The Structure of *cis*-2-Fluoro-4-methyl-1,3,2-dioxaphosphorinane 2-Sulphide*

By A. Miller, M. W. Wieczorek and J. Karolak-Wojciechowska

Institute of General Chemistry, Technical University, 90-924 Łódź, Poland

and M. Mikołajczyk and B. Ziemnicka

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulphur Compounds, 90-362 Łódź, Boczna 5, Poland

Abstract. $C_4H_8FO_2PS$, monoclinic, $P2_1/c$, $a = 5 \cdot 868$ (1), $b = 11 \cdot 353$ (2), $c = 11 \cdot 479$ (2) Å, $\beta = 81 \cdot 27$ (1)°, $V = 755 \cdot 86$ Å^3, $Z = 4$, $D_m = 1 \cdot 49$, $D_c = 1 \cdot 506$ Mg m^{-3}, $F(000) = 352 \cdot 0$, $\mu(\text{Cu } K\alpha) = 5 \cdot 26$ mm^{-1}. The structure has been determined by direct methods and refined by full-matrix least squares to $R = 0 \cdot 032$ for 894 observed reflections. The conformation of the 1,3,2-dioxaphosphorinane ring is briefly discussed.

Introduction. In the course of our studies (Mikołajczyk, Krzywański & Ziemnicka, 1975) on nucleophilic substitution at the thiophosphoryl centre we have prepared the diastereoisomerically pure *cis*-2-fluoro-4-methyl-1,3,2-dioxaphosphorinane 2-sulphide (I). The NMR data (^{1}H, ^{31}P, ^{13}C and ^{19}F) were consistent with a rigid chair conformation in which the thiophosphoryl S and the methyl group are situated in equatorial positions. In the present paper we report the results of the X-ray analysis of (I) undertaken in order to confirm our configurational assignment and to determine the solid-state conformation of the 1,3,2-dioxaphosphorinane ring.

(I)
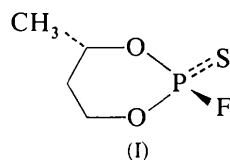
Preliminary unit-cell parameters were obtained from Weissenberg photographs and were refined from diffractometric measurements. The intensity data were collected on a Syntex $P2_1$ four-circle diffractometer (Cu $K\alpha$ radiation, graphite monochromator). Measurements were carried out in the θ–2θ scan mode for $2\theta \leq 116°$. 1028 independent reflections were collected and 894 were considered to be observed ($I \geq 3\sigma$) and included in the refinement. No correction for absorption was applied.

The structure was determined by direct methods with *SHELX* 76 (Sheldrick, 1976). The E map gave the positions of all non-hydrogen atoms. All H atoms were found in the difference Fourier map. The refinement was carried out by full-matrix least squares, refining H atoms isotropically and the non-hydrogen atoms anisotropically. The final R value was 0·032 ($R_w = 0 \cdot 043$);† the weights were given by $w = |\sigma^2(F) +$

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature parameters for the non-hydrogen atoms*

$$B_{eq} = 8\pi^2 (U_{11} U_{22} U_{33})^{1/3}.$$

	x	y	z	B_{eq} (Å^2)
P	3633 (1)	999 (1)	3370 (1)	4·08 (4)
S	5864 (2)	664 (1)	2047 (1)	6·27 (5)
F	2089 (3)	−85 (1)	3781 (2)	5·71 (8)
O(1)	1826 (3)	1951 (2)	3183 (1)	4·23 (8)
O(2)	4612 (3)	1330 (2)	4512 (2)	4·59 (8)
C(1)	219 (4)	2415 (2)	4205 (2)	4·21 (11)
C(2)	1600 (6)	2769 (3)	5147 (3)	5·12 (14)
C(3)	3008 (6)	1771 (3)	5530 (2)	5·02 (13)
C(4)	−1062 (6)	3409 (3)	3744 (3)	5·47 (15)

Table 2. *Positional parameters* ($\times 10^3$) *and isotropic temperature parameters for the hydrogen atoms*

	x	y	z	B (Å^2)
H(11)	−64 (4)	182 (3)	445 (2)	4·1 (5)
H(21)	261 (6)	345 (3)	484 (3)	5·9 (7)
H(22)	70 (6)	297 (3)	580 (3)	6·0 (7)
H(31)	223 (6)	103 (3)	583 (3)	6·2 (7)
H(32)	406 (5)	208 (3)	601 (2)	4·8 (6)
H(41)	4 (5)	398 (2)	332 (3)	5·0 (6)
H(42)	−158 (5)	311 (3)	314 (3)	5·5 (7)
H(43)	−226 (7)	374 (3)	441 (4)	7·4 (8)

Table 3. *Bond lengths* (Å)

