Gartland, G. L., Freeman, G. R. & Bugg, C. E. (1974). *Acta Cryst.* B**30**, 1841–1849.
Ghosh, M., Basak, A. K., Mazumdar, S. K. & Sheldrick, B. (1989). *J. Crystallogr. Spectrosc. Res.* **19**, 289–298.
Grinev, A. N., Shvedov, V. I., Krichevskii, E. S., Romanova, O. B., Altukhova, L. B., Kurilo, G. N., Andreeva, N. I., Golovina, S. M. & Mashkovskii, M. D. (1984). *Khim. Farm. Zh.* **18**, 159–163.
Grinev, A. N., Trofimkin, Yu. I., Lomanova, E. V., Andreeva, N. I. & Mashkovskii, M. D. (1978). *Khim. Farm. Zh.* **12**, 80–84.
Leger, J. M., Alberola, S. & Carpy, A. (1977). *Acta Cryst.* B**33**, 1455–1459.
Merk, P. (1971). *J. Appl. Phys.* **21**, 62–73.
Motherwell, W. D. S. & Clegg, W. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Rodriguez, J. G., Temprano, F., Esteban-Calderon, C., Martinez-Ripoll, M. & Garcia-Blanco, S. (1985). *Tetrahedron*, **41**, 3813–3823.
Sadanandan, S. (1994). Personal communication.
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.
Vijayalakshmi, B. K. & Srinivasan, R. (1975). *Acta Cryst.* B**31**, 999–1003.
Yamane, T., Andou, T. & Ashida, T. (1977). *Acta Cryst.* B**33**, 1650–1653.

Acta Cryst. (1995). C**51**, 80–84

A Macrobicyclic Thiophosphonamide Polyether Ligand

LUC VAN OOSTENRYCK, BERNARD TINANT
AND JEAN-PAUL DECLERCQ

Université Catholique de Louvain, Laboratoire de Chimie Physique Moléculaire et de Cristallographie, Unité CPMC, 1, Place Louis Pasteur,
B 1348 Louvain-la-Neuve, Belgium

JEAN-PIERRE DUTASTA

Stéréochimie et Interactions Moléculaires,
Ecole Normale Supérieure de Lyon,
46 Allée d'Italie, F 69364 Lyon CEDEX 07,
France

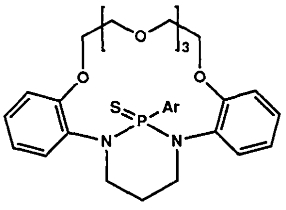
(*Received* 16 *December* 1993; *accepted* 11 *April* 1994)

Abstract

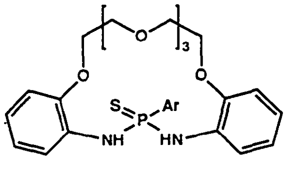
Two crystal structures of a macrobicyclic oligoether compound, 31-phenyl-8,11,14,17,20-pentoxa-1,27-diaza-31-phosphatetracyclo[25.3.1.$0^{2,7}$.$0^{21,26}$]henitriaconta-2,4,6,21,23,25-hexaene 31-sulfide, $C_{29}H_{35}N_2O_5PS$, (1), containing a thiophosphonamide group, are described. The molecules in the two crystals, (I) and (II), exhibit very similar conformations except for a disordered part in crystal form (II). A macrocyclic cavity appears in both conformations, although some O atoms of the $O(CH_2CH_2O)_4$ bridge are turned outwards. The propyl bridge and the phenyl group of the diazaphosphorinane moiety lie close to the sides of the macrocycle. The thiophosphoryl group is directed outwards.

Comment

The introduction of phosphorus binding sites in a host can markedly change its binding power and selectivity towards various guests. The title host, (1), is representative of a new class of organophosphorus ligands containing a crown macrocycle with phosphonamide groups as binding subunits (Dutasta, Declercq, Esteban-Calderon & Tinant, 1989; Dutasta, Van Oostenryck, Tinant & Declercq, 1993; Van Oostenryck, Tinant, Declercq, Dutasta & Simon, 1993). Compound (1) was designed to explore the feasibility and the properties of preorganized ligands based on our previously reported macrocyclic phosphorus host (2) (Dutasta & Simon, 1987). The introduction of the diazaphosphorinane ring enforces rigidity (Dutasta, Esteban-Calderon, Tinant & Declercq, 1990) and can afford two different configurations depending on the orientation of the substituents around the P atom. Therefore, we undertook the solid-state structure determination of compound (1), which was obtained by treatment of precursor (2) with propane diol ditosylate under basic conditions.



