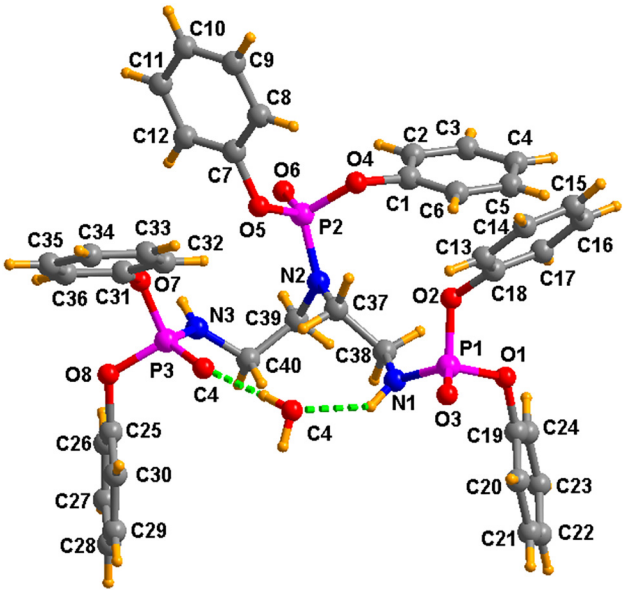
Chao-Jun Du*, Bin Cai and Dan-Xia Li

The crystal structure of diphenyl bis(2-((diphenoxyphosphoryl)amino)ethyl) phosphoramidate monohydrate $C_{40}H_{42}N_3O_{10}P_3$



https://doi.org/10.1515/ncrs-2024-0395
Received October 6, 2024; accepted November 26, 2024;
published online December 9, 2024

Abstract

$C_{40}H_{42}N_3O_{10}P_3$, monoclinic, $P2_1$ (no. 4), a = 9.1649(2) Å, b = 17.1144(3) Å, c = 13.3495(3) Å, β = 109.548(2)°, V = 1973.20(7) Å^3, Z = 2, $R_{gt}(F)$ = 0.0559, $wR_{ref}(F^2)$ = 0.1505, T = 99.99(10) K.

CCDC no.: 2405574

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Chao-Jun Du**, Academy for Mechanical Discipline Studies, Nanyang Institute of Technology, Nanyang 473000, Henan, P.R. China, E-mail: hyperchem@126.com. https://orcid.org/0000-0002-4767-7057

Bin Cai, College of Materials and Chemical Engineering, Henan University of Urban Construction, Pingdingshan, 467036, Henan, P.R. China

Dan-Xia Li, Zhang Zhongjing College of Chinese Medicine, Nanyang Institute of Technology, Nanyang 473000, Henan, P.R. China

Table 1: Data collection and handling.

Crystal:	Metallic dark colourless block
Size:	0.24 × 0.15 × 0.11 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	1.91 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy R, DW system, HyPix, ω
θ_{max}, completeness:	70.1°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18,380, 6,782, 0.066
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 6,103
$N(param)_{refined}$:	508
Programs:	CrysAlis^{PRO},[1] Olex2,[2] SHELX[3,4]

1 Source of materials

An amount of 0.25 mol of diethylenetriamine and 0.80 mol of triethylamine was added to 150 mL of dry chloroform in a 500 mL three-necked round bottom flask equipped with a constant dropping stirring, and spherical condensation reflux tube in a nitrogen atmosphere in an ice water bath. After 10 min, 0.75 mol of diphenyl chlorophosphate dissolved in 150 mL of dry chloroform was added dropwise using the constant pressure dropping funnel in 2 h. About 4 h later, the ice water bath was removed and the reaction stayed overnight at room temperature. The solvent was concentrated under reduced pressure and a white precipitate was obtained. The residue was washed with cold distilled water to remove unreacted diphenyl chlorophosphate, then was recrystallized in THF to obtain colorless block crystals with a yield of 94.8 % (based on diethylenetriamine).

