FELDMANN, R. J. (1974). In *Computer Representation and Manipulation of Chemical Information*, edited by W. T. WIPPKE, S. R. HELLER, R. J. FELDMANN & E. HYDE. New York: John Wiley.

KENNARD, O., ALLEN, F. H., BRICE, M. D., HUMMELINK, T. W. A., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1977). *Pure Appl. Chem.* **49**, 1807–1816.

KENNARD, O., ALLEN, F. H. & WATSON, D. G. (1977). *Molecular Structures and Dimensions*: *Guide to the Literature* 1935–76. Utrecht: Bohn, Scheltema & Holkema.

KENNARD, O. & WATSON, D. G. (1970, 1972). *Molecular Structures and Dimensions: Bibliography.* Vols 1, 2, 3. Utrecht: Oosthoek.

KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, N. W., MOTHERWELL, W. D. S., PETTERSEN, R. C. & TOWN, W. G. (1972). *Molecular Structures and Dimensions.* Vol. *A*1. *Interatomic Distances* 1960–65. Utrecht: Oosthoek.

KENNARD, O., WATSON, D., ALLEN, F., MOTHERWELL, W., TOWN, W. & RODGERS, J. (1975). *Chem. Br.* **11**, 213–216.

KENNARD, O., WATSON, D. G., ALLEN, F. H. & WEEDS, S. (1975–1979). *Molecular Structures and Dimensions*: *Bibliography.* Vols 6, 7, 8, 9, 10. Utrecht and Deventer: Bohn, Scheltema & Holkema.

KENNARD, O., WATSON, D. G. & TOWN, W. G. (1972). *J. Chem. Doc.* **12**, 14–19.

KENNARD, O., WATSON, D. G. & TOWN, W. G. (1973, 1974). *Molecular Structures and Dimensions*: *Bibliography.* Vols 4, 5. Utrecht: Oosthoek.

MACHIN, P. A., MILLS, J. N., MILLS, O. S. & ELDER, M. (1978). *Crystal Structure Search Retrieval Manual.* SRC Daresbury Laboratory, Warrington, England.

MORGAN, H. L. (1965). *J. Chem. Doc.* **5**, 107–113.

MURRAY-RUST, P. & BLAND, R. (1978). *Acta Cryst.* B**34**, 2527–2533.

MURRAY-RUST, P. & MOTHERWELL, S. (1978*a*). *Acta Cryst.* B**34**, 2518–2526.

MURRAY-RUST, P. & MOTHERWELL, S. (1978*b*). *Acta Cryst.* B**34**, 2534–2546.

PENFOLD, B. R., HARPER, B. L., BROWN, T. A. & BOLWELL, A. D. (1977). Proc. R. Aust. Chem. Inst. Melbourne.

SHIMANOUCHI, T. & YAMAMOTO, T. (1976). Proc. 5th Int. CODATA Conf., Boulder, Colorado.

Acta Cryst. (1979). B**35**, 2339–2344

The Crystal and Molecular Structures of Axial–Equatorial and Axial–Axial Bis(4,6-dimethyl-2-thioxo-1,3,2-dioxaphosphorinanyl) Oxide*

BY M. W. WIECZOREK† AND W. S. SHELDRICK

Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, *D*-3300 *Braunschweig–Stöckheim, Federal Republic of Germany*

J. KAROLAK-WOJCIECHOWSKA

Institute of General Chemistry, Technical University, Żwirki 36, 90-924 *Łódź, Poland*

AND M. MIKOŁAJCZYK AND B. ZIEMNICKA

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulphur Compounds, 90-362 *Łódź, Boczna* 5, *Poland*

(*Received* 31 *January* 1979; *accepted* 10 *May* 1979)

