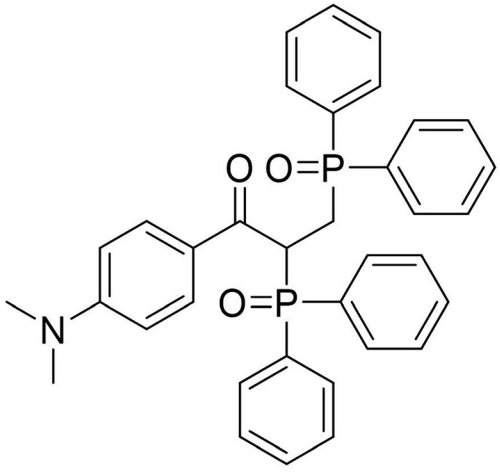
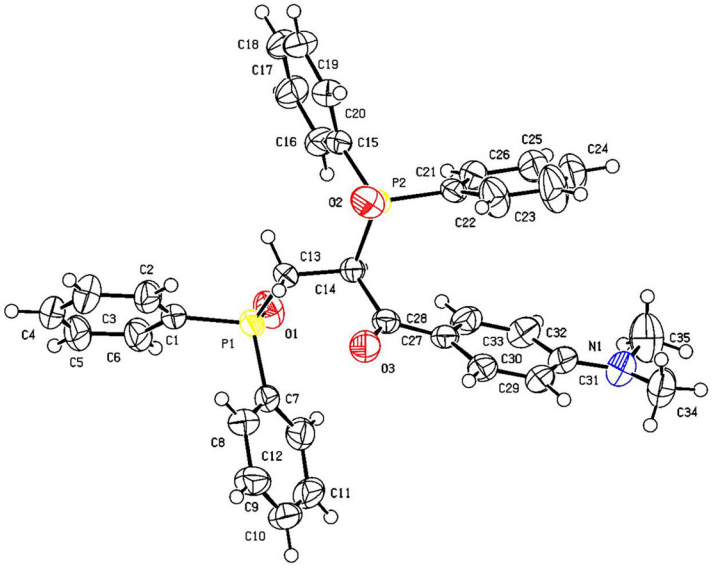
Qianlu Xing, Junhao Ao, Xin Jin and Qiang Huang*

# Crystal structure of 1-(4-(dimethylamino)phenyl)-2,3-bis(diphenylphosphoryl)propan-1-one, $C_{35}H_{33}NO_3P_2$

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**Abstract**

$C_{35}H_{33}NO_3P_2$, orthorhombic, $P2_12_12_1$ (no. 19), $a$ = 5.9926(3) Å, $b$ = 20.7065(10) Å, $c$ = 23.5675(12) Å, $V$ = 2924.4(3) Å$^3$, $Z$ = 4, $T$ = 300 K, $R_{gt}(F)$ = 0.0440, $wR_{ref}(F^2)$ = 0.1232.

**CCDC no.:** 2359284

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.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colourless block |
| Size: | 0.22 × 0.08 × 0.06 mm |
| Wavelength: | Cu *K*α radiation (1.54178 Å) |
| $\mu$: | 1.64 mm$^{-1}$ |
| Diffractometer, scan mode: | $\varphi$ and $\omega$ |
| $\theta_{max}$, completeness: | 68.5°, >99 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 24,523, 5,353, 0.131 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 4,531 |
| $N(param)_{refined}$: | 372 |
| Programs: | Olex2[1,2], SHELX[3] |

## 1 Source of material

1-(4-(dimethylamino)phenyl)-2,3-bis(diphenylphosphoryl) propan-1-one was prepared by the direct difunctionalization of tertiary enaminones with *H*-phosphine oxide. Firstly, the 1-(4-(dimethylamino)phenyl)ethan-1-one reacted with *N*,*N*–dimethylformamide dimethyl acetal at 363 K for overnight to generate (*E*)-3-(dimethylamino)-1-(4-(dimethylamino)phenyl) prop-2-en-1-one. In this reaction, residual *N*,*N*–dimethylformamide dimethyl acetal was removed under vacuum, and then the crude product A was purified by flash column

***Corresponding author: Qiang Huang**, School of Pharmacy, Zunyi Medical University, Zunyi 563000, China, E-mail: huangqiang65@sina.com
**Qianlu Xing**, Department of Pediatric, The Second Affiliated Hospital of Zunyi Medical University, Zunyi 563000, China
**Junhao Ao**, The First Clinical Institute, Zunyi Medical University, Zunyi 563000, China
**Xin Jin**, School of Pharmacy, Zunyi Medical University, Zunyi 563000, China

