

C9	0.9517 (3)	0.0955 (3)	0.1889 (2)	0.0382
C10	0.9463 (2)	0.2326 (3)	0.2264 (2)	0.0372
C11	0.5217 (3)	0.0053 (3)	0.2597 (2)	0.0389
C12	0.5239 (3)	-0.0181 (3)	0.3910 (2)	0.0432
C13	0.3931 (3)	-0.0314 (4)	0.1717 (3)	0.0559
C14	0.9289 (4)	0.3240 (4)	0.1434 (2)	0.0592
C15	0.8465 (3)	0.1684 (3)	0.6614 (2)	0.0387
C16	0.6591 (3)	-0.0594 (3)	-0.0284 (2)	0.0385
C17	0.5835 (3)	-0.0219 (3)	-0.1582 (2)	0.0410
C18	0.5079 (3)	0.1068 (4)	-0.1825 (2)	0.0495
C19	0.5887 (4)	-0.1051 (4)	-0.2466 (2)	0.0600

Table 2. Selected geometric parameters (Å, °)

O3—C6	1.464 (2)	C5—C6	1.516 (3)	
O3—C12	1.336 (2)	C6—C7	1.548 (3)	
C1—C2	1.542 (3)	C7—C8	1.520 (3)	
C1—C5	1.554 (3)	C7—C11	1.496 (3)	
C1—C10	1.524 (3)	C8—C9	1.522 (3)	
C2—C3	1.524 (3)	C9—C10	1.508 (3)	
C3—C4	1.541 (3)	C11—C12	1.474 (3)	
C4—C5	1.557 (2)			
C12—O3—C6	112.0 (2)	C7—C6—O3	105.2 (1)	
C5—C1—C2	104.2 (2)	C7—C6—C5	112.2 (2)	
C10—C1—C2	113.6 (2)	C8—C7—C6	110.6 (2)	
C10—C1—C5	118.5 (2)	C11—C7—C6	103.7 (2)	
C3—C2—C1	107.5 (2)	C11—C7—C8	117.3 (2)	
C4—C3—C2	105.7 (2)	C9—C8—C7	112.3 (2)	
C5—C4—C3	105.4 (1)	C10—C9—C8	114.8 (2)	
C4—C5—C1	101.3 (1)	C9—C10—C1	119.0 (2)	
C6—C5—C1	111.7 (2)	C12—C11—C7	107.9 (2)	
C6—C5—C4	117.6 (2)	C11—C12—O3	109.9 (2)	
C5—C6—O3	110.9 (2)	C4—C15—C11	111.1 (1)	
D—H...A		D...A		D—H...A
O1—H1...O4 ⁱ		2.873 (3)		149 (3)
O2—H2...O7 ⁱⁱ		2.823 (3)		164 (3)
O7—H3...O6 ⁱⁱⁱ		2.888 (4)		177 (3)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, 1 - z$; (ii) $1 + x, y, 1 + z$; (iii) $1 - x, \frac{1}{2} + y, -z$.

Table 3. Conformation of chlorojanerin found in the crystal (X-ray) and in solution (¹H NMR) defined by the interproton dihedral angle $\varphi(H_i, H_j)$

H_i, H_j	$\varphi(H_i, H_j)$ (X-ray)	$^3J(H_i, H_j)$ (Hz)	$\varphi(H_i, H_j)$ (¹ H NMR)*
H1 α /H2 α	-36 (2)	11.3	15
H1 α /H2 β	-154 (2)	7.5	145
H1 α /H5 α	42 (2)	8.5	40
H2 α /H3 α	8 (2)	6.1	30
H2 β /H3 α	123 (2)	0.0	90
H5 α /H6 β	-179 (2)	11.0	170
H6 β /H7 α	-140 (2)	9.0	135
H7 α /H8 β	-173 (2)	9.5	160
H8 β /H9 β	-35 (2)	5.0	40
H8 β /H9 α	82 (2)	1.5	80

* The sign of the interproton dihedral angle cannot be determined due to the periodicity of the Karplus relationship.

The structure was solved by direct methods. All H atoms were refined isotropically, with non-H atoms being refined anisotropically.

Data collection: Syntex R3 software. Cell refinement: Syntex R3 software. Data reduction: CRYSTALS (Watkin, Carruthers & Betteridge, 1985). Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994). Program(s) used to refine structure: CRYSTALS. Molecular graphics: CRYSTAN88 (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: CRYSTALS and local software.