2 Experimental details

The structure was solved by Direct Methods with the SHELXS-2018 program. All H-atoms from C were positioned with idealized geometry and refined isotropically (U_{iso}(H) = 1.2 U_{eq}(C)) using a riding model with C–H = 0.950 and 0.951 (benzene ring), 0.989 and 0.990 Å(methylene), and N–H = 0.880 Å, respectively. The H-atoms from O atoms were positioned with idealized geometry and refined isotropically with U_{iso}(H) = 1.5 U_{eq}(O) and O–H = 0.870 Å.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6563 (6)	0.6484 (3)	0.8625 (4)	0.0252 (11)
C2	0.7107 (7)	0.7243 (3)	0.8777 (5)	0.0280 (11)
H2	0.654635	0.765523	0.833890	0.034*
C3	0.8502 (7)	0.7388 (4)	0.9590 (5)	0.0311 (12)
H3	0.890096	0.790507	0.970451	0.037*
C4	0.9315 (7)	0.6787 (4)	1.0234 (5)	0.0342 (13)
H4	1.026213	0.689262	1.078662	0.041*
C5	0.8741 (7)	0.6036 (4)	1.0068 (5)	0.0342 (12)
H5	0.929332	0.562410	1.051163	0.041*
C6	0.7359 (6)	0.5877 (4)	0.9256 (5)	0.0286 (11)
H6	0.696850	0.535864	0.913695	0.034*
C7	0.1734 (6)	0.6514 (4)	0.6505 (4)	0.0268 (11)
C8	0.1392 (7)	0.6250 (4)	0.7378 (5)	0.0323 (12)
H8	0.198740	0.584639	0.781470	0.039*
C9	0.0161 (7)	0.6586 (4)	0.7603 (5)	0.0353 (13)
H9	−0.010502	0.640725	0.819338	0.042*
C10	−0.0679 (7)	0.7180 (4)	0.6970 (5)	0.0336 (13)
H10	−0.150911	0.741549	0.713644	0.040*
C11	−0.0324 (7)	0.7435 (4)	0.6100 (5)	0.0334 (12)
H11	−0.092168	0.783799	0.566376	0.040*
C12	0.0907 (6)	0.7104 (4)	0.5857 (5)	0.0294 (12)
H12	0.116823	0.727914	0.526316	0.035*
C13	0.6018 (7)	0.3044 (4)	0.9513 (5)	0.0321 (12)
H13	0.519386	0.284917	0.892301	0.038*
C14	0.6193 (8)	0.2809 (4)	1.0551 (5)	0.0370 (13)
H14	0.549157	0.244127	1.066949	0.044*
C15	0.7375 (8)	0.3107 (4)	1.1403 (5)	0.0384 (13)
H15	0.746624	0.295375	1.210509	0.046*
C16	0.8432 (8)	0.3630 (4)	1.1238 (5)	0.0378 (13)
H16	0.925345	0.382714	1.182633	0.045*
C17	0.8288 (7)	0.3863 (4)	1.0213 (5)	0.0318 (12)
H17	0.900672	0.421981	1.009362	0.038*
C18	0.7086 (7)	0.3570 (3)	0.9372 (4)	0.0277 (11)
C19	1.0475 (6)	0.3400 (4)	0.7683 (4)	0.0297 (11)
C20	1.0607 (7)	0.2683 (4)	0.7261 (5)	0.0344 (13)
H20	0.993689	0.226517	0.728639	0.041*
C21	1.1742 (7)	0.2581 (4)	0.6796 (5)	0.0401 (14)
H21	1.184132	0.208959	0.649457	0.048*
C22	1.2730 (8)	0.3186 (5)	0.6766 (5)	0.0446 (15)
H22	1.350217	0.311129	0.644605	0.053*
C23	1.2583 (8)	0.3892 (5)	0.7203 (6)	0.0503 (16)
H23	1.326308	0.430739	0.718834	0.060*
C24	1.1450 (8)	0.4011 (5)	0.7670 (6)	0.0431 (14)
