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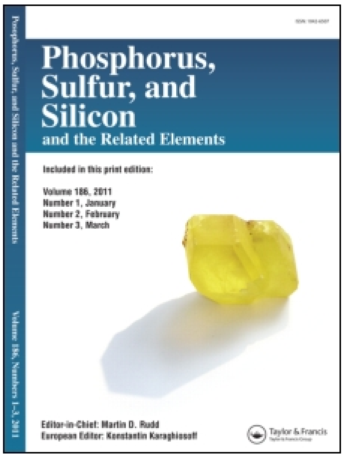

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CRYSTAL AND MOLECULAR STRUCTURES OF 1R,3S,5S-3-(4-METHYLPHENOXY)-3-THIO-1,8,8-TRIMETHYL-2,4,3-DIAZAPHOSPHABICYCCLO[3.2.1]OCTANE AND ITS 1R,3R,5S-DIASTEREOISOMER

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CRYSTAL AND MOLECULAR STRUCTURES OF 1R,3S,5S-3-(4-METHYLPHENOXY)-3-THIO-1,8,8-TRIMETHYL-2,4,3-DIAZAPHOSPHABICYCLO[3.2.1]OCTANE AND ITS 1R,3R,5S-DIASTEREOISOMER

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The crystal and molecular structures of 1R,3S,5S-3-(4-methylphenoxy)-3-thio-1,8,8-trimethyl-2,4,3-diazaphosphabicyclo[3.2.1]octane (1) and its 1R,3R,5S-diastereoisomer (2) have been determined by X-ray diffraction analysis. 1 crystallized in orthorhomic system with space group $P2_12_12_1$, a = 21.286(7), b = 9.009(1), c = 26.395(5) Å; V = 5061.34 Å^3, Z = 12, Dx = 1.222 g/cm^3. 2 crystallized also in ortherhomic system with space group $P2_12_12_1$, but a = 8.624(2), b = 8.374(1), c = 23.522(8) Å; V = 1698.69 Å^3, Z = 4, Dx = 1.214 g/cm^3. The geometric figures of the bicyclic skeletons in both diastereoisomers are similar with the six-membered phosphorus-containing rings in "chaise lounge" conformations. The 4-methylphenoxy group in 1 is equatorial to the six-membered ring, but that in 2 is axial. Three crystallographically independent molecules are present in the asymmetric unit of 1 and have some significant differences in their corresponding torsion angles.

Key words: Diazaphosphabicyclooctane, crystal structure, diastereoisomer, conjugation, torsion angle, conformation.

INTRODUCTION

It has been reported that some dextrorotatory 1,8,8-trimethyl-2,4,3-diazaphosphabicyclo[3.2.1]octanes could be prepared by the asymmetric condensation reaction of thiophosphoryldichlorides with 1R,3S-1,2,2-trimethyl-1,3-diaminocyclopentane.[1] The chiral phosphorus atoms were formed during the synthetic reaction and two classes of the optical isomers of the diazaphosphabicyclooctanes with (1R,3R,5S) and (1R,3S,5S) configurations were produced.[2–4] A preliminary bioassay showed that all of the optical isomers possessed herbicidal activity.[5]

In this paper results of the crystal and molecular structures of 1R,3S,5S-3-(4-methylphenoxy)-3-thio-1,8,8-trimethyl-2,4,3-diazaphosphabicyclo[3.2.1]octane (1) and its (1R,3R,5S)-diastereoisomer (2) are presented.

RESULTS AND DISCUSSION

Three crystallographically independent molecules were found to coexist in the asymmetric unit of 1 in a ratio of 1:1:1 when its crystal and molecular structure was determined by X-ray diffraction method, but in the case of 2 there was only one. The final atomic coordinates of non-hydrogen atoms and their thermal parameters of molecules 1 and 2, the bond lengths and the bond angles are listed in Tables I, II and III respectively. The molecular structures are shown in Figure 1 and 2.

The bicyclic skeleton in each molecule of 1 and 2 similarly consists of a seven-membered ring containing phosphorus and nitrogen atoms in boat form, a six-membered heterocycle taking chaise-lounge conformation and a five-carbon ring in envelope form. There are three chiral atoms in the skeleton, two bridge-head carbon atoms (C-1, C-5) and one phosphorus atom (P-3). The configurations of the two chiral carbon atoms are 1R and 5S, being identical with the chiral carbon atoms in the 1R,3S-1,3-diaminocyclopentane, and the configuration of the phosphorus atom

