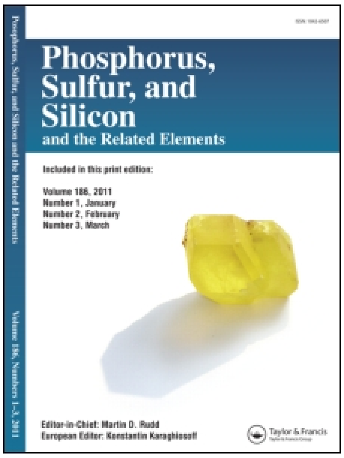

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CRYSTAL AND MOLECULAR STRUCTURE OF (Z)-AND (E)-3-DIPHENYLPHOSPHINOPROPENOIC ACID

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Communication

CRYSTAL AND MOLECULAR STRUCTURE OF (Z)- AND (E)-3-DIPHENYLPHOSPHINOPROPENOIC ACID

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The structures of the title compounds were determined by X-ray diffraction: (Z)-isomer, space group $P2_1/c$, $a = 7.968(1)$, $b = 14.857(2)$, $c = 11.669(2)$, $\beta = 100.44(1)°$, $Z = 4$, $R = 0.048$ for 1785 observed reflections; (E)-isomer, space group $P2_1/c$, $a = 10.169(2)$, $b = 15.910(2)$, $c = 16.234(2)$, $\beta = 93.03(1)°$, $Z = 8$, $R = 0.055$ for 2421 observed reflections. The crystal structure of both isomers is composed of dimeric units in which the individual molecules are joined by twofold hydrogen bonds. While the dimers of the (Z)-isomer are centrosymmetric, those of the (E)-isomer involve two crystallographically independent molecules, differing considerably in conformation of the phenyl groups relatively to the double bond plane. Except for configuration at the double bond, the bond distances and angles are nearly identical for both molecular structures.

Key words: (Z)-3-Diphenylphosphinopropenoic acid; (E)-3-diphenylphosphinopropenoic acid; crystal and molecular structure.

INTRODUCTION

During the study of the properties and structure of phosphinocarboxylic acids,[1] especially with regard to their use as extractants for platinum metals,[2] it showed advisable to dispose sterically the phosphine and carboxyl groups at a distance enabling selective chelation of bulkier metal ions such as Rh(I) in the presence of a large excess of smaller ions, in particular Co(II). The (Z)-isomer of 3-diphenylphosphinopropenoic acid is an obvious candidate for this purpose. The aim of this work was to determine the precise distance between the functional groups of this ligand by X-ray diffraction; for comparison, the structure of the (E)-isomer was determined as well.

RESULTS

Final coordinates of non-hydrogen atoms are given in Table I; Table II compares important geometrical parameters for both structures. Tables of hydrogen atom coordinates, anisotropic displacement parameters and further distances and angles

TABLE I

Fractional coordinates ($\times$ 10^4) of non-hydrogen atoms with estimated standard deviations in parentheses

$$U_{eq} = \sum_i \sum_j \bar{a}_i \bar{a}_j a_i^* a_j^* U_{ij} \times 10^3 \text{ Å}^2$$

