suggest an alternative conformation for the pharmacophore, where $\tau_1 \sim 180°$ and $\tau_2 \sim 130°$, which, on steric arguments, is improbable for 5-methylfurmethide.

The present compound acetylarsenocholine bromide, (I), adopts the *trans–gauche* conformation similar to 5-methylfurmethide with τ_1 and τ_2 angles of 172·4 (9) and 57·6 (12)°, respectively. With the exception of the As—C bonds, the remaining bonds have lengths (Table 2) similar (within experimental error) to those found in the crystalline salts acetylcholine chloride (Herdklotz & Sass, 1970), bromide (Svinning & Sørum, 1975) and iodide (Jagner & Jensen, 1977). Bond angles (Table 2), generally, are also in agreement with these compounds, but there is a significant difference observed between the C(6)—C(5)—O(4) angle [106·9 (9)°] in the present compound and that in acetylcholine bromide [111·6 (3)°]. The compression of this angle in (I) may be due to the relatively close contacts between $Br^-(x, y, 1+z)$ and H(91) (2·95 Å), $Br^-(3/2-x, 1-y, 1/2+z)$ and H(92) (2·89 Å) and between Br^- and C(2) (3·64 Å), all of which are slightly less than the van der Waals radii sum for the pair of atoms involved. In comparison, the crystal structure of acetylcholine bromide shows fewer close contacts suggesting a less compact state for the cation in this structure. The 5° difference in angles between the two structures, noted above, contributes to the shortening of the overall length of the acetylarsenocholine cation relative to acetylcholine in the bromide salt, despite the longer As—C bonds present in the former structure. However, the major factor effecting the decrease in length, as measured between the most distant non-H atoms in the cation, lies in the difference in conformations; acetylcholine bromide exists in the more extended *gauche–gauche* conformation while the arseno analog is of the *trans–gauche* type. This latter conformation for (I) yields an As···O(4) distance of 3·100 (6) Å which is within the range associated with potent muscarinic activity (Chothia & Pauling, 1970).

The geometry about the As atom is perfectly tetrahedral within experimental error; As—C bond lengths and C—As—C angles do not differ significantly from those found in arsenobetaine (Edmonds, Francesconi, Cannon, Raston, Skelton & White, 1977; Cannon *et al.*, 1981), the only other published crystal structure with a trimethylarsonium moiety.

In the crystal structure, the Br^- ion links the arsonium ends of four cations at x, y, z, $3/2-x, 1-y, z-1/2$, $x, y, z-1$ and $1/2+x, 1/2-y, 1-z$ with $Br^-\cdots H$ distances in the range 2·89–3·16 Å where the H atoms are from C(6), C(8), C(9) and C(10). Since the contact distances of the Br^- to the ester end of the cation are greater [closest approach H(13) at 3·55 Å], this suggests that the positive charge is delocalized over the entire cationic head at the arsonium end of the ion. A packing diagram is given in Fig. 2.

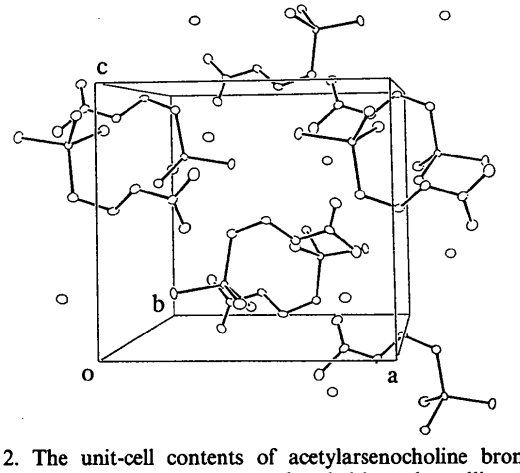

Fig. 2. The unit-cell contents of acetylarsenocholine bromide; bromide ions are shown as non-bonded boundary ellipses.

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A Monoclinic Crystal Form of Tris(triphenylphosphine)platinum(0)

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Abstract. $[Pt\{P(C_6H_5)_3\}_3]$, $M_r = 982{\cdot}0$, monoclinic, $P2_1/c$, $a = 21{\cdot}194\ (2)$, $b = 12{\cdot}432\ (2)$, $c = 18{\cdot}556\ (3)$ Å, $\beta = 112{\cdot}85\ (1)°$, $V = 4505{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}45$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 32{\cdot}8$ cm^{-1}, $F(000) = 1968$, $T = 295$ K, $R = 0{\cdot}033$ and $wR = 0{\cdot}042$ for 5389 reflections with $|F^2| > \sigma(F^2)$. The geometry at Pt is approximately trigonal planar with Pt—P distances ranging from 2·262 (2) to 2·271 (2) Å and P—Pt—P angles varying between 117·20 (6) and 121·83 (6)°. The structure is quite distinct from that previously determined and is not related to it by any simple transformation.

Introduction. A large crystal of $[Pt(PPh_3)_3]$ was isolated from an attempted preparation of $[Pt(PPh_3)_2(dppb)]$ [dppb = 1,4-bis(diphenylphosphino)-butane]. The structure of $[Pt(PPh_3)_3]$ was initially determined more than 20 years ago (Albano, Bellon & Scatturin, 1966), but was apparently never fully refined. There are few literature reports of accurate structure determinations on tris(phosphine)-platinum(0) complexes (Immirzi, Musco & Mann, 1977; van der Knaap *et al.*, 1984) so that an accurate determination of the structure of this important complex was of considerable interest.

Experimental. A large crystal of $[Pt(PPh_3)_3]$ was isolated from a THF solution containing $[Pt(PPh_3)_2(C_2H_4)]$, and a fragment *ca* 0·4 × 0·4 × 0·3 mm was cut from it. Data, Enraf–Nonius CAD-4 diffractometer, cell parameters on least-squares treatment of 25 reflections with $7 < \theta < 10°$, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan mode, $\Delta\theta = (0{\cdot}8 + 0{\cdot}35\tan\theta)°$, maximum scan time 1 min. 8296 unique reflections measured for $2 < \theta < 25°$ and $\pm h + k + l$, and 5389 reflections with $|F^2| > \sigma(F^2)$ used in the refinement, $\sigma(F^2) = [\sigma^2(I) + (0{\cdot}04I)^2]^{1/2}$/Lp. There was no crystal decay. Absorption correction using *DIFABS* (Walker & Stuart, 1983) after isotropic refinement, maximum and minimum corrections of 1·34 and 0·69. The structure was solved by routine heavy-atom methods and refined by full-matrix least squares with the non-H atoms anisotropic (523 parameters). H atoms were fixed at calculated positions with $B_{iso} = 1{\cdot}3\ B_{eq}$ for the C atoms to which they are bonded. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0{\cdot}033$ and $wR = 0{\cdot}042$. $S = 1{\cdot}3$, $(\Delta/\sigma)_{max} = 0{\cdot}01$, $\Delta\rho_{max} = 0{\cdot}9$, $\Delta\rho_{min} - 1{\cdot}1$ e Å^{-3}. Programs from the Enraf–Nonius *SDP-Plus* package (Frenz, 1984) were run on a MicroVAX computer. Atomic scattering

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