Instrumental Achievements

Crystal Structure of *N,N,N′,N′*-Tetrakis(methyldiphenylphosphino)-bis-(2′-phenoxy)-3,6-dioxaoctane

Tuncer HÖKELEK,*† İrfan YAMAK, and Zeynel KILIÇ****

**Hacettepe University, Department of Physics, 06532 Beytepe-Ankara, Turkey*
***Ankara University, Department of Chemistry, 06100 Tandoğan-Ankara, Turkey*

The title molecule, $[C_{70}H_{68}N_2O_4P_4]$, is a polydentate podand consisting of four etheral oxygens, two tertiary amine nitrogens and four diphenylphosphin groups. It crystallizes in the triclinic space group $P\bar{1}$, and there is only one half a molecule in the asymmetric unit. The coordinations around the N and P atoms are pyramidal. The conformations about C20–C21, O2–C21 and O2–C22 are *gauche*, *anti* and *anti*, respectively.

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Forty years ago, application of the Mannich reaction to the synthesis of aminomethylphosphines developed a new research area for the synthesis of novel phosphine ligands.[1,2] The syntheses of some macrocyclic multidentate crown-ethers and podands containing P–C–N linkages have been reported.[3,4]

The title ligand was prepared from a mixture of triethylene glycol bis(2-aminophenyl ether)[5] (2.66 g, 8.00 mmol), diphenylphosphine (5.54 mL, 32.0 mmol) and formaldehyde (7.00 mL, 37% solution in water) in benzene (150 mL) at 55˚C, with argon being passed over for 6 h. After the evaporation of benzene, the residue was crystallized from dichloromethane, yield 5.85 g (65%), m.p. 125˚C.

The structure was solved by direct methods. Since the difference synthesis did not clarify the positions of the H atoms, they were positioned geometrically with C–H distances of 0.97 and 0.93 Å for CH_2 and CH, respectively, and a riding model was used during the refinement.

The results of X-ray structure determination are given in Tables 1 – 3.

The title molecule, which is a polydentate podand (Fig. 2), consists of four etheral oxygens, two tertiary amine nitrogens and four diphenylphosphin groups. It forms stable complexes with some lanthanides and transition-metal cations. The asymmetric unit contains only one half molecule.

The sums of the bond angles, around N1, P1 and P2 atoms [348.2(5), 301.6(3) and 304.2(3)˚, respectively] are the indications of pyramidality. The ϕ_{CC} (O1–C20–C21–O2), ϕ_{CO} (C20–C21–O2–C22) and ϕ_{OC} (C21–O2–C22–C22) torsion angles are –67.9(7), –176.5(5) and 179.9(7)˚, respectively, showing that the conformations about C20–C21 is *gauche* and those around C21–O2 and O2–C22 are *anti*.

The O1–C19 [1.369(7)Å] bond is shorter than the average of the remaining O–C [1.415(7)Å] bonds, due to the electron withdrawing of the phenyl ring. C19–O1–C20 [119.1(5)˚] bond

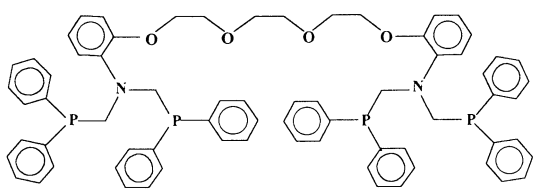

Fig. 1 Chemical diagram.

† To whom correspondence should be addressed.

Table 1 Crystal and experimental data

Formula: $C_{70}H_{68}N_2O_4P_4$
Formula weight = 1125.14
Crystal system: triclinic
Space group: $P\bar{1}$ Z = 1
a = 10.841(2)Å
b = 11.800(2)Å
c = 13.071(2)Å
α = 70.48(2)˚
β = 79.15(2)˚
γ = 78.22(2)˚
V = 1529.7(4)Å^3
D_x = 1.221 g/cm^3
μ(Cu K$_\alpha$) = 1.531 mm^{-1}
T = 294 K
Crystal color: colorless
Crystal size: 0.30 × 0.25 × 0.20 mm
λ(Cu K$_\alpha$) = 1.54184 Å
R = 0.0587 wR = 0.1912
Weighting scheme: $w = 1/[\sigma^2(F_0^2) + (0.0777P)^2 + 0.4613P]$ where $P = (F_0^2 + 2F_c^2)/3$
No. of reflections measured = 5702
No. of reflections used = 3427
[$I > 2\sigma(I)$]
No. of parameters = 362
Goodness-of-fit = 1.199
$(\Delta/\sigma)_{max}$ = 0.007
$(\Delta\rho)_{max}$ = 0.379
$(\Delta\rho)_{min}$ = –0.209
$2\theta_{max}$ = 148.52
Measurements: Enraf-Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: MolEN
Refinement: full matrix least-squares