P–S	1·887 (1)	C(1)–H(11)	0·86 (3)
P–F	1·558 (2)	C(2)–H(21)	1·01 (4)
P–O(1)	1·552 (2)	C(2)–H(22)	0·87 (4)
P–O(2)	1·555 (2)	C(3)–H(31)	0·99 (4)
O(1)–C(1)	1·485 (3)	C(3)–H(32)	0·95 (3)
O(2)–C(3)	1·473 (3)	C(4)–H(41)	0·99 (3)
C(1)–C(2)	1·501 (4)	C(4)–H(42)	0·87 (3)
C(2)–C(3)	1·507 (4)	C(4)–H(43)	1·02 (4)
C(1)–C(4)	1·497 (4)		

Table 4. *Bond angles* (°)

F–P–S	112·7 (1)	C(3)–O(2)–P	118·5 (2)
O(1)–P–S	115·8 (1)	C(2)–C(1)–O(1)	108·4 (2)
O(1)–P–F	102·4 (1)	C(4)–C(1)–O(1)	106·3 (2)
O(2)–P–S	115·3 (1)	C(4)–C(1)–C(2)	114·1 (3)
O(2)–P–F	102·0 (1)	C(3)–C(2)–C(1)	112·8 (3)
O(2)–P–O(1)	107·2 (1)	C(2)–C(3)–O(2)	109·7 (2)
C(1)–O(1)–P	120·2 (1)		
H(11)–C(1)–O(1)	104 (2)	H(32)–C(3)–O(2)	101 (2)
H(11)–C(1)–C(2)	109 (2)	H(32)–C(3)–C(2)	109 (2)
H(11)–C(1)–C(4)	114 (2)	H(32)–C(3)–H(31)	114 (2)
H(21)–C(2)–C(1)	108 (2)	H(41)–C(4)–C(1)	110 (2)
H(21)–C(2)–C(3)	111 (2)	H(42)–C(4)–C(1)	104 (2)
H(22)–C(2)–C(1)	111 (2)	H(42)–C(4)–H(41)	99 (3)
H(22)–C(2)–C(3)	103 (2)	H(43)–C(4)–C(1)	110 (2)
H(22)–C(2)–H(21)	111 (3)	H(43)–C(4)–H(41)	117 (3)
H(31)–C(3)–O(2)	101 (2)	H(43)–C(4)–H(42)	117 (3)
H(31)–C(3)–C(2)	111 (2)		

Table 5. *Geometry of the 1,3,2-dioxaphosphorinane ring*

Plane	Atoms in the plane	Deviations (Å) from plane
(i)	O(1)	–0·006 (1)
	O(2)	0·006 (1)
	C(1)	0·006 (1)
	C(3)	–0·006 (1)
(ii)	O(1), P, O(2)	0·0
(iii)	C(1), C(2), C(3)	0·0
(iv)	S, P, F	0·0

Inclination angles (°)

$$\alpha = \text{(i)/(ii)} = 34\cdot5\ (2)$$
$$\beta = \text{(i)/(iii)} = 53\cdot6\ (3)$$
$$\gamma = \text{(i)/(iv)} = 89\cdot5\ (2)$$

Table 6. *Torsion angles* (°)

C(1)–O(1)–P–O(2)	–40·4 (1)
C(3)–O(2)–P–O(1)	40·7 (2)
C(2)–C(3)–O(2)–P	–51·6 (2)
O(2)–C(3)–C(2)–C(1)	59·2 (2)
C(3)–C(2)–C(1)–O(1)	–57·5 (2)
C(2)–C(1)–O(1)–P	50·0 (2)

$0\cdot002096F^2]^{-1}$. The final positional parameters for the non-hydrogen atoms are given in Table 1 and for the H atoms in Table 2. Bond distances and angles with their standard deviations are given in Tables 3 and 4. The deformation of the ring in relation to the plane of symmetry is $\Delta C_s = 1\cdot4°$.

Discussion. The dioxaphosphorinane ring in (I) adopts a chair conformation with the axial P—F and equatorial C(1)—C(4) bonds as illustrated in Fig. 1. Detailed information on the geometry of the six-membered ring is given in Table 5. The differences ($\alpha - \beta$) are chosen to illustrate the degree of distortion of the chair from the ideal cyclohexane conformation ($\alpha = \beta \simeq 55°$). The conformation of the 1,3,2-dioxaphosphorinane ring may also be described by its torsion angles (see Table 6). The distorted tetrahedral configuration around P is usual for this type of compound (Wieczorek, Sheldrick, Karolak-Wojciechowska, Mikołajczyk & Ziemnicka, 1979). The length of the P=S bond is 1·887 (1) Å; this is shorter than the normally observed length for this type of bond [1·93 Å on average (Corbridge, 1974)]. However, the P—F bond, which in (I) was found to be

1·558 (2) Å, is longer than that normally observed (1·49–1·54 Å) (Corbridge, 1974). These changes in the bond lengths can be accounted for by the presence of the strongly electronegative F. The P—O(1) and P—O(2) single bonds are 1·552 (2) and 1·555 (2) Å respectively. They lie within the normal range (1·522–1·584 Å) for this type of compound (Cameron & Karolak-Wojciechowska, 1977).

