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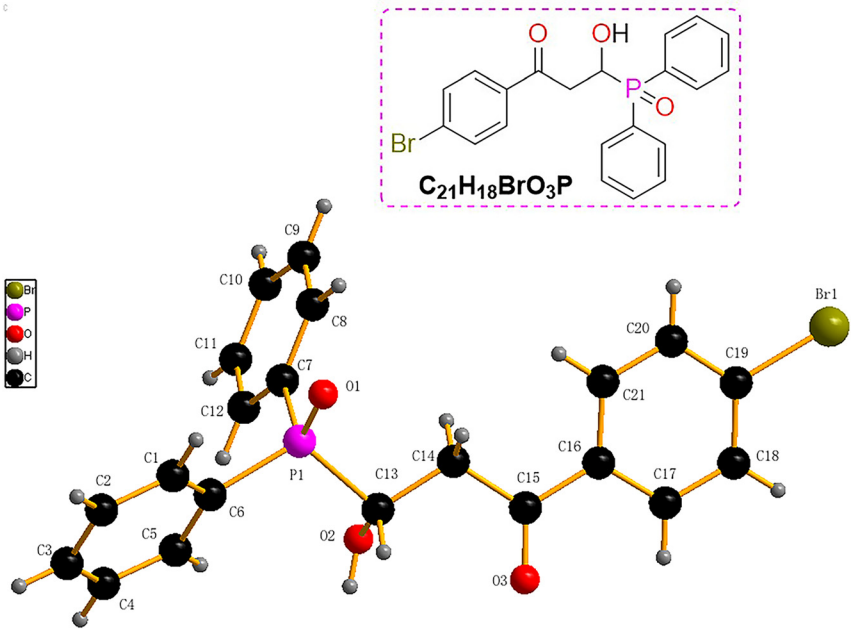
Crystal structure of 1-(4-bromophenyl)-3-(diphenylphosphoryl)-3-hydroxypropan-1-one, $C_{21}H_{18}BrO_3P$



https://doi.org/10.1515/ncrs-2024-0159
Received April 5, 2024; accepted May 12, 2024;
published online June 3, 2024

Abstract

$C_{21}H_{18}BrO_3P$, monoclinic, $P2_1/c$ (no. 14), a = 20.2890(9) Å, b = 5.9736(2) Å, c = 16.1577(8) Å, β = 105.371(2)°, V = 1888.24(14) Å^3, Z = 4, $R_{gt}(F)$ = 0.1359, w$R_{ref}(F^2)$ = 0.1414, T = 298.00 K.

CCDC no.: 2354776

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.18 × 0.17 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.28 mm^{-1}
Diffractometer, scan mode:	Bruker Smart-Apex-II, φ and ω
θ_{max}, completeness:	25.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25,463, 3310, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 2799
N(param)$_{refined}$:	236
Programs:	Olex2,[1,2] SHELX[3]

1 Source of material

3-(Diphenylphosphoryl)-3-hydroxy-1-phenylpropan-1-one was prepared by the direct difunctionalization of tertiary enaminones with H-phosphine oxide and water. Firstly, the (*E*)-1-(4-bromophenyl)-3-(dimethylamino)prop-2-en-1-one (compound A) was synthesized through the reaction between 1-(4-bromophenyl)ethan-1-one and N,N–dimethylformamide dimethyl acetal (DMF–DMA) at 363 K for overnight. In this reaction, residual DMF–DMA was