Abstract

The structures of the axial–equatorial (*a*,*e*) and axial–axial (*a*,*a*) isomers of bis(4,6-dimethyl-2-thioxo-1,3,2-dioxaphosphorinanyl) oxide (2) have been determined. (*a*,*e*)-(2) crystallizes in the monoclinic space group $P2_1/c$ with $a = 9{\cdot}076\,(3)$, $b = 14{\cdot}134\,(4)$, $c = 13{\cdot}555\,(3)$ Å, $\beta = 103{\cdot}88\,(3)^\circ$, $Z = 4$; (*a*,*a*)-(2) is monoclinic, $P2_1/n$, with $a = 14{\cdot}966\,(3)$, $b = 9{\cdot}887\,(2)$, $c = 12{\cdot}325\,(3)$ Å, $\beta = 113{\cdot}38\,(3)^\circ$, $Z = 4$. The structures were refined to $R = 0{\cdot}056$ and $0{\cdot}070$ respectively. The dioxaphosphorinane rings all display chair conformations flattened at P and the opposite ring C, the degree of flattening being much more pronounced at P. This flattening is accentuated in the ring with an equatorially sited P=S bond. The exocyclic P—O distance is significantly longer and the endocyclic O—P—O angle significantly wider for the P bonded to

---

* Stereochemistry of Organophosphorus Cyclic Compounds. X.

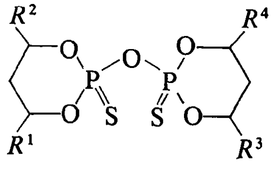
† Permanent address: Institute of General Chemistry, Technical University, 90-924 Łódź, Poland.

0567-7408/79/102339-06$01.00

the equatorially sited S atom than for those bonded to the axially sited S atom.

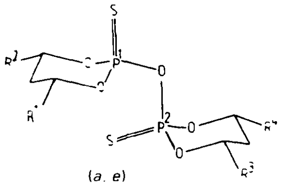
Introduction

This work is part of a general study on the synthesis, geometrical isomerism and ring conformations of the bis(2-thioxodioxaphosphorinanyl) oxides.

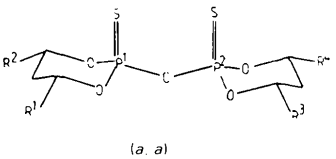


(1) $R^1 = R^4 = \text{Me}$
$R^2 = R^3 = \text{H}$
(2) $R^1 = R^2 = R^3 = R^4 = \text{Me}$

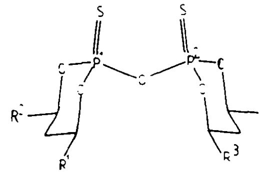
For derivatives with symmetrical *R* substituents equatorially sited with respect to the best plane of the six-membered dioxaphosphorinane rings there are three possible geometrical isomers, namely with the P=S bonds axial–equatorial (*a,e*), axial–axial (*a,a*) and equatorial–equatorial (*e,e*) to the ring planes. We have already reported the X-ray structural analyses of the (*a,e*) and (*e,e*) isomers of (1) (Karolak-Wojciechowska, Wieczorek, Mikołajczyk & Ziemnicka, 1979). We now present a comparative study of the (*a,e*) and (*a,a*) isomers of (2).



(*a*. *e*)



(*a*. *a*)



(*e*. *e*)

Experimental

Single crystals of axial–equatorial bis(4,6-dimethyl-2-thioxo-1,3,2-dioxaphosphorinanyl) oxide [(*a,e*)-(2)] and axial–axial bis(4,6-dimethyl-2-thioxo-1,3,2-dioxaphosphorinanyl) oxide [(*a,a*)-(2)] were grown from benzene/cyclohexane solutions. Crystal and refinement data for compounds (*a,e*)-(2) and (*a,a*)-(2) are summarized in Table 1. Intensity data for (*a,e*)-(2) and (*a,a*)-(2) were collected on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator) [crystals of compound (*a,a*)-(2) were sealed in a Lindemann-glass capillary tube]. Measurements were carried out in the θ–2θ scan mode for $2\theta \leq 50°$. No absorption correction was applied.

