of the planes Mn—P(2)—C(22) and Mn—P(2)—C(23) respectively.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
ULIBARRI, M. & FAYOS, J. (1982). *Acta Cryst.* B38, 952–954.
USON, R., RIERA, V., GIMENO, J. & LAGUNA, M. (1977). *Transition Met. Chem.* 2, 123–130.

2-Chloro-4,4,6,6-tetramethyl-1,3,2-dioxarsenane

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Abstract. $C_7H_{14}AsClO_2$, monoclinic, $P2_1/n$, $Z = 4$, $a = 7\cdot867$ (9), $b = 10\cdot730$ (14), $c = 11\cdot738$ (9) Å, $\beta = 92\cdot67$ (5)°, $D_c = 1\cdot614$ Mg m^{-3} at 150 K. The structure was solved by conventional techniques to $R_w = 0\cdot041$ for 1005 observed reflections. The dioxarsenane ring adopts a twist-boat conformation with the As—Cl pointing in an axial direction.

Introduction. Recently, the spatial structure of six-membered cyclic esters containing CH_3 groups in the 4,4,6,6 positions was investigated by NMR and dipole-moment methods (Samitov, Yuldasheva & Anonimova, 1982). As a result of this work it was shown that 2-chloro-4,4,6,6-tetramethyl-1,3,2-dioxarsenane has a flexible conformation in solution. However, even at temperatures below 175 K the spectra gave no clear evidence about the type of flexible form. Therefore, an X-ray investigation of the solid phase was undertaken. This would give extra information about the title compound as well as information about dioxarsenane geometry. To our knowledge this is the first crystallographic report on a cyclic ester containing As.

The title compound was synthesized by a method described by Kamai & Chadaeva (1951) and purified by distillation *in vacuo* under argon (b.p. 365 K/ 1·47 kPa). It crystallized spontaneously upon standing (m.p. 316–317·5 K).

A total of 1198 independent reflections ($0 \le \theta \le 22°$) was measured at 150 K on an Enraf–Nonius CAD-4 diffractometer employing Mo radiation ($\lambda = 0\cdot7107$ Å), a monochromator and a pure ω scan. Even under a continuous stream of cold nitrogen gas, with the crystal sealed inside a Lindemann-glass capillary, a slight decrease in standard intensity was noticed and corrected for. Intensities were corrected for Lorentz and polarization effects, but no absorption correction was applied in view of the size of the crystal (0·2 × 0·2 × 0·2 mm) and the absorption coefficient ($\mu = 3\cdot84$ mm^{-1} for Mo $K\alpha$).

A set of 1005 reflections with $I > 2\sigma(I)$ was used in the analysis. The structure was solved by conventional Patterson and (difference) Fourier techniques. Isotropic temperature parameters of the H atoms were fixed at $B_{iso} = 2\cdot5$ Å^2 during the least-squares refinement. A weighting scheme based on counting statistics was used. No extinction correction was made.

The refinement converged to $R_w = 0\cdot041$, with R_w defined as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ for observed reflections. The maximum noise level in the final

difference electron-density map was 0.4 e Å^{-3}. Positional parameters are presented in Table 1, the numbering of the atoms is given in Fig. 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38044 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters of the molecule in fractions of the cell edges and isotropic thermal parameters*

The e.s.d.'s, given in parentheses, refer to the last digit. $H(x,j)$ (with $j = 1,2,3$) is attached to $C(x)$. Isotropic temperature factors (Å²) for non-H atoms are calculated from anisotropic temperature parameters assuming equal volume of the 50% probability region according to Lipson & Cochran (1968): $B_{\text{Iso}} = 8\pi^2(U_{11}^0 \ U_{22}^0 \times U_{33}^0)^{1/3}$. All anisotropic thermal parameters were physically acceptable.

