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9,9,10,10-Tetrafluoro-1,3,5,7-tetrathio-2,4,6,8-tetraoxa-1,3,5,7-tetraphosphatricyclo[3.3.1.1^{3,7}]decane, $P_4O_4(CF_2)_2S_4$: a Cage Structure Related to P_4O_6

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Abstract

The title structure is formally derived from the P_4O_6 cage structure by sulfuration of the P atoms (as in the known structure $P_4O_6S_4$) and replacement of two bridging O atoms by CF_2 groups. The molecule possesses crystallographic twofold symmetry. The main effect of introducing the CF_2 groups is to widen the remaining P—O—P angles and shorten the P—O bonds; the P—C bonds are longer than the P—O bonds and the P—C—P angles narrower than the P—O—P angles.

Comment

The cage structure of 'phosphorus trioxide', P_4O_6, may be regarded as one of the classic structures in inorganic chemistry and has been well established for many years (Wells, 1984). A single-crystal X-ray structure analysis, however, has been performed only recently (Jansen & Moebs, 1984). Closely related structures are observed in species where some or all of the P atoms bear additional terminal substituents such as =O or =S, *e.g.* P_4O_7 (Jansen & Voss, 1981; Jost & Schneider, 1981), P_4O_9 (Jansen & Lüer, 1991), P_4O_{10} (Jansen & Lüer, 1986), P_4O_6S (Frick, Jansen, Bruna & Peyerimhoff, 1991), and $P_4O_6S_4$ (Mijlhoff, Portheine & Romers, 1967).

Recent work in this Institute (Groddeck, 1990) involved the sulfuration of difluoromethanebis(dichlorophosphonate), $[Cl_2P(=O)]_2CF_2$, with P_4S_{10}. Among the products was a colourless crystalline solid, which is shown by this X-ray investigation to be the title compound (1).

As shown in Fig. 1, the structure of (1) is based on the P_4O_6 cage. All four P atoms bear an additional terminal sulfur (=S) substituent, and CF_2 groups take the place of two of the bridging O atoms. The molecule possesses crystallographic twofold symmetry, whereby the atoms O(1) and O(2) occupy special positions $\frac{1}{4}, y, \frac{1}{4}$.

Despite the apparent suitability of cage structures for rigid-body libration corrections, R_{lib} (Schomaker & Trueblood, 1968) was high (0.11), perhaps because of the CF_2 groups, and the associated bond-length corrections of 0.003–0.004 Å may not be reliable. We prefer to discuss uncorrected bond lengths.

The incorporation of the CF_2 groups introduces the expected distortions into the cage structure. The P—C—P angles (113.5°) are much narrower than the P—O—P angles [average 130.7°; *cf.* average 127.0° in P_4O_6 (Jansen & Moebs, 1984)] and the P—C bonds (average 1.870 Å) are longer than the P—O bonds (average 1.616 Å; *cf.* average 1.647 Å in P_4O_6). The molecular dimensions involving P^{III} in the other related phosphorus–oxygen cages mentioned above display similar values to those in P_4O_6. Their P^V—O single bonds are slightly shorter, typically in the range 1.58–1.60 Å, which is consistent with the values observed in (1), whereas their P—O—P angles involving at least one P^V atom are narrower than the P—O—P angles in P_4O_6 (123–124°).

The terminal P=S bonds (1.869 Å) in (1) are slightly shorter than in P_4O_6S [1.890 (1) Å (Frick, Jansen, Bruna & Peyerimhoff, 1991)] and P_4S_{10} [average 1.908 Å (Vos, Olthof, van Bolhuis & Botterweg, 1965)].

There are no unusually short intermolecular contacts; the shortest are F(2)···F(2) ($\frac{3}{2} - x$, y, $\frac{1}{2} - z$) 2.80 (1) Å and O(2)···O(1) (x, $-1 + y$, z) 2.88 (1) Å.

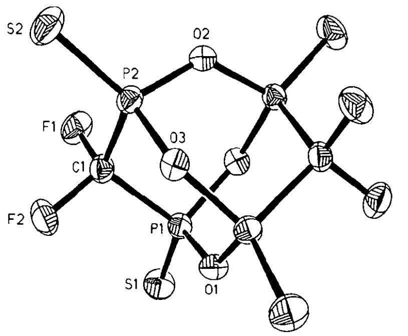

Fig. 1. The molecule of the title compound, showing the atom-numbering scheme of the asymmetric unit. Ellipsoids are drawn at the 50% level.