Structure solution and refinement

The structures were solved by direct methods (*SHELX* 76; Sheldrick, 1976) and refined by blocked-full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms. For (*a,e*)-(2) the H atoms were freely refined with individual temperature factors, whereas for (*a,a*)-(2) they were assigned group isotropic temperature factors and the methyl H atoms were refined as a part of rigid methyl groups. The weights were given by $w = k/[\sigma^2(F_o) + gF^2]$. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Tables 2 and 3 give the final positional parameters, Tables 4 and 5 the bond lengths and angles. Figs. 1 and 2 show (*a,e*)-(2) and (*a,a*)-(2), respectively, in perspective with the numbering scheme used and Figs. 3 and 4 show the unit-cell contents.*

Table 1. *Crystal and refinement data*

a = axial and *e* = equatorial position for S relative to the plane of the dioxaphosphorinane ring.

	(*a,e*)-(2)	(*a,a*)-(2)
Stoichiometry	$C_{10}H_{20}O_5P_2S_2$	$C_{10}H_{20}O_5P_2S_2$
Conformation	chair, chair	chair, chair
Space group	$P2_1/c$	$P2_1/n$
a (Å)	9·076 (3)	14·966 (3)
b (Å)	14·134 (4)	9·887 (2)
c (Å)	13·555 (3)	12·325 (3)
β (°)	103·88 (3)	113·38 (3)
U (Å^3)	1688·1 (7)	1674·0 (6)
Z	4	4
M_r	346·32	346·32
D_c (Mg m^{-3})	1·37	1·38
Radiation	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0·46	0·46
2θ range (°)	$3·0 \leq 2\theta \leq 50·0$	$3·0 \leq 2\theta \leq 50·0$
F rejection criterion	$<4·0\sigma(F)$	$<4·0\sigma(F)$
Number of reflexions	1692	1504
R	0·056	0·070
R_w ($\sum w^{1/2}\Delta/\sum w^{1/2}F_o$)	0·049	0·069
k	2·1248	1·2072
g	0·000235	0·002

---

* Lists of structure factors and anisotropic thermal parameters for both compounds and bond lengths involving H atoms for (*a,e*)-(2) and (*a,a*)-(2) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34463 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Molecular geometry

The conformation of both dioxaphosphorinane rings for the two derivatives is a chair. The structural analyses confirm the (*a*,*e*) and (*a*,*a*) geometries for the two isomers. Detailed information on the geometries of (*a*,*e*)-(2) and (*a*,*a*)-(2) is given in Table 6. The differences ($\alpha - \beta$) are chosen to illustrate the degree of distortion of the chair from the idealized cyclohexane conformation ($\alpha = \beta \simeq 55°$). With respect to this idealized conformation, the rings are flattened at both the P and the opposite ring C atoms [C(12) or C(22)], the degree of flattening being very significantly more marked for the P than for the C atoms. For that ring with an equatorial S atom, α is 16·2° smaller than β; for the three rings with S axial the difference between α and β is less pronounced, being 11·8, 8·6 and 10·9° respectively. Similar ring distortions have been observed for (*a*,*e*)-(1), (*e*,*e*)-(1) and the analogous derivatives bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulphide (3) (Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976) and bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) oxide (4) (Bukowska-Strzyżewska & Dobrowolska, 1976, 1978). The α values are 43·5 and 26·1° for (*a*,*e*)-(1), 36·8 and 33·6° for (*e*,*e*)-(1), 31·1 and 31·1° for (3)