TABLE I

Positional parameters and their estimated standard deviations

Atom	X	Y	Z	Beq
1R,3S,5S-Isomer				
S(1)	0.2248(2)	0.9984(4)	0.4030(1)	5.27(8)
P(1)	0.2232(2)	0.7822(4)	0.4004(1)	4.47(7)
O(1)	0.2850(4)	0.7191(8)	0.3702(3)	5.1(2)
N(1)	0.1682(5)	0.702(1)	0.3691(4)	4.5(2)
N(2)	0.2205(5)	0.704(1)	0.4564(3)	4.4(2)
C(11)	0.1170(5)	0.606(1)	0.3912(5)	5.3(3)
C(12)	0.0761(6)	0.704(2)	0.4287(6)	7.0(4)
C(13)	0.1071(7)	0.697(2)	0.4824(5)	6.9(4)
C(14)	0.1678(6)	0.604(2)	0.4722(5)	5.6(3)
C(15)	0.1508(6)	0.493(1)	0.4288(5)	5.6(3)
C(16)	0.0823(6)	0.535(1)	0.3467(5)	5.4(3)
C(17)	0.2071(5)	0.409(1)	0.4050(5)	5.4(3)
C(18)	0.1010(6)	0.380(2)	0.4494(6)	7.2(4)
C(21)	0.3454(5)	0.781(1)	0.3763(5)	4.5(3)
C(22)	0.3765(6)	0.767(1)	0.4228(5)	5.3(3)
C(23)	0.4376(6)	0.823(2)	0.4255(5)	5.7(4)
C(24)	0.4655(6)	0.898(2)	0.3842(5)	5.9(3)
C(25)	0.4325(6)	0.910(2)	0.3396(5)	6.4(4)
C(26)	0.3692(7)	0.853(1)	0.3343(5)	5.9(4)
C(27)	0.5319(6)	0.964(2)	0.3888(6)	7.3(4)
S(2)	0.2241(2)	0.8760(4)	0.2280(1)	6.08(9)
P(2)	0.2157(2)	1.0882(4)	0.2351(1)	4.65(8)
O(2)	0.1407(4)	1.127(1)	0.2353(4)	7.0(2)
N(3)	0.2399(5)	1.197(1)	0.1894(4)	4.9(2)
N(4)	0.2474(5)	1.160(1)	0.2864(3)	5.0(3)
C(31)	0.2923(6)	1.313(1)	0.1941(4)	4.6(3)
C(32)	0.3568(7)	1.228(2)	0.2011(6)	7.0(4)
C(33)	0.3601(6)	1.192(2)	0.2585(6)	8.0(4)
C(34)	0.2989(6)	1.270(1)	0.2834(5)	6.1(4)
C(35)	0.2827(7)	1.393(1)	0.2466(4)	5.3(3)
C(36)	0.2887(7)	1.413(1)	0.1473(4)	6.2(3)
C(37)	0.2154(6)	1.462(1)	0.2543(6)	6.6(4)

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TABLE I (*Continued*)

Atom	X	Y	Z	Beq
C(38)	0.3329(6)	1.519(1)	0.2516(5)	6.5(4)
C(41)	0.0937(5)	1.048(1)	0.2630(5)	5.8(3)
C(42)	0.0854(6)	1.089(2)	0.3142(5)	5.4(3)
C(43)	0.0360(6)	1.022(1)	0.3391(5)	5.6(4)
C(44)	-0.0053(6)	0.921(1)	0.3143(5)	5.8(4)
C(45)	0.0093(6)	0.882(2)	0.2629(5)	6.5(4)
C(46)	0.0569(6)	0.946(1)	0.2371(5)	6.2(4)
C(47)	-0.0587(6)	0.849(2)	0.3399(6)	7.1(4)
S(3)	0.2591(2)	0.8962(4)	0.5657(1)	6.32(9)
P(3)	0.2689(2)	1.1075(4)	0.5535(1)	4.89(8)
O(3)	0.2001(4)	1.1849(9)	0.5484(3)	5.6(2)
N(5)	0.3077(4)	1.200(1)	0.5973(4)	4.6(2)
N(6)	0.3014(5)	1.157(1)	0.5011(4)	4.8(3)
C(51)	0.3722(6)	1.260(1)	0.5874(4)	5.4(3)
C(52)	0.4184(6)	1.127(2)	0.5793(5)	7.6(4)
C(53)	0.4128(6)	1.095(2)	0.5191(5)	6.8(4)
C(54)	0.3678(6)	1.219(1)	0.4974(5)	5.3(3)
C(55)	0.3728(6)	1.349(1)	0.5365(5)	5.5(4)
C(56)	0.3794(7)	1.260(2)	0.4426(5)	6.4(4)
C(57)	0.3189(7)	1.467(2)	0.5330(6)	7.0(4)
C(58)	0.4369(6)	1.429(2)	0.5302(5)	8.0(5)
C(61)	0.1497(5)	1.148(1)	0.5806(5)	4.7(3)
C(62)	0.1000(6)	1.067(2)	0.5549(5)	6.6(4)
C(63)	0.0479(6)	1.034(2)	0.5866(6)	6.5(4)
C(64)	0.0469(6)	1.071(1)	0.6374(6)	6.3(4)
C(65)	0.0978(6)	1.146(2)	0.6609(6)	6.3(4)
C(66)	0.1488(7)	1.188(2)	0.6315(5)	6.4(4)
C(67)	-0.0118(7)	1.028(2)	0.6705(7)	8.8(5)
1R,3R,5S-Isomer				
S	0.0604(3)	1.356(3)	0.0104(9)	4.9(5)
P	0.0792(3)	1.130(3)	0.0254(8)	3.9(4)
O	0.1363(6)	1.036(7)	-0.0315(2)	4.7(1)
N(1)	0.2142(8)	1.075(9)	0.0709(3)	4.7(2)
N(2)	-0.0785(8)	1.052(8)	0.0506(3)	3.9(1)
C(11)	0.191 (1)	0.921(1)	0.1039(4)	5.1(2)
C(12)	0.176(1)	0.772(1)	0.0672(4)	5.9(3)
C(13)	-0.007(1)	0.763(1)	0.0526(4)	5.2(2)
C(14)	-0.080(1)	0.902(1)	0.0858(3)	4.5(2)
C(15)	0.034(1)	0.933(1)	0.1371(3)	5.1(2)
C	-0.250(1)	0.874(1)	0.1020(4)	5.8(2)
C(21)	0.023(1)	0.784(1)	0.1795(4)	7.2(3)
C(22)	0.004(1)	1.089(1)	0.1702(4)	6.3(3)
C(31)	0.088(1)	1.072(1)	-0.0870(3)	4.5(2)
C(32)	-0.070(1)	1.081(1)	-0.1008(4)	5.6(2)
C(33)	-0.106(1)	1.111(2)	-0.1587(4)	7.2(3)
C(34)	0.011(1)	1.130(2)	-0.1990(4)	6.9(3)
C(35)	0.164(1)	1.126(2)	-0.1830(4)	6.8(3)
C(36)	0.205(1)	1.094(1)	-0.1254(3)	5.6(3)
C(37)	-0.035(2)	1.159(2)	-0.2613(4)	10.2(4)