The other bond lengths and angles in the dioxaphosphorinane ring in (I) are consistent with the literature data (Corbridge, 1974).
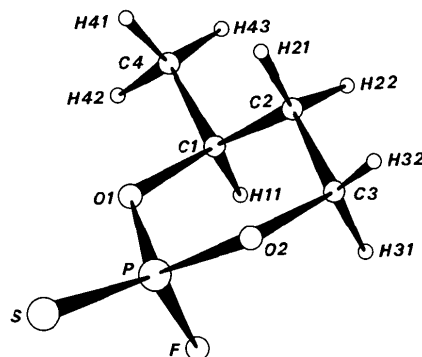

Fig. 1. A perspective view of a molecule of (I).

References

CAMERON, S. & KAROLAK-WOJCIECHOWSKA, J. (1977). *Acta Cryst.* B33, 2342–2344.

CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phosphorus*, pp. 219, 276, 407. Amsterdam: Elsevier.

MIKOŁAJCZYK, M., KRZYWAŃSKI, J. & ZIEMNICKA, B. (1975). *Tetrahedron Lett.* pp. 1607–1610.

SHELDRICK, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.

WIECZOREK, M. W., SHELDRICK, W. S., KAROLAK-WOJCIECHOWSKA, J., MIKOŁAJCZYK, M. & ZIEMNICKA, B. (1979). *Acta Cryst.* B35, 2339–2344.

1,2,3,4,7,7-Hexachloro-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene [Alodan (Hoechst)®]*

BY COLIN H. L. KENNARD

Department of Chemistry, University of Queensland, Brisbane 4067, Australia

GRAHAM SMITH

Department of Chemistry, Queensland Institute of Technology, Brisbane 4000, Australia

AND TOR BJÖRN PALM

Arrhenius Laboratory, University of Stockholm, Fack, Stockholm, Sweden

Abstract. $C_9H_6Cl_8$, $M_r = 397.8$, orthorhombic, *Pbca*, $a = 16.596$ (3), $b = 11.893$ (4), $c = 14.379$ (5) Å, $Z = 8$, $D_x = 1.86$ Mg m^{-3}, μ(Mo $K\alpha$) = 1.55 mm^{-1}, $R = 0.047$, 1858 observed reflections. The configuration of the hexachloro-8,9,10-trinorbornene moiety is similar to that found in other cyclodiene insecticides. The Cl atoms of the *endo*-chloromethyl groups in the cyclopentene ring adopt different relative conformations, thus destroying the mirror symmetry of the molecule. One C–Cl bond adopts a parallel, the other a perpendicular orientation with respect to the plane containing the bridgehead chlorines.

Introduction. Alodan† is the trademark (Hoechst–Roussell) given to the simplest 'cyclodiene' compound having insecticidal properties. Activity appears in Alodan and compounds with a single halomethyl group at the unsubstituted positions of the hexachloro-8,9,10-trinorbornene moiety, the activity increasing I > Br (Bromodan) > Cl (Alodan) (Soloway, 1965). Alodan has low mammalian toxicity and some acaricidal activity and was introduced as a dusting powder or a solution concentrate for control of animal ectoparasites (Brooks, 1974). The X-ray structure was determined as part of a continuing investigation of the systematics of structural features of agriculturally important chemicals.

Colourless prismatic crystals (m.p. 376 K) were grown from aqueous isopropyl alcohol. 1858 unique reflections with $I > 2.5\sigma(I)$ were considered observed out of a reduced data set of 2471 ($2\theta_{max} = 54°$) from a total of 6912 reflections ($2\theta_{max} = 70°$) collected from one crystal on a Philips PW1100 four-circle diffractometer. Monochromatized Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation was used. The data were corrected for Lorentz and monochromator polarization effects and for absorption.

The structure was solved by the multisolution Σ_2 sign-expansion direct-methods approach of *SHELX* (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms reduced R ($= \sum \|F_o| - |F_c\|/\sum F_o$) from an initial value of 0.30 to 0.047 and R_w $[= (\sum w\|F_o| - |F_c\|^2/\sum w|F_o|^2)^{1/2}]$ to 0.051. $w = 1.77[(\sigma F_o)^2 + 0.00127(F_o)^2]$ was found to be suitable. H atoms were located in a difference-Fourier synthesis and their parameters were allowed to refine. A final difference-Fourier map revealed no features higher than 0.19 e Å^{-3}. No corrections were made for extinction.

* Cyclodienes. VIII. Part VII: Isodrin (Kennard, Smith & Hovmöller, 1979).

† Common name: 5,6-bis(chloromethyl)-1,2,3,4,7,7-hexachloronorborn-2-ene.