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.66013 (3)	0.64869 (13)	0.84335 (5)	0.1050 (3)
P1	0.19263 (4)	0.50494 (13)	0.83262 (5)	0.0269 (2)
O1	0.20754 (13)	0.7311 (4)	0.87214 (15)	0.0391 (6)
O2	0.25202 (15)	0.1153 (4)	0.82354 (17)	0.0462 (6)
H2	0.2424	0.0100	0.8507	0.069*
O3	0.39309 (16)	0.1252 (6)	0.9478 (2)	0.0724 (10)
C7	0.18357 (16)	0.5077 (5)	0.7182 (2)	0.0296 (7)
C6	0.11412 (16)	0.3961 (5)	0.84973 (19)	0.0287 (7)
C5	0.07667 (18)	0.5478 (6)	0.8844 (2)	0.0352 (7)
H5	0.0941	0.6903	0.8999	0.042*
C13	0.26336 (17)	0.3087 (5)	0.8756 (2)	0.0322 (7)
H13	0.2658	0.2702	0.9353	0.039*
C1	0.08802 (17)	0.1817 (6)	0.8285 (2)	0.0350 (7)
H1	0.1130	0.0773	0.8067	0.042*
C8	0.1549 (2)	0.3315 (6)	0.6641 (2)	0.0403 (8)
H8	0.1375	0.2079	0.6863	0.048*
C16	0.45737 (18)	0.3828 (6)	0.8899 (2)	0.0384 (8)
C14	0.32857 (17)	0.4248 (6)	0.8696 (2)	0.0373 (8)
H14A	0.3251	0.4563	0.8097	0.045*
H14B	0.3320	0.5671	0.8993	0.045*
C12	0.2089 (2)	0.6902 (6)	0.6836 (2)	0.0404 (8)
H12	0.2281	0.8096	0.7186	0.048*
C10	0.1771 (2)	0.5203 (7)	0.5442 (2)	0.0448 (9)
H10	0.1748	0.5249	0.4860	0.054*
C17	0.45987 (19)	0.5876 (7)	0.8498 (3)	0.0461 (9)
H17	0.4203	0.6731	0.8322	0.055*
C4	0.01363 (19)	0.4884 (7)	0.8962 (2)	0.0441 (9)
H4	−0.0111	0.5911	0.9192	0.053*
C9	0.1520 (2)	0.3387 (7)	0.5777 (2)	0.0470 (9)
H9	0.1329	0.2199	0.5423	0.056*
C2	0.02481 (19)	0.1242 (6)	0.8398 (2)	0.0441 (9)
H2A	0.0072	−0.0181	0.8245	0.053*
C21	0.51713 (19)	0.2585 (7)	0.9160 (3)	0.0483 (9)
H21	0.5165	0.1215	0.9431	0.058*
C15	0.39300 (19)	0.2946 (7)	0.9061 (2)	0.0439 (9)
C3	−0.01232 (18)	0.2771 (7)	0.8737 (3)	0.0473 (9)
H3	−0.0547	0.2373	0.8813	0.057*
C18	0.5196 (2)	0.6661 (7)	0.8357 (3)	0.0524 (10)
H18	0.5207	0.8031	0.8087	0.063*
C11	0.2055 (2)	0.6950 (7)	0.5963 (2)	0.0478 (9)
H11	0.2227	0.8178	0.5734	0.057*
C19	0.57808 (19)	0.5382 (8)	0.8624 (3)	0.0509 (10)
C20	0.5774 (2)	0.3354 (7)	0.9021 (3)	0.0557 (11)
H20	0.6171	0.2507	0.9195	0.067*

removed by reduced pressure distillation, and then the crude product A was purified by flash column chromatography on silicagel (ethyl acetate/petroleum ether = 1:4) to obtain white solid target compound A in 72 % yield. Next, the obtained (*E*)-1-(4-bromophenyl)-3-(dimethylamino) prop-2-en-1-one (A, 254 mg, 1 mmol) reacted with diphenylphosphine oxide (303 mg, 1.5 mmol) using dried aluminum muriate (266 mg, 2 mmol) in the mixed solvent of tetrahydrofuran (8 ml) and pure water (1 ml) was stirred at 323 K for 3 h. After completion of reaction, the above mixture was filtrated and washed three times by ethyl acetate. The organic liquid was evaporated under vacuum to obtain the residue. The residue was purified by flash column chromatography on silicagel (ethyl acetate/petroleum ether = 1:1) to obtain white solid B as the target compound in 92 % yield. The product B is stable in air.

2 Experimental details

Using Olex2,[1] the structure was solved with the Olex2.solve[2] structure solution program using Charge Flipping and refined with the ShelXL[3] refinement package using CGLS minimization. All hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

3 Comment

Organic phosphorous is attractive because of wide applications in organic and medicinal chemistry.[4–6] For example, various α-aminophosphine oxides can be synthesied through the substitution of the OH-group in α-hydroxylphosphorus compounds using amines.[7]

In the molecules forming the title crystal structure, the key bond lengths and angles are within normal ranges, and are consistent with those previously reported in similar structures.[8] The C–P bond is confirmed by the distance of P1–C6, P1–C7, P2–C13. Their lengths are 1.808(3) Å°, 1.809(3) Å°, and 1.841(3) Å, respectively. The bond angles for O1–P1–C6, O1–P1–C7, O1–P1–C13 are 110.33(14) Å°, 112.57(14) Å°, and 111.48(15) Å°, which is consistent with O=P–C group. Additionally, the bond angles for C7–P1–C13, C6–P1–C7, C6–P1–C13 at 104.42(15) Å°, 107.73(14) Å°, and 110.10(15) Å° were observed. Meanwhile, the hydroxyl and carbonyl groups are also found by the distance of O2–C13, O3=C15. The bond lengths are 1.412(4) Å° and 1.215(5) Å°.

Acknowledgments: This research was supported by National Key Clinical Specialties Construction Program, and the Natural Science Foundation of Guizhou Province (No. QKHJC-ZK[2022]592).

Author contributions: Yifan Liu drafted most parts of the manuscript and conducted the experiments of crystal analysis. Ronghai Cui coordinated the work. Jialing Kang and Jian Zhang co-revised the manuscript. Xin Jin cultured the crystal of

compound. Qiang Huang contributed to the analysis of results. All authors agreed to the final version of the manuscript. All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: National Key Clinical Specialties Construction Program, the Natural Science Foundation of Guizhou Province (No. QKHJC-ZK[2022]592).

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

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