Financial support from BASF Aktiengesellschaft, Ludwigshafen, and Fonds der Chemischen Industrie are gratefully acknowledged. We also wish to thank Mr V. Brecht for carefully measuring the NMR spectra.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1793–1795

(Bromodifluoromethyl)diphenylphosphine Sulfide

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(Received 14 March 1996; accepted 1 April 1996)

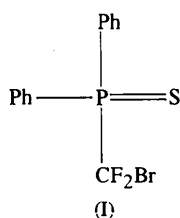
Abstract

The P—S bond in C₁₃H₁₀BrF₂PS is somewhat shorter [1.9348 (11) Å] and the P—CF₂Br bond longer [1.884 (3) Å] than standard values, which may reasonably be attributed to the halogen substituents. The conformation about the P—CF₂Br bond is *gauche*.

Comment

Surprisingly few compounds containing the moiety Ph₂P(=S)R have been subjected to structure determi-

nation; as far as we are aware there are none where *R* is a halogen-substituted alkyl group.



The title compound [(I), Fig. 1] adopts the expected *gauche* conformation about the P—C1 bond; a typical torsion angle is S—P—C1—Br $-65.4(2)^\circ$. The phenyl rings subtend an interplanar angle of $67.16(12)^\circ$.

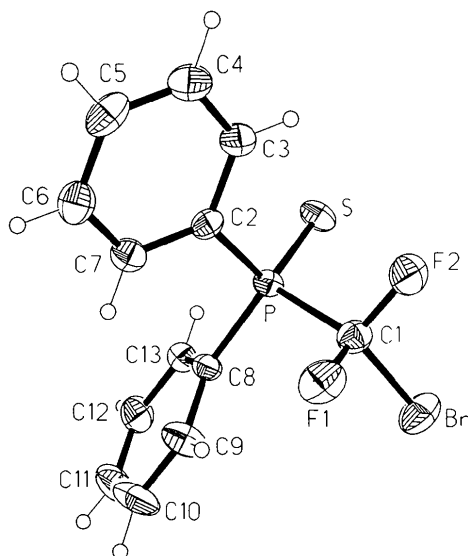


Fig. 1. The molecule of the title compound in the crystal. Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.

As is usual for thiophosphoryl compounds, repulsion from the electrons of the P=S double bond causes the S—P—C angles to be the widest angles at phosphorus; the smallest such angle is S—P—C1, which is probably attributable to the effect of the halogen substituents at C1, which remove electron density from the P—C bond and thus lower the electrostatic repulsion.

The P=S bond [$1.9348(11)$ Å] is slightly shorter than the normal value for C₃P=S systems (1.954 Å; Allen *et al.*, 1987), which is also consistent with the electron-withdrawing substituent at phosphorus (O or N substituents at phosphorus also decrease the P=S bond length). The P—CF₂Br bond is rather long at $1.884(3)$ Å. However, it would be unwise to consider the effects on bond lengths as general in the absence of further examples.

There are no unusually short intermolecular contacts.

Experimental

The title compound was obtained from Ph₂PCF₂Br and P(=S)Cl₃ and recrystallized from dichloromethane/petroleum ether (Ruhnau, 1992).

Crystal data

C₁₃H₁₀BrF₂PS

M_r = 347.15

Monoclinic

C2/*c*

a = $15.312(5)$ Å

b = $10.300(3)$ Å

c = $17.554(5)$ Å

β = $93.68(3)^\circ$

V = $2762.8(14)$ Å³

Z = 8

D_x = 1.669 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 50 reflections

θ = 10 – 11.3°

μ = 3.243 mm⁻¹

T = $173(2)$ K

Prism

$0.70 \times 0.48 \times 0.44$ mm

Colourless

Data collection

Siemens R3 diffractometer

ω-scans

Absorption correction:

ψ scans (XEMP; Nicolet, 1987)