may be 3R or 3S. The main difference between the molecular structures of 1 and 2 is that the methylphenoxy group in 1 is equatorial to the six-membered ring, but in 2 it is axial, which not only makes 1 and 2 the geometrical isomers but also makes

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TABLE II

Bond distances in angstroms*

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
1R,3S,5S-Isomer					
S(1)	P(1)	1.949(3)	P(1)	O(1)	1.639(6)
P(1)	N(1)	1.604(6)	P(1)	N(2)	1.641(6)
O(1)	C(21)	1.41(1)	N(1)	C(11)	1.52(2)
N(2)	C(14)	1.50(1)	C(11)	C(12)	1.59(1)
C(11)	C(15)	1.59(1)	C(11)	C(16)	1.52(2)
C(12)	C(13)	1.58(1)	C(13)	C(14)	1.56(1)
C(14)	C(15)	1.56(1)	C(15)	C(17)	1.55(1)
C(15)	C(18)	1.57(1)	C(21)	C(22)	1.40(2)
C(21)	C(26)	1.38(1)	C(22)	C(23)	1.40(1)
C(23)	C(24)	1.41(1)	C(24)	C(25)	1.38(1)
C(24)	C(27)	1.54(1)	C(25)	C(26)	1.45(1)
S(2)	P(2)	1.930(3)	P(2)	O(2)	1.634(6)
P(2)	N(3)	1.635(6)	P(2)	N(4)	1.647(6)
O(2)	C(41)	1.426(9)	N(3)	C(31)	1.54(1)
N(4)	C(34)	1.480(9)	C(31)	C(32)	1.58(1)
C(31)	C(35)	1.58(1)	C(31)	C(36)	1.54(2)
C(32)	C(33)	1.55(1)	C(33)	C(34)	1.62(1)
C(34)	C(35)	1.52(2)	C(35)	C(37)	1.57(1)
C(35)	C(38)	1.57(2)	C(41)	C(42)	1.41(1)
C(41)	C(46)	1.39(1)	C(42)	C(43)	1.38(2)
C(43)	C(44)	1.43(1)	C(44)	C(45)	1.43(1)
C(44)	C(47)	1.47(1)	C(45)	C(46)	1.36(2)
S(3)	P(3)	1.942(3)	P(3)	O(3)	1.628(5)
P(3)	N(5)	1.647(6)	P(3)	N(6)	1.610(6)
O(3)	C(61)	1.41(2)	N(5)	C(51)	1.50(1)
N(6)	C(54)	1.52(1)	C(51)	C(52)	1.58(1)
C(51)	C(55)	1.56(2)	C(52)	C(53)	1.63(1)
C(53)	C(54)	1.58(1)	C(54)	C(55)	1.57(1)
C(54)	C(56)	1.51(2)	C(55)	C(57)	1.57(1)
C(55)	C(58)	1.56(1)	C(61)	C(62)	1.45(1)
C(61)	C(66)	1.39(2)	C(62)	C(63)	1.42(1)
C(63)	C(64)	1.39(3)	C(64)	C(65)	1.42(1)
C(64)	C(67)	1.57(2)	C(65)	C(66)	1.39(1)
1R,3R,5S-Isomer					
S	P	1.931(3)	P	O	1.631(5)
P	N(1)	1.644(6)	P	N(2)	1.626(2)
O	C(31)	1.399(7)	N(1)	C(11)	1.52(2)
N(2)	C(14)	1.503(8)	C(11)	C(12)	1.53(1)
C(11)	C(15)	1.57(1)	C(12)	C(13)	1.61(2)
C(13)	C(14)	1.54(2)	C(14)	C(15)	1.572(9)
C(14)	C	1.54(1)	C(15)	C(21)	1.60(2)
C(15)	C(22)	1.55(1)	C(31)	C(32)	1.40(2)
C(31)	C(36)	1.37(1)	C(32)	C(33)	1.42(2)
C(33)	C(34)	1.40(2)	C(34)	C(35)	1.37(2)
C(34)	C(37)	1.54(2)	C(35)	C(36)	1.42(1)

