C1*A* —C2*A* —N3*A*	114.2 (8)	C1*B* —C2*B* —N3*B*	115.3 (8)
C1*A* —C2*A* —N7*A*	114.1 (8)	C1*B* —C2*B* —N7*B*	114.8 (8)
N3*A* —C2*A* —N7*A*	131.7 (8)	N3*B* —C2*B* —N7*B*	129.9 (8)
C2*A* —N3*A* —N4*A*	110.9 (6)	C2*B* —N3*B* —N4*B*	110.9 (6)
N3*A* —N4*A* —C5*A*	115.2 (7)	N3*B* —N4*B* —C5*B*	117.2 (7)
N4*A* —C5*A* —C6*A*	119.0 (8)	N4*B* —C5*B* —C6*B*	120.8 (8)

Data collection: *P3/PC Diffractometer Program* (Siemens, 1989). Cell refinement: *P3/PC Diffractometer Program.* Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN, MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS.* Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH.* Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71831 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1087]

References

Abdul-Ghani, M. (1988). MSc thesis, Univ. of Manchester, England.
Abdul-Ghani, M. (1992). PhD thesis, Univ. of Manchester, England.
Barlow, M. G., Bell, D., O'Reilly, N. J. & Tipping, A. E. (1983). *J. Fluorine Chem.* **23**, 293-299.
CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual.* SERC Daresbury Laboratory, Warrington, England.
Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42-46.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.
O'Reilly, N. J. (1984). PhD thesis, Univ. of Manchester, England.
Siemens (1989). *P3/PC Diffractometer Program.* Version 3.13. Siemens Analytical Instruments, Inc., Madison, Wisconsin, USA.
Siemens (1990). *XDISK. Data Reduction Program.* Siemens Analytical Instruments, Inc., Madison, Wisconsin, USA.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558-564.

Acta Cryst. (1994). C**50**, 724–726

Diethyl 5,6-Dihydro-2*H*-1,3-dithiolo[4,5-*b*]-[1,4]dithiin-2-ylphosphonate, $C_9H_{15}O_3PS_4$

Shripad V. Kelkar, Jeremy D. Kilburn
and Michael Webster

Department of Chemistry, University of Southampton, Southampton SO9 5NH, England

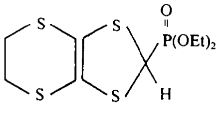
(*Received* 30 *July* 1993; *accepted* 27 *October* 1993)

Abstract

The two molecules in the asymmetric unit are very similar, apart from one P—O—C—C torsion angle. The five-membered ring is in the envelope conformation and the S—C_{sp^3} bonds [average 1.819 (7) Å] are longer than the S—C_{sp^2} bonds [average 1.76 (1) Å].

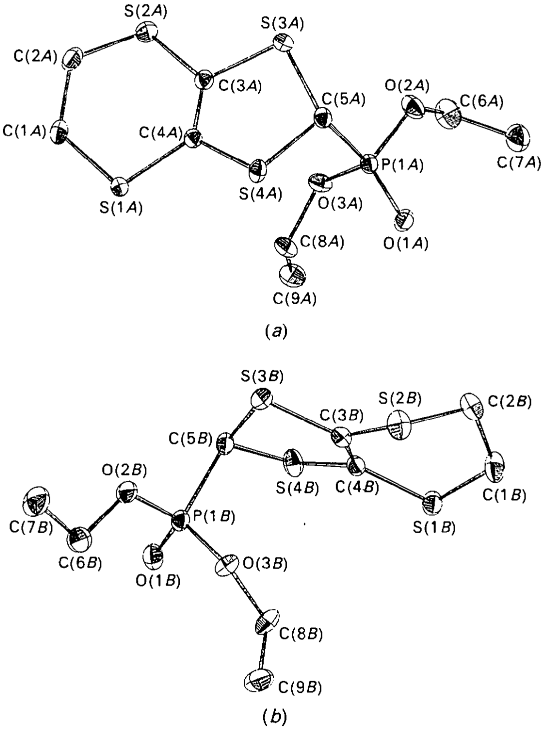
Comment

Phosphoranes of 1,3-dithiole derivatives are useful synthetic intermediates, particularly for the preparation of tetrathiafulvalene derivatives (Moore & Bryce, 1991).