Experimental

Crystal data

$C_2F_4O_4P_4S_4$
M_r = 416.1
Monoclinic
$P2/n$
a = 8.283 (2) Å
b = 6.428 (2) Å
c = 12.707 (3) Å
β = 101.39 (2)°

D_x = 2.084 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 50 reflections
θ = 10–12.5°
μ = 1.2 mm^{-1}
T = 178 K
Prism

$V = 663.3$ (3) Å^3
$Z = 2$

0.7 × 0.4 × 0.2 mm
Colourless

Data collection

Siemens *R*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.91$, $T_{\max} = 1.11$
3067 measured reflections
1538 independent reflections
1416 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.018$
$\theta_{\max} = 27.5°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 147 reflections intensity variation: <1.5%

Refinement

Refinement on *F*
Final $R = 0.027$
$wR = 0.038$
$S = 2.0$
1416 reflections
84 parameters
$w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.4$ e Å^{-3}

$\Delta\rho_{\min} = -0.4$ e Å^{-3}
Extinction correction: $F_{\rm corr} = F/(1+0.002xF^2/\sin2\theta)^{-0.25}$
Extinction coefficient: $x = 0.0017$ (5)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The structure was solved by direct methods and refined by full-matrix techniques with all atoms anisotropic. The program system *SHELXTL-Plus* (Sheldrick, 1990) was employed.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	$U_{\rm eq}$
P(1)	0.26261 (5)	0.41095 (6)	0.13623 (3)	0.0222 (1)
P(2)	0.42706 (5)	0.06743 (6)	0.29648 (3)	0.0228 (1)
S(1)	0.26484 (6)	0.59362 (7)	0.02213 (4)	0.0353 (2)
S(2)	0.60060 (6)	−0.11384 (8)	0.34939 (4)	0.0372 (2)
O(1)	0.25000	0.51488 (24)	0.25000	0.0246 (5)
O(2)	0.25000	−0.03744 (24)	0.25000	0.0241 (5)
O(3)	0.38255 (14)	0.23951 (17)	0.37926 (8)	0.0241 (3)
C(1)	0.44559 (19)	0.23870 (25)	0.18067 (12)	0.0245 (4)
F(1)	0.46540 (14)	0.11746 (17)	0.09698 (8)	0.0349 (3)
F(2)	0.58028 (12)	0.36018 (18)	0.20892 (9)	0.0353 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

P(1)—S(1)	1.869 (1)	P(1)—O(1)	1.615 (1)
P(1)—C(1)	1.872 (2)	P(2)—S(2)	1.869 (1)
P(2)—O(2)	1.616 (1)	P(2)—O(3)	1.618 (1)
P(2)—C(1)	1.868 (2)	O(3)—P(1$^{\rm i}$)	1.614 (1)
C(1)—F(1)	1.354 (2)	C(1)—F(2)	1.351 (2)
S(1)—P(1)—O(1)	116.6 (1)	S(1)—P(1)—C(1)	118.3 (1)
O(1)—P(1)—C(1)	99.6 (1)	S(1)—P(1)—O(3$^{\rm i}$)	117.1 (1)
O(1)—P(1)—O(3$^{\rm i}$)	102.3 (1)	C(1)—P(1)—O(3$^{\rm i}$)	99.9 (1)
S(2)—P(2)—O(2)	116.7 (1)	S(2)—P(2)—O(3)	116.7 (1)
O(2)—P(2)—C(1)	99.7 (1)	S(2)—P(2)—C(1)	118.3 (1)
P(1)—O(1)—P(1$^{\rm i}$)	131.1 (1)	O(3)—P(2)—C(1)	100.0 (1)
P(2)—O(3)—P(1$^{\rm i}$)	130.3 (1)	P(2)—O(2)—P(2$^{\rm i}$)	130.7 (1)
P(1)—C(1)—F(1)	108.7 (1)	P(1)—C(1)—P(2)	113.5 (1)
P(1)—C(1)—F(2)	108.4 (1)	P(2)—C(1)—F(1)	108.7 (1)
F(1)—C(1)—F(2)	108.6 (1)	P(2)—C(1)—F(2)	108.9 (1)

Symmetry code: (i) $\frac{1}{2} - x, y, \frac{1}{2} - z$.

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Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71200 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1040]

References

Frick, F., Jansen, M., Bruna, P. J. & Peyerimhoff, S. D. (1991). *Chem. Ber.* **124**, 1711–1714.
Groddeck, A. (1990). PhD thesis, Technical Univ. of Braunschweig, Germany.
Jansen, M. & Lüer, B. (1986). *Z. Kristallogr.* **177**, 149–151.
Jansen, M. & Lüer, B. (1991). *Z. Kristallogr.* **197**, 247–248.
Jansen, M. & Moebs, M. (1984). *Inorg. Chem.* **23**, 4486–4488.
Jansen, M. & Voss, M. (1981). *Angew. Chem.* **93**, 120–121.
Jost, K. H. & Schneider, M. (1981). *Acta Cryst.* B**37**, 222–224.
Mijlhoff, F. C., Portheine, J. & Romers, C. (1967). *Receuil*, **86**, 257–262.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Vos, A., Olthof, R., van Bolhuis, F. & Botterweg, R. (1965). *Acta Cryst.* **19**, 864–867.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Wells, A. F. (1984). *Structural Inorganic Chemistry*, p. 855. Oxford: Clarendon Press.

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Structure of 2,3-Diphenyl-2-norbornene: Comparison with Data for a *cis*-Stilbene

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Abstract

The molecule 2,3-diphenyl-2-norbornene (2,3-diphenylbicyclo[2.2.1]hept-2-ene) (1) has been prepared as a model for *cis*-stilbene (2) in which single-bond but not double-bond torsion (within the π system) is sterically possible on both the ground-state and lowest triplet-state surfaces. A comparison of the crystal structure of (1) with previously published data for a derivative of (2) shows that the non-planar π-system geometries of (1) and (2) are indeed similar. This has allowed definitive conclusions to be

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