*:Numbers in parentheses are estimated standard deviations in the least significant digits.

their phosphorus atoms in different configurations. The absolute configuration of the phosphorus atom in 2 was established as 3R by using the appropriate anomalous scattering effect of phosphorus and sulfur atoms.[3] The configuration of the phospho-

TABLE III

Bond angles in degrees*

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
1R,3S,5S-Isomer							
S(1)	P(1)	O(1)	110.5(2)	S(1)	P(1)	N(1)	118.6(3)
S(1)	P(1)	N(2)	113.6(2)	O(1)	P(1)	N(1)	100.4(3)
P(1)	O(1)	C(21)	122.5(5)	P(1)	N(1)	C(11)	125.9(5)
P(1)	N(2)	C(14)	122.4(5)	N(1)	C(11)	C(12)	108.0(6)
N(2)	C(14)	C(13)	110.1(8)	N(2)	C(14)	C(15)	110.7(6)
C(11)	C(12)	C(13)	108.1(8)	C(11)	C(15)	C(14)	99.1(7)
C(11)	C(15)	C(17)	114.0(7)	C(11)	C(15)	C(18)	109.0(6)
C(12)	C(11)	C(15)	102.3(6)	C(12)	C(11)	C(16)	116.6(7)
C(12)	C(13)	C(14)	102.4(7)	C(13)	C(14)	C(15)	106.1(6)
C(14)	C(15)	C(17)	115.5(6)	C(14)	C(15)	C(18)	108.5(7)
C(15)	C(11)	C(16)	116.0(7)	C(17)	C(15)	C(18)	110.1(8)
O(1)	C(21)	C(22)	119.8(8)	O(1)	C(21)	C(26)	115.4(8)
C(21)	C(22)	C(23)	116.9(9)	C(21)	C(26)	C(25)	115.5(8)
C(22)	C(21)	C(26)	125.0(8)	C(22)	C(23)	C(24)	121.7(9)
C(23)	C(24)	C(25)	118.8(8)	C(23)	C(24)	C(27)	120.8(8)
C(24)	C(25)	C(26)	122.0(9)	C(25)	C(24)	C(27)	120.4(8)
S(2)	P(2)	O(2)	107.6(3)	S(2)	P(2)	N(3)	119.5(3)
S(2)	P(2)	N(4)	115.5(3)	O(2)	P(2)	N(3)	100.6(3)
O(2)	P(2)	N(4)	108.3(3)	N(3)	P(2)	N(4)	104.1(3)
P(2)	N(4)	C(34)	121.5(5)	N(3)	C(31)	C(32)	108.0(7)
N(3)	C(31)	C(35)	106.8(6)	N(3)	C(31)	C(36)	107.5(6)
N(4)	C(34)	C(33)	109.3(7)	N(4)	C(34)	C(35)	111.0(7)
C(31)	C(32)	C(33)	104.9(8)	C(31)	C(35)	C(34)	101.4(6)
C(31)	C(35)	C(37)	114.3(7)	C(31)	C(35)	C(38)	108.6(7)
C(32)	C(31)	C(35)	103.4(7)	C(32)	C(31)	C(36)	115.0(7)
C(32)	C(33)	C(34)	105.6(7)	C(33)	C(34)	C(35)	103.9(7)
C(34)	C(35)	C(37)	114.3(7)	C(34)	C(35)	C(38)	106.8(7)
C(35)	C(31)	C(36)	115.6(6)	C(37)	C(35)	C(38)	109.1(6)
O(2)	C(41)	C(42)	116.8(9)	O(2)	C(41)	C(46)	118(2)
C(41)	C(42)	C(43)	116.2(8)	C(41)	C(46)	C(45)	117(1)
C(42)	C(41)	C(46)	124.9(9)	C(42)	C(43)	C(44)	122(1)
C(43)	C(44)	C(45)	117.2(9)	C(43)	C(44)	C(47)	123.1(9)
C(44)	C(45)	C(46)	122.4(9)	C(45)	C(44)	C(47)	119.7(9)
S(3)	P(3)	O(3)	109.6(2)	S(3)	P(3)	N(5)	115.7(3)
S(3)	P(3)	N(6)	117.5(3)	O(3)	P(3)	N(5)	107.0(3)
O(3)	P(3)	N(6)	101.4(3)	N(5)	P(3)	N(6)	104.3(3)
P(3)	O(3)	C(61)	122.3(5)	P(3)	N(5)	C(51)	121.4(5)
P(3)	N(6)	C(54)	123.8(5)	N(5)	C(51)	C(52)	108.6(7)
N(5)	C(51)	C(55)	110.1(7)	N(6)	C(54)	C(53)	106.3(7)
N(6)	C(54)	C(55)	107.2(7)	N(6)	C(54)	C(56)	107.5(6)
C(51)	C(52)	C(53)	102.9(8)	C(51)	C(55)	C(54)	100.5(7)
C(51)	C(55)	C(57)	112.9(7)	C(51)	C(55)	C(58)	109.7(7)
C(52)	C(51)	C(55)	105.8(7)	C(52)	C(53)	C(54)	105.9(8)
C(53)	C(54)	C(55)	104.6(6)	C(53)	C(54)	C(56)	114.7(7)
C(54)	C(55)	C(57)	114.8(7)	C(54)	C(55)	C(58)	109.8(7)
C(55)	C(54)	C(56)	116.0(7)	C(57)	C(55)	C(58)	108.9(7)
O(3)	C(61)	C(62)	113.2(7)	O(3)	C(61)	C(66)	122.0(7)
C(62)	C(61)	C(66)	124.8(8)	C(62)	C(63)	C(64)	122.(1)
C(63)	C(64)	C(65)	121.8(9)	C(63)	C(64)	C(67)	119.7(7)
C(64)	C(65)	C(66)	118.8(9)	C(65)	C(64)	C(67)	118.6(7)
1R,3R,5S-Isomer							
S	P	O	110.5(3)	S	P	N(1)	116.8(3)
S	P	N(2)	113.3(2)	O	P	N(1)	100.7(3)