(I)

The title compound (I) has been prepared previously in four steps from 4,5-ethylenedithio-1,3-dithiole-2-thione, and was reported to be an oil (Hansen, Lakshmikantham, Cava, Metzger & Becher, 1991). By heating 4,5-ethylenedithio-1,3-dithiole-2-thione in the presence of excess triethyl phosphite at 483 K for 6 h, the title compound was prepared in one step and purified by column chromatography [silica gel; 0-50% ethyl acetate/petroleum ether (40-60), gradient elution] to obtain a viscous oil. Trituration with the same solvents gave crystals (m.p. 337-338 K) and crystals suitable for X-ray examination were obtained by crystallization from ethyl acetate/petroleum ether (30/70 *v*/*v*).



(*a*)

(*b*)

Fig. 1. Views of $C_9H_{15}O_3PS_4$, showing the two molecules (*A* and *B*) in the asymmetric unit and the atom-labelling scheme. H atoms are excluded and the displacement ellipsoids are drawn at the 50% probability level.

The structure was solved by direct methods (Sheldrick, 1985), which revealed the expected molecule. The asymmetric unit contains two independent molecules (*A* and *B*) with very similar geometries. The atoms S1, S2, S3, S4, C3 and C4 are essentially coplanar, as expected, and C1 and C2 lie on the same side of the six-membered ring. The five-membered ring is in an envelope conformation with C5 out of the plane and on the opposite side to the out-of-plane atoms of the six-membered ring. The major difference between the two molecules is in the value of the P1—O2—C6—C7 torsion angle (see Table 2).

Experimental

Crystal data

$C_9H_{15}O_3PS_4$
$M_r = 330.43$
Monoclinic
$P2_1/a$
$a = 16.197\ (6)$ Å
$b = 9.141\ (2)$ Å
$c = 19.540\ (1)$ Å
$\beta = 99.28\ (1)°$
$V = 2855.2\ (1.2)$ Å^3
$Z = 8$
$D_x = 1.536$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 3\text{–}26°$
$\mu = 0.74$ mm^{-1}
$T = 150$ K
Air-stable blocks
0.24 × 0.18 × 0.10 mm
Colourless

Data collection

Enraf-Nonius FAST area detector diffractometer
ω scans
Absorption correction: none
14 911 measured reflections
7339 independent reflections
3607 observed reflections $[F > 3\sigma(F)]$

$R_{\text{int}} = 0.054$
$\theta_{\max} = 30.0°$
$h = -22 \rightarrow 22$
$k = -11 \rightarrow 12$
$l = -26 \rightarrow 12$
Standard reflections not applicable for FAST data collection

Refinement

Refinement on *F*
$R = 0.0265$
$wR = 0.0367$
$S = 0.31$
3607 reflections
320 parameters
Only H-atom *U*'s refined

$w = 1/[\sigma^2(F) + 0.0015F^2]$
$(\Delta/\sigma)_{\max} = 0.1$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