Table 2. *Positional parameters* ($\times 10^4$) *for the nonhydrogen atoms*

	Compound (*a*,*e*)-(2)			Compound (*a*,*a*)-(2)		
	x	*y*	*z*	*x*	*y*	*z*
P(1)	4386 (1)	2534 (1)	7374 (1)	2943 (2)	−1753 (2)	11156 (2)
S(1)	4778 (2)	2474 (1)	8812 (1)	2675 (2)	−3263 (3)	10173 (2)
O(11)	3324 (3)	3360 (2)	6849 (2)	2099 (3)	−1222 (6)	11504 (4)
O(12)	5795 (3)	2565 (2)	6904 (2)	3851 (4)	−1811 (7)	12362 (5)
C(11)	4019 (6)	4288 (3)	6783 (4)	1961 (6)	−1960 (10)	12449 (7)
C(12)	5332 (6)	4164 (3)	6296 (4)	2896 (6)	−1913 (9)	13536 (6)
C(13)	6503 (6)	3478 (4)	6821 (4)	3752 (7)	−2469 (12)	13345 (7)
C(14)	2772 (7)	4914 (4)	6224 (5)	1095 (6)	−1340 (10)	12582 (8)
C(15)	7750 (6)	3308 (4)	6291 (4)	4700 (7)	−2328 (15)	14387 (8)
P(2)	1962 (2)	1128 (1)	6545 (1)	2841 (2)	251 (2)	9374 (2)
S(2)	1250 (2)	779 (1)	7690 (1)	1473 (2)	313 (3)	8571 (2)
O	3593 (3)	1639 (2)	6777 (2)	3233 (4)	−407 (6)	10659 (4)
O(21)	2282 (3)	286 (2)	5886 (2)	3374 (4)	1646 (5)	9724 (4)
O(22)	890 (3)	1815 (2)	5815 (2)	3420 (4)	−539 (5)	8772 (4)
C(23)	1074 (6)	2002 (4)	4789 (4)	3596 (6)	174 (9)	7820 (6)
C(22)	1324 (6)	1083 (4)	4286 (3)	4140 (6)	1461 (8)	8337 (7)
C(21)	2584 (6)	482 (4)	4891 (4)	3612 (6)	2383 (8)	8833 (7)
C(24)	−315 (6)	2548 (4)	4248 (4)	4170 (7)	−798 (9)	7423 (9)
C(25)	2828 (6)	−445 (4)	4422 (4)	4187 (8)	3610 (9)	9455 (8)

Table 3. *Hydrogen-atom positional parameters* ($\times 10^4$)

	Compound (*a*,*e*)-(2)			Compound (*a*,*a*)-(2)		
	x	*y*	*z*	*x*	*y*	*z*
H(111)	4306 (47)	4484 (30)	7535 (33)	1806 (6)	−3024 (10)	12270 (7)
H(121)	4845 (46)	3943 (29)	5623 (29)	2802 (6)	−2495 (9)	14224 (6)
H(122)	5739 (41)	4758 (26)	6250 (28)	3046 (6)	−873 (9)	13814 (6)
H(131)	6896 (41)	3626 (25)	7505 (26)	3600 (7)	−3536 (12)	13183 (7)
H(141)	3229 (56)	5456 (35)	6148 (35)	940 (6)	−2006 (10)	13181 (8)
H(142)	1992 (56)	4984 (35)	6511 (39)	486 (6)	−1339 (10)	11735 (8)
H(143)	2324 (52)	4738 (34)	5592 (34)	1217 (6)	−328 (10)	12939 (8)
H(151)	8408 (51)	3823 (35)	6424 (32)	4605 (7)	−2940 (15)	15061 (8)
H(152)	8354 (43)	2822 (27)	6589 (28)	4926 (7)	−1324 (15)	14728 (8)
H(153)	7403 (74)	3059 (48)	5571 (49)	5248 (7)	−2780 (15)	14139 (8)
H(211)	3473 (40)	809 (24)	5064 (27)	2979 (6)	2721 (8)	8085 (7)
H(221)	1481 (37)	1177 (23)	3707 (23)	4268 (6)	1993 (8)	7646 (7)
H(222)	400 (49)	752 (32)	4102 (32)	4829 (6)	1196 (8)	9033 (7)
H(231)	1917 (47)	2320 (27)	4915 (30)	2944 (6)	463 (9)	7073 (6)
H(241)	−1195 (50)	2161 (32)	4233 (33)	4230 (7)	−306 (9)	6673 (9)
H(242)	−127 (62)	2644 (37)	3614 (44)	3771 (7)	−1733 (9)	7140 (9)
H(243)	−380 (54)	3121 (35)	4581 (35)	4889 (7)	−1014 (9)	8079 (9)
H(251)	2976 (44)	−368 (28)	3804 (29)	4409 (8)	4141 (9)	8837 (8)
H(252)	3620 (55)	−790 (32)	4918 (36)	4822 (8)	3360 (9)	10237 (8)
H(253)	1987 (48)	−757 (27)	4270 (30)	3708 (8)	4246 (9)	9696 (8)

