Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a stereopacking diagram, have been deposited with the IUCr (Reference: TA1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Espenbetov, A. A., Struchkov, Yu. T., Poplavskaya, I. A. & Kurmangalieva, R. G. (1985). *Izv. Akad. Nauk Kaz. SSR Ser. Khim.* pp. 56–57.
Grigereit, T. E., Ramakrishna, B. L., Place, H., Willett, R. D., Pellacani, G. C., Manfredini, T., Menabue, L., Bonamartini-Corradi, A. & Battaglia, L. P. (1987). *Inorg. Chem.* **26**, 2235–2243.
Place, H. & Willett, R. D. (1987*a*). *Acta Cryst.* C**43**, 1050–1053.
Place, H. & Willett, R. D. (1987*b*). *Acta Cryst.* C**43**, 1497–1500.
Roman, P., Beitia, J. I. & Luque, A. (1993). *Acta Cryst.* C**49**, 584–587.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1990). *SHELXTL/PC.* Release 4.1. Siemens Crystallographic Research Systems, Madison, Wisconsin, USA.
Siemens (1991). *XSCANS Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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2,8-Dithia-1-phospha-5-arsabicyclo[3.3.0]-octane 1-Oxide

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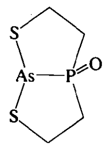
Abstract

The title compound, $C_4H_8AsOPS_2$, obtained by oxidation of $As(SCH_2CH_2)_2P$, shows a bicyclooctane structure with an As—P bond distance of 2.345 (1) Å. The compound shows weak intermolecular As···O interactions of 2.882 (2) Å.

Comment

In 1982, we reported a number of 2,8-dithia-1-phospha-5-arsabicyclo[3.3.0]octanes (Jurkschat, Mügge, Tzschach, Uhlig & Zschunke, 1982). A detailed conformational study of these compounds in solution, followed later by NMR spectroscopic analysis (Zschunke, Mügge, Meyer, Tzschach & Jurkschat, 1983), suggested that they exist in a preferred conformer with strong puckering of the fused five-membered rings. No single crystals of any of these compounds has been obtained thus far. However, oxide $As(SCH_2CH_2)_2PO$, hereafter (1), was obtained as a minor product by recrystallization of $As(SCH_2CH_2)_2P$ from toluene in the presence of air. Its ^{31}P NMR spectrum shows a singlet at 128.8 p.p.m., which is consistent with the presence of pentavalent phosphorus.



(1)

The twist conformation of the two fused five-membered rings, As—S1—C1—C2—P1 [$\varphi(2) = -118.9\,(4)^\circ$] and As—S2—C4—C3—P1 [$\varphi(2) = 94.6\,(3)^\circ$], of (1) in the solid state resembles that predicted for $As(SCH_2CH_2)_2P$ in solution (Zschunke *et al.*, 1983). The As—P distance of 2.345 (1) Å may be regarded as normal; it resembles those reported for other As—P compounds (Baudler, Aktalay, Heinlein & Tebbe, 1982; Weber, Bungardt & Boese, 1989; Jutzi, Meyer, Opiela, Olmstead & Power, 1990; Märkl, Dietl, Ziegl & Nuber, 1988; Sheldrick, 1975). The same holds for the As—S bond distances (Dräger, 1975). An interesting feature of the structure of (1) is the weak intermolecular As···O interaction of 2.882 (2) Å resulting in head-to-tail dimers. This distance is at the upper limit of such contacts (Dräger, 1975) and reflects the ambivalent character of (1), with weak Lewis acidity at the As atom and Lewis basicity at the P═O function. The P═O bond length of 1.490 (2) Å is not affected by the weak coordination and resembles those found in functional substituted organotin compounds (Weichmann, Rensch, Dargatz & Meunier-Piret, 1989; Weichmann & Meunier-Piret, 1993).

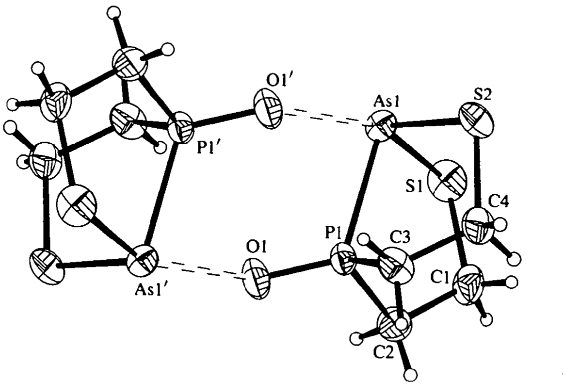


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound showing the atom-numbering scheme with 50% probability ellipsoids.

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Experimental

Crystals of the title compound were obtained by recrystallization of $As(SCH_2CH_2)_2P$ from toluene in the presence of air.