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TABLE III (*Continued*)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O	P	N(2)	111.1(3)	N(1)	P	N(2)	103.9(3)
P	O	C(31)	125.0(4)	P	N(1)	C(11)	118.3(5)
P	N(2)	C(14)	123.2(6)	N(1)	C(11)	C(12)	114.7(7)
N(1)	C(11)	C(15)	108.8(7)	C(12)	C(11)	C(15)	105.1(7)
C(11)	C(12)	C(13)	103.7(8)	C(12)	C(13)	C(14)	105.2(7)
N(2)	C(14)	C(13)	110.2(5)	N(2)	C(14)	C(15)	106.2(6)
N(2)	C(14)	C	105.9(6)	C(13)	C(14)	C(15)	105.0(7)
C(13)	C(14)	C	113.9(7)	C(15)	C(14)	C	115.4(5)
C(11)	C(15)	C(14)	98.3(5)	C(11)	C(15)	C(21)	108.3(7)
C(11)	C(15)	C(22)	116.5(7)	C(14)	C(15)	C(21)	108.4(6)
C(14)	C(15)	C(22)	115.1(6)	C(21)	C(15)	C(22)	109.7(6)
O	C(31)	C(32)	120.8(6)	O	C(31)	C(36)	115.4(6)
C(32)	C(31)	C(36)	123.9(6)	C(31)	C(32)	C(33)	116.2(8)
C(32)	C(33)	C(34)	120.9(8)	C(33)	C(34)	C(35)	120.5(8)
C(33)	C(34)	C(37)	118.7(8)	C(35)	C(34)	C(37)	120.8(8)
C(34)	C(35)	C(36)	120.3(8)	C(31)	C(36)	C(35)	118.0(7)

*:Numbers in parentheses are estimated standard deviations in the least significant digits.

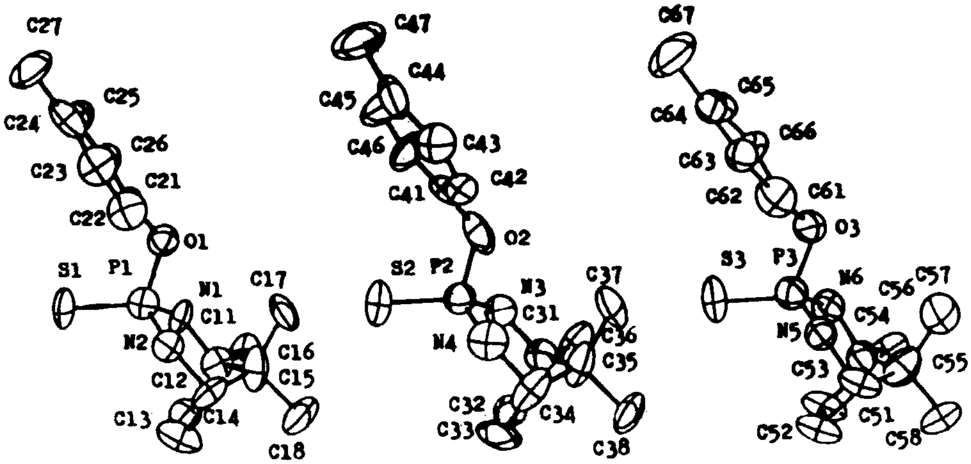

FIGURE 1 The structures of three crystallographically independent molecules of 1.

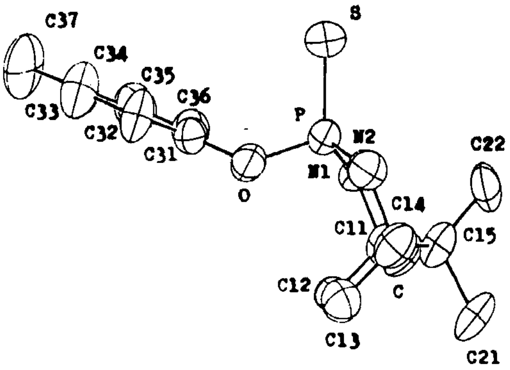

FIGURE 2 The molecular structure of 2.

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rus in 1 is 3S. So that 1 has (1R,3S,5S) configuration and 2 is (1R,3R,5S). They are diastereoisomers.

