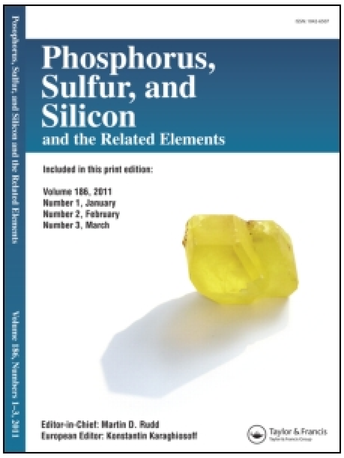

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THE CRYSTAL STRUCTURE AND STEREOCHEMISTRY OF 2,3-DIPHENYL-4-DIPHENYLPHOSPHINYLISOXAZOLIDINE

K. Michal Pietrusiewicz[a]; Michal W. Wieczorek[b]; Grzegorz Bujacz[b]; Alberto Brandi[c]
[a] The Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Lódź, Poland [b] Institute of General Chemistry, Technical University of Lódź, Lódź, Poland [c] Centro dei Composti Eterociclici-C. N. R., Dipartimento di Chimica Organica, Universita' di Firenze, Firenze, Italy

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THE CRYSTAL STRUCTURE AND STEREOCHEMISTRY OF 2,3-DIPHENYL-4-DIPHENYLPHOSPHINYLISOXAZOLIDINE

K. MICHAL PIETRUSIEWICZ†
The Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Lódź, Poland

MICHAL W. WIECZOREK and GRZEGORZ BUJACZ
Institute of General Chemistry, Technical University of Lódź, Zwirki 36, 90-924 Lódź, Poland

ALBERTO BRANDI[1]
Centro dei Composti Eterociclici—C.N.R., Dipartimento di Chimica Organica, Universita' di Firenze, via G. Capponi 9, 50121 Firenze, Italy

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The structure of the major product of the 1,3-dipolar cycloaddition of diphenylvinylphosphine oxide to C,N-diphenylnitrone was analyzed by a single-crystal X-ray diffraction technique. $C_{27}H_{24}NO_2P$, monoclinic, space group $P2_{1/c}$, $a = 9.396\,(1)$Å, $b = 22.057\,(2)$Å, $c = 11.171\,(2)$Å, $V = 2244.9\,(3)$Å^3 and $Z = 4$. The structure was solved by direct methods and was refined by full matrix least-squares calculations to $R = 0.040$ and $R_w = 0.037$ using 2905 unique reflections with $I > 3\sigma(I)$. The studied molecule was identified as the 4-substituted regioisomer possessing C_3-phenyl and diphenylphosphinyl substituents in the trans arrangement.

Key words: 1,3-Dipolar cycloaddition; diphenylvinylphosphine oxide; regioselective addition; stereochemical assignment; X-ray crystal structure; 2,3-diphenyl-4-diphenylphosphinylisoxazolidine.

INTRODUCTION

Diphenylvinylphosphine oxide, diphenylvinylphosphine sulfide and diphenylvinylphosphine selenide have recently been found to cycloadd to C,N-diphenylnitrone **1** with predominant formation of the corresponding 4-diphenylphosphinyl isoxazolidines **3**.[2,3] The three dipolarophiles join thus the small but growing number of monosubstituted olefins which are capable of producing prevailing amounts of the 4-substituted isoxazolidines in their reactions with certain nitrones.[4–6] The increasing supply of such isoxazolidines offers many novel synthetic possibilities[6–8] and an accurate knowledge of their stereochemistry is therefore becoming of considerable importance. In all the cases reported heretofore such 4-substituted isoxazolidines were found to be configurationally homogeneous and were most often represented in the trans configuration. The proposed stereochemical assignments were usually suggested by the pertinent

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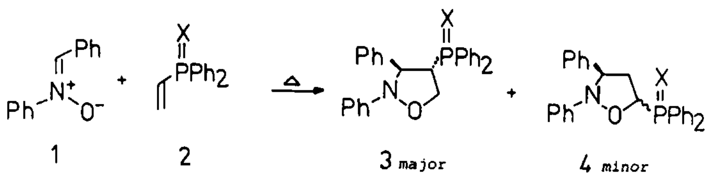
† Author to whom all correspondence should be addressed.



