Heteroatom Chemistry
Volume 2, Number 6, 1991

Crystal Structure and Stereochemistry of (P*S**, 2*S**, 3a*S**)-Hexahydro-2-(*tert*-butylvinylthiophosphinyl)-6,6-dimethylpyrrolo[1,2-*b*]isoxazole

K. Michał Pietrusiewicz*

Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

Wanda Wieczorek

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

Stefano Cicchi and Alberto Brandi*

Dipartimento di Chimica Organica and Centro Composti Eterociclici, Universita di Firenze, via G. Capponi 9, 50121 Firenze, Italy

Received 21 May 1991.

ABSTRACT

*The structure of the major product of the cycloaddition of 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole* N*-oxide to* tert*-butyldivinylphosphine sulfide was analyzed by means of single-crystal X-ray diffraction technique. The analysis revealed two crystallographically independent molecules that differed in conformation of the fused five-membered heterocyclic rings. These rings were found to be two envelopes in one molecule and two half-chairs in the other. The studied compound was identified as an exo adduct of the expected erythro configuration and was found to favor a conformation in which the P=S and ring C–O bonds were anti and the C=C–P=S moiety was in the s-cis array. $C_{14}H_{26}NOPS$, space group $P\bar{1}$, $a = 10.6004(7)$ Å, $b = 12.3225(6)$ Å, $c = 13.4404(7)$ Å, $\alpha = 104.073(4)°$, $\beta = 92.758(4)°$, $\gamma = 95.968(5)°$, $V = 1688.802(4)$ Å^3, $Z = 4$.*

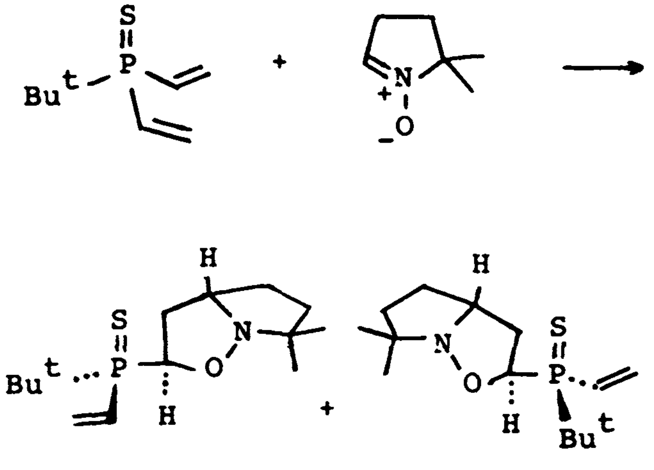
INTRODUCTION

In a recent paper we demonstrated that cycloaddition of nitrones to *P*-chiral and *P*-prochiral vinyl phosphine derivatives can proceed with remarkably high and predictable diastereofacial selectivity provided that the substituents at phosphorus are properly adjusted [1]. The reaction involving divinylphosphine sulfide possessing the *tert*-butyl group as the large substituent at phosphorus gave the best results in this respect and also made the best case for an asymmetric process that effectively converts a *P*-prochiral phosphine derivative into the chiral one (Equation 1). The single-crystal X-ray diffraction analysis of the major product of this reaction, **1**, is reported in this paper. The analysis was meant to substantiate the recently proposed [1] stereochemical assignment to **1** as well as to provide an insight into the preferred conformation of vinyl phosphine sulfides. Very recently vinyl phosphine oxides were found to favor *s*-cis arrangement in the ground state [2, 3] and were also implied to comply with this preference in their reactive conformations [1, 4, 5].

---

*To whom correspondence should be addressed.

1042-7163/92/$3.50 + .25



1 (23:1) **2**

RESULTS AND DISCUSSION

The X-ray diffraction experiment discerned two crystallographically independent molecules of **1**. The perspective view of the molecules is displayed in Figure 1. The pertinent positional parameters, bond lengths, and bond angles are listed in Tables 1, 2, and 3, respectively.

Inspection of Figure 1 proves unequivocally that the recent stereochemical assignment of **1** was correct: **1** is an exo adduct and has the erythro configuration at the thiophosphinyl–isoxazolidine junction.

