During the collection of the intensity data a loss of intensity of about 30% and a shift of the peak position was detected in two of the three standard reflections (after 612 reflections). The centering of the crystal in the X-ray beam was checked optically. After recentering all 25 control reflections, the data collection was continued with a loss of 10% in the intensity of all three standard reflections. A linear decay correction (Kopf, 1987) was applied to the data to compensate for this. The decay of the crystal and other problems with the crystal quality (only a miniscule amount of the compound was available) may explain the rather high values of R. From the systematic absences (hkl: $h + k = 2n$) the possible space groups $C2$ (No. 5), Cm (No. 8) and $C2/m$ (No. 12) were deduced. With $Z = 4$ and $|E^2 - 1| = 0.727$ (the theoretical value for a non-centrosymmetric space group being 0.736), and given the knowledge that the title compound was chiral, the only possible space group was $C2$. The positions of all H atoms were refined with distance restraints for the C—H bonds (Sheldrick, 1993). Friedel opposites were collected for each reflection. These Friedel pairs were regarded as symmetry independent and were not merged. The absolute structure was determined by refinement of the Flack enantiomorph parameter, x, which refined to $-0.4\,(4)$ (Flack, 1983). Polar-axis restraints were applied using the method of Flack & Schwarzenbach (1988) in order to fix the origin in y.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *CADSHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *CIF2TEX* (Kopf, 1992*a*) and *FCF2FOC* (Kopf, 1992*b*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Edgar, J. A., Culvenor, C. C. J. & Pliske, T. E. (1976). *J. Chem. Ecol.* **2**, 263–270.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.
Kopf, J. (1987). *CADSHEL. Program for Reduction of Enraf–Nonius CAD-4 Data.* Univ. of Hamburg, Germany.
Kopf, J. (1992*a*). *CIF2TEX. Program for the Automatic Preparation of Deposition Data.* Univ. of Hamburg, Germany.
Kopf, J. (1992*b*). *FCF2FOC. Program for Printing* F_c*-squared and* F_o*-squared.* Univ. of Hamburg, Germany.
Schulz, S. (1992). *Liebigs Ann. Chem.* pp. 829–834.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1992). *SHELXTL-Plus*. Release 4.21/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Acta Cryst. (1995). C**51**, 86–88

A Chiral Bicyclic 1-Acetoxy Phosphonamide

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Abstract

The crystal structure of a chiral non-racemic 1-acetoxy phosphonamide, 2-(1-acetoxy-3-methylbutyl)-1,3-(2,2-dimethylpropyl)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 2-oxide, m.p. = 385.5–386 K, $C_{23}H_{45}N_2O_3P$, has been determined by X-ray diffraction. The title compound consists of a five-membered ring with a tetrahedrally coordinated P atom. In addition to the two N atoms of the five-membered ring, the P atom is bonded to an O atom and the C_1 atom of the acetoxyalkyl chain. The five-membered ring is *trans* fused to a cyclohexane ring in a chair conformation.

Comment

Recently, we reported the preparation and reactions of chiral phosphorous acid diamides (Koeller & Spilling, 1991; Blazis, De la Cruz, Koeller & Spilling, 1993). Treatment of phosphorous acid diamide (1) with LDA in THF solution followed by addition of isovaleraldehyde to the resulting anion gave the 1-hydroxy phosphonamides (2) in a 3.4:1 ratio of diastereoisomers (Fig. 1). Treatment of (2) with acetic anhydride, triethylamine and DMAP in CH_2Cl_2 gave the acetates (3*a*) and (3*b*), which could be separated by chromatography on silica gel. The more polar acetate (3*b*) crystallized from diethyl ether and hexane to give crystals suitable for X-ray diffraction analysis. Evidence for the relative configuration of C(1) was not available by standard spectroscopic methods, but single-crystal X-ray diffraction analysis allowed assignment of the relative configuration of the new chiral center as *S*, resulting from the *R*,*R* diamide. The phosphorous acid diamide showed the same facial selectivity as previously observed in the reaction with cinnamaldehyde (Koeller, Rath & Spilling, 1993). The molecular structure is shown in Fig. 2.