T_{min} = 0.716 , *T_{max}* =

0.776

2496 measured reflections

2412 independent reflections

1980 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0247

θ_{max} = 25.00°

h = -18 → 18

k = 0 → 12

l = 0 → 20

3 standard reflections

monitored every 147

reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0313

wR(*F*²) = 0.0856

S = 1.065

2410 reflections

163 parameters

H atoms riding

w = $1/[\sigma^2(F_o^2) + (0.0406P)^2 + 5.8511P]$

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = -0.001

Δρ_{max} = 0.468 e Å⁻³

Δρ_{min} = -0.491 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Br	0.36198 (3)	0.74855 (4)	0.44550 (2)	0.04484 (14)
P	0.31079 (5)	0.55957 (7)	0.30711 (4)	0.0214 (2)
S	0.38556 (5)	0.42131 (8)	0.34777 (5)	0.0298 (2)
F1	0.31595 (14)	0.8201 (2)	0.30150 (11)	0.0424 (5)
F2	0.44153 (13)	0.7274 (2)	0.31488 (12)	0.0405 (5)
C1	0.3593 (2)	0.7214 (3)	0.3367 (2)	0.0290 (7)
C2	0.3053 (2)	0.5729 (3)	0.2046 (2)	0.0238 (6)
C3	0.3810 (2)	0.5458 (3)	0.1673 (2)	0.0323 (7)
C4	0.3800 (2)	0.5534 (4)	0.0888 (2)	0.0404 (8)
C5	0.3039 (2)	0.5874 (3)	0.0469 (2)	0.0387 (8)
C6	0.2284 (2)	0.6139 (3)	0.0836 (2)	0.0346 (7)
C7	0.2292 (2)	0.6071 (3)	0.1620 (2)	0.0278 (7)
C8	0.2011 (2)	0.5621 (3)	0.3393 (2)	0.0238 (6)

C9	0.1476 (2)	0.6716 (4)	0.3348 (2)	0.0403 (8)
C10	0.0636 (2)	0.6645 (4)	0.3591 (2)	0.0513 (10)
C11	0.0320 (2)	0.5500 (4)	0.3869 (2)	0.0481 (10)
C12	0.0844 (2)	0.4418 (4)	0.3915 (2)	0.0380 (8)
C13	0.1692 (2)	0.4475 (3)	0.3676 (2)	0.0281 (7)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Br—C1	1.927 (3)	P—S	1.9348 (11)
P—C2	1.801 (3)	F1—C1	1.343 (4)
P—C8	1.807 (3)	F2—C1	1.341 (4)
P—C1	1.884 (3)		
C2—P—C8	109.04 (14)	F2—C1—F1	106.2 (2)
C2—P—C1	101.57 (14)	F2—C1—P	108.8 (2)
C8—P—C1	105.00 (14)	F1—C1—P	111.6 (2)
C2—P—S	114.42 (10)	F2—C1—Br	108.4 (2)
C8—P—S	115.82 (10)	F1—C1—Br	109.0 (2)
C1—P—S	109.62 (11)	P—C1—Br	112.6 (2)

Data collection: *P3* (Nicolet, 1987). Cell refinement: *P3*. Data reduction: *XDISK* (Nicolet, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

Crystals of the title compound were kindly provided by Dr C. Ruhnau and Professor M. Fild of this Institute. I thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauff for technical assistance.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1795–1797

A Diaza Analogue of Benzo-15-crown-5

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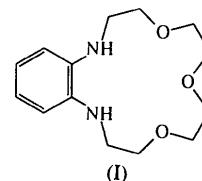
(Received 1 February 1996; accepted 4 March 1996)

Abstract

The title compound, 2,3-benzo-7,10,13-trioxa-1,4-diaza-2-pentadecene, $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$, is a derivative of benzo-15-crown-5 in which the two O atoms flanking the aromatic ring are replaced by NH groups. Except for the rigidly near-planar $\text{OC}_6\text{H}_4\text{O}$ segment, the macrocycle contains *gauche* C—C and a mixture of *gauche* and *anti* C—O and C—N linkages.

Comment

The title compound, (I), was prepared as part of a study of selective complexation of a range of metal ions by crown ethers and their derivatives. Many complexes are known which incorporate 15-crown-5 as a ligand, covering a wide range of over 30 different metal ions; a search of the Cambridge Structural Database (Allen & Kennard, 1993) produced a substantial list.



Substitution of one or more of the O atoms by NH groups alters the complexing ability of the ligand, since the basicity of the NH group in such macrocycles has been found to be lower than that of the replaced O atom (Frensdorff, 1971; Blackborow, Lockhart, Thompson & Thompson, 1978), with even the remaining O atoms showing reduced basicity compared with the parent crown ether (Lockhart, Atkinson, Marshall & Davies, 1979).

Although the Cambridge Structural Database contains around twenty structures related to 15-crown-5 (free or complexed to a metal) in which one O atom has been replaced by NH or NR and almost as many in which two non-adjacent O atoms have been replaced, there are no previous reports of disubstitution in adjacent positions, except where the two N atoms act as bridgeheads in a bicyclic molecule.