

Structure of *N,N'*-Dibenzyl-*N*-(4-methyl-2-oxo-1,3λ⁵, 2-dioxaphosphorinan-2-yl)thiourea, C₁₉H₂₃N₂O₃PS

BY JANINA KAROLAK-WOJCIECHOWSKA AND MICHAŁ W. WIECZOREK

Institute of General Chemistry, Technical University, 90–362 Łódź, Zwirki 36, Poland

MARIAN MIKOŁAJCZYK, ANNA SUT AND PIOTR KIELBASINSKI

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

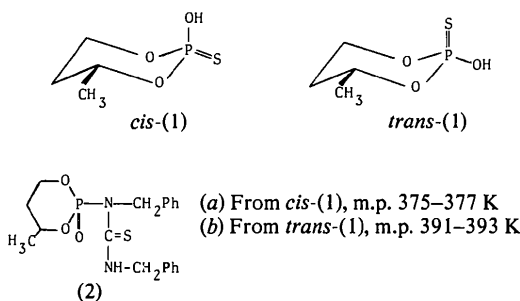
AND YURIU T. STRUCHKOV AND MICHAEL Y. ANTIPIN

Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov Street, Moscow 117312, USSR

(Received 5 November 1982; accepted 17 December 1982)

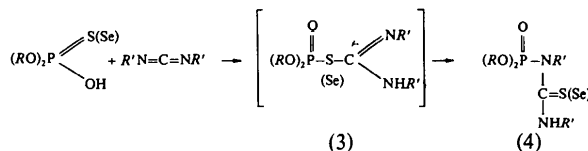
Abstract. $M_r = 390.44$, monoclinic, space group $P2_1/a$, $a = 17.423$ (9), $b = 15.089$ (3), $c = 7.582$ (2) Å, $\beta = 112.96$ (4)°, $V = 1835.36$ Å³, $Z = 4$, $D_x = 1.337$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.36$ cm⁻¹, $F(000) = 824$, $T = 153$ K. Final $R = 0.051$ for 1663 observed reflections. The atoms forming the thiourea system are coplanar. The 1,3,2-dioxaphosphorinane ring has a chair conformation with the N atom in an equatorial position. There is an intramolecular hydrogen bond between the phosphoryl O atom and the secondary N atom.

Introduction. As a continuation of a research programme on the reaction of carbodiimides with phosphorothio(seleno)ic acids (Mikołajczyk, Kielbasinski & Goszczynska, 1977) we have synthesized two diastereoisomeric *N*-phosphorylthioureas (2), starting from *N,N'*-dibenzylcarbodiimide and both *cis*- and *trans*-diastereoisomers of a model cyclic thioacid: 2-hydroxy-4-methyl-2-thioxo-1,3,2-dioxaphosphorinane (1).



The aim of the present study was to determine the stereochemistry of the rearrangement of *S*(Se)-phosphorylthio(seleno)ureas (3), which are formed in the first step of the reaction between carbodiimides

and phosphorothio(seleno)ic acids, to the stable and isolable *N*-phosphorylthio(seleno)ureas (4).



In this paper we report an X-ray analysis of *N*-phosphorylthiourea (2a) obtained from *cis*-(1). The analysis was undertaken to compare the configuration at the P atom in the adduct and in the parent thioacid.

Recently we have also described an X-ray analysis of *N,N'*-dibenzyl-*N*-diphenoxyphosphorylthiourea (Karolak-Wojciechowska, Wieczorek, Mikołajczyk, Kielbasinski, Struchkov & Antipin, 1979).

Experimental. Space group and approximate unit-cell parameters determined photographically using Cu $K\alpha$ radiation and the latter adjusted by a least-squares fit of the optimized diffractometer setting angles of 15 selected reflections; Syntex $P1$ diffractometer, no absorption correction applied, $2\theta \leq 50^\circ$, θ - 2θ scan technique, Mo $K\alpha$ radiation; intensities of three standard reflections monitored at frequent intervals showed no significant fluctuations during data collection; of the 2323 reflections measured 1663 classified as observed using criterion $|F_o| \geq 4\sigma|F_o|$, these 1663 observations used in final refinement of the structure; structure solved by the automatic centrosymmetric direct methods from *SHELX* 76 system of programs (Sheldrick, 1976); structure refined by full-matrix least squares for non-H with anisotropic temperature factors and with isotropic temperature factors for H atoms, which were located in a difference map in the expected positions; isotropic thermal parameters of H atoms

taken as for their parent C atoms not refined; process of refining stopped when changes in all parameters became less than $\frac{1}{15}$ of their respective e.s.d.'s; final conventional $R = 0.051$ and $R_w = 0.046$, weighting scheme $w = k/[\sigma^2(F_o) + gF_o^2]$; in final difference map no significant density observed; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations performed on an Odra 1305 computer using *SHELX 76*.