|	x	y	z	B_{Iso}
O(1)	0.1849 (6)	0.0076 (4)	0.2758 (4)	2.15
As(2)	0.2646 (1)	0.01128 (7)	0.41682 (6)	1.89
O(3)	0.4619 (6)	0.0805 (4)	0.4012 (4)	1.66
C(4)	0.5161 (9)	0.1347 (6)	0.2927 (6)	1.36
C(5)	0.3617 (9)	0.1881 (6)	0.2271 (5)	1.36
C(6)	0.2164 (9)	0.1001 (7)	0.1873 (5)	1.44
C(7)	0.616 (1)	0.0355 (7)	0.2339 (6)	2.45
C(8)	0.634 (1)	0.2420 (7)	0.3295 (6)	2.57
C(9)	0.057 (1)	0.1729 (7)	0.1665 (6)	2.47
C(10)	0.254 (1)	0.0246 (7)	0.0815 (6)	2.38
Cl	0.1276 (3)	0.1794 (2)	0.4831 (2)	3.47
H(5,1)	0.296 (8)	0.253 (5)	0.274 (5)	2.50
H(5,2)	0.400 (8)	0.229 (5)	0.163 (5)	2.50
H(7,1)	0.715 (7)	0.023 (5)	0.292 (5)	2.50
H(7,2)	0.528 (8)	−0.040 (5)	0.221 (5)	2.50
H(7,3)	0.657 (7)	0.070 (5)	0.167 (5)	2.50
H(8,1)	0.564 (8)	0.292 (5)	0.362 (5)	2.50
H(8,2)	0.687 (7)	0.288 (5)	0.258 (5)	2.50
H(8,3)	0.728 (8)	0.218 (6)	0.379 (5)	2.50
H(9,1)	−0.059 (8)	0.128 (5)	0.141 (5)	2.50
H(9,2)	0.059 (8)	0.233 (5)	0.099 (5)	2.50
H(9,3)	0.019 (8)	0.210 (6)	0.227 (5)	2.50
H(10,1)	0.377 (8)	−0.037 (5)	0.088 (5)	2.50
H(10,2)	0.147 (8)	−0.035 (5)	0.055 (5)	2.50
H(10,3)	0.273 (7)	0.081 (5)	0.021 (5)	2.50
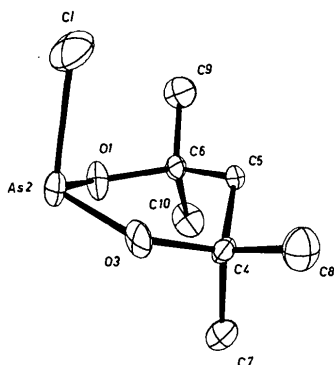
Fig. 1. Conformation of the molecule and numbering of the atoms.

Discussion. The dioxarsenane ring is in a twist-boat form with the As—Cl group in the axial position, with a pseudo C_2 axis through O(3) and C(6) and flattened around As(2). This can be seen from the torsion angles and the ring-puckering parameters listed in Tables 2 and 3, respectively.

This conformation could also be dominant in solution. Using the bond moments of As—O and As—Cl (Arbusov, Anonimova, Vul'fson, Yuldasheva, Chadaeva & Vereshchagin, 1974) and the X-ray geometry, a dipole moment of 1.03×10^{-29} C m is calculated. This value correlates well with the experimental dipole moment, 1.10×10^{-29} C m.

A similar conformation was observed in the crystal structure of 4,4-dimethyl-6,6-diphenyl-1,3,2-dioxa-thiane 2-oxide (MPS; Petit, 1982) and of *trans*-5-chloro-*cis,trans*-4,6-di-*tert*-butyl-1,3,2-dioxathiane 2-oxide (CBTS, Carbonelle, Jeannin & Robert, 1978). They can be explained in terms of the anomeric effect.