(1)



(2)

Two crystal forms of (1) exist and both are presented here. The first crystal form, (I), was obtained by evaporation from dichloromethane/hexane. The second, (II), appeared during unsuccessful attempts to complex potassium thiocyanate; it was obtained by evaporation from an acetone solution containing equimolar amounts of ligand (1) and potassium salt. As shown by the crystal structure analysis, no cation was included in this second crystal form.

The general folding of the molecule is very similar in the two structures. However, its must be noted that in the crystal form (II), disorder appeared involving four adjacent atoms of the polyether chain (C21–C24), with relative occupancies 0.72:0.28. This disorder implies two different conformations, which are reported in this discussion as (II*A*) and (II*B*). Fig. 1 is a view of structure (II*A*) giving the numbering of the atoms. In Fig. 2, the non-H atoms of (I) and (II*A*) are superimposed.

Acta Crystallographica Section C
ISSN 0108-2701 © 1995

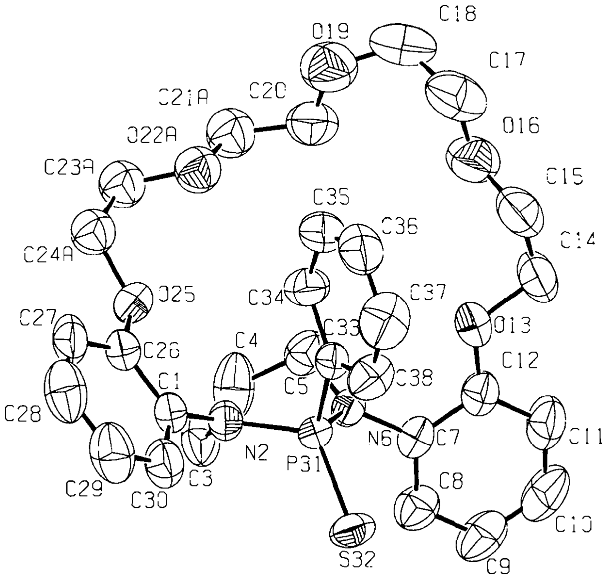


Fig. 1. View of molecule (II*A*) showing the numbering of the atoms. Displacement ellipsoids are plotted at the 50% probability level.

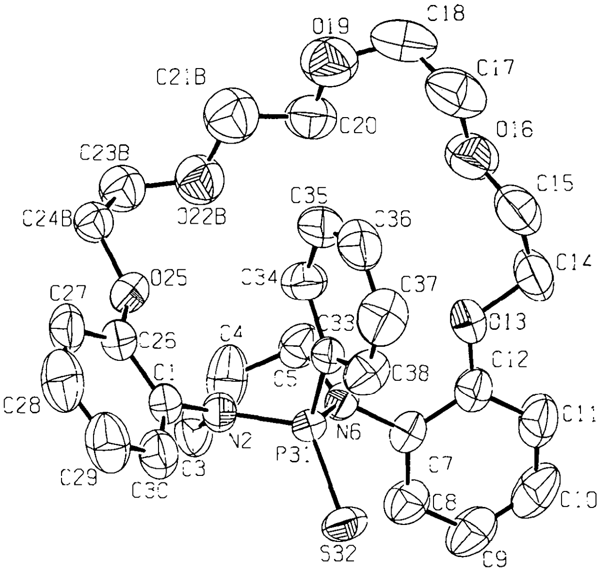


Fig. 3. View of molecule (II*B*) showing the numbering of the atoms. Displacement ellipsoids are plotted at the 50% probability level..

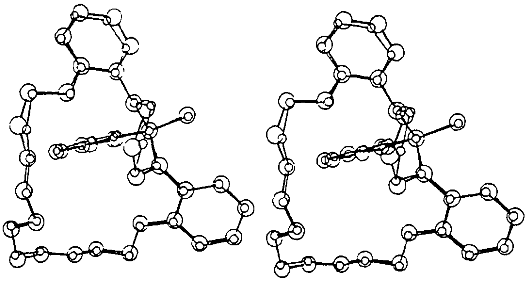


Fig. 2. Superposition picture of molecules (I) and (II*A*).