X= O,S,Se

NMR data[5,6] and accorded also with the assumption, that in the cycloaddition transition state leading to such adducts the olefin and the nitrone C-substituents were oriented away from each other in order to avoid unfavorable steric interactions. In this paper we report the single-crystal X-ray diffraction analysis of **3** (X=O), the major product of the reaction of diphenylvinylphosphine oxide with nitrone **1**. The results unequivocally confirm the regio- and stereochemical assignments discussed above.

RESULTS AND DISCUSSION

A three-dimensional view of the investigated molecule with the numbering system is shown in Figure 1. The final positional parameters together with estimated standard deviations are given in Table I. Bond lengths and bond angles are listed in Table II and Table III, respectively.

Inspection of Figure 1 reveals that the structural assignment proposed recently[2] for **3** (X = O) is fully confirmed. Diphenylphosphinyl substituent resides on C1 (C4 in the isoxazolidine ring numbering), and is found in the trans relationship with respect to the C3-phenyl group. The detailed arrangement of atoms within this part of the molecule is displayed in the two Newman projections which are shown in Figure 2. As can be seen from this Figure, the hydrogen atoms H11 and

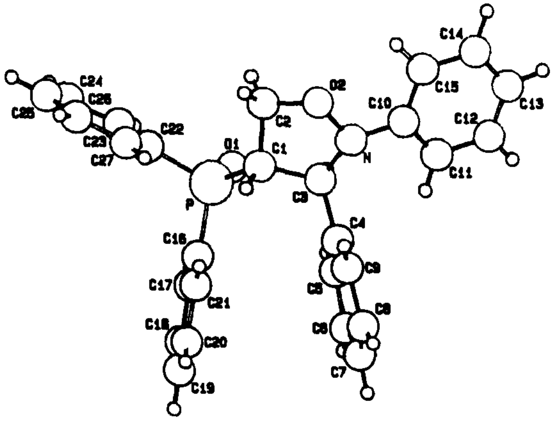


FIGURE 1 Three-dimensional view of 2,3-diphenyl-4-diphenylphosphinylisoxazolidine **3** (X = O) with atom numbering.

TABLE I

Positional parameters and their estimated standard deviations

Atom	*x*	*y*	*z*	B(A2)
P	0.97890(6)	0.23123(3)	0.23529(5)	2.99(1)
O1	0.9641(2)	0.24339(8)	0.1018(1)	3.95(4)
O2	0.2670(3)	0.6353(2)	0.6740(3)	5.51(8)
O2′	0.2972(3)	0.6481(2)	0.7756(3)	4.27(8)
N	0.8434(2)	0.3958(1)	0.2962(2)	5.36(5)
C1	0.9140(2)	0.2936(1)	0.3141(2)	3.07(4)
C2	0.7467(2)	0.2995(1)	0.2846(2)	4.65(6)
C3	0.9589(2)	0.3561(1)	0.2721(2)	3.33(5)
C4	0.118	0.375	0.325	2.9
C4′	0.102	0.379	0.357	4.0
C5	0.219	0.364	0.259	4.8
C5′	0.229	0.372	0.309	6.2
C6	0.368	0.375	0.309	5.9
C6′	0.368	0.389	0.386	8.1
C7	0.414	0.400	0.430	7.1
C7′	0.352	0.412	0.477	7.9
C8	0.316	0.414	0.514	7.6
C8′	0.237	0.427	0.534	10.9
C9	0.166	0.395	0.451	4.8
C9′	0.101	0.409	0.460	6.1
C10	0.8071(3)	0.4481(1)	0.2213(2)	4.07(5)
C11	0.9102(3)	0.4779(1)	0.1738(3)	5.33(7)
C12	0.8739(3)	0.5303(1)	0.1055(3)	5.83(7)
C13	0.7377(3)	0.5532(1)	0.0837(3)	6.72(8)
C14	0.6340(3)	0.5238(2)	0.1271(4)	9.2(1)
C15	0.6676(3)	0.4712(1)	0.1969(3)	7.36(8)
C16	1.1676(2)	0.2174(1)	0.3159(2)	3.00(4)
C17	1.2648(2)	0.1995(1)	0.2473(2)	3.83(5)
C18	1.4114(2)	0.1898(1)	0.3035(2)	4.58(5)
C19	1.4621(3)	0.1982(1)	0.4280(3)	4.62(6)
C20	1.3666(3)	0.2151(1)	0.4986(2)	4.58(6)
C21	1.2193(2)	0.2246(1)	0.4429(2)	3.82(5)
C22	0.8748(2)	0.1652(1)	0.2580(2)	3.21(5)
C23	0.8345(3)	0.1250(1)	0.1598(2)	4.52(6)
C24	0.7620(3)	0.0716(1)	0.1744(3)	5.49(7)
C25	0.2719(3)	0.5589(1)	0.2156(3)	5.26(7)
C26	0.7646(3)	0.0993(1)	0.3810(2)	4.55(6)
C27	0.8396(2)	0.1518(1)	0.3691(2)	3.66(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2 * B(1,1) + b2 * B(2,2) + c2 * B(3,3) + ab(cos gamma) * B(1,2) + ac(cos beta) * B(1,3) + bc(cos alpha) * B(2,3)]

