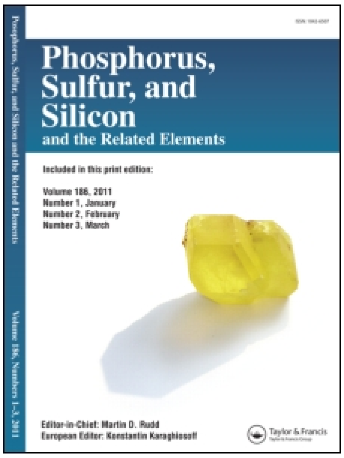

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ASSIGNMENT OF THE ABSOLUTE CONFIGURATION TO ENANTIOMERIC 2, 3-DIHYDRO-1-PHENYL-1*H*-PHOSPHOLE 1-SULFIDES. X-RAY STRUCTURE OF ( )-(1*S*,3A*R*,7*S*8*S*,8A*R*)-7, 8-DI(*TERT*-BUTOXY)-1-PHENYLOCTAHYDRO-1*H*-PYRROLO[1, 2-*B*]-1*H*-PHOSPHOLO[2, 3-*D*]-ISOXAZOLE 1-SULFIDE

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ASSIGNMENT OF THE ABSOLUTE CONFIGURATION TO ENANTIOMERIC 2,3-DIHYDRO-1-PHENYL-1*H*-PHOSPHOLE 1-SULFIDES. X-RAY STRUCTURE OF (+)-(1*S*,3a*R*,7*S*,8*S*,8a*R*,8b*R*)-7,8-DI(*TERT*-BUTOXY)-1-PHENYLOCTAHYDRO-1*H*-PYRROLO[1,2-*b*]-1*H*-PHOSPHOLO[2,3-*d*]-ISOXAZOLE 1-SULFIDE[1]

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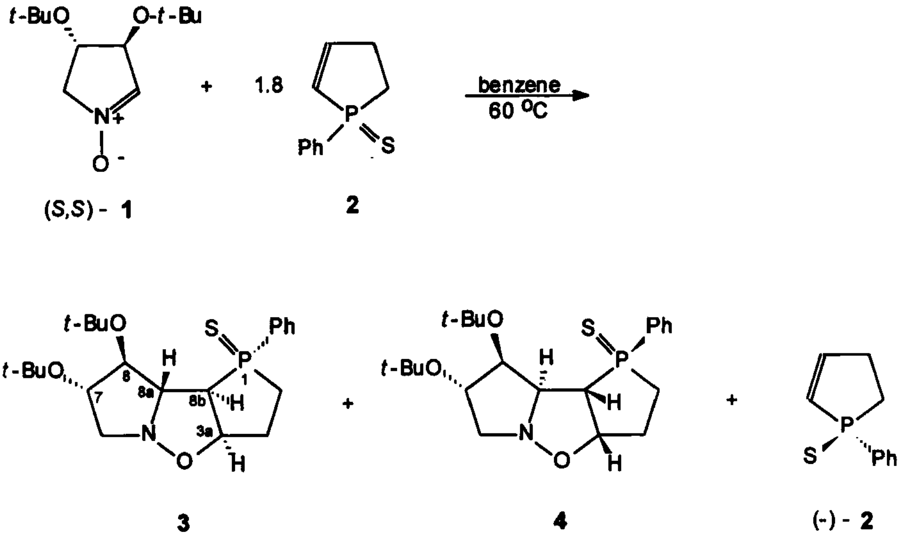
The structure and absolute configuration of the predominant of the two diastereomeric 7,8-di-*tert*-butoxy-1-phenyloctahydro-1*H*-pyrrolo[1,2-*b*]phospholo[2,3-*d*]isoxazole 1-sulfides obtained in the kinetic resolution experiment involving cycloaddition reaction of (*S*,*S*)-3,4-di-*tert*-butoxy-3,4-dihydro-2*H*-pyrrole 1-oxide (**1**) with an excess of racemic 2,3-dihydro-1-phenyl-1*H*-phosphole 1-sulfide (**2**), was determined by a single-crystal X-ray diffraction technique. $C_{22}H_{34}O_3NPS$, trigonal, space group $P3_1$, $a = b = 11.831(1)$, $c = 14.761(2)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1789(4)$ Å^3, $Z = 3$. The structure was solved by direct methods and was refined by full matrix least-squares calculations to $R = 0.031$ and $R_w = 0.036$ using 3737 unique reflections with $I > 3\sigma(I)$. The absolute configuration of the studied molecule was determined by calculation of the ETA (η) parameter and was found to be 1*S*, 3a*R*, 7*S*, 8*S*, 8a*R*, 8b*R*. This finding assigns unequivocally the *S* configuration to the faster reacting enantiomer of **2** and correspondingly the *R* configuration to the isolated slower reacting (−)-**2**. It also confirms fully the notion that in the cycloaddition transition state **1** and **2** prefer to approach each other in the *exo* mode and from the ring faces opposite to P-Ph and C3-O-*t*-Bu substituents, respectively.