The only significant difference between (I) and (II) concerns the conformation of the diazaphosphorinane ring. Both six-membered heterocycles have an approximate twist conformation (Duax, Weeks & Rhorer, 1976). The succession of intracyclic torsion angles (N6—P31—N2—C3—C4—C5—N6) is 23, −64, 41, 16, −60 and 38°, respectively, for (I), and 36, −66, 25, 35, −67 and 29°, respectively, for (II). The conformation of the oligoether chain can be described qualitatively, according to Dale (1980), as a succession of groups of three torsion angles in each oxyethylene unit. Molecules (I) and (II*A*) are characterized by exactly the same $(ag^-a)(ag^+g^-)(ag^-a)(ag^-a)$ arrangement. The succession of (*aga*) torsion angles is usually favourable for good convergence of the O atoms towards the cavity. In the present study, a 'pseudo-corner' (ag^+g^-) appears, so that the O atoms are only moderately well oriented towards the cavity. The conformation of the minor component (II*B*) (Fig. 3) is rather different. In the succession $(ag^-a)(ag^+g^-)(aaa)(g^-g^-a)$, there appears a pseudo-corner (ag^+g^-), an all *trans* sequence (*aaa*) and a 'genuine' corner (g^-g^-a).

The following conformational features, common to both structures, are of interest: (i) a macrocyclic cavity defined in all cases by the oligoether chain and the phosphonamide group; (ii) this cavity is partially occupied on one side by the phenyl substituent of the P atom, whereas the other side is crowded by the CH_2—CH_2—CH_2 linkage of the six-membered heterocycle; (iii) the P═S bond turns away from the cavity and is almost coplanar with the P—Ph group; and (iv) the N atoms are close to planarity with the sum of their bond angles being greater than 357°.

With the exception of the disordered part of molecule (II), the distances and angles in the polyether chain show the usual features of such chains, *i.e.* shortened C—C bond distances and widened C—O—C bond angles. Some of the bond angles in molecule (II*B*) are very distorted, probably resulting from the weak occupation which does not allow very accurate refinement of the atoms involved. The coordination of the P atom is distorted tetrahedral. The observed distances around this atom are in good agreement with the mean values we have calculated from fifty thiophosphonamide groups found in the Cambridge Structural Database (Allen *et al.*, 1979): P═S 1.93, P—C 1.80 and P—N 1.68 Å. The large mean value of the C—P═S angle (113°) and the small mean value of the N—P—N angle (95°) calculated from these fifty thiophosphonamide groups also agree with our results. More surprisingly, we observed large dissymmetries in the S═P—N and C—P—N angles: approximately 120° for S32═P31—N2 compared with 112° for S32═P31—N6, and approximately 103° for C33—P31—N2 and 112° for C33—P31—N6 in both structures. The corresponding calculated mean values are 116 and 107°, respectively. This dissymmetry may be attributed to the very different orientations of the phenyl rings bonded to N2 and N6. The orientation of the first brings H30 into a steric interaction with S32, which could be responsible for the opening of the S32═P31—N2 angle.

The conformation of the free molecule does not seem very favourable for complexation. If in fact a cation was in the cavity, a more suitable molecular conformation would be one where the P—Ph group is directed outwards (*exo* position) and all O atoms and the P═S bond are turned inwards. In this case the cavity could accomodate a guest with participation of the thiophosphoryl binding site. Such a situation could be attained by the rotation of the entire six-membered ring around the N—C(aromatic) bonds independently of its own conformation, *i.e.* its twist or even chair conformation, although in the latter case axial or equatorial orientations of the P═S bond should be considered. This process would, however, be of high energy as the phenyl group or the propyl part of the six-membered heterocycle would have to go through the macrocyclic cavity. Such a conformational reorganization has been observed upon complexation of parent compounds (Van Oostenryck, Declercq, Dutasta & Tinant, 1994). However, solution studies of the free ligand did not allow characterization of the second form where the P═S and P—Ph groups are exchanged from an *exo–endo* to an *endo–exo* conformation.