The conjugation between the phosphorus and nitrogen atoms in phosphoryl amides can take place either by a pπ-dπ delocalization along the P—N bond or by a resonance interaction of the nonbonding electrons of nitrogen with the P═Oπ system.[6,7] The P—N bond lengths in 1 are 1.604–1.647 Å, and in 2 are 1.621–1.644 Å respectively, which are shorter than the typical P—N single bond length (1.78 Å).[8] There must be pπ-dπ conjugations between the phosphorus and nitrogen atoms in 1 and 2 because their P═S bond lengths (1.930–1.949 Å) and P—O bond lengths (1.628–1.639 Å) are longer than the typical P═S double bond length (1.878 Å) and P—O single bond length (1.564 Å) respectively.

The S—P—O—C bonds in the four molecules are not co-planar and the torsion angles are about ±40°. Their torsional directions in 1 are clockwise and in 2 counterclockwise (−38.26°). The situation is shown below (Figure 3).

The phenoxy groups in 1 and 2 are rotated about the P—O bond axes apart from the S—P—O bond planes, and the rotational directions are all from N(1,3,6) to

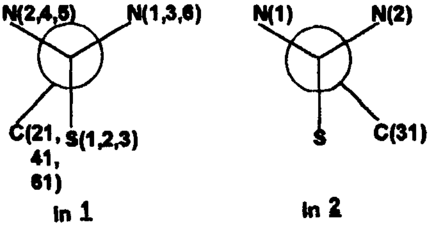

FIGURE 3 The torsional directions of the S—P—O—C bonds.

TABLE IV

Phosphorus-containing torsion angles in degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
1R,3S,5S-Isomer				
S(1)	P(1)	O(1)	C(21)	40.07(0.87)
N(1)	P(1)	O(1)	C(21)	166.11(0.83)
N(2)	P(1)	O(1)	C(21)	-84.92(0.88)
S(1)	P(1)	N(1)	C(11)	-114.63(0.88)
O(1)	P(1)	N(1)	C(11)	125.05(0.93)
N(2)	P(1)	N(1)	C(11)	12.77(1.06)
S(1)	P(1)	N(2)	C(14)	120.21(0.84)
O(1)	P(1)	N(2)	C(14)	-116.62(0.91)
N(1)	P(1)	N(2)	C(14)	-10.29(1.02)
P(1)	O(1)	C(21)	C(22)	67.44(1.26)
P(1)	O(1)	C(21)	C(26)	-112.72(1.03)
P(1)	N(1)	C(11)	C(12)	62.70(1.24)
P(1)	N(1)	C(11)	C(15)	-46.57(1.28)
P(1)	N(1)	C(11)	C(16)	-171.19(0.81)
P(1)	N(2)	C(14)	C(13)	-72.99(1.15)
P(1)	N(2)	C(14)	C(15)	44.07(1.21)
S(2)	P(2)	O(2)	C(41)	44.50(1.01)
N(3)	P(2)	O(2)	C(41)	170.32(0.95)

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TABLE IV (*Continued*)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
N(4)	P(2)	O(2)	C(41)	-80.97(1.01)
S(2)	P(2)	N(3)	C(31)	-117.87(0.83)
O(2)	P(2)	N(3)	C(31)	124.76(0.90)
N(4)	P(2)	N(3)	C(31)	12.76(1.01)
S(2)	P(2)	N(4)	C(34)	118.23(0.85)
O(2)	P(2)	N(4)	C(34)	-121.10(0.92)
N(3)	P(2)	N(4)	C(34)	-14.74(1.03)
P(2)	O(2)	C(41)	C(42)	83.73(1.25)
P(2)	O(2)	C(41)	C(46)	-100.62(1.22)
P(2)	N(3)	C(31)	C(32)	68.77(1.21)
P(2)	N(3)	C(31)	C(35)	-41.86(1.21)
P(2)	N(3)	C(31)	C(36)	-166.54(0.82)
P(2)	N(4)	C(34)	C(33)	-64.55(1.24)
P(2)	N(4)	C(34)	C(35)	49.36(1.28)
S(3)	P(3)	O(3)	C(61)	41.58(0.92)
N(5)	P(3)	O(3)	C(61)	-84.60(0.92)
N(6)	P(3)	O(3)	C(61)	166.48(0.86)
S(3)	P(3)	N(5)	C(51)	109.51(0.86)
O(3)	P(3)	N(5)	C(51)	-128.03(0.88)
N(6)	P(3)	N(5)	C(51)	-21.11(1.00)
S(3)	P(3)	N(6)	C(54)	-106.77(0.88)
O(3)	P(3)	N(6)	C(54)	133.79(0.90)
N(5)	P(3)	N(6)	C(54)	22.80(1.02)
P(3)	O(3)	C(61)	C(62)	70.62(1.40)
P(3)	O(3)	C(61)	C(66)	-110.48(1.05)
P(3)	N(5)	C(51)	C(52)	-65.44(1.16)
P(3)	N(5)	C(51)	C(55)	49.79(1.27)
P(3)	N(6)	C(54)	C(53)	59.70(1.21)
P(3)	N(6)	C(54)	C(55)	-51.73(1.25)
P(3)	N(6)	C(54)	C(56)	-176.96(0.87)
1R,3R,5S-Isome				
S	P	O	C(31)	-38.26(0.69)
N(1)	P	O	C(31)	-162.26(0.66)
N(2)	P	O	C(31)	88.22(0.69)
S	P	N(1)	C(11)	152.88(0.53)
O	P	N(1)	C(11)	-87.59(0.64)
N(2)	P	N(1)	C(11)	27.45(0.69)
S	P	N(2)	C(14)	155.80(0.50)
O	P	N(2)	C(14)	79.25(0.61)
N(1)	P	N(2)	C(14)	-28.11(0.66)
P	O	C(31)	C(32)	-52.89(1.09)
P	O	C(31)	C(36)	127.85(0.81)
P	N(1)	C(11)	C(12)	60.39(0.90)
P	N(1)	C(11)	C(15)	-56.92(0.84)
P	N(2)	C(14)	C(13)	-57.96(0.84)
P	N(2)	C(14)	C(15)	55.20(0.76)
P	N(2)	C(14)	C	178.35(0.55)