(which displays crystallographic C_2 symmetry) and 36·0 and 36·2° for (4). The β values all lie between 51 and 56°. Thus the α values are about 5–10° smaller for equatorial as opposed to axial placement of the doubly bonded atom at P, whereas the β angles are relatively impervious to the substitution pattern and somewhat smaller than for cyclohexane (1–6°). The conformations of 1,3,2-dioxaphosphorinane rings may also be described by their torsion angles [Figs. 5 and 6 for (*a*,*e*)-(2) and (*a*,*a*)-(2)].

Detailed information for the axial and equatorial positions of C(14), C(15), S(1) and C(24), C(25), S(2) are given in Table 7. As a result of short non-bonded distances, the angles made between the C–C bonds to the methyl substituents and the best plane of ring *B* in (*a*,*e*)-(2) differ by 10·3°. The axial–axial siting of S(1) and S(2) in compound (*a*,*a*)-(2) leads to a larger twist angle between the two halves of the molecule [dihedral angle between planes through P(1)S(1)O and

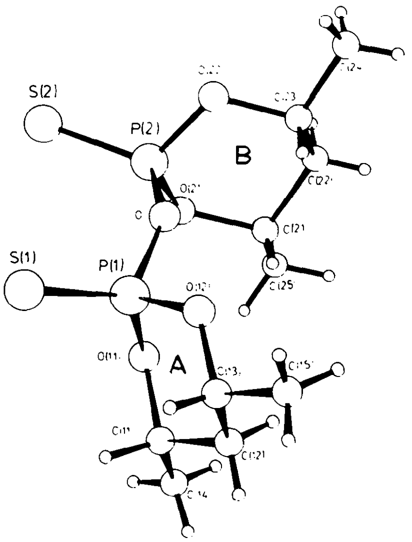


Fig. 1. (*a*,*e*)-(2) in perspective with the numbering scheme.

Table 4. *Bond lengths* (Å)

	(*a*,*e*)-(2)	(*a*,*a*)-(2)
P(1)–O	1·580 (3)	1·579 (5)
S(1)–P(1)	1·896 (2)	1·879 (3)
O(11)–P(1)	1·571 (3)	1·569 (5)
O(12)–P(1)	1·561 (4)	1·568 (5)
C(13)–O(12)	1·458 (6)	1·434 (9)
C(11)–O(11)	1·467 (6)	1·457 (9)
C(12)–C(13)	1·488 (7)	1·496 (11)
C(11)–C(12)	1·505 (8)	1·506 (10)
C(15)–C(13)	1·497 (8)	1·495 (12)
C(14)–C(11)	1·492 (7)	1·499 (11)
P(2)–O	1·608 (3)	1·594 (5)
S(2)–P(2)	1·884 (2)	1·888 (3)
O(22)–P(2)	1·552 (3)	1·557 (5)
O(21)–P(2)	1·556 (3)	1·566 (5)
C(23)–O(22)	1·464 (6)	1·479 (8)
C(21)–O(21)	1·467 (7)	1·474 (9)
C(22)–C(23)	1·509 (8)	1·509 (10)
C(21)–C(22)	1·501 (7)	1·488 (10)
C(24)–C(23)	1·511 (7)	1·496 (10)
C(25)–C(21)	1·496 (8)	1·509 (11)

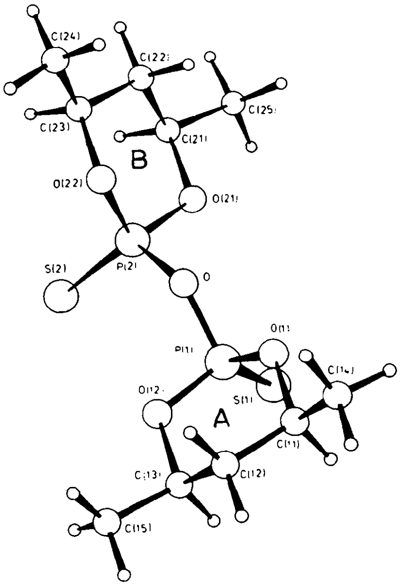


Fig. 2. (*a*,*a*)-(2) in perspective with the numbering scheme.