TABLE 1 Positional Parameters ($\times 10^4$) for the Nonhydrogen Atoms in **1** with Estimated Standard Deviations in Parentheses

	x	*y*	*z*
Molecule A			
P1	1982(1)	2243(1)	2866(1)
S1	882(1)	3196(1)	3705(1)
O1	4451(3)	2122(3)	2578(3)
N1	5272(3)	1833(3)	3383(3)
C1	2074(5)	906(4)	3149(4)
C2	1237(5)	500(4)	3703(5)
C3	1528(4)	1941(4)	1475(4)
C6	1641(6)	3065(5)	1168(4)
C5	143(5)	1408(5)	1295(4)
C4	2337(5)	1147(5)	844(4)
C7	3651(4)	2906(4)	3067(4)
C8	4130(4)	3283(5)	4202(4)
C9	5452(4)	2922(4)	4170(4)
C10	6474(4)	3692(4)	3799(4)
C11	6998(5)	2934(4)	2889(5)
C12	6509(4)	1734(4)	2926(4)
C13	7342(5)	1315(4)	3671(5)
C14	6352(4)	892(4)	1884(5)
Molecule B			
P1′	3466(1)	6829(1)	2161(1)
S1′	4635(1)	5898(1)	2603(1)
N1′	302(3)	7540(3)	3122(3)
O1′	1015(3)	7170(3)	2208(3)
C1′	3688(5)	8281(4)	2880(4)
C2′	4612(6)	8705(5)	3560(5)
C3′	3501(5)	6868(5)	794(5)
C4′	2631(6)	7657(6)	526(5)
C5′	4873(5)	7211(5)	605(5)
C6′	3110(6)	5672(6)	139(5)
C7′	1819(4)	6375(4)	2379(5)
C8′	1678(4)	6289(4)	3472(5)
C9′	364(4)	6629(3)	3662(5)
C10′	−761(5)	5725(4)	3191(5)
C11′	−1446(5)	6190(5)	2389(6)
C12′	−1043(4)	7443(4)	2715(4)
C13′	−1761(5)	7995(5)	3611(5)
C14′	−1156(5)	8047(6)	1878(5)

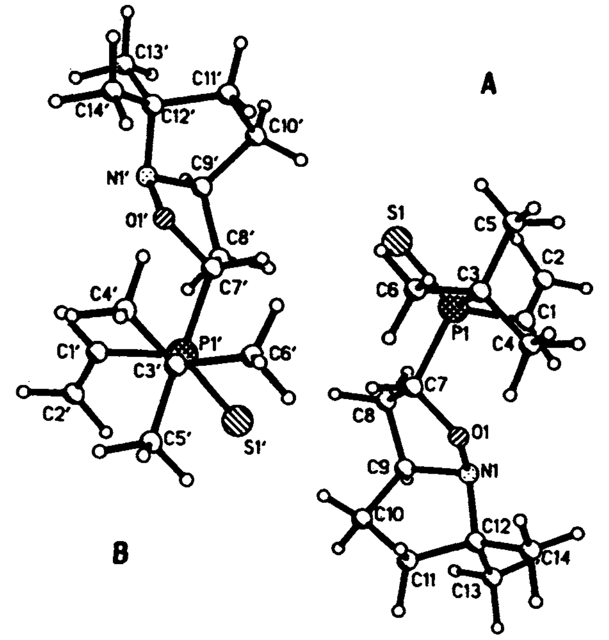


FIGURE 1 The perspective view of the two independent molecules of **1** with atom labelling.

The bond lengths and valency angles listed in Tables 2 and 3 are similar to the literature values and are the same in both molecules within 3σ. It should only be noted that in both molecules the phosphorus tetrahedron is deformed in the usual way showing somewhat increased S–P–C angles [111.2(2)–115.0(2)] and correspondingly decreased C–P–C angles [102.4(2)–107.6(2)°].

As indicated by the S1–P1–C1–C2 and S1′–P1′–C1′–C2′ torsion angles equal to 15.3(5) and 6.6(6)°, respectively, the relative arrangement of the P=S and the C=C groups in both molecules is *s*-cis, albeit somewhat more distorted from co-planarity in molecule A than in molecule B. Besides this particular difference, the overall conformations of the acyclic fragments in A and B are closely similar and are the staggered ones with the P=S bond anti to the ring C–O, as indicated by the pertinent $\theta_{S\text{–}P\text{–}C\text{–}O}$ angles of 170.7 and 170.6° in A and B, respectively.

TABLE 2 Bond Lengths (Å) in **1** with Estimated Standard Deviations in Parentheses

Molecule A			
S1–P1	1.944(2)	C1–P1	1.789(6)
C3–P1	1.845(5)	C7–P1	1.848(4)
N1–O1	1.489(6)	C7–O1	1.414(4)
C9–N1	1.481(5)	C12–N1	1.479(5)
C2–C1	1.321(8)	C4–C3	1.501(7)
C5–C3	1.528(7)	C6–C3	1.533(8)
C8–C7	1.527(7)	C9–C8	1.513(6)
C10–C9	1.546(7)	C11–C10	1.515(7)
C12–C11	1.528(7)	C13–C12	1.520(8)
C14–C12	1.517(7)		
Molecule B			
S1′–P1′	1.939(2)	C3′–P1′	1.852(7)
C1′–P1′	1.800(5)	O1′–N1′	1.475(5)
C7′–P1′	1.836(5)	C12′–N1′	1.484(5)
C9′–N1′	1.483(8)	C2′–C1′	1.282(8)
C7′–O1′	1.415(6)	C5′–C3′	1.523(8)
C4′–C3′	1.500(9)	C8′–C7′	1.512(9)
C6′–C3′	1.525(8)	C10′–C9′	1.540(6)
C9′–C8′	1.511(6)	C12′–C11′	1.508(7)
C11′–C10′	1.526(9)	C14–C12′	1.499(9)
C13′–C12′	1.513(8)		