N(2,4,5). It seems that the phenoxy groups are strongly excluded by the methyl groups, in which the central carbon atoms are C(16, 36, 56) in 1 and C in 2, attached to the bridge-head carbon atoms, C(11, 31, 54) in 1 and C(11) in 2.

The corresponding phosphorus-containing torsion angles in the three different molecules of 1 are not the same (Table IV). In the cases shown in Figure 4 the differences

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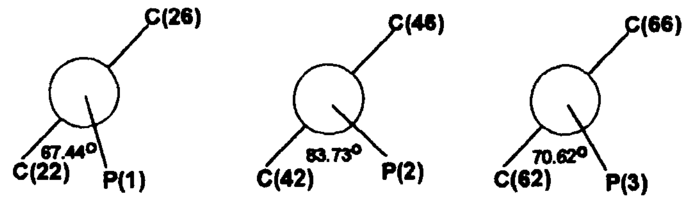

FIGURE 4 Differences of some phosphorus-containing torsion angles in the molecules of 1.

TABLE V

Selected differences of the corresponding torsion angles in the three independent molecules of 1

Corresponding structural subunit	Difference (°)
S(1)-P(1)-O(1)-C(21) / S(2)-P(2)-O(2)-C(41)	-4.43
N(1)-P(1)-O(1)-C(21) / N(3)-P(2)-O(2)-C(41)	-4.31
N(2)-P(1)-O(1)-C(21) / N(4)-P(2)-O(2)-C(41)	-3.93
S(2)-P(2)-N(3)-C(31) / S(3)-P(3)-N(6)-C(54)	-11.10
O(2)-P(2)-N(3)-C(31) / O(3)-P(3)-N(6)-C(54)	-9.03
N(4)-P(2)-N(3)-C(31) / N(5)-P(3)-N(6)-C(54)	-10.06
S(1)-P(1)-N(2)-C(14) / S(3)- P(3)-N(5)-C(51)	10.70
O(1)-P(1)-N(2)-C(14) / O(3)-P(3)-N(5)-C(51)	-11.41
N(1)-P(1)-N(2)-C(14) / N(6)-P(3)-N(5)-C(51)	10.82
P(1)-O(1)-C(21)-C(22) / P(2)-O(2)-C(41)-C(42)	-16.29
P(1)-O(1)-C(21)-C(26) / P(2)-O(2)-C(41)-C(46)	-12.10
P(2)-N(3)-C(31)-C(32) / P(3)-N(6)-C(54)-C(53)	9.07
P(2)-N(3)-C(31)-C(35) / P(3)-N(6)-C(54)-C(55)	9.87
P(2)-N(3)-C(31)-C(36) / P(3)-N(6)-C(54)-C(56)	10.42
P(1)-N(2)-C(14)-C(13) / P(2)-N(4)-C(34)-C(33)	-8.44
P(1)-N(2)-C(14)-C(15) / P(3)-N(5)-C(51)-C(55)	5.72

of the corresponding torsion angles are worth notice, two of which are more than ten degrees.

Some selected differences in degrees of the corresponding phosphorus-containing torsion angles are listed in Table V.

Similar cases are also observed in the bicyclic systems. Between the two corresponding subunits shown in Figure 5, there is a four-degree difference in the rotations about the C—C bond axes although both have a staggered arrangement.

It is obvious that the three independent molecules of 1 can not coincide geometrically because of their structural differences, which are introduced by the rotations of the methylphenoxy groups about the P—O bond axes, the methylphenyl groups about the O—C bond axes and the some other groups about the C—C bond axes. It is concluded that the three molecules of 1 are not only crystallographically independent but also conformationally different even if 1 is in the solid state.

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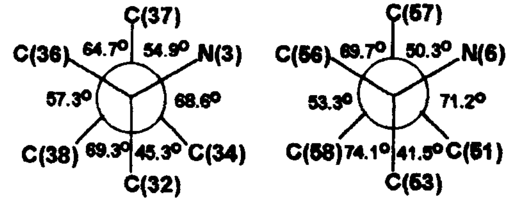

FIGURE 5 Rotation about the C—C bond in the bicyclic systems.