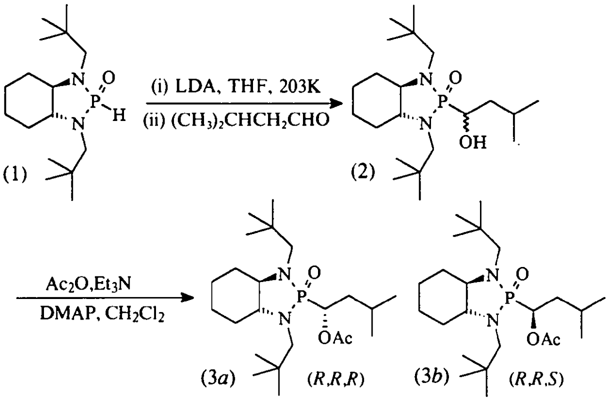

Fig. 1. Preparation of the 1-acetoxy phosphonamide.

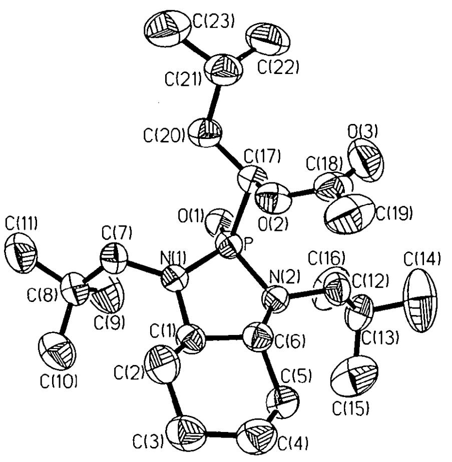

Fig. 2. The molecular structure (*SHELXTL-Plus*; Sheldrick, 1991) of the 1-acetoxy phosphonamide, showing 50% probability ellipsoids (H atoms have been omitted for clarity).

The X-ray crystal structures of related *N*,*N*-dimethyl bicyclic phosphonamides (Bélanger-Gariépy, Delorme, Hanessian & Brisse, 1986; Bélanger-Gariépy, Bennani, Hanessian & Brisse, 1989; Bennani, Bélanger-Gariépy & Hanessian, 1990; Bennani & Hanessian, 1991; Bélanger-Gariépy, Bennani, Beaudoin & Hanessian, 1992; Simard, Beaudoin & Hanesian, 1992) have been published. The bond distances for the acetoxyalkyl phosphonamide (3*b*) are consistent with the published structures of related bicyclic phosphonamides.

Experimental

Crystal data

$C_{23}H_{45}N_2O_3P$
$M_r = 428.6$
Orthorhombic
$P2_12_12_1$
$a = 9.970$ (2) Å
$b = 14.049$ (3) Å
$c = 19.013$ (4) Å
$V = 2663.1$ (10) Å^3
$Z = 4$
$D_x = 1.069$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 8.75$–10°
$\mu = 0.126$ mm^{-1}
$T = 298$ K
Irregular
0.6 × 0.5 × 0.4 mm
Colorless
Crystal source: recrystallized from Et_2O/hexane

Data collection

Siemens *R*3*m*/*V* diffractometer
θ–2θ scans
Absorption correction: none
5622 measured reflections
4152 independent reflections
3209 observed reflections [$F > 3.0\sigma(F)$]

$R_{\rm int} = 0.0315$
$\theta_{\rm max} = 27.5°$
$h = -8 \rightarrow 12$
$k = -11 \rightarrow 18$
$l = 0 \rightarrow 24$
3 standard reflections monitored every 50 reflections intensity variation: <2%

Refinement

Refinement on F
$R = 0.0495$
$wR = 0.0593$
$S = 1.2$
3209 reflections
276 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0010F^2]$