Crystal data

$C_4H_8AsOPS_2$
$M_r = 242.11$
Triclinic
$P\bar{1}$
$a = 6.522\,(3)$ Å
$b = 6.852\,(1)$ Å
$c = 10.539\,(1)$ Å
$\alpha = 71.24\,(1)°$
$\beta = 78.88\,(3)°$
$\gamma = 63.29\,(3)°$
$V = 397.7\,(2)$ Å^3
$Z = 2$
$D_x = 2.022$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 75 reflections
$\theta = 14–15°$
$\mu = 4.917$ mm^{-1}
$T = 298\,(2)$ K
Rectangular prism
0.90 × 0.64 × 0.50 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.330$, $T_{max} = 1.000$
2495 measured reflections
2307 independent reflections
2069 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0201$
$\theta_{max} = 14.99°$
$h = 0 \rightarrow 9$
$k = -8 \rightarrow 9$
$l = -14 \rightarrow 14$
3 standard reflections frequency: 50 min intensity decay: 5%

Refinement

Refinement on F^2
$R[F_o > 4\sigma(F_o)] = 0.0297$
$wR(F^2) = 0.0826$
$S = 1.120$
2307 reflections
86 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.3211P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.543$ e Å^{-3}
$\Delta\rho_{min} = -0.682$ 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 (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
As	0.17165 (4)	0.39448 (4)	0.16387 (3)	0.02818 (9)
S1	0.18837 (14)	0.19937 (13)	0.38312 (8)	0.0399 (2)
S2	−0.08575 (11)	0.74476 (12)	0.16791 (8)	0.0356 (2)
P	0.47165 (10)	0.48049 (10)	0.18397 (6)	0.02427 (13)
O1	0.6894 (3)	0.3959 (4)	0.1013 (2)	0.0376 (4)
C1	0.3144 (5)	0.3337 (5)	0.4495 (3)	0.0377 (6)
C2	0.5210 (5)	0.3568 (6)	0.3619 (3)	0.0372 (6)
C3	0.3264 (5)	0.7861 (4)	0.1514 (3)	0.0346 (6)
C4	0.0819 (5)	0.8663 (5)	0.2119 (3)	0.0348 (6)

Table 2. *Selected geometric parameters (Å, °)*

As—S2	2.2354 (12)	P—O1	1.490 (2)
As—S1	2.2623 (8)	P—C3	1.811 (3)
As—P	2.3447 (11)	P—C2	1.817 (3)
As—O1^i	2.882 (2)	C1—C2	1.521 (4)
S1—C1	1.824 (3)	C3—C4	1.516 (4)
S2—C4	1.834 (3)		
S2—As—S1	103.13 (4)	O1—P—C2	110.83 (13)
S2—As—P	90.83 (4)	C3—P—C2	108.9 (2)
S1—As—P	90.09 (4)	O1—P—As	118.06 (10)
S2—As—O1^i	85.77 (5)	C3—P—As	100.97 (10)
S1—As—O1^i	160.32 (5)	C2—P—As	102.01 (10)
P—As—O1^i	72.05 (5)	C2—C1—S1	111.6 (2)
C1—S1—As	101.05 (10)	C1—C2—P	114.5 (2)
C4—S2—As	103.58 (9)	C4—C3—P	112.8 (2)
O1—P—C3	114.86 (14)	C3—C4—S2	112.7 (2)
S2—As—S1—C1	−66.38 (11)	S1—As—P—C2	−3.51 (11)
P—As—S1—C1	24.50 (11)	O1^i—As—P—C2	−175.09 (12)
O1^i—As—S1—C1	48.9 (2)	As—S1—C1—C2	−46.8 (2)
S1—As—S2—C4	81.24 (11)	S1—C1—C2—P	49.4 (3)
P—As—S2—C4	−9.05 (11)	O1—P—C2—C1	−151.4 (2)
O1^i—As—S2—C4	−80.99 (12)	C3—P—C2—C1	81.4 (3)
S2—As—P—O1	−138.69 (10)	As—P—C2—C1	−24.8 (3)
S1—As—P—O1	118.18 (10)	O1—P—C3—C4	166.3 (2)
O1^i—As—P—O1	−53.40 (13)	C2—P—C3—C4	−68.8 (2)
S2—As—P—C3	−12.63 (11)	As—P—C3—C4	38.1 (2)
S1—As—P—C3	−115.76 (11)	P—C3—C4—S2	−50.8 (3)
O1^i—As—P—C3	72.65 (12)	As—S2—C4—C3	35.4 (2)
S2—As—P—C2	99.63 (11)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CELSIUS* (Svenson, 1974). Data reduction: *CORINC* (Dräger & Gattow, 1971). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baudler, M., Aktalay, Y., Heinlein, T. & Tebbe, K.-F. (1982). *Z. Naturforsch. Teil B*, **37**, 299–305.

Dräger, M. (1975). *Z. Anorg. Allg. Chem.* **411**, 79–89.

Dräger, M. & Gattow G. (1971). *Acta Chem. Scand.* **25**, 761–762. [Revised version by L. Wiehl & D. Schollmeyer D. (1994). Universität Mainz, Germany.]

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Jurkschat, K., Mügge, C., Tzschach, A., Uhlig, W. & Zschunke, A. (1982). *Tetrahedron Lett.* **23**, 1345–1348.