Key words: Phospholene sulfide, kinetic resolution, perhydro-1*H*-pyrrolo[1,2-*b*]phospholo[2,3-*d*]isoxazole, absolute configuration, X-ray analysis.

INTRODUCTION

Resolved P-chiral phosphine sulfides are potentially highly attractive as precursors to resolved phosphines because they can be readily reduced with complete preservation of their stereochemical integrity at phosphorus.[2,3] However, due to the low polarity of their P=S function access to the resolved phosphine sulfides *via* direct resolution or *via* stereoselective synthesis has proved to be very difficult and it is most frequently the case that the resolved phosphines serve to synthesize optically active phosphine sulfides rather than *vice versa*.[4] In a recent study[5] we have demonstrated that optically active 2,3-dihydro-1-phenyl-1*H*-phosphole 1-sulfide (**2**) can be readily obtained by means of the kinetic resolution involving its 1,3-dipolar cycloaddition to an enantiomeric five-membered ring nitrone derived from tartaric acid.[6] The pertinent resolution experiment which led to the formation of the two diastereomeric cycloadducts **3** and **4** in unequal amounts, and from which the unreacted laevorotatory **2** was conveniently isolated is shown in the Equation.[5]



In this report we wish to present a single-crystal X-ray diffraction study of the major cycloadduct **3**. The study provides an insight into the preferred mode of approach of the two reactants and establishes directly the configuration of the faster reacting enantiomer of **2** and, by default, the configuration of the isolated slower reacting (−)-**2**. It also provides the first crystallographic description of the novel heterocyclic perhydro-1*H*-pyrrolo[1,2-*b*]phospholo[2,3-*d*]isoxazole ring system.

RESULTS AND DISCUSSION

The molecular structure of **3** is displayed in Figure 1 which shows also its absolute configuration. According to the Cahn-Ingold-Prelog rules[7] the configuration of **3** has been found to be P*S*, 3*R*, 5*S*, 6*S*, 7*R*, 8*R* (arbitrary numbering corresponding with Figure 1). It follows unequivocally from this finding that the preferred stereochemical pathway of the cycloaddition of **1** to **2** involves an *exo* transition state in which the two five-membered ring reactants attack each other from the faces opposite to the P-Ph and C3-O-*t*-Bu substituents, respectively. It further follows that in the studied reaction involving nitrone **1** of the *S*,*S* configuration the *S*

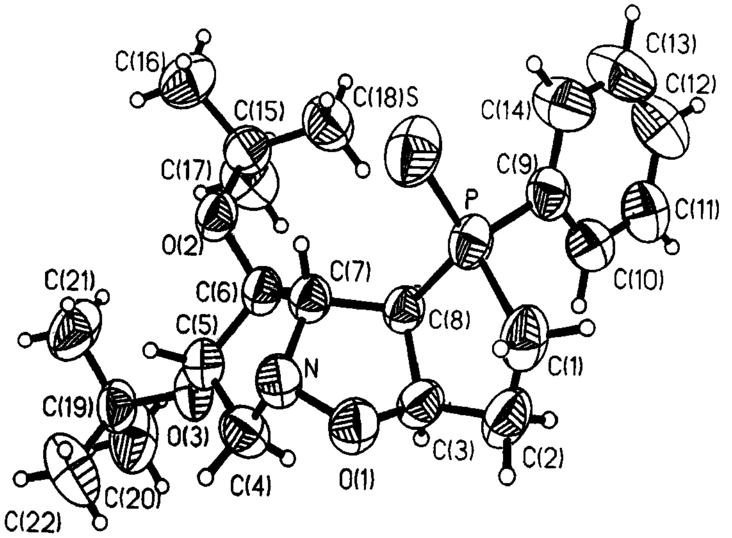


FIGURE 1 ORTEP view of 3 showing 50% probability ellipsoids.

enantiomer of dihydrophosphole sulfide was consumed preferentially and therefore the isolated unreacted laevorotatory **2** can be assigned unambiguously as *R*.