	(Z)-isomer				(E)-isomer							
					Molecule A				Molecule B			
Atom	x	y	z	U_{eq}	x	y	z	U_{eq}	x	y	z	U_{eq}
P	3092(1)	2621(1)	1147(1)	29(1)	11738(1)	1090(1)	7584(1)	48(1)	3055(1)	59(1)	2378(1)	51(1)
O1	1867(3)	5245(2)	-719(2)	61(1)	7530(4)	1490(2)	5721(2)	60(1)	7093(4)	-270(2)	4394(2)	67(1)
O2	975(2)	4051(1)	172(2)	50(1)	8645(3)	298(2)	5582(2)	64(1)	5883(3)	872(2)	4550(2)	76(1)
C1	4222(4)	3256(2)	189(3)	48(1)	10427(4)	816(3)	6842(2)	47(2)	4259(4)	360(3)	3179(3)	50(2)
C2	3690(4)	4005(2)	-384(3)	49(1)	9483(4)	1320(3)	6530(3)	48(2)	5276(4)	-89(3)	3482(3)	52(2)
C3	2056(4)	4426(2)	-295(3)	46(1)	8522(5)	998(3)	5905(3)	46(2)	6110(5)	212(3)	4189(3)	51(2)
C4	1422(4)	2031(2)	140(2)	41(1)	11003(4)	1908(3)	8189(2)	43(2)	3915(4)	-737(3)	1801(3)	48(2)
C5	1448(3)	1910(2)	-1034(2)	51(1)	11677(5)	2658(3)	8274(3)	57(2)	3706(5)	-1568(3)	2021(3)	64(2)
C6	161(4)	1445(2)	-1741(2)	58(1)	11178(6)	3329(3)	8688(3)	69(2)	4256(5)	-2215(3)	1595(3)	71(2)
C7	-1177(4)	1102(2)	-1284(2)	64(1)	9970(6)	3264(3)	9025(3)	64(2)	5004(5)	-2052(3)	936(3)	65(2)
C8	-1229(4)	1220(2)	-136(3)	76(1)	9266(5)	2524(3)	8945(3)	62(2)	5236(5)	-1239(3)	721(3)	72(2)
C9	58(4)	1681(2)	582(3)	65(1)	9766(5)	1845(3)	8528(3)	56(2)	4700(5)	-579(3)	1142(3)	65(2)
C10	4660(3)	1727(2)	1611(2)	44(1)	11735(4)	150(3)	8230(3)	47(2)	3032(5)	1000(3)	1735(3)	49(2)
C11	4439(4)	832(2)	1306(3)	55(1)	11660(5)	172(3)	9084(3)	66(2)	1839(5)	1203(3)	1318(3)	62(2)
C12	5649(5)	192(2)	1772(3)	72(1)	11815(6)	-549(4)	9546(3)	81(3)	1739(7)	1935(4)	861(3)	84(3)
C13	7101(5)	460(3)	2534(3)	78(2)	12039(6)	-1310(4)	9172(4)	85(3)	2792(8)	2473(4)	814(3)	86(3)
C14	7339(4)	1343(3)	2851(3)	73(1)	12090(5)	-1345(3)	8336(4)	74(2)	3977(7)	2270(4)	1223(3)	77(2)
C15	6123(4)	1981(3)	2394(3)	61(1)	11953(5)	-632(3)	7861(3)	62(2)	4100(5)	1534(3)	1669(3)	60(2)

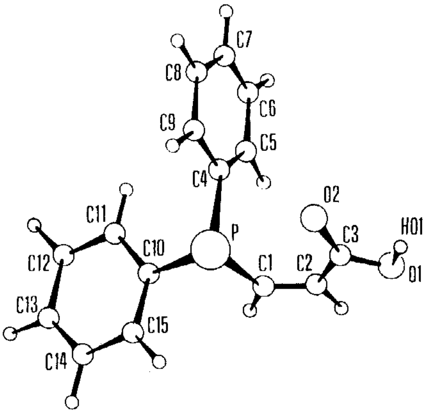

FIGURE 1 Perspective view of the molecule of (Z)-isomer.

are available from the authors upon request. Pertinent data have been deposited at Cambridge Structural Database. Figures 1 and 2 show perspective views on the asymmetric units; crystal packing is obvious from Figures 3 and 4.

TABLE II

Important distances (Å) and angles (°) with estimated standard deviations in parentheses

Distance (angle)	(Z)-isomer	(E)-isomer	
		Molecule A	Molecule B
P-C1	1.824(3)	1.803(4)	1.803(5)
P-C4	1.833(3)	1.816(5)	1.826(5)
P-C10	1.873(3)	1.827(5)	1.825(5)
C1-P-C4	103.6(1)	102.9(2)	103.3(2)
C1-P-C10	99.8(1)	99.4(2)	100.5(2)
C4-P-C10	102.7(1)	105.2(2)	105.5(2)
C1-C2	1.328(4)	1.330(6)	1.329(6)
C2-C3	1.465(5)	1.467(7)	1.471(7)
P-C1-C2	126.6(2)	127.0(3)	127.5(3)
C1-C2-C3	121.9(3)	119.7(4)	121.2(4)
P-C1-C2-C3 [a]	0.5(4)	177.6(7)	-174.5(7)
C3-O1	1.313(4)	1.300(6)	1.290(6)
C3-O2	1.233(4)	1.239(6)	1.230(6)
C2-C3-O1	114.3(2)	115.5(4)	114.5(4)
C2-C3-O2	122.7(2)	121.9(4)	122.4(4)
O1-C3-O2	123.0(2)	122.6(4)	123.1(4)
O1...O2	2.675(3)	2.654(5)	
O2...O1		2.589(5)	
A/B [b]	135.8(3)	153.2(5)	124.8(5)
A/C [b]	109.9(3)	70.8(5)	58.9(6)
B/C [b]	104.5(5)	135.8(7)	109.9(8)
A/D [b]	15.1(3)	9.2(5)	4.0(6)