H31 are in the anti array and the corresponding dihedral angle H11–C1–C3–H31 is equal to 153°. The diphenylphosphinyl group is found in the conformation in which the smallest phosphorus substituent, i.e., O1, is placed against the isoxazolidine ring, as could have been expected.

Examination of Figure 1 and Table III shows the isoxazolidine ring to have conformation between an envelope and a half-chair. The torsion angles in the ring are displayed in Figure 3 and the corresponding deformation factors are

TABLE II

Bond distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
P	O1	1.488(2)	C8	C9	1.466(2)
P	C1	1.817(2)	C8'	C9'	1.399(4)
P	C16	1.808(2)	C10	C11	1.380(4)
P	C22	1.806(2)	C10	C15	1.371(4)
N	C3	1.470(3)	C11	C12	1.381(4)
N	C10	1.416(3)	C12	C13	1.341(4)
C1	C2	1.531(4)	C13	C14	1.356(5)
C1	C3	1.547(3)	C14	C15	1.389(5)
C4	C5	1.355(3)	C16	C17	1.385(3)
C4	C9	1.448(4)	C16	C21	1.391(3)
C4'	C5'	1.434(3)	C17	C18	1.384(4)
C4'	C9'	1.334(4)	C18	C19	1.368(4)
C5	C6	1.397(2)	C19	C20	1.383(4)
C5'	C6'	1.431(6)	C20	C21	1.389(4)
C6	C7	1.424(3)	C22	C23	1.390(3)
C6'	C7'	1.178(3)	C22	C27	1.391(3)
C7	C8	1.492(4)	C23	C24	1.390(4)
C7'	C8'	1.419(4)	C26	C27	1.379(4)
C3	C4	1.525(4)	C3	C4'	1.529(4)

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

listed below:

$$\Delta C_s(N) = 51.54 \qquad \Delta C_2(N) = 6.67$$

$$\Delta C_s(O2) = 37.81 \qquad \Delta C_2(O2) = 43.97$$

$$\Delta C_s(C1) = 20.26 \qquad \Delta C_2(C1) = 60.33$$

$$\Delta C_s(C2) = 10.41 \qquad \Delta C_2(C2) = 64.45$$

$$\Delta C_s(C3) = 43.81 \qquad \Delta C_2(C3) = 33.18$$

In addition, an envelope conformation of the studied isoxazolidine ring which shows the smallest deviation from the idealized envelope has been selected by the least-squares plane calculations. It is the one which possesses the C1, C3, N, O2 atoms in one plane and the C2 carbon in a 0.63 Å distance from that plane.

EXPERIMENTAL

Phosphinylisoxazolidine **3** ($X = O$) was available from previous work[2] and the appropriate crystals were obtained by slow evaporation of the benzene solution. $C_{27}H_{24}NO_2P$, monoclinic, space group $P2_{1/c}$ with $a = 9.396$ (1)Å, $b = 22.057$ (2)Å, $c = 11.171$ (2)Å, $\beta = 104.12$ (1)°, $Z = 4$, $V = 2244.9$ (3)Å^3, $\mu = 12.5\,mm^{-1}$ and $D_x = 1.259\,g/cm^3$. Intensity data were collected on a small single crystal using CAD4 diffractometer in the range of $1 < \theta < 75°$ with graphite monochromatized Cu-K_α radiation ($\lambda = 1.54178$ Å) in the $\omega/2\theta$ scan mode. Lattice constants were refined by the least-squares fit of 25 reflections in the θ range of 20.3–27.6°. No absorption correction was applied at the stage of data collection. Out of 3260 integrated reflections collected up to $\sin\theta/\lambda = 0.751$ Å^{-1}, 2905 observed reflections [$I > 3\sigma(I)$] were used to solve the structure by direct methods and to refine it by the full matrix least-squares using F's. H atoms were found on the Fourier map and were refined with isotropic thermal parameters. For all other atoms anisotropic thermal parameters. For all other atoms