Inspection of the bond angles in **3** collected in Table I reveals that the $R_3P{=}S$ tetrahedron exhibits a deformation consisting of an increase of the S-P-C and simultaneous decrease of the C-P-C valency angles. The most distorted is the endocyclic angle C1-P-C8 [95.9(1)°]. Similar deformation of the endocyclic angles of $R_3P{=}O$ tetrahedrons in the related bicyclic fused phospholane structures (perhydrophospholo[2,3-*d*]isoxazoles) have been observed.[8]

The two peripheral heterocyclic rings in **3**, i.e., phospholane and pyrrolidine, exist in the conformation of a deformed envelope with C2 and C4 atoms deviating from the planes of the respective remaining four atoms. The corresponding asymmetry parameters[9] in relation to the corresponding planes of symmetry are $\Delta C_s(C2) = 5.4$ and $\Delta C_s(C4) = 3.3°$. The found conformation of the phospholane ring in **3** is similar to the conformations found for this ring in the related fused bicyclic phospholane structures,[8] except for the position of the P=X bond as related to the phospholane ring. The torsion angle S-P-C8-C3 in **3** is 118.5(2)°. Also, the P=S bond and phenyl ring in **3** are strictly coplanar [S-P-C9-C14 = 0.5(3)°].

The conformations of the two $OC(CH_3)_3$ groups are alike; the conformations around the C6-O2 and C5-O3 bonds in relation to the O2-C15 and O3-C19 bonds are *ac*. The C15, C19 and O2 atoms of these groups are involved in the two shortened intramolecular contacts: C5-H51 . . . C19 of 2.41 Å, and C7-H71 . . . O2 of 2.41 A.

Inspection of the molecular packing in the unit cell of **3** revealed that there are no shortened intermolecular contacts less than the sums of van der Waals' radii.

EXPERIMENTAL

A crystal with approximate dimensions of 0.28, 0.30, 0.25 mm, obtained by slow evaporation of an diisopropyl ether solution, was used for data collection. Accurate unit cell dimensions were obtained

TABLE I

Bond lengths and angles for 3

P-S	1.946 (1)	P-C(1)	1.826 (3)
P-C(8)	1.856 (3)	P-C(9)	1.813 (3)
O(1)-N	1.442 (3)	O(1)-C(3)	1.445 (4)
O(2)-C(6)	1.428 (2)	O(2)-C(15)	1.444 (4)
O(3)-C(5)	1.414 (4)	O(3)-C(19)	1.450 (5)
N-C(4)	1.473 (4)	N-C(7)	1.489 (3)
C(1)-C(2)	1.508 (5)	C(2)-C(3)	1.527 (5)
C(3)-C(8)	1.525 (3)	C(4)-C(5)	1.507 (3)
C(5)-C(6)	1.526 (4)	C(6)-C(7)	1.555 (4)
C(7)-C(8)	1.540 (4)	C(9)-C(10)	1.385 (4)
C(9)-C(14)	1.382 (4)	C(10)-C(11)	1.381 (6)
C(11)-C(12)	1.368 (6)	C(12)-C(13)	1.366 (6)
C(13)-C(14)	1.384 (7)	C(15)-C(16)	1.524 (4)
C(15)-C(17)	1.525 (5)	C(15)-C(18)	1.506 (6)
C(19)-C(20)	1.501 (6)	C(19)-C(21)	1.502 (4)
C(19)-C(22)	1.509 (7)		