Discussion. Table 1 lists the final positional and isotropic thermal parameters.*

The numbering scheme of the compound investigated is presented in Fig. 1. The bond lengths and angles are listed in Table 2.

The molecule contains the six-membered 1,3,2-dioxaphosphorinane and two benzene rings joined by the thiourea skeleton. The deviations of the atoms from the weighted mean planes for both benzene rings and the plane of the thiourea moiety are listed in the Supplementary Publication.*

An analysis of the thermal vibrations of both benzene rings was carried out in the TLS approximation of rigid-body motion (Schomaker & Trueblood, 1968). Bond lengths corrected for libration do not differ significantly from the uncorrected values (the deviations do not exceed the corresponding e.s.d.'s). The changes in bond lengths are given in the Supplementary Publication.* Nevertheless, only uncorrected values will be used in the following discussion.

The atoms N(1), N(2), C(1) and S from the thiourea skeleton form a plane and the remaining atoms C(2), H(3), P and C(3), bonded to N(2) and N(1), are slightly out of this plane. The benzene rings are inclined to this plane at 85.1 (6)° and 75.2 (6)° respectively.

The conformation of the 1,3,2-dioxaphosphorinane ring can be described as a chair on the basis of torsion angles (Table 3). The ring is flattened at the phosphorus end and the angle between the planes passing through the atoms (i): O(1), O(2), C(4) and C(6) and (ii): P, O(1), O(2) is 36.5 (8)°. This flattening can be found in other compounds containing the 1,3,2-dioxaphosphorinane ring (Cameron & Karolak-Wojciechowska, 1977). The phosphoryl oxygen occupies an axial position. The angle between the bond vector P—O(3) and the plane defined above as (i) is 72.1 (6)°. The bonds P—N(1) and C(6)—C(7) are equatorial and the angles between these bonds and plane (i) are 39.8 (8)° and 29.3 (8)° respectively.

Table 1. Positional ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters ($\times 10^3$)

$$U_{eq} = \frac{U_{11} + U_{22}\sin^2\beta + U_{33}\cos\beta}{3(1-\cos^2\beta)}$$

	x	y	z	$U_{eq}/U(\text{\AA}^2)$
P	7474 (1)	9403 (1)	2695 (2)	22 (1)
S	7043 (1)	12040 (1)	440 (2)	26 (1)
O(1)	8322 (2)	8938 (2)	2992 (4)	27 (1)
O(2)	7506 (2)	9568 (2)	4757 (4)	26 (1)
O(3)	6731 (2)	8946 (2)	1408 (4)	28 (1)
N(1)	7590 (3)	10419 (2)	1912 (5)	20 (2)
N(2)	6222 (3)	10525 (2)	-321 (5)	20 (2)
C(1)	6927 (3)	10939 (3)	661 (6)	21 (2)
C(2)	5446 (3)	10978 (3)	-1431 (6)	22 (2)
C(3)	8432 (3)	10824 (3)	2794 (6)	22 (2)
C(4)	8609 (4)	8201 (3)	4399 (7)	29 (2)
C(5)	8664 (4)	8545 (3)	6309 (7)	29 (2)
C(6)	7849 (4)	8880 (3)	6279 (6)	28 (2)
C(7)	7883 (4)	9317 (4)	8101 (7)	32 (2)
C(11)	5262 (3)	11145 (3)	-3533 (6)	20 (2)
C(12)	4525 (3)	11538 (3)	-4638 (7)	26 (2)
C(13)	4304 (3)	11697 (3)	-6573 (7)	29 (2)
C(14)	4858 (4)	11474 (3)	-7423 (6)	26 (2)
C(15)	5608 (3)	11091 (3)	-6317 (7)	27 (2)
C(16)	5821 (3)	10919 (3)	-4380 (6)	22 (2)
C(21)	8724 (3)	11090 (3)	4890 (6)	24 (2)
C(22)	8180 (3)	11485 (3)	5619 (6)	22 (2)
C(23)	8463 (3)	11741 (3)	7524 (7)	25 (2)
C(24)	9292 (4)	11624 (3)	8721 (7)	31 (2)
C(25)	9842 (4)	11247 (4)	7991 (7)	37 (2)
C(26)	9537 (4)	10977 (3)	6096 (7)	31 (2)
H(1)	496 (3)	1064 (3)	-138 (5)	23
H(2)	548 (3)	1152 (3)	-71 (6)	23
H(3)	620 (3)	997 (3)	-26 (6)	20
H(4)	841 (3)	1138 (3)	190 (6)	22
H(5)	893 (3)	1041 (3)	276 (5)	22
H(12)	415 (3)	1166 (3)	-417 (6)	28
H(13)	378 (3)	1197 (3)	-738 (6)	29
H(14)	468 (3)	1160 (3)	-880 (6)	25
H(15)	600 (3)	1089 (3)	-688 (6)	27
H(16)	643 (3)	1069 (3)	-359 (6)	25
H(22)	769 (3)	1156 (3)	488 (6)	21
H(23)	804 (3)	1202 (3)	791 (6)	28
H(24)	954 (3)	1174 (3)	1014 (6)	28
H(25)	1049 (3)	1117 (3)	902 (6)	37
H(26)	988 (3)	1079 (3)	552 (6)	31
H(41)	815 (3)	768 (3)	378 (6)	28
H(42)	923 (3)	814 (3)	471 (6)	28
H(51)	891 (3)	808 (3)	738 (6)	26
H(52)	919 (3)	907 (3)	693 (6)	26
H(61)	738 (3)	836 (3)	589 (6)	25
H(71)	821 (3)	892 (3)	925 (7)	29
H(72)	830 (3)	983 (3)	830 (6)	29
H(73)	716 (3)	951 (3)	772 (6)	29