Table 5. *Bond angles* (°)

	(*a*,*e*)-(2)	(*a*,*a*)-(2)		(*a*,*e*)-(2)	(*a*,*a*)-(2)
O–P(2)–S(2)	116·0 (1)	115·4 (2)	O(21)–P(2)–S(2)	114·9 (2)	116·4 (3)
O(21)–P(2)–O	99·5 (2)	98·0 (3)	O(22)–P(2)–S(2)	113·8 (2)	117·4 (2)
O(22)–P(2)–O	104·5 (2)	102·3 (3)	O(22)–P(2)–O(21)	106·7 (2)	104·7 (3)
P(1)–O–P(2)	138·1 (2)	132·5 (3)	C(21)–O(21)–P(2)	119·1 (3)	118·5 (4)
C(23)–O(22)–P(2)	121·5 (3)	116·5 (4)	C(22)–C(23)–O(22)	109·7 (4)	107·6 (6)
C(24)–C(23)–O(22)	106·3 (4)	105·0 (6)	C(24)–C(23)–C(22)	114·8 (4)	113·3 (7)
C(21)–C(22)–C(23)	114·7 (4)	113·8 (7)	C(22)–C(21)–O(21)	108·9 (4)	109·2 (6)
C(25)–C(21)–O(21)	107·7 (4)	106·0 (6)	C(25)–C(21)–C(22)	115·8 (4)	114·4 (7)
S(1)–P(1)–O	116·1 (1)	116·1 (2)	O(11)–P(1)–O	102·0 (2)	102·4 (3)
O(11)–P(1)–S(1)	116·3 (2)	116·5 (3)	O(12)–P(1)–O	97·5 (2)	98·1 (3)
O(12)–P(1)–S(1)	116·8 (1)	117·0 (3)	O(12)–P(1)–O(11)	105·5 (2)	104·2 (3)
C(11)–O(11)–P(1)	117·8 (3)	116·3 (5)	C(13)–O(12)–P(1)	118·5 (3)	118·8 (5)
C(12)–C(11)–O(11)	108·7 (4)	108·6 (6)	C(14)–C(11)–O(11)	106·0 (4)	106·6 (7)
C(14)–C(11)–C(12)	115·5 (5)	115·4 (7)	C(13)–C(12)–C(11)	114·6 (4)	113·7 (7)
C(12)–C(13)–O(12)	109·6 (4)	110·3 (7)	C(15)–C(13)–O(12)	107·1 (4)	107·7 (8)
C(15)–C(13)–C(12)	114·3 (4)	114·2 (8)			

Table 6. *Ring geometries of compounds* (*a*, *e*)-(2) *and* (*a*, *a*)-(2)

Plane	Atoms in the plane	Deviations (Å) from plane (*a*,*e*)-(2)	Deviations (Å) from plane (*a*,*a*)-(2)	Inclination angles (°) (*a*,*e*)-(2)	Inclination angles (°) (*a*,*a*)-(2)
(i)	O(11)	−0·005 (3)	0·019 (6)		
	O(12)	0·005 (3)	−0·019 (7)	α = (i)/(ii) = 39·9 (6)	42·5 (7)
	C(11)	0·007 (6)	−0·025 (10)		
	C(13)	−0·007 (6)	0·025 (10)		
(ii)	P(1)O(11)O(12)	0·0	0·0	β = (i)/(iii) = 51·7 (7)	51·1 (10)
(iii)	C(11)C(12)C(13)	0·0	0·0	α = (j)/(jj) = 34·3 (6)	42·3 (7)
(j)	O(22)	−0·021 (3)	0·019 (6)		
	O(21)	0·021 (3)	−0·019 (6)	β = (j)/(jjj) = 50·5 (7)	53·2 (10)
	C(21)	0·028 (6)	0·025 (9)		
	C(23)	−0·028 (6)	−0·025 (9)		
(jj)	P(2)O(21)O(22)	0·0	0·0	(j)/(i) = 62·9 (8)	78·7 (11)
(jjj)	C(21)C(22)C(23)	0·0	0·0		