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

| Atom | x | y | z | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.6539 (6) | 0.31761 (16) | 0.74636 (13) | 0.0405 (7) |
| C2 | 0.8674 (7) | 0.3219 (2) | 0.76726 (16) | 0.0541 (9) |
| H2 | 0.974115 | 0.345949 | 0.747933 | 0.065* |
| C3 | 0.9243 (8) | 0.2902 (3) | 0.81739 (19) | 0.0652 (11) |
| H3 | 1.068221 | 0.293995 | 0.831796 | 0.078* |
| C4 | 0.7698 (8) | 0.2535 (2) | 0.84559 (17) | 0.0602 (10) |
| H4 | 0.809264 | 0.232149 | 0.878846 | 0.072* |
| C5 | 0.5571 (9) | 0.2482 (2) | 0.82475 (19) | 0.0660 (12) |
| H5 | 0.452222 | 0.223036 | 0.843645 | 0.079* |
| C6 | 0.4990 (7) | 0.2804 (2) | 0.77551 (18) | 0.0553 (10) |
| H6 | 0.353976 | 0.277133 | 0.761737 | 0.066* |
| C7 | 0.5902 (6) | 0.29212 (16) | 0.62920 (14) | 0.0427 (7) |
| C8 | 0.7858 (7) | 0.25651 (18) | 0.62706 (17) | 0.0528 (8) |
| H8 | 0.902495 | 0.266603 | 0.651504 | 0.063* |
| C9 | 0.8096 (9) | 0.2058 (2) | 0.5887 (2) | 0.0650 (11) |
| H9 | 0.941357 | 0.182035 | 0.587709 | 0.078* |
| C10 | 0.6386 (9) | 0.1909 (2) | 0.55248 (18) | 0.0666 (13) |
| H10 | 0.654004 | 0.157103 | 0.526837 | 0.080* |
| C11 | 0.4453 (10) | 0.2259 (2) | 0.55399 (19) | 0.0669 (12) |
| H11 | 0.329380 | 0.215528 | 0.529362 | 0.080* |
| C12 | 0.4200 (7) | 0.2771 (2) | 0.59226 (18) | 0.0547 (9) |
| H12 | 0.288431 | 0.300855 | 0.592731 | 0.066* |
| C13 | 0.7510 (6) | 0.41949 (14) | 0.66680 (14) | 0.0400 (7) |
| H13A | 0.768391 | 0.446049 | 0.700414 | 0.048* |
| H13B | 0.895560 | 0.401296 | 0.657472 | 0.048* |
| C14 | 0.6693 (6) | 0.46177 (15) | 0.61714 (13) | 0.0365 (6) |
| H14 | 0.507448 | 0.468006 | 0.619622 | 0.044* |
| C15 | 0.7308 (6) | 0.57520 (15) | 0.68955 (14) | 0.0411 (7) |
| C16 | 0.5275 (7) | 0.5654 (2) | 0.71596 (16) | 0.0533 (9) |
| H16 | 0.421816 | 0.538219 | 0.699612 | 0.064* |
| C17 | 0.4814 (8) | 0.5965 (2) | 0.76747 (17) | 0.0601 (11) |
| H17 | 0.344030 | 0.590141 | 0.785000 | 0.072* |
| C18 | 0.6356 (8) | 0.6359 (2) | 0.79217 (16) | 0.0647 (12) |
| H18 | 0.604269 | 0.655606 | 0.826707 | 0.078* |
| C19 | 0.8375 (9) | 0.6464 (2) | 0.76598 (19) | 0.0654 (12) |
| H19 | 0.941142 | 0.674089 | 0.782436 | 0.079* |
| C20 | 0.8869 (7) | 0.61591 (19) | 0.71517 (19) | 0.0542 (9) |
| H20 | 1.024746 | 0.622595 | 0.698034 | 0.065* |
| C21 | 0.7021 (6) | 0.59349 (15) | 0.56905 (14) | 0.0405 (7) |
| C22 | 0.8394 (9) | 0.6101 (3) | 0.5239 (2) | 0.0676 (12) |
| H22 | 0.983491 | 0.593545 | 0.522064 | 0.081* |
| C23 | 0.7644 (11) | 0.6510 (3) | 0.4819 (2) | 0.0882 (18) |
| H23 | 0.856963 | 0.660989 | 0.451462 | 0.106* |
| C24 | 0.5543 (10) | 0.6769 (2) | 0.4847 (2) | 0.0713 (13) |
| H24 | 0.505664 | 0.705168 | 0.456622 | 0.086* |
| C25 | 0.4161 (8) | 0.6611 (2) | 0.52870 (18) | 0.0571 (9) |
| H25 | 0.273243 | 0.678528 | 0.530353 | 0.069* |
| C26 | 0.4877 (7) | 0.61928 (19) | 0.57095 (16) | 0.0497 (9) |
| H26 | 0.392214 | 0.608454 | 0.600575 | 0.060* |
| C27 | 0.7312 (6) | 0.43180 (16) | 0.55935 (14) | 0.0402 (7) |
| C28 | 0.6032 (6) | 0.44987 (16) | 0.50851 (14) | 0.0417 (7) |
| C29 | 0.7065 (7) | 0.44192 (18) | 0.45553 (15) | 0.0481 (8) |
| H29 | 0.845247 | 0.421959 | 0.453457 | 0.058* |
| C30 | 0.6049 (7) | 0.46329 (19) | 0.40651 (15) | 0.0524 (9) |
| H30 | 0.676705 | 0.457040 | 0.371953 | 0.063* |
| C31 | 0.3979 (7) | 0.49400 (19) | 0.40719 (17) | 0.0518 (9) |
| C32 | 0.2889 (8) | 0.4980 (2) | 0.46001 (18) | 0.0563 (9) |
| H32 | 0.145291 | 0.514944 | 0.461727 | 0.068* |
| C33 | 0.3908 (7) | 0.4772 (2) | 0.50934 (16) | 0.0504 (9) |
| H33 | 0.316280 | 0.481638 | 0.543740 | 0.060* |
| C34 | 0.4384 (11) | 0.5232 (3) | 0.3074 (2) | 0.0805 (15) |
| H34A | 0.566812 | 0.549556 | 0.315060 | 0.121* |
| H34B | 0.351728 | 0.542698 | 0.277678 | 0.121* |
| H34C | 0.485952 | 0.481022 | 0.295663 | 0.121* |
| C35 | 0.1161 (11) | 0.5618 (4) | 0.3619 (3) | 0.100 (2) |
| H35A | 0.000094 | 0.542415 | 0.384315 | 0.150* |
| H35B | 0.060594 | 0.570595 | 0.324523 | 0.150* |
| H35C | 0.163145 | 0.601358 | 0.379425 | 0.150* |
| N1 | 0.3037 (8) | 0.5179 (2) | 0.35826 (16) | 0.0672 (10) |
| O1 | 0.3194 (5) | 0.37708 (15) | 0.68649 (14) | 0.0613 (7) |
| O2 | 1.0626 (5) | 0.53455 (13) | 0.61782 (13) | 0.0540 (6) |
| O3 | 0.8929 (6) | 0.39639 (15) | 0.55652 (12) | 0.0603 (8) |
| P1 | 0.55567 (15) | 0.35463 (4) | 0.68158 (3) | 0.0391 (2) |
| P2 | 0.81379 (15) | 0.54031 (4) | 0.62261 (4) | 0.0382 (2) |