Experimental

Compound (I)

Crystal data

$C_{29}H_{35}N_2O_5PS$
$M_r = 554.62$
Monoclinic
$P2_1/n$
$a = 12.674\ (3)$ Å
$b = 20.023\ (4)$ Å
$c = 11.494\ (3)$ Å
$\beta = 96.11\ (2)°$
$V = 2900.3\ (12)$ Å^3
$Z = 4$
$D_x = 1.270$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 2.5–12.5°$
$\mu = 0.207$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
0.32 × 0.24 × 0.18 mm

Data collection

Syntex $P2_1$ four-circle diffractometer
ω scans
5699 measured reflections
5699 independent reflections
4197 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 26.00°$

$h = 0 \rightarrow 15$
$k = 0 \rightarrow 24$
$l = -14 \rightarrow 14$
1 standard reflection monitored every 50 reflections intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0487$
$wR(F^2) = 0.1306$
$S = 1.176$
5699 reflections
344 parameters
All H-atom parameters refined with a common $U = 0.085\ (2)$ Å^2 for all H atoms

$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.5425P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.618$ e Å^{-3}
$\Delta\rho_{min} = -0.211$ 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) *for* (I)

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

	x	y	z	U_{eq}
C1	0.1505 (2)	0.39840 (11)	0.0528 (2)	0.0430 (5)
N2	0.25703 (13)	0.41084 (9)	0.10272 (15)	0.0409 (4)
C3	0.3060 (2)	0.47596 (13)	0.0853 (2)	0.0606 (7)
C4	0.3508 (3)	0.50617 (14)	0.2003 (3)	0.0811 (9)
C5	0.4059 (2)	0.45701 (13)	0.2828 (2)	0.0597 (7)
N6	0.43065 (13)	0.39406 (9)	0.22482 (15)	0.0404 (4)
C7	0.5363 (2)	0.36838 (11)	0.2493 (2)	0.0422 (5)
C8	0.6061 (2)	0.37151 (14)	0.1657 (2)	0.0560 (6)
C9	0.7095 (2)	0.3473 (2)	0.1893 (3)	0.0697 (8)
C10	0.7412 (2)	0.3211 (2)	0.2969 (3)	0.0690 (8)
C11	0.6739 (2)	0.31843 (13)	0.3825 (2)	0.0585 (6)
C12	0.5702 (2)	0.34165 (11)	0.3593 (2)	0.0459 (5)
O13	0.49632 (13)	0.34053 (9)	0.43701 (14)	0.0584 (5)
C14	0.5297 (2)	0.31799 (15)	0.5534 (2)	0.0641 (7)
C15	0.4347 (3)	0.3124 (2)	0.6178 (2)	0.0722 (8)
O16	0.4003 (2)	0.37632 (10)	0.6490 (2)	0.0711 (5)
C17	0.3165 (3)	0.3720 (2)	0.7218 (3)	0.0849 (10)
C18	0.2800 (3)	0.4408 (2)	0.7512 (3)	0.0817 (9)
O19	0.2124 (2)	0.47107 (11)	0.6623 (2)	0.0780 (6)
C20	0.2653 (2)	0.5030 (2)	0.5765 (2)	0.0660 (7)
C21	0.1903 (3)	0.5445 (2)	0.4998 (3)	0.0763 (8)
O22	0.1284 (2)	0.50509 (10)	0.4205 (2)	0.0714 (5)
C23	0.0599 (2)	0.5441 (2)	0.3403 (3)	0.0781 (9)
C24	0.0104 (2)	0.5002 (2)	0.2477 (2)	0.0696 (8)
O25	0.09359 (12)	0.47589 (9)	0.18402 (15)	0.0571 (4)
C26	0.0664 (2)	0.43083 (13)	0.0976 (2)	0.0492 (6)
C27	−0.0377 (2)	0.4166 (2)	0.0533 (3)	0.0651 (7)
C28	−0.0565 (2)	0.3707 (2)	−0.0357 (3)	0.0726 (8)
C29	0.0245 (2)	0.33947 (15)	−0.0821 (3)	0.0679 (7)
C30	0.1282 (2)	0.35316 (12)	−0.0379 (2)	0.0533 (6)
P31	0.33351 (4)	0.34850 (3)	0.15775 (5)	0.0386 (2)
S32	0.38609 (5)	0.28272 (4)	0.05509 (6)	0.0651 (2)
C33	0.2528 (2)	0.30994 (12)	0.2601 (2)	0.0472 (5)
C34	0.1959 (2)	0.3491 (2)	0.3304 (2)	0.0670 (8)
C35	0.1360 (3)	0.3199 (2)	0.4101 (3)	0.0965 (12)
C36	0.1299 (3)	0.2532 (2)	0.4197 (4)	0.1028 (14)
C37	0.1844 (3)	0.2133 (2)	0.3499 (4)	0.0928 (12)
C38	0.2477 (2)	0.24121 (14)	0.2697 (3)	0.0667 (7)