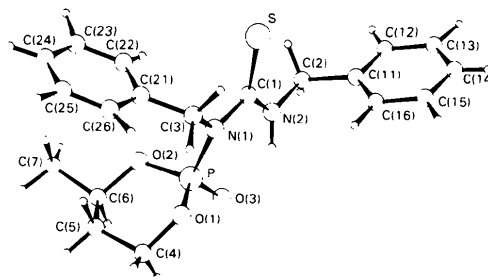


Fig. 1. The molecule of *N,N'*-dibenzyl-*N*-(4-methyl-2-oxo-1,3λ²,2-dioxaphosphorinan-2-yl)thiourea (2a).

* Lists of structure factors, anisotropic thermal parameters, deviations of atoms from weighted mean planes, benzyl-group bond lengths corrected for libration and distances involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38297 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

O(1)—P	1.572 (4)	O(2)—P	1.562 (4)
O(3)—P	1.456 (3)	N(1)—P	1.684 (4)
C(1)—S	1.690 (4)	C(4)—O(1)	1.487 (6)
C(6)—O(2)	1.493 (5)	C(1)—N(1)	1.412 (5)
C(3)—N(1)	1.486 (6)	C(1)—N(2)	1.320 (6)
C(2)—N(2)	1.455 (6)	C(11)—C(2)	1.519 (7)
C(21)—C(3)	1.522 (6)	C(5)—C(4)	1.506 (8)
C(6)—C(5)	1.499 (9)	C(7)—C(6)	1.511 (8)
C(12)—C(11)	1.365 (7)	C(16)—C(11)	1.402 (9)
C(13)—C(12)	1.385 (7)	C(14)—C(13)	1.395 (9)
C(15)—C(14)	1.375 (7)	C(16)—C(15)	1.391 (7)
C(22)—C(21)	1.403 (8)	C(26)—C(21)	1.363 (7)
C(23)—C(22)	1.386 (6)	C(24)—C(23)	1.385 (7)
C(25)—C(24)	1.401 (9)	C(26)—C(25)	1.384 (7)
O(2)—P—O(1)	105.3 (2)	O(3)—P—O(1)	115.2 (2)
O(3)—P—O(2)	115.0 (2)	N(1)—P—O(1)	102.7 (2)
N(1)—P—O(2)	104.2 (2)	N(1)—P—O(3)	113.1 (2)
C(4)—O(1)—P	118.1 (4)	C(6)—O(2)—P	120.7 (3)
C(1)—N(1)—P	124.3 (3)	C(3)—N(1)—P	116.7 (3)
C(3)—N(1)—C(1)	118.6 (4)	C(2)—N(2)—C(1)	123.6 (4)
N(1)—C(1)—S	121.0 (3)	N(2)—C(1)—S	122.1 (3)
N(2)—C(1)—N(1)	116.9 (4)	C(11)—C(2)—N(2)	116.9 (5)
C(21)—C(3)—N(1)	116.6 (5)	C(5)—C(4)—O(1)	108.0 (4)
C(6)—C(5)—C(4)	113.4 (4)	C(5)—C(6)—O(2)	109.7 (5)
C(7)—C(6)—O(2)	105.4 (4)	C(7)—C(6)—C(5)	115.8 (4)
C(12)—C(11)—C(2)	118.6 (5)	C(16)—C(11)—C(2)	122.7 (4)
C(16)—C(11)—C(12)	118.7 (4)	C(13)—C(12)—C(11)	122.1 (6)
C(14)—C(13)—C(12)	119.4 (5)	C(15)—C(14)—C(13)	118.9 (5)
C(16)—C(15)—C(14)	121.4 (6)	C(15)—C(16)—C(11)	119.5 (4)
C(22)—C(21)—C(3)	121.4 (4)	C(26)—C(21)—C(3)	120.3 (5)
C(26)—C(21)—C(22)	118.3 (4)	C(23)—C(22)—C(21)	120.5 (4)
C(24)—C(23)—C(22)	120.3 (6)	C(25)—C(24)—C(23)	119.4 (5)
C(26)—C(25)—C(24)	119.0 (5)	C(25)—C(26)—C(21)	122.5 (6)