[a] Torsional angle

[b] Angles between least-squares planes defined as follows:
A: C1,C2,C3,P; B: C4 to C9; C: C10 to C15; D: C3,O1,O2

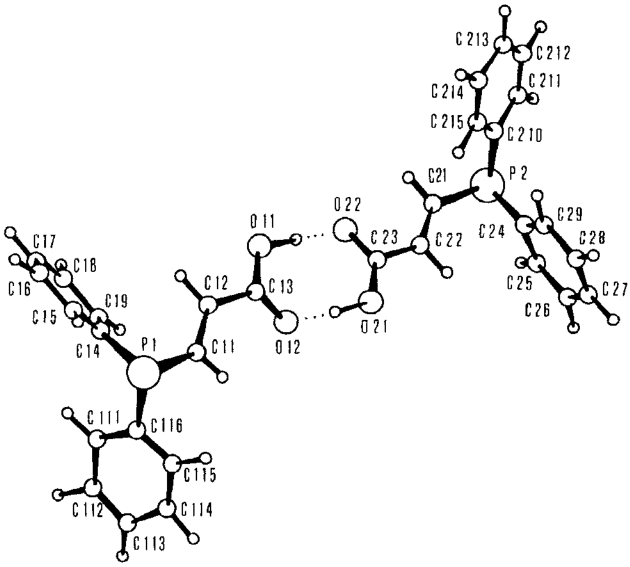

FIGURE 2 Perspective view of two crystallographically independent molecules of (E)-isomer.

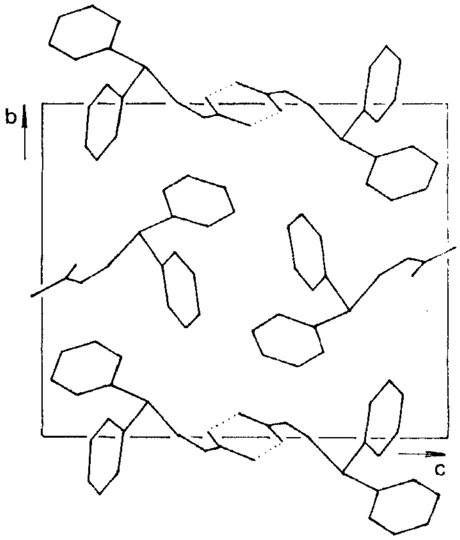

FIGURE 3 Projection of the unit cell of (Z)-isomer onto the bc plane.

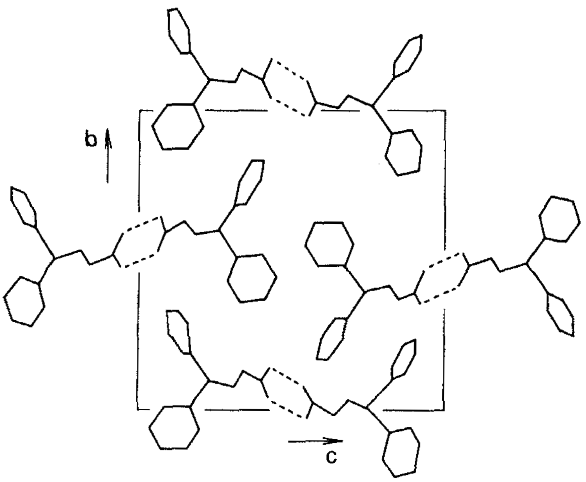

FIGURE 4 Projection of the unit cell of (E)-isomer onto the bc plane.