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

C1—C30	1.387 (3)	C17—C18	1.504 (5)
C1—C26	1.393 (3)	C18—O19	1.400 (4)
C1—N2	1.432 (3)	O19—C20	1.404 (3)
N2—C3	1.467 (3)	C20—C21	1.480 (4)
N2—P31	1.663 (2)	C21—O22	1.384 (3)
C3—C4	1.509 (4)	O22—C23	1.430 (3)
C4—C5	1.489 (4)	C23—C24	1.470 (4)
C5—N6	1.475 (3)	C24—O25	1.431 (3)
N6—C7	1.434 (3)	O25—C26	1.359 (3)
N6—P31	1.655 (2)	C26—C27	1.392 (3)
C7—C8	1.374 (3)	C27—C28	1.376 (4)
C7—C12	1.399 (3)	C28—C29	1.359 (4)
C8—C9	1.397 (4)	C29—C30	1.385 (3)
C9—C10	1.363 (4)	P31—C33	1.812 (2)
C10—C11	1.370 (4)	P31—S32	1.9336 (9)
C11—C12	1.394 (3)	C33—C34	1.382 (4)
C12—O13	1.361 (3)	C33—C38	1.383 (4)
O13—C14	1.432 (3)	C34—C35	1.380 (4)

C14—C15	1.484 (4)	C35—C36	1.342 (6)
C15—O16	1.410 (4)	C36—C37	1.370 (6)
O16—C17	1.423 (3)	C37—C38	1.401 (4)
C30—C1—C26	118.7 (2)	C18—O19—C20	114.1 (2)
C30—C1—N2	121.5 (2)	O19—C20—C21	110.4 (2)
C26—C1—N2	119.8 (2)	O22—C21—C20	110.8 (2)
C1—N2—C3	119.6 (2)	C21—O22—C23	112.0 (2)
C1—N2—P31	120.56 (14)	O22—C23—C24	108.8 (2)
C3—N2—P31	118.75 (15)	O25—C24—C23	107.0 (2)
N2—C3—C4	111.2 (2)	C26—O25—C24	117.1 (2)
C5—C4—C3	113.6 (2)	O25—C26—C27	124.1 (2)
N6—C5—C4	112.6 (2)	O25—C26—C1	115.8 (2)
C7—N6—C5	117.2 (2)	C27—C26—C1	120.1 (2)
C7—N6—P31	121.76 (14)	C28—C27—C26	119.5 (3)
C5—N6—P31	119.89 (15)	C29—C28—C27	121.3 (3)
C8—C7—C12	119.4 (2)	C28—C29—C30	119.5 (3)
C8—C7—N6	120.3 (2)	C29—C30—C1	120.9 (3)
C12—C7—N6	120.3 (2)	N6—P31—N2	97.93 (9)
C7—C8—C9	120.6 (3)	N6—P31—C33	112.07 (10)
C10—C9—C8	119.2 (3)	N2—P31—C33	102.72 (9)
C9—C10—C11	121.4 (2)	N6—P31—S32	111.84 (7)
C10—C11—C12	119.8 (3)	N2—P31—S32	120.25 (7)
O13—C12—C11	124.8 (2)	C33—P31—S32	111.17 (9)
O13—C12—C7	115.7 (2)	C34—C33—C38	119.1 (2)
C11—C12—C7	119.5 (2)	C34—C33—P31	120.2 (2)
C12—O13—C14	117.5 (2)	C38—C33—P31	120.7 (2)
O13—C14—C15	108.3 (2)	C35—C34—C33	120.4 (3)
O16—C15—C14	110.4 (2)	C36—C35—C34	121.1 (4)
C15—O16—C17	111.3 (2)	C35—C36—C37	119.6 (3)
O16—C17—C18	110.0 (3)	C36—C37—C38	120.8 (3)
O19—C18—C17	114.3 (3)	C33—C38—C37	119.0 (3)