The anomeric effect accounts for the stabilizing non-bonding 'interaction of lone-pair orbitals with an anti-bonding σ^* or π^* orbital on adjacent atoms. The interaction stabilizes the rotamer having the largest number of lone pairs in the antiperiplanar position to electronegative groups. In six-membered rings with O atoms in 1 and 3 positions the effect is at a maximum when the most electronegative group on atom 2 is in the axial position. Therefore, in the absence of other factors, the chair conformation with an axial electronegative substituent is normally preferred. Increase of steric hindrance, such as in *cis,cis*-4,6-dimethyl-1,3,2-dioxathiane 2-oxide (Petit, Lenstra & Geise, 1978), causes a change in conformation towards the chair form with an equatorial substituent. If such a transition does not produce relief in steric strain, as in MPS, CBTS and the present structure, a (twist)-boat

Table 2. *Torsion angles* (°) *in the dioxarsenane ring*

C(6)–O(1)–As(2)–O(3)	−33.5 (8)	O(3)–C(4)–C(5)–C(6)	−62.6 (8)
O(1)–As(2)–O(3)–C(4)	8.1 (8)	C(4)–C(5)–C(6)–O(1)	40.0 (8)
As(2)–O(3)–C(4)–C(5)	32.5 (8)	C(5)–C(6)–O(1)–As(2)	12.4 (8)
$\alpha_1{}^a$	17.0 (8)		
$\alpha_2{}^b$	47.2 (8)		

(*a*) α_1 is the angle between the plane O(1)As(2)O(3) and the least-squares plane through O(1)O(3)C(4)C(6). (*b*) α_2 is the angle between the plane C(4)C(5)C(6) and the least-squares plane through O(1)O(3)C(4)C(6).

Table 3. *Ring-puckering parameters* (*Cremer & Pople, 1975; Cremer, 1975*) *of the dioxarsenane ring*

The e.s.d.'s were calculated as described by Norrestam (1981).

	q_2 (Å)	q_3 (Å)	Q (Å)	θ (°)	φ (°)
Dioxarsenane ring	0.577 (6)	−0.100 (6)	0.586 (6)	99.9 (6)	33.9 (6)
Ideal chair^a	0	0.560	0.560	0 / 180	
Ideal boat^a	0.7	0	0.7	90	$n\pi/3$
Ideal twist-boat^a	0.7	0	0.7	90	$(2n + 1)\pi/6$

(*a*) The values for the idealized forms refer to a ring with equal bond lengths (1.535 Å) and tetrahedral valence angles.

Table 4. *Bond lengths (Å) and valence angles (°) with e.s.d.'s in parentheses*

O(1)—As(2)	1·743 (4)	O(3)—As(2)	1·738 (4)
O(1)—C(6)	1·466 (6)	O(3)—C(4)	1·481 (6)
C(5)—C(6)	1·538 (8)	C(4)—C(5)	1·520 (8)
C(6)—C(9)	1·490 (10)	C(4)—C(7)	1·510 (8)
C(6)—C(10)	1·523 (8)	C(4)—C(8)	1·530 (10)
As(2)—Cl	2·258 (2)	⟨C—H⟩	1·00 (6)

As(2)—O(1)—C(6)	126·3 (4)	As(2)—O(3)—C(4)	123·6 (3)
O(1)—As(2)—Cl	100·9 (2)	O(3)—As(2)—Cl	97·9 (1)
O(1)—C(6)—C(5)	110·4 (5)	O(3)—C(4)—C(5)	109·2 (5)
O(1)—C(6)—C(9)	107·5 (5)	O(3)—C(4)—C(7)	107·1 (5)
O(1)—C(6)—C(10)	105·2 (5)	O(3)—C(4)—C(8)	104·4 (5)
C(5)—C(6)—C(9)	109·7 (6)	C(5)—C(4)—C(7)	117·1 (6)
C(5)—C(6)—C(10)	113·9 (6)	C(5)—C(4)—C(8)	108·6 (5)
C(9)—C(6)—C(10)	109·8 (6)	C(7)—C(4)—C(8)	109·7 (6)
O(1)—As(2)—O(3)	101·1 (2)	⟨C—C—H⟩	110 (3)
C(4)—C(5)—C(6)	119·2 (5)	⟨H—C—H⟩	108 (5)

