Synthesis, Spectroscopic Study and Crystal Structure of a New Amidophosphonate, $(C_6H_5O)_2P(O)(NHCH(CH_3)(C_2H_5))$

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The crystal structure of diphenyl (2-butylamido) phosphonate has been determined. This crystal belongs to the space group $P2_1/c$, and the asymmetric unit of the structure is composed of one complete molecule. The P atom has a distorted tetrahedral configuration with the O–P–O angle as the minimum bond angle at the P atom (97.74(18)°) and one of the O=P–O angles as the maximum angle (115.2(2)°). The oxygen atom of the P–O–C_6H_5 moiety may be ascribed with the sp^2 character, reflected in the P–O–C angles (120.8(3)° and 125.4(3)°). In the crystal structure, the molecules are aggregated through the N–H···O=P hydrogen bond (N1···O1 = 2.971(5)Å) in a one-dimensional chain along the *b* axis.

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Phosphorus-containing compounds play a vital role in different domains of chemistry,[1] because of their applications in medicine and pharmacology,[2,3] coordination chemistry[4,5] and biochemistry.[6] Recently, crystal structures of some phosphoramides have been reported.[7,8]

Here, we report on the synthesis and single-crystal X-ray determination of diphenyl (2-butylamido) phosphonate (I), with the chemical structure as shown in Fig. 1. For the synthesis of (I), a solution of 2-butylamine (0.37 g, 5 mmol) in dry acetonitrile (10 ml) was added to a solution of diphenyl phosphoryl chloride (0.67 g, 2.5 mmol) in the same solvent (20 ml) at 273 K. After stirring for 3 h, the solvent was removed *in vacuo* and the solid obtained was washed with distilled water. Single crystals of (I) were obtained from a solution of the product in methanol–heptane (4:1 v/v) after slow evaporation at room temperature. IR (KBr, cm^{-1}): 3242, 2972, 2928, 1742, 1592, 1490, 1375, 1250, 1203, 1151, 1071, 1025, 930, 767, 688. MS (70 eV): 305 (12) $[M]^+$, 304 (35) $[M–1]^+$, 289 (32) $[M–CH_4]^+$, 275 (100) $[M–C_2H_6]^+$, 182 (15) $[M–C_2H_6–C_6H_5O]^+$, 95 (44) $[C_6H_7O]^+$, 30 (90) $[C_2H_6]^+$. $^{31}P\{^1H\}$-NMR (DMSO-d_6, 121.78 MHz, δ_{ppm}): 0.05 (s). ^{1}H-NMR: (DMSO-d_6, 300.85 MHz, δ_{ppm}): 0.76 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3), 1.01 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 1.34 (m, 2H, CH_2), 3.14 (m, 1H, CH), 5.70 (m, 1H, NH), 7.22 (m, 6H, Ar-H), 7.40 (m, 4H, Ar-H). ^{13}C-NMR (DMSO-d_6, 75.66 MHz, δ_{ppm}): 10.77 (s), 22.73 (d, $^3J_{PC}$ = 4.5 Hz), 31.24 (d, $^3J_{PC}$ = 6.8 Hz), 49.68 (s), 120.56 (d, $^3J_{PC}$ = 5.3 Hz), 120.58 (d, $^3J_{PC}$ = 4.5 Hz), 125.05 (s), 130.15 (s), 151.32 (d, $^2J_{PC}$ = 6.1 Hz), 151.34 (d, $^2J_{PC}$ = 6.8 Hz). The ^{13}C NMR spectrum is discussed in Supporting Information.

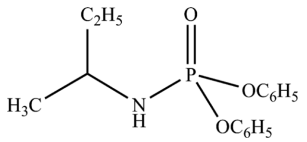

Fig. 1 Chemical structure of the title amidophosphonate.

The crystallographic data and details of the X-ray analysis are presented in Table 1. Selected bond lengths and angles are given in Table 2. The asymmetric unit of structure (I) contains one complete molecule (Fig. 2). The P=O bond length (1.465(3)Å) is slightly longer than the P=O double bond length (1.45 Å)[1] and the P–N bond length (1.595(4)Å) is shorter than the standard P–N single bond length (1.77 Å).[1] The phosphorus

Table 1 Crystal and experimental data

Empirical formula: $C_{16}H_{20}NO_3P$	
Formula weight = 305.30	
Temperature = 100(2)K	
Crystal system: Monoclinic	Space group: $P2_1/c$
a = 13.277(2)Å	α = 90°
b = 5.2887(7)Å	β = 99.542(6)°
c = 21.962(5)Å	γ = 90°
V = 1520.8(5)Å^3	Z = 4
D_x = 1.333 g/cm^3	
Radiation: Mo K_α (λ = 0.71073 Å)	
μ(Mo K_α) = 0.190 mm^{-1}	F(0 0 0) = 648
Crystal size = 0.1 × 0.08 × 0.08 mm^3	
No. of reflections collected = 2661	
No. of independent reflections = 2661	
θ range for data collection: 2.233 to 25.045°	
Data/restraints/parameters = 2661/15/193	
Goodness-of-fit on F^2 = 1.074	
R indices $I > 2\sigma(I)$: R_1 = 0.0725, wR_2 = 0.1485	
R indices (all data): R_1 = 0.1093, wR_2 = 0.1651	
$(\Delta/\sigma)_{max}$ < 0.001	
$(\Delta\rho)_{max}$ = 1.240 eÅ^{-3}	$(\Delta\rho)_{min}$ = –0.577 eÅ^{-3}
Measurement: Bruker D8 Venture	
Program system: SHELXTL	
Structure determination: SHELXS[9]	
CCDC deposition number: 1485675	