The conformations of the fused five-membered rings in the two molecules are different. Both rings in molecule A exist in a half-chair conformation while in molecule B they are envelopes. The half-chair rings in A are more deformed than the corresponding envelopes in B. For A, the asymmetry parameters calculated in relation to the two-fold axes are $\Delta C_2(\mathrm{N1{-}C12}) = 3.2$ and $\Delta C_2(\mathrm{N1{-}C9}) = 6.4°$ for the pyrrolidine and isoxazolidine ring, respectively, whereas for B the corresponding asymmetry parameters calculated in relation to the symmetry planes are $\Delta C_s(\mathrm{C9'{-}C10'}) = 1.1$ and $\Delta C_s(\mathrm{O1'{-}C7'}) = 4.3°$, respectively. In A, deviations of N1 and C9 atoms from the mean plane of the isoxazolidine ring are −0.181(4) and 0.308(5) Å, respectively, while in the pyrrolidine ring of the same molecule atoms N1 and C12 deviate from the mean plane by 0.136(4) and −0.229(5) Å, respectively. In B, atoms C9′ and C12′ are deviated from the mean planes of the corresponding envelopes by 0.289(5) and −0.204(5) Å, respectively. The dihedral angle between the mean planes of the two five-membered rings in molecule A and molecule B is 79.5(2) and 77.9(2)°, respectively.

TABLE 3 Bond Angles (°) in **1** with Estimated Standard Deviations in Parentheses

Molecule A			
C1–P1–S1	115.0(2)	C3–P1–S1	113.2(2)
C3–P1–C1	106.2(2)	C7–P1–S1	111.2(2)
C7–P1–C1	103.6(2)	C7–P1–C3	106.9(2)
C7–O1–N1	108.6(3)	C9–N1–O1	100.5(3)
C12–N1–O1	103.6(3)	C12–N1–C9	105.2(3)
C2–C1–P1	121.4(4)	C6–C3–P1	107.8(4)
C5–C3–P1	107.7(4)	C5–C3–C6	109.4(4)
C4–C3–P1	112.4(4)	C4–C3–C6	110.5(4)
C4–C3–C5	108.9(4)	O1–C7–P1	109.6(3)
C8–C7–P1	112.7(3)	C8–C7–O1	106.8(4)
C9–C8–C7	101.6(4)	C8–C9–N1	103.0(4)
C10–C9–N1	106.5(4)	C10–C9–C8	115.9(4)
C11–C10–C9	105.4(4)	C12–C11–C10	105.2(4)
C11–C12–N1	104.7(4)	C13–C12–N1	105.6(4)
C13–C12–C11	111.5(4)	C14–C12–N1	110.8(4)
C14–C12–C11	114.0(5)	C14–C12–C13	109.9(4)
Molecule B			
C1′–P1′–S1′	114.4(2)	C3′–P1′–S1′	114.9(2)
C3′–P1′–C1′	105.3(3)	C7′–P1′–S1′	111.2(2)
C7′–P1′–C1′	102.4(2)	C7′–P1′–C3′	107.6(2)
C9′–N1′–O1′	103.6(3)	C12′–N1′–O1′	105.1(3)
C12′–N1′–C9′	105.8(3)	C7′–O1′–N1′	109.6(4)
C2′–C1′–P1′	123.6(5)	C4′–C3′–P1′	111.8(4)
C5′–C3′–P1′	107.6(4)	C5′–C3′–C4′	111.4(5)
C6′–C3′–P1′	107.6(4)	C6′–C3′–C4′	110.5(5)
C6′–C3′–C5′	107.7(5)	O1′–C7′–P1′	110.1(3)
C8′–C7′–P1′	112.4(3)	C8′–C7′–O1′	106.4(4)
C9′–C8′–C7′	102.3(4)	C8′–C9′–N1′	102.9(4)
C10′–C9′–N1′	106.5(4)	C10′–C9′–C8′	116.2(4)
C11′–C10′–C9′	105.0(4)	C12′–C11′–C10′	104.4(5)
C11′–C12′–N1′	104.0(4)	C13′–C12′–N1′	106.1(4)
C13′–C12′–C11′	110.8(4)	C14′–C12′–N1′	110.9(4)
C14′–C12′–C11′	115.1(5)	C14′–C12′–C13′	109.5(5)

The intermolecular distances between nonbonded atoms for the two molecules were found either close to or greater than the pertinent sums of van der Waals radii.