form occurs. In this conformation the steric hindrance due to ring substituents is relieved, while an intermediate stabilization *via* the anomeric interaction can remain. Bond lengths and valence angles are given in Table 4. The As—Cl bond is longer than normal [2·258 *vs* 2·161 Å in $AsCl_3$ and $As(CH_3)_2Cl$ (Sutton, 1965)] in accordance with the anomeric effect. The $n(O)—\sigma^*$ (As—Cl) delocalization causes an increase in electron density in the anti-bonding σ^* (As—Cl) orbital with a consequent lengthening of the bond and a decrease of the force constant. One also notices that the C—O bonds are longer than those normally encountered in ethers and alcohols (1·43–1·44 Å). The same phenomenon was observed in cyclic sulfites (Petit, 1982) and cyclic phosphates (Van Nuffel, Lenstra & Geise, 1980, 1981, 1982).

Bond angles are found to be normal. The As—O—C angles (123·6 and 126·3°) may seem large, but similar values were observed for P—O—C in 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-oxide (Silver & Rudman, 1972) and in 2α-bromo-5β-bromoethyl-5α-methyl-1,3,2-dioxaphosphorinane 2-oxide

(Beineke, 1969). Again, such values fit in with the anomeric effect, since the delocalization increases the sp^2 character of the O atoms in the ring.

References

ARBUSOV, B. A., ANONIMOVA, I. V., VUL'FSON, S. G., YULDASHEVA, L. K., CHADAEVA, N. A. & VERESHCHAGIN, A. N. (1974). *Phosphorus*, **5**, 17–20.
BEINEKE, T. A. (1969). *Acta Cryst.* B**25**, 413–419.
CARBONELLE, A. C., JEANNIN, Y. & ROBERT, F. (1978). *Acta Cryst.* B**34**, 1631–1634.
CREMER, D. (1975). *Quantum Chem. Program Exch.* **11**, 288.
CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
KAMAI, G. KH. & CHADAEVA, N. A. (1951). *Dokl. Akad. Nauk SSSR*, **81**, 837–840.
LIPSON, H. & COCHRAN, W. (1968). *The Determination of Crystal Structures*, p. 301. London: Bell.
NORRESTAM, R. (1981). *Acta Cryst.* A**37**, 764–765.
PETIT, G. H. (1982). PhD Thesis, Univ. of Antwerp.
PETIT, G. H., LENSTRA, A. T. H. & GEISE, H. J. (1978). *Bull. Soc. Chim. Belg.* **87**, 659–666.
SAMITOV, YU. YU., YULDASHEVA, L. K. & ANONIMOVA, I. V. (1982). *Zh. Org. Khim.* **18**, 406–415.
SILVER, L. & RUDMAN, R. (1972). *Acta Cryst.* B**28**, 574–578.
SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*, p. 535. London: The Chemical Society.
VAN NUFFEL, P., LENSTRA, A. T. H. & GEISE, H. J. (1980). *Cryst. Struct. Commun.* **9**, 733–738.
VAN NUFFEL, P., LENSTRA, A. T. H. & GEISE, H. J. (1981). *Acta Cryst.* B**37**, 133–136.
VAN NUFFEL, P., LENSTRA, A. T. H. & GEISE, H. J. (1982). *Bull. Soc. Chim. Belg.* **91**, 43–48.

catena-Poly{copper(I)-di-μ-bromo-copper(I)-2,3 : 2,4-[bis-μ-(1,4-oxathiane-S : S)]-[di-μ-bromo-dicopper(I)]-3,1 : 4,1-[bis-μ-(1,4-oxathiane-S : S)]}

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Abstract. $(C_4H_8BrCuOS)_n$, orthorhombic, *Fdd*2, $a = 37·91$ (2), $b = 15·11$ (1), $c = 9·95$ (1) Å, $V = 5699·6$ Å^3, $F(000) = 3839$, $D_c = 2·31$ g cm^{-3}, $Z = 32$, μ(Cu $K\alpha$) = 121·7 cm^{-1}. Final $R = 0·067$ for 1302 observed reflexions. The structure contains Cu_2Br_2 rings linked by S-bridging 1,4-oxathiane molecules into