chromatography on silicagel to obtain yellow solid target compound in 65 % yield. Next, the obtained (*E*)-3-(dimethylamino)-1-(4-(dimethylamino)phenyl)prop-2-en-1-one (218 mg, 1 mmol) reacted with diphenylphosphine oxide (505 mg, 2.5 mmol) in the chlorine hydride tetrahydrofuran solution (8 mL, 0.5 mol/L) at 323 K for 12 h. After completion of reaction, the mixture was quenched by 30 mL water, and extracted three times by ethyl acetate. After the organic phase was dried by anhydrous sodium sulfate, the solvent was evaporated under vacuum to obtain the crude product. The residue was further purified by flash column chromatography on silicagel (dichloromethane/methanol = 50:1) to obtain white product as the target compound in 89 % yield.

## 2 Experimental details

Single crystals of 1-(4-(dimethylamino)phenyl)-2,3-bis(diphenylphosphoryl)propan-1-one were cultured in a mixed solvent of dichloromethane and petroleum ether for 15 days. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using least squares minimisation. All hydrogen atoms bound to carbon, phosphine, and bromide atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

## 3 Comment

The synthetic research toward organic phosphorous and their derivatives is attractive due to their wide applications in organic catalysis,[4] medicinal chemistry,[5] and materials science.[6] In this context, vicinal diphosphorylation of enaminones with *H*-phosphine oxides was developed in an acid medium. The prepared compound is air stable, and it can be further converted into (3-(4-(dimethylamino)phenyl)-3-hydroxypropane-1,2-diyl)bis(diphenylphosphine oxide) using sodium borohydride.

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.[7,8] The C–P bonds are confirmed by the distance of P1–C1, P1–C7, P1–C13, P2–C14, P2–C15, P2–C21. Their lengths are 1.807(3) Å, 1.801(4) Å, 1.815(3) Å, 1.847(3) Å, 1.805(3) Å, and 1.804(4) Å respectively. Addtionally, the lengths of P1–O1 and P2–O2 are 1.495(3) Å and 1.500(3) Å. The bond angle of C27–C14–P2 measures 107.6(2)°, which is almost identical to the bond angle of C13–C14–P2. Here, the bond angle of C14–C13–P1 measures 111.2(2)°, which is slightly larger than the bond angle of C13–C14–P2. The bond angles at 112.67(19)°, 113.31(16)°, 112.04(18) Å are consistent with the O=P–C group bearing O1–P1–C7, O1–P1–C13, and O1–P1–C1 bonds. Meanwhile, the amino and carbonyl groups are also found by the distance of N1–C31, O3=C27 at 1.376(5) Å and 1.217(5) Å, respectively.

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

**Author contribution:** Qianlu Xing and Junhao Ao drafted most parts of the manuscript and conducted the experiments of crystal analysis. 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.

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