$(\Delta/\sigma)_{\rm max} = 0.019$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
P	0.9071 (1)	0.7709 (1)	0.7731 (1)	0.042 (1)
O(1)	0.9602 (2)	0.6732 (2)	0.7736 (1)	0.053 (1)
O(2)	0.8016 (3)	0.8880 (2)	0.6761 (1)	0.055 (1)
O(3)	0.9396 (4)	0.9058 (2)	0.5838 (2)	0.088 (1)
N(1)	0.7927 (3)	0.8014 (2)	0.8323 (1)	0.046 (1)
N(2)	1.0116 (3)	0.8601 (2)	0.7919 (1)	0.044 (1)
C(1)	0.8315 (3)	0.8875 (2)	0.8714 (2)	0.045 (1)
C(2)	0.7223 (4)	0.9563 (3)	0.8923 (2)	0.065 (1)
C(3)	0.7869 (4)	1.0373 (3)	0.9332 (2)	0.06 (1)
C(4)	0.8998 (5)	1.0848 (3)	0.8926 (2)	0.072 (1)
C(5)	1.0044 (4)	1.0142 (2)	0.8655 (2)	0.056 (1)
C(6)	0.9316 (3)	0.9379 (2)	0.8241 (2)	0.046 (1)
C(7)	0.6845 (3)	0.7383 (3)	0.8546 (2)	0.053 (1)
C(8)	0.6953 (4)	0.6834 (3)	0.9250 (2)	0.063 (1)
C(9)	0.8254 (5)	0.6285 (4)	0.9279 (3)	0.102 (2)
C(10)	0.6838 (6)	0.7481 (3)	0.9889 (2)	0.093 (2)
C(11)	0.5763 (5)	0.6161 (3)	0.9259 (3)	0.100 (2)
C(12)	1.1181 (3)	0.8877 (3)	0.7417 (2)	0.054 (1)
C(13)	1.2618 (3)	0.8617 (3)	0.7635 (2)	0.062 (1)
C(14)	1.3540 (5)	0.8991 (5)	0.7074 (3)	0.136 (3)
C(15)	1.3015 (5)	0.9111 (4)	0.8308 (3)	0.105 (2)
C(16)	1.2785 (4)	0.7573 (3)	0.7723 (3)	0.093 (2)
C(17)	0.8369 (4)	0.7890 (2)	0.6839 (2)	0.044 (1)
C(18)	0.8620 (5)	0.9395 (3)	0.6242 (2)	0.064 (1)
C(19)	0.8159 (6)	1.0402 (3)	0.6275 (2)	0.094 (2)
C(20)	0.7157 (3)	0.7283 (3)	0.6695 (2)	0.054 (1)
C(21)	0.6604 (4)	0.7312 (3)	0.5938 (2)	0.067 (1)
C(22)	0.7565 (5)	0.6930 (3)	0.5408 (2)	0.093 (2)
C(23)	0.5315 (5)	0.6743 (4)	0.5905 (3)	0.104 (2)

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

P—O(1)	1.471 (2)	P—N(1)	1.659 (3)
P—N(2)	1.669 (3)	P—C(17)	1.853 (3)
O(2)—C(17)	1.442 (4)	O(2)—C(18)	1.364 (5)
O(3)—C(18)	1.189 (5)	N(1)—C(1)	1.472 (4)

N(1)—C(7)	1.459 (4)	N(2)—C(6)	1.484 (4)
N(2)—C(12)	1.479 (4)	C(1)—C(2)	1.508 (5)
C(1)—C(6)	1.519 (5)	C(2)—C(3)	1.521 (5)
C(3)—C(4)	1.520 (6)	C(4)—C(5)	1.529 (5)
C(5)—C(6)	1.516 (5)	C(7)—C(8)	1.550 (5)
C(8)—C(9)	1.510 (7)	C(8)—C(10)	1.522 (5)
C(8)—C(11)	1.517 (6)	C(12)—C(13)	1.535 (5)
C(13)—C(14)	1.503 (7)	C(13)—C(15)	1.508 (7)
C(13)—C(16)	1.486 (6)	C(17)—C(20)	1.504 (5)
C(18)—C(19)	1.488 (6)	C(20)—C(21)	1.542 (5)
C(21)—C(22)	1.491 (6)	C(21)—C(23)	1.514 (7)
O(1)—P—N(1)	118.9 (1)	O(1)—P—N(2)	118.3 (1)
N(1)—P—N(2)	95.1 (1)	O(1)—P—C(17)	105.7 (1)
N(1)—P—C(17)	109.0 (1)	N(2)—P—C(17)	109.2 (1)
C(17)—O(2)—C(18)	118.6 (3)	P—N(1)—C(1)	112.0 (2)
P—N(1)—C(7)	123.2 (2)	C(1)—N(1)—C(7)	123.2 (2)
P—N(2)—C(6)	107.8 (2)	P—N(2)—C(12)	120.4 (2)
C(6)—N(2)—C(12)	117.3 (3)	N(1)—C(1)—C(2)	118.0 (3)
N(1)—C(1)—C(6)	104.8 (3)	C(2)—C(1)—C(6)	109.4 (3)
C(1)—C(2)—C(3)	107.9 (3)	C(2)—C(3)—C(4)	112.5 (3)
C(3)—C(4)—C(5)	113.0 (3)	C(4)—C(5)—C(6)	107.9 (3)
N(2)—C(6)—C(1)	104.8 (3)	N(2)—C(6)—C(5)	118.5 (3)
C(1)—C(6)—C(5)	109.6 (3)	N(1)—C(7)—C(8)	120.1 (3)
C(7)—C(8)—C(9)	110.2 (3)	C(7)—C(8)—C(10)	112.8 (3)
C(9)—C(8)—C(10)	109.9 (4)	C(7)—C(8)—C(11)	105.4 (3)
C(9)—C(8)—C(11)	110.8 (4)	C(10)—C(8)—C(11)	107.7 (4)
N(2)—C(12)—C(13)	115.7 (3)	C(12)—C(13)—C(14)	107.2 (4)
C(12)—C(13)—C(15)	111.4 (3)	C(14)—C(13)—C(15)	106.3 (4)
C(12)—C(13)—C(16)	111.7 (3)	C(14)—C(13)—C(16)	110.9 (4)
C(15)—C(13)—C(16)	109.2 (4)	P—C(17)—O(2)	108.6 (2)
P—C(17)—C(20)	113.1 (2)	O(2)—C(17)—C(20)	109.4 (3)
O(2)—C(18)—O(3)	123.0 (4)	O(2)—C(18)—C(19)	109.7 (4)
O(3)—C(18)—C(19)	127.3 (4)	C(17)—C(20)—C(21)	116.2 (3)
C(20)—C(21)—C(22)	113.0 (3)	C(20)—C(21)—C(23)	109.2 (3)
C(22)—C(21)—C(23)	109.1 (4)		