To conclude, the presented crystallographic analysis provides the unequivocal proof for the assignment of stereochemistry to **1** [1]. It reveals in addition that, in analogy to vinyl phosphine oxides [2, 3], the studied vinyl phosphine sulfide prefers the *s*-cis conformation in the ground state. The observed preference is likely to have a bearing on the reactive conformation of such compounds in thermal reactions [1, 5].

EXPERIMENTAL

A crystal suitable for X-ray diffraction measurement was obtained by crystallization of **1** [1] from benzene. Accurate cell dimensions were obtained by the least-squares fit to the θ values of 25 reflections measured on the Enraf-Nonius CAD4 diffractometer. The intensity data were collected using graphite-monochromated CuKα radiation and ω-2θ scan technique. The data were corrected for Lorentz, polarization, and absorption effects. The crystal data and experimental details are listed in Table 4.

The structure was solved by direct methods using the SHELX S-86 program [6] and was refined by full-matrix least squares. All nonhydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms of CH_3 groups were revealed in difference Fourier maps and their fixed parameters were included in the last stages of the refinement. The other hydrogen atoms were placed in geometrically calculated positions and were refined in the riding mode. The weighting scheme used was $w = 1/\sigma^2(F)$. An empirical isotropic extinction correction was introduced and the parameter x was refined to the value of 0.0007(1). Refinement was terminated when the maximum shift in any parameter was $<0.1\ \sigma$. The final difference Fourier map did not show any peaks higher than 0.18 eÅ^3. The computations were performed with SHELX-76 crystal structure determination program [7] on an AMSTRAD 1512 minicomputer [8].

TABLE 4 Crystal Data and Experimental Parameters for **1**

Molecular formula	$C_{14}H_{26}ONPS$
M_r	287.404
a (Å)	10.6004(7)
b (Å)	12.3225(6)
c (Å)	13.4404(7)
α (deg)	104.073(4)
β (deg)	92.758(4)
γ (deg)	95.968(5)
V (Å^3)	1688.802(4)
Space group	$P\bar{1}$
Z	4
F(000)	624
D_x (Mgm^{-3})	1.13
D_m (Mgm^{-3})	1.12
μ(CuKα) (cm^{-1})	25.00
Radiation	CuKα
Scan mode	ω-2θ
θ range	1-75°
Reflections measured	4008
Reflections $I > 4\sigma(I)$	3501
R	0.056
R_W	0.057

ACKNOWLEDGMENTS

The authors wish to thank the Polish Academy of Sciences (CPBP-01.13), the Ministry of National Education (Pr-II.10)—Poland and Consiglio Nazionale delle Richerche—Italy for financial support.

REFERENCES AND NOTES

[1] A. Brandi, S. Cicchi, A. Goti, K. M. Pietrusiewicz, M. Zabłocka, W. Wiśniewski, *J. Org. Chem., 56,* 1991, 4383.

[2] K. M. Pietrusiewicz, M. Zabłocka, M. Kuźnikowski, W. Wieczorek, W. Maniukiewicz, M. Rospenk, *Heteroatom Chem., 2,* 1991, 111.

[3] K. M. Pietrusiewicz, M. Zabłocka, W. Wieczorek, A. Brandi, *Tetrahedron: Asymmetry, 2,* 1991, 419.

[4] A. Brandi, P. Cannavo', K. M. Pietrusiewicz, M. Zabłocka, M. Wieczorek, *J. Org. Chem., 54,* 1989, 3073.

[5] Cf.: D. P. Curran, B. H. Kim, H. P. Piyasena, R. J. Loncharich, K. N. Houk, *J. Org. Chem., 52,* 1987, 2137; G. S. Pyne, R. Griffith, M. Edwards, *Tetrahedron Lett., 29,* 1988, 2089; T. Koizumi, Y. Arai, H. Takayama, K. Kuriyama, M. Shiro, *Tetrahedron Lett., 28,* 1987, 3689; H. Waldmann, M. Dräger, *Tetrahedron Lett., 30,* 1989, 4227, and references cited in these papers.

[6] G. M. Sheldrick, C. Kruger, R. Goddard: *Crystallographic Computing 3,* Oxford University Press, England, pp. 175–189 (1985).

[7] G. M. Sheldrick: *SHELX 76. Program for Crystal Structure Determination,* University of Cambridge, England, 1976.

[8] Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.