Compound (II)

Crystal data

$C_{29}H_{35}N_2O_5PS$
$M_r = 554.62$
Monoclinic
$P2_1/n$
$a = 16.791\ (12)$ Å
$b = 15.927\ (11)$ Å
$c = 10.922\ (6)$ Å
$\beta = 100.31\ (5)°$
$V = 2873.7\ (33)$ Å^3
$Z = 4$
$D_x = 1.282$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 2.5–12.5°$
$\mu = 0.209$ mm^{-1}
$T = 293\ (2)$ K
Plate-like
0.48 × 0.48 × 0.10 mm

Data collection

Syntex $P2_1$ four-circle diffractometer
ω scans
5658 measured reflections
5658 independent reflections
3747 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max} = 26.03°$

$h = 0 \rightarrow 20$
$k = 0 \rightarrow 19$
$l = -13 \rightarrow 13$
1 standard reflection monitored every 50 reflections intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0560$
$wR(F^2) = 0.1511$
$S = 1.190$
5656 reflections
341 parameters
All H-atom parameters refined with a common $U = 0.093\ (2)$ Å^2 for all H atoms

$w = 1/[\sigma^2(F_o^2) + (0.0932P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.346$ e Å^{-3}
$\Delta\rho_{\min} = -0.341$ 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 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

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

	x	y	z	$U_{\rm eq}$
C1	0.0168 (2)	0.0998 (2)	0.2906 (2)	0.051 (1)
N2	−0.0212 (1)	0.1800 (1)	0.2772 (2)	0.048 (1)
C3	−0.0951 (2)	0.1929 (2)	0.3295 (3)	0.072 (1)
C4	−0.0899 (2)	0.2717 (2)	0.4099 (4)	0.090 (1)
C5	−0.0329 (2)	0.3347 (2)	0.3734 (2)	0.065 (1)
N6	−0.0351 (1)	0.3331 (1)	0.2375 (2)	0.048 (1)
C7	−0.0694 (2)	0.4043 (2)	0.1677 (2)	0.051 (1)
C8	−0.1483 (2)	0.4024 (2)	0.1046 (3)	0.067 (1)
C9	−0.1820 (2)	0.4719 (2)	0.0381 (3)	0.083 (1)
C10	−0.1360 (2)	0.5421 (2)	0.0365 (3)	0.090 (1)
C11	−0.0577 (2)	0.5463 (2)	0.0994 (3)	0.079 (1)
C12	−0.0241 (2)	0.4772 (2)	0.1678 (2)	0.059 (1)
O13	0.0525 (1)	0.4735 (1)	0.2346 (2)	0.069 (1)
C14	0.1026 (2)	0.5466 (2)	0.2387 (3)	0.082 (1)
C15	0.1861 (2)	0.5221 (2)	0.2965 (3)	0.088 (1)
O16	0.1927 (1)	0.5146 (2)	0.4275 (2)	0.092 (1)
C17	0.2723 (2)	0.4920 (3)	0.4871 (4)	0.108 (1)
C18	0.2758 (2)	0.4794 (3)	0.6230 (4)	0.108 (1)
O19	0.2449 (2)	0.4038 (2)	0.6569 (3)	0.103 (1)
C20	0.1611 (2)	0.3994 (2)	0.6388 (3)	0.087 (1)
C21*A*	0.1287 (3)	0.3286 (3)	0.7055 (5)	0.081 (1)
O22*A*	0.1389 (2)	0.2531 (2)	0.6426 (3)	0.072 (1)
C23*A*	0.1054 (3)	0.1843 (3)	0.6956 (4)	0.072 (1)
C24*A*	0.1091 (3)	0.1087 (3)	0.6145 (4)	0.067 (1)
C21*B*	0.1679 (9)	0.3089 (9)	0.6846 (16)	0.103 (5)
O22*B*	0.0845 (5)	0.2819 (5)	0.6566 (8)	0.082 (3)
C23*B*	0.0664 (8)	0.2040 (7)	0.7039 (10)	0.072 (3)
C24*B*	0.0876 (7)	0.1275 (6)	0.6333 (9)	0.053 (3)
O25	0.0534 (1)	0.1303 (1)	0.5010 (2)	0.066 (1)
C26	0.0568 (2)	0.0745 (2)	0.4082 (3)	0.056 (1)
C27	0.0962 (2)	−0.0025 (2)	0.4236 (3)	0.073 (1)
C28	0.0959 (2)	−0.0531 (2)	0.3213 (4)	0.087 (1)
C29	0.0580 (2)	−0.0292 (2)	0.2055 (4)	0.089 (1)
C30	0.0180 (2)	0.0468 (2)	0.1906 (3)	0.070 (1)
P31	−0.0012 (1)	0.2497 (1)	0.1740 (1)	0.043 (1)
S32	−0.0482 (1)	0.2373 (1)	−0.0014 (1)	0.063 (1)
C33	0.1081 (1)	0.2480 (1)	0.1971 (2)	0.046 (1)
C34	0.1545 (2)	0.2524 (2)	0.3165 (3)	0.065 (1)
C35	0.2375 (2)	0.2543 (2)	0.3338 (3)	0.077 (1)
C36	0.2757 (2)	0.2508 (2)	0.2347 (4)	0.081 (1)
C37	0.2318 (2)	0.2455 (2)	0.1180 (4)	0.088 (1)
C38	0.1479 (2)	0.2441 (2)	0.0981 (3)	0.067 (1)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