TABLE III

Bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	P	C1	112.9(1)	O1	P	C16	111.7(1)	O1	P	C22	111.39(9)
C1	P	C16	106.90(9)	C5	C6	C7	119.63(9)	C1	P	C22	106.6(2)
C5′	C4′	C9′	124.1(2)	C16	P	C22	107.0(1)	C3	N	C10	117.4(2)
P	C1	C2	114.1(2)	P	C1	C3	112.3(2)	C4	C5	C6	120.8(2)
C2	C1	C3	101.6(2)	N	C3	C1	102.0(2)	C5′	C6′	C7′	110.5(2)
N	C3	C4	117.9(3)	N	C3	C4′	105.5(3)	C1	C3	C4	115.8(3)
C5	C4	C9	119.7(2)	C4′	C5′	C6′	117.7(2)	C6	C7	C8	125.3(2)
C7	C8	C9	108.6(2)	N	C10	C11	121.6(2)	N	C10	C15	120.1(2)
C6′	C7′	C8′	139.1(2)	C11	C10	C15	118.2(2)	C10	C11	C12	120.6(2)
C11	C12	C13	120.0(3)	C12	C13	C14	119.4(3)	C4	C9	C8	125.6(3)
C13	C14	C15	121.0(3)	C10	C15	C14	119.9(3)	P	C16	C17	118.1(1)
P	C16	C21	123.0(2)	C17	C16	C21	118.9(2)	C16	C17	C18	120.7(3)
C17	C18	C19	120.1(2)	C7′	C8′	C9′	111.0(2)	C18	C19	C20	120.2(3)
C19	C20	C21	120.0(2)	C16	C21	C20	120.1(2)	P	C22	C23	117.1(2)
P	C22	C27	123.5(2)	C23	C22	C27	119.3(2)	C22	C23	C24	119.7(2)
C22	C27	C26	120.2(2)	C4′	C9′	C8′	116.9(2)	C1	C3	C4′	111.5(3)

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

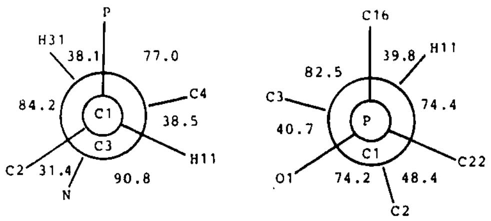


FIGURE 2 Newman projections along C_1—C_3 and P—C_1 bonds with relevant dihedral angles (°).

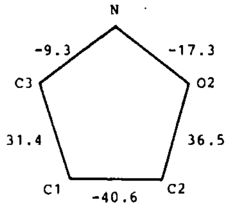


FIGURE 3 Torsional angles in the isoxazolidine ring (°).

anisotropic thermal parameters were applied. Difabs program was used to perform absorption correction. Refinement converged to $R = 0.040$ and $R_w = 0.037$ with the unitweight for 307 refined parameters. The largest shift over e.s.d. in the last cycle was 0.11. The largest residual peak in the final difference Fourier map was 0.224 e $Å^{-3}$. The aromatic ring C4–C5–C6–C7–C8 as well as the oxygen O2 have multiplicity of 0.53/0.47. All calculations were carried out with an Enraf-Nonius SDP crystallographic computing package (Frenz, 1984). Scattering factors were taken from the International Tables for X-Ray Crystallography.

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SUPPLEMENTARY MATERIAL AVAILABLE

Table of Torsional Angles, Table of Least-Squares Planes, Table of General Displacement Parameter Expressions—U's and B's, Table of Refined Displacement Parameter Expressions—Beta's, Table of Root-Mean-Square Amplitudes of Thermal Vibration and Values of F_{obs} and $F_{calc.}$ have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Requests should be accompanied by the full literature citation for this paper.

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