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	U_{iso}
P1	0.9284(2)	0.3063(1)	0.3751(1)	0.0602(5)
P2	0.6204(2)	0.7212(1)	0.2927(1)	0.0609(5)
O1	0.9001(4)	0.6308(4)	0.0549(3)	0.064(1)
O2	0.9645(4)	0.8672(4)	-0.0179(4)	0.068(1)
N1	0.8194(5)	0.5364(4)	0.2687(4)	0.057(1)
C1	1.0832(6)	0.3538(6)	0.3669(5)	0.062(2)
C2	1.1757(7)	0.2823(7)	0.4343(6)	0.081(2)
C3	1.2907(7)	0.3189(9)	0.4226(7)	0.093(3)
C4	1.3193(8)	0.4256(9)	0.3451(8)	0.092(2)
C5	1.2299(8)	0.4947(8)	0.2760(7)	0.091(2)
C6	1.1143(7)	0.4586(7)	0.2877(6)	0.075(2)
C7	0.9010(6)	0.2161(5)	0.5201(5)	0.060(1)
C8	0.8741(7)	0.1006(6)	0.5459(6)	0.076(2)
C9	0.8543(8)	0.0271(7)	0.6551(8)	0.091(2)
C10	0.8624(8)	0.0708(8)	0.7375(7)	0.092(3)
C11	0.8896(9)	0.1871(8)	0.7143(6)	0.091(2)
C12	0.9084(8)	0.2588(6)	0.6059(6)	0.078(2)
C13	0.8198(6)	0.4498(5)	0.3788(5)	0.062(2)
C14	0.7661(5)	0.5084(5)	0.1904(5)	0.051(1)
C15	0.6768(6)	0.4298(6)	0.2193(6)	0.068(2)
C16	0.6255(7)	0.4072(7)	0.1393(7)	0.080(2)
C17	0.6589(7)	0.4644(7)	0.0310(7)	0.074(2)
C18	0.7523(7)	0.5408(6)	-0.0005(5)	0.066(2)
C19	0.8065(6)	0.5601(5)	0.0793(5)	0.056(1)
C20	0.9403(7)	0.6921(6)	-0.0566(5)	0.065(2)
C21	1.0310(7)	0.7721(6)	-0.0598(6)	0.074(2)
C22	1.0398(6)	0.9529(6)	-0.0228(6)	0.069(2)
C23	0.5691(6)	0.7733(5)	0.1557(5)	0.060(1)
C24	0.6371(6)	0.8420(6)	0.0612(6)	0.065(2)
C25	0.5896(9)	0.8791(7)	-0.0379(6)	0.085(2)
C26	0.474(1)	0.8478(8)	-0.0434(8)	0.098(3)
C27	0.4079(9)	0.7830(8)	0.0475(9)	0.097(3)
C28	0.4552(7)	0.7444(7)	0.1486(7)	0.077(2)
C29	0.6231(7)	0.8690(6)	0.3088(5)	0.064(2)
C30	0.5052(8)	0.9299(8)	0.3413(7)	0.087(2)
C31	0.498(1)	1.041(1)	0.3598(9)	0.116(3)
C32	0.604(2)	1.0911(8)	0.3446(7)	0.113(4)
C33	0.720(1)	1.0325(8)	0.3149(7)	0.091(2)
C34	0.7289(8)	0.9212(7)	0.2962(6)	0.078(2)
C35	0.7927(6)	0.6649(5)	0.2661(5)	0.059(1)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Bond distances (Å) and angles with torsion angles (˚)

P1	C7	1.840(6)	C20	C21	1.48(1)
P1	C1	1.850(7)	N1	C14	1.420(7)
P1	C13	1.865(6)	N1	C13	1.460(7)
P2	C29	1.831(7)	N1	C35	1.475(7)
P2	C23	1.843(6)	O1	C19	1.369(7)
P2	C35	1.859(6)	O1	C20	1.422(7)
C22	C22'	1.48(1)	O2	C22	1.403(7)
			O2	C21	1.419(8)
C1-P1-C13		100.0(3)	C23-P2-C35		103.2(3)
C7-P1-C1		101.9(3)	C29-P2-C23		99.3(3)
C7-P1-C13		99.7(3)	C29-P2-C35		101.7(3)
C13-N1-C35		114.0(5)	N1-C13-P1		110.2(4)
C14-N1-C13		118.3(5)	N1-C35-P2		113.2(4)
C14-N1-C35		115.9(4)	O1-C20-C21		108.2(5)
C19-O1-C20		119.1(5)	O2-C21-C20		108.8(6)
C22-O2-C21		113.8(5)	O2-C22-C22'		108.7(7)
C13-N1-C35-P2		-81.6(5)	C29-P2-C35-N1		170.0(4)
C14-N1-C13-P1		67.3(6)	C35-N1-C13-P1		-151.2(4)
C14-N1-C35-P2		60.8(6)	N1-C14-C19-O1		2.7(8)
C21-O2-C22-C22'		179.9(7)	O1-C20-C21-O2		-67.9(7)
C23-P2-C35-N1		-87.3(4)			

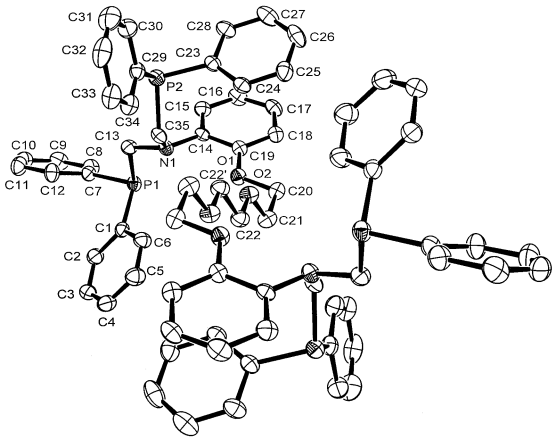

Fig. 2 Molecular structure of the title compound with atom-numbering scheme. The thermal ellipsoids are drawn at the 20% probability level.

angle is larger than C21–O2–C22 [113.8(5)˚]. On the other hand, the exocyclic angles O1–C19–C14 [116.2(5)] and N1–C14–C19 [118.8(5)˚] are unexpectedly narrowed, while the O1–C19–C18 [122.9(6)] and C15–C14–N1 [122.9(6)˚] angles are broadened.

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