S-P-C(1)	114.7(1)	S-P-C(8)	117.8(1)
C(1)-P-C(8)	95.9(1)	S-P-C(9)	114.0(1)
C(1)-P-C(9)	106.6(1)	C(8)-P-C(9)	105.9(1)
N-O(1)-C(3)	106.7(2)	C(6)-O(2)-C(15)	119.0(2)
C(5)-O(3)-C(19)	119.1(2)	O(1)-N-C(4)	110.2(2)
O(1)-N-C(7)	105.7(2)	C(4)-N-C(7)	106.6(2)
P-C(1)-C(2)	106.9(2)	C(1)-C(2)-C(3)	108.6(2)
O(1)-C(3)-C(2)	107.2(2)	O(1)-C(3)-C(8)	103.3(2)
C(2)-C(3)-C(8)	112.2(3)	N-C(4)-C(5)	102.7(2)
O(3)-C(5)-C(4)	111.3(2)	O(3)-C(5)-C(6)	111.3(2)
C(4)-C(5)-C(6)	103.5(3)	O(2)-C(6)-C(5)	108.5(2)
O(2)-C(6)-C(7)	112.7(2)	C(5)-C(6)-C(7)	104.6(2)
N-C(7)-C(6)	105.0(2)	N-C(7)-C(8)	105.6(2)
C(6)-C(7)-C(8)	116.8(2)	P-C(8)-C(3)	105.0(2)
P-C(8)-C(7)	114.3(2)	C(3)-C(8)-C(7)	103.9(2)
P-C(9)-C(10)	120.7(2)	P-C(9)-C(14)	120.4(2)
C(10)-C(9)-C(14)	118.9(3)	C(9)-C(10)-C(11)	121.2(3)
C(10)-C(11)-C(12)	119.1(3)	C(11)-C(12)-C(13)	120.5(5)
C(12)-C(13)-C(14)	120.8(4)	C(9)-C(14)-C(13)	119.5(3)
O(2)-C(15)-C(16)	102.8(3)	O(2)-C(15)-C(17)	110.0(3)
C(16)-C(15)-C(17)	110.9(3)	O(2)-C(15)-C(18)	111.1(2)
C(16)-C(15)-C(18)	110.8(3)	C(17)-C(15)-C(18)	110.9(3)
O(3)-C(19)-C(20)	103.1(3)	O(3)-C(19)-C(21)	110.0(3)
C(20)-C(19)-C(21)	110.3(3)	O(3)-C(19)-C(22)	110.7(3)
C(20)-C(19)-C(22)	111.0(4)	C(21)-C(19)-C(22)	111.5(3)

TABLE II

Crystal data and experimental parameters for 3

Molecular formula	$C_{22}H_{34}O_3NPS$
M_r	423.55
Space group	$P3_1$
a, Å	11.831(1)
b, Å	11.831(1)
c, Å	14.761(2)
$\alpha = \beta$, deg	90
γ, deg	120
V, $Å^3$	1789.4(4)
Z	3
D_{calc}, $g \cdot cm^{-3}$	1.179
μ_{calc}, cm^{-1}	19.8
Radiation, graphite monochromator	CuK_α
2θ range, deg	2 - 150
Reflections observed [$I>3\sigma(I)$]	3737
R	0.031
R_w	0.036

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 the ω-2θ scan technique. The measured intensities were corrected for Lorentz and polarization effects. Crystal data and experimental details are listed in Table II.

The structure was solved by direct methods, using the SHELXS-86 program[10] and was refined by the full-matrix least-squares method using the SHELXTL System.[11] The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, and in the final cycles of refinement a weighting scheme based on counting statistics was used with $w = [\sigma^2(F_o) + 0.0001(F_o)^2]^{-1}$. An empirical isotropic extinction correction was introduced, and the parameter x was refined to the value 0.0042(4). During the refinement of the nonhydrogen atoms with anisotropic thermal parameters, the hydrogen atom contributions were included in the structure factors after calculation of their positions on the basis of idealized geometry. H atoms were refined in the riding mode. Refinement was terminated when maximum shift in any parameter was less than 0.1σ. The final difference Fourier map showed no peaks higher than 0.22 $Å^{-3}$. Convergence was obtained at $R = 0.031$ and $R_w = 0.036$.

The absolute configuration was determined by calculation of the ETA (η) parameter.[12] This parameter for the *S* configuration at P atom was 1.08(6).

Atomic coordinates for the 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.

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