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

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

	x	y	z	U_{eq}
S1*A*	0.12926 (4)	0.59609 (6)	0.03763 (4)	0.0195 (3)
S2*A*	0.18492 (4)	0.32845 (7)	0.16330 (4)	0.0227 (3)
S3*A*	0.34226 (4)	0.30766 (6)	0.10434 (4)	0.0187 (3)
S4*A*	0.29113 (4)	0.52483 (6)	−0.00605 (3)	0.0171 (3)
P1*A*	0.44751 (4)	0.58225 (6)	0.09249 (4)	0.0147 (3)
O1*A*	0.4819 (1)	0.6772 (2)	0.0435 (1)	0.0203 (8)
O2*A*	0.5110 (1)	0.4880 (2)	0.1434 (1)	0.0230 (9)
O3*A*	0.3971 (1)	0.6660 (2)	0.1428 (1)	0.0188 (8)
C1*A*	0.0647 (1)	0.5128 (3)	0.0949 (2)	0.0225 (13)
C2*A*	0.0833 (1)	0.3531 (3)	0.1112 (1)	0.0220 (12)
C3*A*	0.2450 (1)	0.3957 (2)	0.1040 (1)	0.0171 (12)
C4*A*	0.2224 (1)	0.4951 (2)	0.0545 (1)	0.0150 (11)
C5*A*	0.3810 (1)	0.4411 (2)	0.0481 (1)	0.0155 (11)
C6*A*	0.5659 (2)	0.5493 (3)	0.2030 (2)	0.0293 (14)
C7*A*	0.6482 (2)	0.5910 (3)	0.1851 (2)	0.0313 (15)
C8*A*	0.3511 (2)	0.8007 (2)	0.1217 (1)	0.0213 (12)
C9*A*	0.3711 (2)	0.9109 (3)	0.1789 (2)	0.0271 (14)
S1*B*	0.86313 (4)	0.58945 (7)	0.46053 (4)	0.0212 (3)
S2*B*	0.79525 (4)	0.36666 (8)	0.32297 (4)	0.0267 (3)
S3*B*	0.64058 (4)	0.32970 (6)	0.38656 (4)	0.0223 (3)
S4*B*	0.70227 (4)	0.51688 (7)	0.50683 (4)	0.0215 (3)
P1*B*	0.54712 (4)	0.60806 (6)	0.41364 (4)	0.0164 (3)
O1*B*	0.5241 (1)	0.7059 (2)	0.4671 (1)	0.0226 (9)
O2*B*	0.4726 (1)	0.5288 (2)	0.3666 (1)	0.0225 (9)
O3*B*	0.5942 (1)	0.6850 (2)	0.3594 (1)	0.0192 (8)
C1*B*	0.9293 (2)	0.4909 (3)	0.4086 (2)	0.0285 (14)
C2*B*	0.8955 (2)	0.3468 (3)	0.3790 (2)	0.0264 (14)
C3*B*	0.7381 (1)	0.4159 (2)	0.3874 (1)	0.0183 (12)
C4*B*	0.7666 (1)	0.4994 (2)	0.4424 (1)	0.0169 (12)
C5*B*	0.6084 (1)	0.4533 (2)	0.4501 (1)	0.0185 (12)
C6*B*	0.4064 (2)	0.6175 (3)	0.3270 (2)	0.0268 (13)
C7*B*	0.3455 (2)	0.5194 (3)	0.2857 (2)	0.0357 (16)
C8*B*	0.6462 (2)	0.8150 (3)	0.3766 (2)	0.0259 (13)
C9*B*	0.6251 (2)	0.9239 (3)	0.3197 (2)	0.0342 (15)

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

S1*A*—C1*A*	1.817 (3)	S1*B*—C1*B*	1.828 (3)
S1*A*—C4*A*	1.753 (2)	S1*B*—C4*B*	1.752 (2)
S2*A*—C2*A*	1.805 (3)	S2*B*—C2*B*	1.815 (3)
S2*A*—C3*A*	1.742 (3)	S2*B*—C3*B*	1.737 (3)
S3*A*—C3*A*	1.767 (2)	S3*B*—C3*B*	1.762 (2)
S3*A*—C5*A*	1.820 (2)	S3*B*—C5*B*	1.816 (3)
S4*A*—C4*A*	1.772 (3)	S4*B*—C4*B*	1.766 (3)
S4*A*—C5*A*	1.825 (2)	S4*B*—C5*B*	1.827 (2)
C1*A*—C2*A*	1.514 (3)	C1*B*—C2*B*	1.506 (4)
C3*A*—C4*A*	1.334 (3)	C3*B*—C4*B*	1.339 (4)
P1*A*—C5*A*	1.810 (2)	P1*B*—C5*B*	1.807 (2)
P1*A*—O1*A*	1.466 (2)	P1*B*—O1*B*	1.468 (2)
C2*A*—S2*A*—C3*A*	97.9 (1)	C2*B*—S2*B*—C3*B*	96.8 (1)
C4*A*—S1*A*—C1*A*	103.1 (1)	C4*B*—S1*B*—C1*B*	103.9 (1)
S4*A*—C4*A*—C3*A*	117.3 (2)	S4*B*—C4*B*—C3*B*	117.2 (2)
C4*A*—C3*A*—S3*A*	117.0 (2)	C4*B*—C3*B*—S3*B*	117.0 (2)
C3*A*—S3*A*—C5*A*	95.0 (1)	C3*B*—S3*B*—C5*B*	94.1 (1)
S3*A*—C5*A*—S4*A*	108.1 (1)	S3*B*—C5*B*—S4*B*	108.1 (1)
C5*A*—S4*A*—C4*A*	94.4 (1)	C5*B*—S4*B*—C4*B*	93.9 (1)
P1*A*—O2*A*—C6*A*—C7*A*	−92.3 (3)	P1*B*—O2*B*—C6*B*—C7*B*	178.3 (2)
P1*A*—O3*A*—C8*A*—C9*A*	−133.4 (2)	P1*B*—O3*B*—C8*B*—C9*B*	−133.9 (2)