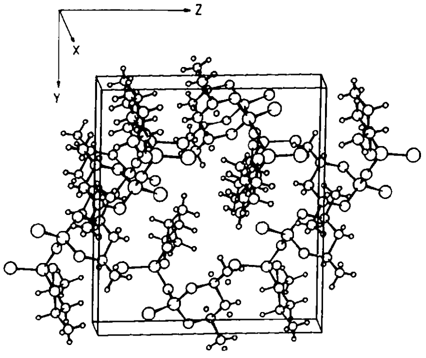


Fig. 3. The unit-cell contents of (*a*,*e*)-(2).

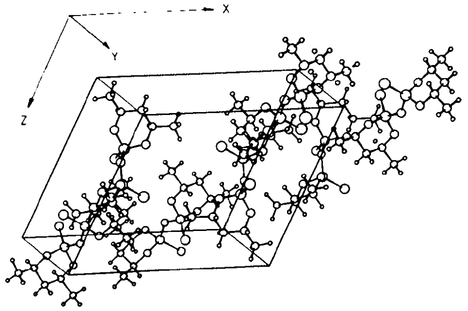


Fig. 4. The unit-cell contents of (*a*,*a*)-(2).

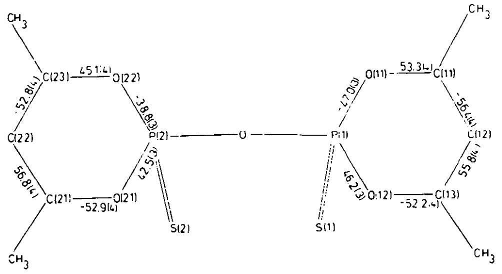


Fig. 5. Torsion angles (°) of (*a*,*e*)-(2).

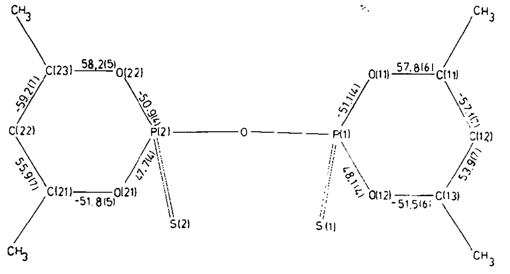


Fig. 6. Torsion angles (°) of (*a*,*a*)-(2).

Table 7. *Angles* (°) *between bonds and ring least-squares planes*

Plane	Atoms	(*a*,*e*)-(2)	(*a*,*a*)-(2)
O(11)O(12)C(11)- C(13)C(12)P(1)	C(11)···C(14)	−19·9 (6)	−18·4 (7)
	C(13)···C(15)	−21·5 (6)	−21·7 (7)
	P(1)···S(1)	63·4 (7)	67·6 (8)
O(21)O(22)C(21)- C(23)C(22)P(2)	C(23)···C(24)	−24·8 (6)	−22·1 (7)
	C(21)···C(25)	−14·5 (6)	−23·2 (7)
	P(2)···S(2)	−28·8 (7)	66·9 (8)

P(2)S(2)O]. Detailed information on the dihedral angles of (*a*,*e*)-(2) and (*a*,*a*)-(2) is given in Table 8. Considering the bonds and angles around the P atoms the following conclusions may be drawn for the two isomers of (2).

(1) The exocyclic O—P distance to the P bonded to the equatorially sited S in (*a*,*e*)-(2) is significantly longer than that to the P bonded to the axially sited S [1·608 (3) *versus* 1·580 (3) Å]. The O—P distances to the P bonded to an axially sited S are not significantly different [1·580(3), 1·579 (5), 1·594 (5) Å].