H24	1.135031	0.450235	0.797296	0.052*
C25	0.2536 (7)	0.5354 (4)	0.1509 (5)	0.0299 (12)
C26	0.3269 (7)	0.5932 (4)	0.1149 (5)	0.0368 (13)
H26	0.322693	0.645968	0.135779	0.044*
C27	0.4075 (8)	0.5727 (4)	0.0471 (6)	0.0447 (15)
H27	0.459898	0.611901	0.021819	0.054*
C28	0.4122 (8)	0.4958 (4)	0.0163 (6)	0.0409 (14)
H28	0.466742	0.482279	−0.030516	0.049*
C29	0.3365 (8)	0.4383 (4)	0.0541 (5)	0.0383 (13)
H29	0.339823	0.385473	0.033128	0.046*
C30	0.2565 (7)	0.4578 (4)	0.1220 (5)	0.0333 (13)
H30	0.204689	0.418799	0.148141	0.040*
C31	−0.0210 (7)	0.5287 (4)	0.3718 (5)	0.0338 (13)
C32	0.0042 (8)	0.4773 (4)	0.4550 (6)	0.0397 (14)
H32	0.100362	0.476861	0.511657	0.048*
C33	−0.1127 (9)	0.4263 (4)	0.4547 (6)	0.0466 (15)
H33	−0.097308	0.390791	0.511944	0.056*
C34	−0.2495 (9)	0.4266 (4)	0.3730 (7)	0.0479 (15)
H34	−0.327884	0.390154	0.372577	0.057*
C35	−0.2758 (8)	0.4795 (5)	0.2908 (7)	0.0483 (16)
H35	−0.373103	0.480312	0.235363	0.058*
C36	−0.1597 (7)	0.5318 (4)	0.2889 (5)	0.0387 (14)
H36	−0.175688	0.568127	0.232439	0.046*
C37	0.5676 (6)	0.5159 (3)	0.6275 (5)	0.0256 (11)
H37A	0.495124	0.493097	0.561430	0.031*
H37B	0.527947	0.503461	0.686120	0.031*
C38	0.7255 (6)	0.4784 (3)	0.6507 (5)	0.0265 (11)
H38A	0.770888	0.494265	0.596190	0.032*
H38B	0.795809	0.495757	0.721030	0.032*
C39	0.6212 (6)	0.6320 (3)	0.5289 (4)	0.0256 (11)
H39A	0.732957	0.620713	0.546470	0.031*
H39B	0.608631	0.689485	0.526319	0.031*
C40	0.5357 (6)	0.5992 (4)	0.4199 (4)	0.0275 (11)
H40A	0.582467	0.620351	0.368596	0.033*
H40B	0.548377	0.541760	0.421766	0.033*
N1	0.7081 (5)	0.3930 (3)	0.6500 (4)	0.0276 (10)
H1	0.669108	0.369276	0.588270	0.033*
N2	0.5700 (5)	0.6011 (3)	0.6154 (4)	0.0240 (10)
N3	0.3698 (5)	0.6180 (3)	0.3827 (4)	0.0303 (11)
H3A	0.340373	0.666913	0.383018	0.036*
O1	0.9361 (4)	0.3549 (2)	0.8176 (3)	0.0275 (9)
O2	0.6875 (4)	0.3852 (2)	0.8345 (3)	0.0276 (9)
O3	0.7129 (5)	0.2584 (2)	0.7383 (3)	0.0300 (9)
O4	0.5121 (4)	0.6296 (2)	0.7874 (3)	0.0261 (8)
O5	0.2967 (4)	0.6159 (2)	0.6247 (3)	0.0262 (8)
O6	0.4690 (4)	0.7382 (2)	0.6478 (3)	0.0283 (9)
O7	0.0987 (5)	0.5813 (2)	0.3726 (3)	0.0309 (9)
O8	0.1639 (4)	0.5559 (3)	0.2151 (3)	0.0288 (9)
O9	0.2948 (5)	0.4719 (3)	0.3774 (3)	0.0336 (9)
P1	0.75639 (15)	0.34067 (8)	0.75578 (11)	0.0238 (3)
P2	0.46376 (15)	0.65409 (8)	0.66534 (11)	0.0234 (3)
P3	0.23987 (16)	0.55039 (8)	0.34105 (11)	0.0267 (3)
O10	0.4465 (5)	0.3407 (3)	0.4801 (3)	0.0318 (9)
H10A	0.460388	0.313930	0.428628	0.048*
H10B	0.397117	0.382368	0.449432	0.048*