H atoms were placed in calculated positions (C—H = 0.95 Å) and were assigned a common refined displacement parameter. In the refinement, data were truncated to $\theta_{\max} = 25°$. Data collection and reduction, and cell refinement: *CAD*-4 *Software* (Enraf-Nonius, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

We thank the SERC for financial support (SVK) and Professor M. B. Hursthouse and the SERC for the X-ray data collection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71791 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1077]

References

Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
Hansen, T. K., Lakshmikantham, M. V., Cava, M. P., Metzger, R. M. & Becher, J. (1991). *J. Org. Chem.* **56**, 2720-2722.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Moore, A. J. & Bryce, M. R. (1991). *Synthesis*, pp. 26-28.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1994). C**50**, 726–727

A D-Homotestosterone Derivative

Mathias Noltemeyer*

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

Lutz F. Tietze and János Wölfling

Institut für Organische Chemie der Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany

Gyula Schneider

Department of Organic Chemistry, József Attila University, Dóm tér 8, H-6720 Szeged, Hungary

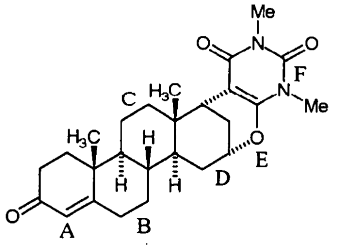
(*Received* 19 *July* 1993; *accepted* 9 *November* 1993)

Abstract

The structure of [6*R*-(6α,7aβ,7bα,13aα,13bβ,15aα,16α)]-4,6,7,7a,7b,8,9,11,12,13,13a,13b,14,15,15a,16-hexadecahydro-2,4,13a,15a-tetramethyl-6,16-methano-1*H*-phenanthro[2',1':5,6]oxocino[2,3-*d*]pyrimidine-1,3(2*H*),11-trione, $C_{26}H_{34}N_2O_4$, is reported.

Comment

Rings *B* and *C* and rings *C* and *D* are *trans* fused, whereas rings *D* and *E* are *cis* fused (6α,16α). Rings *B* and *C* adopt chair conformations, whereas rings *A*, *D* and *E* show a 1α,2β-half-chair, a distorted chair and a 17α-sofa conformation, respectively.



(I)

For some related reactions see Tietze (1984), Tietze, Wölfling & Schneider (1991), and Tietze & Beifuss (1993). For the structure of testosterone see Roberts, Pettersen, Sheldrick, Isaacs & Kennard (1973), and for several testosterone derivatives see Duax & Norton (1975), and Griffin, Duax & Weeks (1984).

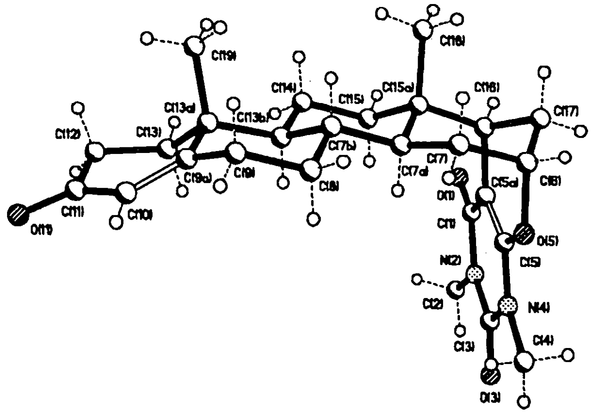


Fig. 1. View of the title compound with atomic numbering scheme.

Experimental

The synthesis of the title compound *via* a tandem-Knoevenagel hetero-Diels–Alder reaction will be published elsewhere (Tietze, Wölfling & Schneider, 1994).

Crystal data

$C_{26}H_{34}N_2O_4$
M_r = 438.57
Orthorhombic
$P2_12_12_1$
a = 10.532 (2) Å
b = 13.812 (3) Å
c = 16.048 (3) Å
V = 2334.5 (8) Å^3
Z = 4
D_x = 1.248 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 35 reflections
θ = 10–12.5°
μ = 0.084 mm^{-1}
T = 293 (2) K
Plates
1.00 × 1.00 × 0.70 mm
Light yellow

Data collection

Stoe AED2 four-circle diffractometer
Profile fitting collection method
Absorption correction: none
2275 measured reflections
2028 independent reflections
1830 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0166
$\theta_{\rm max}$ = 22.49°
$h = -2 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0419
$wR(F^2)$ = 0.1140
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.153 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.159 e Å^{-3}

Acta Crystallographica Section C
ISSN 0108-2701 ©1994