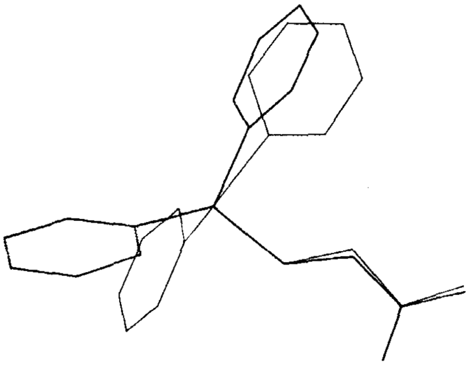

FIGURE 5 Superposition of two independent molecules of (E)-isomer with the double bond plane taken as reference (molecule A in bold lines).

Both structures are composed of dimeric units which are typical for solid carboxylic acids. The pseudocentrosymmetric dimers of the (E)-isomer are composed of two independent molecules labeled A and B (Figure 5). The main difference between these two molecules consists, obviously as a result of crystal packing effects, in the conformation of the phenyl and, in a lesser extent, of the carboxyl groups relatively to the olefinic plane. The other intramolecular and hydrogen-bonding parameters are normal and typical for 1,2-disubstituted olefins[3] as well as for carboxylic acids[4] and for an uncoordinated Ph_2P group.[5] The key distance between phosphorus and oxygen in the (Z)-isomer is 2.823(2) and therefore ideal for selective chelation since the atomic diameters in question are 2.90 and 2.66 for Rh and Co respectively.

TABLE III

Crystal data, measurement and refinement details

Crystal dimensions (mm)	0.55x0.15x0.12	0.47x0.15x0.12
Space group	$P2_1/c$ (No.14)	
a (Å)	7.968(1)	10.169(2)
b (Å)	14.857(2)	15.910(2)
c (Å)	11.669(2)	16.234(2)
β (°)	100.44(1)	93.03(1)
V (Å^3), Z	1358.4(3), 4	2622.8(7), 8
D_c, D_m (g cm^{-3})	1.253, 1.24(1)	1.297, 1.29(1)
Radiation	Mo K_α , λ = 0.71073	
Absorption correction	None, μ = 0.192 mm^{-1}	
F(000)	536	1072
Temperature (K)	293(1)	
No.of reflections for latt. param.determination	18 (30° <2Θ <37°)	19(27° <2Θ <33°)
Diffractometer, scan mode	CAD4, ω / 2 Θ	
$(\sin \Theta/\lambda)_{max}$	0.60	
Stand.reflections (var.)	2 after every 2 h (< 0.5%)	
Interval h; k; l	-9,9;0,17;-13;13	-12,12;0,18;-19,19
No.of reflctions measured	3825	9560
independent by symmetry	2069	4789
used [I > 1.96 σ(I)]	1785	2421
Resid.electr.density (eÅ^{-3})	0.25;-0.24	0.22;-0.21
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Weight	$A/(\sigma^2(F_o) + 0.0009 F^2)$	
A	1.436	0.630
R, wR	0.048, 0.051	0.055,0.057
R_{int}, S	0.029, 1.0358	0.033, 0.9794

EXPERIMENTAL

Polycrystalline samples of both isomers were synthesized according to the literature.[6] Because of limited stability in solution, single crystals were obtained by as rapid crystallization as possible for forming X-ray-quality crystals: solutions saturated at 50°C in toluene ((Z)-isomer) or methanol ((E)-isomer) were cooled to 20°C during 1 h, followed by immediate isolation by decantation, washing with a little cold solvent and drying in vacuo. The melting points of the pure isomers are 109°C (Z-) and 114°C (E-) and the parameters of their NMR spectra agree with the published values.[6] The density was determined by flotation in aqueous $ZnCl_2$ solution. Crystal data and details of measurement and refinement are summarized in Table III. The structures were solved by direct methods (SHELXS-86[7]) and refined by full-matrix least-squares (SHELX 76,[8] for the (E)-isomer in two blocks). All hydrogen atoms were clearly discernible in difference maps but, except for H(01) and its H(011) and H(021) analogues, they were constrained in theoretical positions since they proved to be unstable towards free refinement.

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