SHELXTL-Plus (Sheldrick, 1991) was used for data reduction, structure solution and refinement. The structure was solved by direct methods. Full-matrix least-squares refinement was carried out minimizing $w(F_o-F_c)^2$. All non-H atoms were refined anisotropically to convergence. H atoms except those on assymmetric C atoms were included in their calculated positions. Atoms H(1), H(6) and H(17) were refined isotropically. Roger's (1981) η test was used [η = 1.2 (3)] for absolute-structure determination.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bélanger-Gariépy, F., Bennani, Y. L., Beaudoin, S. & Hanessian, S. (1992). *Acta Cryst.* C**48**, 1533–1535.

Bélanger-Gariépy, F., Bennani, Y. L., Hanessian, H. & Brisse, F. (1989). *Acta Cryst.* C**45**, 289–291.

Bélanger-Gariépy, F., Delorme, D., Hanessian, H. & Brisse, F. (1986). *Acta Cryst.* C**42**, 856–860.

Bennani, Y. L., Bélanger-Gariépy, F. & Hanessian, H. (1990). *Acta Cryst.* C**46**, 653–656.

Bennani, Y. L. & Hanessian, S. (1991). *Acta Cryst.* C**47**, 1230–1234.

Blazis, V. J., De la Cruz, A., Koeller, K. J. & Spilling, C. D. (1993). *Phosphorus Sulfur Silicon*, **75**, 159–162.

Koeller, K. J., Rath, N. P. & Spilling, C. D. (1993). *Acta Cryst.* C**49**, 1547–1549.

Koeller, K. J. & Spilling, C. D. (1991). *Tetrahedron Lett.* **32**, 6297–6300.

Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Simard, M., Beaudoin, S. & Hanesian, S. (1992). *Acta Cryst.* C**48**, 1535–1537.

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2,4,6-Trihexyl-1,3,5-trithiane

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Abstract

The crystal structure of the title compound, $C_{21}H_{42}S_3$, comprises two independent pseudo-enantiomeric molecules, related by an approximate *n*-glide plane operation perpendicular to the *b* axis followed by a rotation of 4.2 (1)° about the *b*-axis direction. This slight but significant deviation from space group $P2_1/n$ to the non-centrosymmetric space group $P2_1$ avoids unrealistically short van der Waals contacts in the chain packing. The trithiane rings have chair conformations.

Comment

Ethylene-bridged cyclic polysulfides are flexible and are often found to possess a *trans* orientation of the S atoms (Cooper & Rawle, 1990). In contrast, methylene-based derivatives exhibit greater rigidity (Edema, Hoogenraad, Kellogg, Kooijman & Spek, 1993) and are often arranged in a crown-type configuration (Edema, Buter, van Bolhuis, Meetsma, Kellogg, Kooijman & Spek, 1993). Trithianes all have three *cis*-oriented S atoms and this rigidity prevents them 'wrapping around' a metal ion and is the cause of their poor solubility in organic solvents (Edema, Hoogenraad, Schoonbeek, Kellogg, Kooijman & Spek, 1993). In order to overcome this