Table 3. Torsion angles (°) in the 1,3,2-dioxaphosphorinane ring

E.s.d.'s are in the range 0.5–1.0°.			
P—O(2)—C(6)—C(5)	47.8	C(5)—C(4)—O(1)—P	−56.7
O(2)—C(6)—C(5)—C(4)	−55.0	C(4)—O(1)—P—O(2)	45.7
C(6)—C(5)—C(4)—O(1)	59.8	O(1)—P—O(2)—C(6)	−41.2

As in other *N,N'*-dibenzyl trisubstituted thioureas (Karolak-Wojciechowska *et al.*, 1979, 1983), the P and H(3) atoms are *trans* oriented with respect to sulphur.

Acta Cryst. (1983). C39, 589–592

Polarized Ethylenes: Structures of [Dimethylamino(methylthio)methylene]malononitrile (I), C₇H₉N₃S, and [Bis(dimethylamino)methylene]malononitrile (II), C₈H₁₂N₄

BY D. ADHIKESAVALU AND K. VENKATESAN

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

(Received 7 September 1982; accepted 15 December 1982)

Abstract. (I): $M_r = 167$, orthorhombic, $Pna2_1$, $Z = 4$, $\lambda = 0.7107 \text{ \AA} = 0.299 \text{ mm}^{-1}$, $F(000) = 352$, $T = 293 \text{ K}$. (II): $M_r = 164$, orthorhombic, $Pcab$, $Z = 8$, $a = 7.899 (3)$, $b = 8.670 (2)$, $c = 12.956 (6) \text{ \AA}$, $V = 887.2 \text{ \AA}^3$, $D_m = 1.25$, $D_x = 1.250 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha)$, $a = 7.876 (2)$, $b = 14.430 (4)$, $c = 16.312 (5) \text{ \AA}$, $V =$

0108-2701/83/050589-04\$01.50

The molecular configuration in the present structure is sterically favoured and is stabilized by an intramolecular hydrogen bond between N(1) and O(3) of 2.623 (6) Å.

The C=S bond length of 1.690 (4) Å has a similar value to that found for thiourea [1.70 (1) Å, Truter, 1967].

In the molecule there are two C(*sp*²)-N bonds. The C(1)-N(1) bond of 1.412 (5) Å is longer by 0.09 Å than C(1)-N(2) = 1.320 (6) Å. This lengthening is a consequence of the presence of the electronegative phosphoryl group bonded to N(1). For the same reason the P-N(1) bond of 1.684 (4) Å is shorter than the generally accepted single P-N bond (1.77 Å).

The configuration at the P atom in *N*-phosphorylthiourea (2a) is identical with that in the parent thioacid [*cis*-(1)] (the methyl group in the 4-position of the dioxaphosphorinane ring is in both cases *trans* with respect to the phosphoryl oxygen). This result proves that the S→N migration of the phosphoryl group in *S*-phosphorylisothiourea (3) proceeds with retention of configuration at the P atom.

References

- CAMERON, T. S. & KAROLAK-WOJCIECHOWSKA, J. (1977). *Acta Cryst.* B33, 2342–2344.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KAROLAK-WOJCIECHOWSKA, J., WIECZOREK, M., MIKOŁAJCZYK, M., KIELBASINSKI, P., STRUCHKOV, Y. T. & ANTIPIN, M. Y. (1979). *Acta Cryst.* B35, 877–881.
- KAROLAK-WOJCIECHOWSKA, J., WIECZOREK, M., MIKOŁAJCZYK, M., KIELBASINSKI, P., STRUCHKOV, Y. T. & ANTIPIN, M. Y. (1983). *Phosphorus Sulphur*. In the press.
- MIKOŁAJCZYK, M., KIELBASINSKI, P. & GOSZCZYNSKA, Z. (1977). *J. Org. Chem.* 42, 3629–3630.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.
- SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- TRUTER, M. R. (1967). *Acta Cryst.* 22, 556–559.

© 1983 International Union of Crystallography