C1—C30	1.383 (4)	C20—C21*A*	1.498 (5)
C1—C26	1.398 (4)	C20—C21*B*	1.523 (13)
C1—N2	1.424 (3)	C21*A*—O22*A*	1.410 (6)
N2—C3	1.470 (3)	O22*A*—C23*A*	1.405 (5)
N2—P31	1.658 (2)	C23*A*—C24*A*	1.502 (6)
C3—C4	1.526 (5)	C24*A*—O25	1.454 (5)
C4—C5	1.489 (4)	C21*B*—O22*B*	1.44 (2)
C5—N6	1.478 (3)	O22*B*—C23*B*	1.398 (12)
N6—C7	1.429 (3)	C23*B*—C24*B*	1.518 (14)
N6—P31	1.646 (2)	C24*B*—O25	1.457 (10)
C7—C8	1.380 (4)	O25—C26	1.357 (3)
C7—C12	1.388 (4)	C26—C27	1.389 (4)
C8—C9	1.387 (4)	C27—C28	1.377 (5)
C9—C10	1.362 (5)	C28—C29	1.365 (5)
C10—C11	1.372 (5)	C29—C30	1.380 (4)
C11—C12	1.392 (4)	P31—C33	1.807 (3)
C12—O13	1.361 (3)	P31—S32	1.9464 (14)
O13—C14	1.433 (3)	C33—C38	1.371 (4)
C14—C15	1.482 (5)	C33—C34	1.396 (4)
C15—O16	1.420 (4)	C34—C35	1.372 (4)
O16—C17	1.425 (4)	C35—C36	1.355 (5)
C17—C18	1.488 (5)	C36—C37	1.355 (5)
C18—O19	1.388 (5)	C37—C38	1.387 (4)
O19—C20	1.387 (4)		
C30—C1—C26	118.5 (3)	O22*A*—C21*A*—C20	108.5 (4)
C30—C1—N2	122.4 (2)	C23*A*—O22*A*—C21*A*	111.8 (3)