Jutzi, P., Meyer, U., Opiela, S., Olmstead, M. M. & Power, P. P. (1990). *Organometallics*, **9**, 1459–1463.

Märkl, G., Dietl, S., Ziegl, M. L. & Nuber, B. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 709–710.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structure*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for Crystal Structure Refinement*. University of Göttingen, Germany.

Sheldrick, W. S. (1975). *Acta Cryst.* **B31**, 1789–1791.

Svenson, C. (1974). *CELSIUS*. *Program for Refinement of Lattice Parameters*. Lund, Sweden.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Weber, L., Bungardt, D. & Boese, R. (1989). *Z. Anorg. Allg. Chem.* **578**, 205–224.
Weichmann, H. & Meunier-Piret, J. (1993). *Organometallics*, **12**, 4097–4103.
Weichmann, H., Rensch, B., Dargatz, M. & Meunier-Piret, J. (1989). *Bull. Soc. Chim. Belg.* **98**, 1–8.
Zschunke, A., Mügge, C., Meyer, H., Tzschach, A. & Jurkschat, K. (1983). *Org. Magn. Reson.* **21**, 315.

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N-(*p*-Tolyl)-amine-1-D-fructose from a Small Crystal

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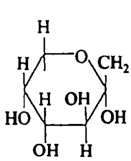
Abstract

Non-enzymatic glycation (reaction of an amino group with a sugar) is the first step in a complex, poorly understood, series of Maillard reactions. The reaction can also serve as a model for the general non-enzymatic processing of proteins. The structure of the title compound, $C_{13}H_{19}NO_5$, is a model for the product in such a process. Despite the small volume of the crystal, the use of a Cu $K\alpha$ rotating-anode source allowed the collection of sufficient data to solve and refine the structure.

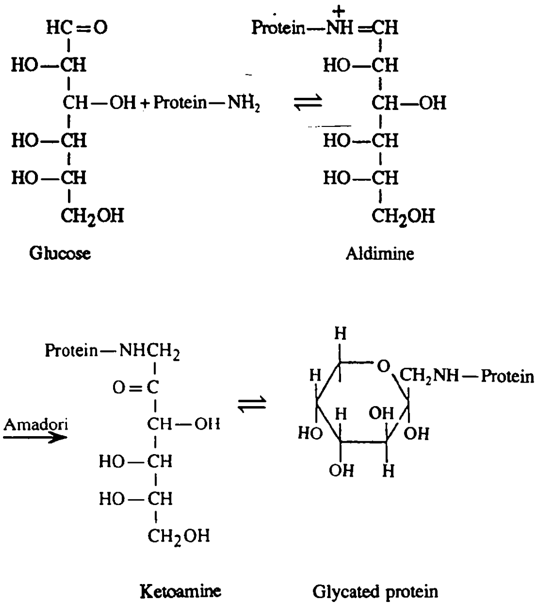
Comment

The title compound (1) is formed by a process like that occurring in the reaction of glucose with amino groups in proteins, which occurs non-enzymatically, *in vivo* (Cohen, 1986).



(1)

This intrinisically very slow process appears to be critical in the pathogenesis of various secondary complications associated with diabetes Mellitus (Cohen, 1986; Baynes, Thorpe & Murtiashaw, 1984; Lowrey, Lyness & Soeldner, 1985) and the process of aging (Monnier, Kohn & Cerami, 1984). Glycation is initiated by the condensation of the acyclic form of glucose with protein amino groups to yield a Schiff-base intermediate (aldimine). This aldimine can undergo the practically irreversible Amadori rearrangement to a stable ketoamine derivative, which then cyclizes to the hemiketal structure (Neglia, Cohen, Garber, Thorpe & Baynes, 1985). Although the Schiff-base and Amadori compounds of small organic amines are known to assume cyclic pyranose and furanose conformations in solution (Funcke & Klemer, 1976), relatively little is known about the structures which exist in proteins either *in vivo* or *in vitro*. ^{13}C NMR spectroscopy has been used to characterize Amadori ketoamine adducts formed by the reaction of glucose with amino groups of proteins (Neglia, Cohen, Garber, Thorpe & Baynes, 1985) and with small molecules (Neglia, Cohen, Garber, Ellis, Thorpe & Baynes, 1983). The pyranose form appears to be the predominant structure in solution.



Glycated proteins have been reported to undergo either conformational changes (Shaklai, Garlick & Bunn, 1984) and/or functional changes (Watkins, Thorpe & Baynes, 1987; Cerami, Vlassara & Browlee, 1987). Non-enzymatic glycation of a large polypeptide at a single site can have marked effects on both the conformation as well as the biological properties of the protein. In order to have a much clearer understanding, we have prepared (1) and performed an X-ray crystallographic analysis which can serve as a structural model for the product in the general non-enzymatic processing of proteins. A diagram showing the molecular structure of $C_{13}H_{19}NO_5$ is shown in Fig. 1. Short intermolecular distances between a number of atom pairs indicate hydrogen-bonding interactions between these pairs (Table 2).

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