(2) The endocyclic O—P—O angle for the equatorially sited S is significantly larger than those for

Table 8. *Some dihedral angles (°) between planes defined by three atoms*

		Dihedral angle between planes 1 and 2	
Plane 1	Plane 2	(*a*,*e*)-(2)	(*a*,*a*)-(2)
S(2)P(2)O	S(1)P(1)O	39·0 (2)	103·4 (3)
S(2)P(2)O	P(1)OP(2)	55·9 (2)	45·4 (3)
S(1)P(1)O	P(1)OP(2)	69·3 (3)	39·9 (3)

the axially sited S atoms [106·7 (3) *versus* 105·0 (2), 104·2 (3) and 104·7 (3)°].

(3) The P(1)—O—P(2) angle in (*a*,*e*)-(2) is 5·6° larger than that in (*a*,*a*)-(2), presumably as a result of the shorter S···S contact in this isomer [3·99 *versus* 4·10 Å].

These conclusions are similar to those drawn for the axial–equatorial and equatorial–equatorial bis(4-methyl-2-thioxo-1,3,2-dioxaphosphorinanyl) oxide isomers [(*a*,*e*)-(1) and (*e*,*e*)-(1)]. The P—O ring bonds for the rings with an axial P=S bond are significantly longer than those in rings with an equatorial thiophosphoryl group. The P=S bond lengths are within the range (1·85–1·96 Å) typically observed for substituted phosphates (Corbridge, 1974).

References

Bukowska-Strzyżewska, M. & Dobrowolska, W. (1976). *Cryst. Struct. Commun.* **5**, 733–737.

Bukowska-Strzyżewska, M. & Dobrowolska, W. (1978). *Acta Cryst.* B**34**, 1357–1360.

Bukowska-Strzyżewska, M., Michalski, J., Młotkowska, B. & Skoweranda, J. (1976). *Acta Cryst.* B**32**, 2605–2608.

Corbridge, D. E. C. (1974). *The Structural Chemistry of Phosphorus*, p. 218. Amsterdam: Elsevier.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Karolak-Wojciechowska, J., Wieczorek, M. W., Mikołajczyk, M. & Ziemnicka, B. (1979). *Acta Cryst.* B**35**. Submitted.

Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination . Univ. of Cambridge, England.

Acta Cryst. (1979). B**35**, 2344–2347

The Crystal and Molecular Structure of 4-Thiobenzoylmorpholine at 200 K

By K. Ann Kerr* and Patrick M. A. O. Van Roey

Departments of Chemistry and Physics, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

(*Received* 26 *March* 1979; *accepted* 8 *June* 1979)

Abstract

$C_{11}H_{13}NOS$ crystallizes from benzene as yellow needles elongated in the *c* direction with space group $P2_12_12_1$. Crystal data at 200 K are: a = 10·770 (3), b = 17·401 (5), c = 5·661 (2) Å, V = 1060·9 Å^3, D_c = 1·298 Mg m^{-3}, Z = 4. The structure refined to an *R* value of 0·0364. The C—N length of 1·326 (3) Å and the C—S length of 1·683 (2) Å indicate extensive delocalization of the N lone pair. However the torsional angle of 64·8 (2)° between the phenyl and thiocarbonyl groups minimizes interaction between the two π systems.

Introduction

Substituents capable of conjugation with the thiocarbonyl group in thioamides can influence the interaction of the N lone pair with the π system of the thiocarbonyl. It has been shown by IR and NMR studies (Krueger & Fulea, 1975; Berg, 1976) that such substituents can either raise or lower the barrier to rotation about the C—N bond. This work is part of a crystallographic study of several related thioamides undertaken to provide a structural basis for evaluating the interaction between the thioamide moiety and the substituents in terms of electronic and steric effects in this class of compounds.

Since the structure of 4-thiobenzoylmorpholine was intended to be the reference structure for the series it was disappointing to find extremely high thermal motion in the room-temperature structure. In order to gain the required precision, the data were recollected at 200 K. Although the amplitude of vibration is considerably reduced at this temperature, thermal parameters are still significantly anisotropic.

---

* To whom correspondence should be addressed.

0567-7408/79/102344-04$01.00