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Table 2 Selected bond lengths [Å] and angles [°]

P1-O2	1.596(3)	O2-C5	1.397(6)
P1-O1	1.465(3)	N1-C1	1.484(6)
P1-N1	1.595(4)	O3-C11	1.406(5)
P1-O3	1.582(4)	C1-C2	1.651(8)
O1-P1-O2	115.2(2)	C1-N1-P1	127.8(3)
O1-P1-N1	115.0(2)	C11-O3-P1	125.4(3)
O1-P1-O3	114.6(2)	C10-C5-O2	119.1(4)
N1-P1-O2	106.7(2)	C6-C5-O2	119.1(4)
O3-P1-O2	97.74(18)	C16-C11-O3	122.6(4)
O3-P1-N1	105.8(2)	N1-C1-C2	107.4(5)
C5-O2-P1	120.8(3)	C3-C1-N1	112.4(5)

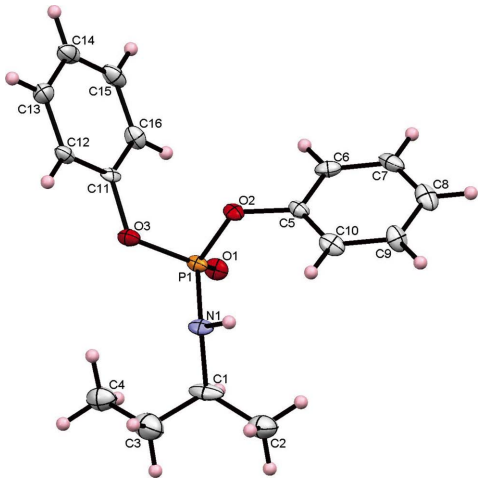

Fig. 2 Displacement ellipsoid plot (50% probability level) and the atom numbering scheme. H atoms are drawn as spheres of arbitrary radii.

atom has a distorted tetrahedral configuration. The bond angles around the phosphorus atom are in the range of 97.74(18)° (∠O3-P1-O2) to 115.2(2)° (∠O1-P1-O2). The oxygen atom of the P-O-C_6H_5 moiety may be ascribed with the sp^2 character, which is reflected to the C-O-P bond angles close to the sp^2 value of 120° (∠C5-O2-P1: 120.8(3)° and ∠C11-O3-P1: 125.4(3)°). The P-O bond lengths of the C-O-P fragments (1.582(4)Å and 1.596(3)Å) are shorter than the standard value well-known for the P-O single bond (1.64 Å).[1] The dihedral angle between two phenyl rings is 54.20°.

The C1-N1-P1 angle of 127.8(3)° is similar to the values reported for analogous structures with the $(O)_2P(O)(NHC)$ skeleton.[8] The NH group adopts a *gauche* orientation relative to the phosphoryl group (dihedral angle between H1N1P1 plane and O1P1N1 plane is 63.80°). The molecules are aggregated through the N1-H1···O1-P1 hydrogen bond (with *d*(N1···O1) = 2.971(5)Å) in a one-dimensional chain along the *b* axis. The unit-cell packing is shown in Fig. 3 and hydrogen bonding data of the structure are presented in Table 3.

Acknowledgements

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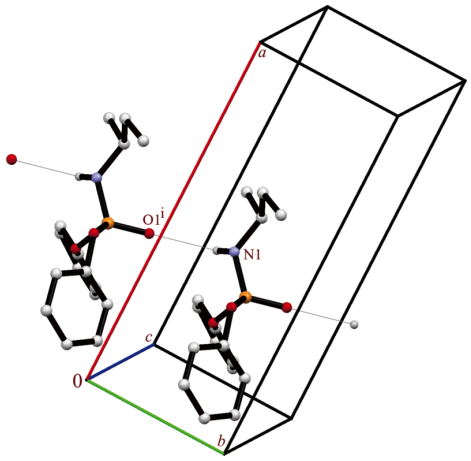

Fig. 3 Partial view of the crystal packing of (I), showing the linear arrangement built from the N-H···O=P hydrogen bonds (symmetry operation (i) *x*, *y*–1, *z*). The hydrogen bonds are shown as dotted lines. Only the H atoms involved in hydrogen bonding are shown.

Table 3 Hydrogen-bonding geometry (e.s.d. is given in parentheses)

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (°)
N1-H1···O1^{i}	0.88	2.37	2.971(5)	126.2

Symmetry operation (i) *x*, *y*–1, *z*.

Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

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