EXPERIMENTAL

Preparations of 1 *and* 2: Chiral reagent cis-1R,3S-1,2,2-trimethyl-1,3-cyclopentadiamine[9] (0.5 g, 3.52 mmol) was dissolved in 20 ml of acetonitrile. A solution of 4-methyl-phenoxy thiophosphoryldichloride (0.8 g, 3.32 mmol) in 10 ml of acetonitrile was dropped in slowly at 0–5°C under stirring after 4 ml of triethyl amine was added previously. The reaction mixture was then stirred at room temperature for 10 hours. Amine salt formed was filtered off and the solvent was removed by vacuum evaporation. 1, Rf = 0.4, and 2, Rf = 0.6 were separated from the residue by thin-layer chromatograph with a 1:5 ethyl acetate and cyclohexane as developing agent.

The experimental data of 1: m.p. 94–95°C. Anal. Calcd. for $C_{15}H_{23}N_2OPS$: C, 58.06; H, 7.42; N, 9.03. Found: C, 58.17; H, 7.61; N, 9.27. $[\alpha]^7_D(CHCl_3, 0.20) = +41.71°$. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4): δ 66.30 ppm. ^1H NMR ($CDCl_3$, TMS): δ 0.94–1.17 (6H, 2s, $2CH_3$); δ 1.39 (3H, d, CH_3); δ 1.78 (4H, m, $2CH_2$); δ 2.30 (3H, d, CH_3); δ 2.41 (1H, m, CH); δ 2.61–3.47 (2H, m, 2NH); δ 7.09–7.27 (4H, 2s, C_6H_4) [ppm]. IR: ν 3240, 2940, 1510, 1215, 1053, 818, 700, 584 cm^{-1}.

The experimental data of 2: m.p. 98–99°C. Anal. Calcd. for $C_{15}H_{23}N_2OPS$: C, 58.06; H, 7.42; N, 9.03. Found: C, 58.12; H, 7.44; N, 9.27. $[\alpha]^7_D(CHCl_3, 0.20) = +13.51°$. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4): δ 62.19 ppm. ^1H NMR ($CDCl_3$, TMS): δ 0.89 (3H, s, CH_3); δ 1.19 (6H, m, $2CH_3$); δ 1.75 (4H, m, $2CH_2$); δ 2.30 (3H, s, CH_3); δ 2.40 (1H, m, CH); δ 2.61–3.38 (2H, m, 2NH); δ 7.14–7.20 (4H, 2s, C_6H_4) [ppm]. IR: ν 3240, 2940, 1510, 1215, 1053, 818, 700, 584 cm^{-1}.

The specific rotations were measured on a Perkin Elmer 241Mc polarimeter. ^1H and ^{31}P NMR spectrum were measured on a JEOL FX-90Q NMR spectrometer. IR spectrum were recorded by a Shimadzu IR-435 spectrophotometer with KBr wafer. The thermometer was uncorrected.

Crystallographic data to* 1: The single crystals of 1 were obtained by crystallization from ethanol solution. A colorless crystal of $(C_{15}H_{23}N_2OPS)_3$ having approximate dimensions of 0.2 × 0.2 × 0.3 mm was mounted on a glass fiber in a random orientation. The determination of unit cell and the data collection were performed with Mo kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromater situated in the incident beam. A total of 5428 independent reflections was collected in the range of $2° \leq \theta \leq 25°$ by ω-2θ scan technique at room temperature, in which reflections with 2874 $I \geq 3\delta(I)$ were considered to be observed and used in the succeeding refinement. The correction for LP factors was applied to the data.

The crystal is orthorhombic, space group $P2_12_12_1$, with a = 21.286(7), b = 9.009(1), c = 26.393(5) Å, α = 90, β = 90, γ = 90°, V = 5061.34 $Å^3$, Mr = 931.20, Z = 12, Dx = 1.222 g/cm^3, μ = 2.75 cm^{-1}, F(000) = 1992.

The structure was solved by direct method (MULTAN 82). Most atoms were located from an E-map. The other non-hydrogen atoms were determined with successive differential Fourier syntheses. The hydrogen atoms were then added in geometrically ideal positions. The final refinement by full matrix least-square method with anisotropic thermal parameters for non-hydrogen atoms converged with unweighted and weighted agreement factors of 0.059 and 0.067. The highest peak on the final difference Fourier map had a height of 0.47 $e/Å^3$.

All calculations were performed on a PDP11/44 computer using SDP-PLUS program system.

Crystallographic data to* 2: The single crystals of 2 were obtained by crystallization from ethanol solution also. A colorless crystal of $C_{15}H_{23}N_2OPS$ having approximate dimensions of 0.2 × 0.2 × 0.25 mm was mounted on a glass fiber in a random orientation. The procedures of the determination of unit cell and the data collection were the same as mentioned above except that the collected independent

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*The torsion angles have been deposited with the Cambridge Crystallographic Data Centre (CCCD), UK.

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reflections were 3214 and in which reflections with 1711 I $\geq 3\delta(I)$ were considered to be observed and used in the succeeding refinement.

The crystal is orthorhombic, space group $P2_12_12_1$, with a = 8.624(2), b = 8.374(1), c = 23.522(8) Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, V = 1698.69 $Å^3$, Mr = 310.4, Z = 4, Dx = 1.214 g/cm^3, μ = 2.73 cm^{-1}, F(000) = 664.

The structure of 2 was solved by MULTAN 82 method. The unweighted and weighted agreement factors were 0.068 and 0.077 respectively. The highest peak on the final difference Fourier map had a height of 0.54 e/$Å^3$.

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