C26—C1—N2	119.1 (2)	O22*A*—C23*A*—C24*A*	108.7 (4)
C1—N2—C3	118.6 (2)	O25—C24*A*—C23*A*	103.0 (4)
C1—N2—P31	121.9 (2)	O22*B*—C21*B*—C20	101.5 (10)
C3—N2—P31	117.3 (2)	C23*B*—O22*B*—C21*B*	117.0 (9)
N2—C3—C4	111.9 (2)	O22*B*—C23*B*—C24*B*	116.0 (9)
C5—C4—C3	111.9 (2)	O25—C24*B*—C23*B*	113.1 (8)
N6—C5—C4	110.8 (3)	C26—O25—C24*A*	112.0 (3)
C7—N6—C5	117.2 (2)	C26—O25—C24*B*	131.2 (5)
C7—N6—P31	123.5 (2)	O25—C26—C27	124.8 (3)
C5—N6—P31	119.2 (2)	O25—C26—C1	114.8 (2)
C8—C7—C12	119.7 (2)	C27—C26—C1	120.4 (3)
C8—C7—N6	120.6 (2)	C28—C27—C26	119.1 (3)
C12—C7—N6	119.6 (2)	C29—C28—C27	121.5 (3)
C7—C8—C9	120.6 (3)	C28—C29—C30	119.4 (3)
C10—C9—C8	118.9 (3)	C29—C30—C1	121.2 (3)
C9—C10—C11	121.9 (3)	N6—P31—N2	97.26 (11)
C10—C11—C12	119.4 (3)	N6—P31—C33	111.82 (11)
O13—C12—C7	115.4 (2)	N2—P31—C33	102.68 (11)
O13—C12—C11	125.1 (3)	N6—P31—S32	112.74 (8)
C7—C12—C11	119.4 (3)	N2—P31—S32	120.37 (8)
C12—O13—C14	118.3 (2)	C33—P31—S32	110.99 (10)
O13—C14—C15	107.8 (3)	C38—C33—C34	118.0 (2)
O16—C15—C14	110.4 (3)	C38—C33—P31	121.1 (2)
C15—O16—C17	112.3 (3)	C34—C33—P31	120.9 (2)
O16—C17—C18	110.9 (3)	C35—C34—C33	120.9 (3)
O19—C18—C17	115.7 (3)	C36—C35—C34	120.2 (3)
C20—O19—C18	115.1 (3)	C35—C36—C37	119.9 (3)
O19—C20—C21*A*	114.5 (3)	C36—C37—C38	121.0 (3)
O19—C20—C21*B*	89.1 (6)	C33—C38—C37	120.1 (3)

Data collection, cell refinement and data reduction: local programs. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978); *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

The National Fund for Scientific Research, Belgium, is gratefully acknowledged for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* B**35**, 2331–2339.

Dale, J. (1980). *Isr. J. Chem.* **20**, 3–11.

Duax, W. L., Weeks, C. M. & Rhorer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, pp 271–383. New York: John Wiley.

Dutasta, J.-P., Declercq, J.-P., Esteban-Calderon, C. & Tinant, B. (1989). *J. Am. Chem. Soc.* **111**, 7136–7144.

Dutasta, J.-P., Esteban-Calderon, C., Tinant, B. & Declercq, J.-P. (1990). *Acta Cryst.* C**46**, 68–71.

Dutasta, J.-P. & Simon, P. (1987). *Tetrahedron Lett.* **28**, 3577–3580.

Dutasta, J.-P., Van Oostenryck, L., Tinant, B. & Declercq, J.-P. (1993). *Phosphorus Sulfur Silicon*, **75**, 63–66.

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

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

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

Van Oostenryck, L., Declercq, J.-P., Dutasta, J.-P. & Tinant, B. (1994). Unpublished results.

Van Oostenryck, L., Tinant, B., Declercq, J.-P., Dutasta, J.-P. & Simon, P. (1993). *J. Incl. Phenom. Mol. Recognit. Chem.* **16**, 383–402.

Acta Cryst. (1995). C**51**, 84–86

(1′*R*,2*S*,3*R*)-2-Hydroxy-2-(1-hydroxyethyl)-3-methyl-γ-butyrolactone

Jürgen Kopf

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Stefan Schulz

Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

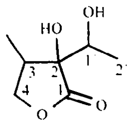
(*Received* 13 *May* 1994; *accepted* 14 *July* 1994)

Abstract

The determination of the structure of the title compound, $C_7H_{12}O_4$, allowed the unambiguous elucidation of the absolute configuration of a pheromone produced by the tropical butterfly *Prittwitzia hymaenea*. This unique pheromone is the 1′-epimer of the title compound. The lactone ring adopts a rather flat, almost ideal envelope conformation. The structure is stabilized by hydrogen bonds.

Comment

2-Hydroxy-2-(1-hydroxyethyl)-3-methyl-γ-butyrolactone, (I), has been identified as an Ithomiine butterfly pheromone, but no absolute or relative configuration has been reported (Edgar, Culvenor & Pliske, 1976). It is likely that this lactone is produced from 2,3-dihydroxy-2-(1-methylethyl)butanoic acids (viridifloric and trachelantic acids), obtained by the cleavage of pyrrolizidine alkaloids taken up from the plants that the butterflies feed upon (Edgar, Culvenor & Pliske, 1976). All enantiomers of the acids occur in these plant alkaloids.



(I)

Acta Crystallographica Section C
ISSN 0108-2701 ©1995