3 Comment

It is well known that many crystal structures of diphenyl phosphoryl based monophosphoramidate,[5–7] some diphosphoramidate[8–12] and one tetraphosphoramidate[13] have been reported. Only, one tin(IV) complex[14] containing this type of diphosphoramidate was reported. To date, there is not any single crystal structure of triphosphoramidate published anywhere.

As shown in the figure, the asymmetrical unit is made of three diphenyl phosphoryl groups, one diethylenetriamine moiety losing three protons from different amine groups and one crystal water molecule. All nitrogen atoms are in a planar configuration. All atoms on all six phenyl groups are nearly co-planar.

The two kinds of hydrogen bonds N1–H1···O10, N3–H3···O3, O10–H10A···O9, O10–H10B···O6, are linked to generate an one-dimensional double-chain structure. A three dimensional supramolecular structure was obtained by linking the 1D double-chains through the C–H···π, van der Waals and other weak intermolecular force. All bond lengths and angles are consistent with the reported results.[5–14]

Conflict of interest: The authors declare no conflicts of interest regarding this article.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

References

1. CrysAlis^{PRO} 1.171.43.92a. Rigaku OD, Oxfordshire, England, 2023.
2. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment-Olex2 Dissected. *Acta Cryst.* **2015**, *A71*, 59–75.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
4. Sheldrick, G. Using Phases to Determine the Space Group. *Acta Cryst.* **2018**, *A74*, A353.
5. Hasija, A.; Som, S.; Chopra, D. Investigation of Crystal Structures, Energetics and Isostructurality in Halogen-Substituted Phosphoramidates. *Acta Crystallogr.* **2022**, *B78*, 179–194.
6. Das, D.; Rao, C. V. S. B.; Sivaraman, N.; Sivaramakrishna, A.; Vijayakrishna, K. Synthesis and Extraction Behavior of Alkyl and Cyclic Aminophosphonates Towards Actinides. *Inorg. Chim. Acta* **2018**, *482*, 597–604.
7. Sabbaghi, F.; Pourayoubi, M.; Necas, M.; Bartos, P. Diphenyl (Methylamido)Phosphate. *Acta Crystallogr.* **2012**, *E68*, o2934.
8. Gholivand, K.; Valmoozi, A. A. E.; Mahzouni, H. R. Structural and Electronic Aspects of Hydrogen Bonding in Two Polymorphs of Butylene-*N*,*N*′-bis(*O*,*O*′-Diarylphosphoramidate). *Acta Crystallogr*. **2013**, *B69*, 55–61.
9. Zhang, N.; Cheng, C.-M.; Wang, R.-J. Synthesis and Crystal Structure Analysis of 2-Amino-4,6-Bis(Diphenoxyl Phosphoramide)-1,3,5-Triazine. *Chin. J. Struct. Chem.* **2012**, *31*, 1042–1046.
10. Pourayoubi, M.; Zargaran, P. Tetraphenyl Piperazine-1,4-Diyldiphosphonate. *Acta Crystallogr.* **2010**, *E66*, o3273–o3274.
11. Smolobochkin, A. V.; Turmanov, R. A.; Abdullaeva, D. S.; Gazizov, A. S.; Voronina, J. K.; Appazov, N. O.; Buzyurova, D. N.; Burilov, A. R.; Pudovik, M. A. 2-(Het)aryl-*N*-phosphorylpyrrolidines via Cyclization of Phosphorus Acid Amides: A Regioselective Approach. *Chem. Sel.* **2020**, *5*, 12045–12050.
12. Alviri, B. V.; Pourayoubi, M.; Farhadipour, A.; Necas, M.; Bertolasi, V. A Combined X-Ray Crystallography and Theoretical Study of N–H···OX (X is = P and –C) Hydrogen Bonds in Two New Structures with a (C–O)2(N)P(=Y) (Y is O and S) Skeleton. *Acta Crystallogr.* **2018**, *C74*, 1610–1621.
13. Feng, C.; Cao, M. A.; Zhao, Q. Synthesis and Structural Analysis of Two Cyclam Derivatives. *J. Mol. Struct.* **2021**, *1224*, 128842.
14. Gholivand, K.; Gholami, A.; Ebrahimi, A. A. V.; Abolghasemi, S. T.; Esrafili, M. D.; Fadaei, F. T.; Schenk, K. J. Triphenyltin(iv) Adducts of Diphosphoryl Ligands: Structural, Electronic and Energy Aspects from X-ray Crystallography and Theoretical Calculations. *RSC Adv.* **2015**, *5*, 17482–17492.