

CRYSTAL STRUCTURE OF *N*-(NAPHTHALENE-1-YL)-*P,P*-DIPHENYLPHOSPHINOTHIOIC AMIDE

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Abstract

Refluxing of the $C_{10}H_7-1-HNPPh_2$ with elemental sulfur in toluene (1:1 molar ratio) afforded $C_{10}H_7-1-HNP(S)Ph_2$ (**1**). The crystal structure of **1** has been characterized by single X-ray diffraction method. **1** crystallized in the triclinic space group $P-1$, $a = 9.986(5) \text{ \AA}$, $b = 10.306(5) \text{ \AA}$, $c = 10.837(5) \text{ \AA}$, $\alpha = 66.350(5)^\circ$, $\beta = 72.961(5)^\circ$, $\gamma = 67.828(5)^\circ$, $Z = 2$. The structure was solved by direct methods, and refined by full-matrix least squares techniques to an R factor of 0.015 for 3538 observed reflections. In the crystal the P-atom showed a distorted tetrahedral environment.

Keywords: Aminophosphine; molecular structure; sulfur; phosphorus

Introduction

As a continuation of our interest on the synthesis and solid-state structures of phosphorus(III) ligands containing direct P–N bonds (Al-Masri, 2012; Al-Masri, 2013), as these are interesting starting materials for the preparation of transition metal–phosphorus complexes or in the field of medicinal chemistry and catalytic chemistry (Gopalakrishnan, 2009; Fei, 2005; Kafarski, 1984), thereof, we herein report the crystal structure of *N*-(naphthalene-1-yl)-*P,P*-diphenylphosphinothioic amide (**1**).

2. Materials and Methods:

All experiments were carried out under purified dry nitrogen using standard Schlenk and vacuum line techniques. Solvents were dried and freshly distilled under nitrogen (Perrin, 1988). $C_{10}H_7-1-HNPPh_2$ were prepared according to the method described previously by our group (Al-Masri, 2012). Crystallographic data are given in *Table 1*. Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area

detector. Data were collected at 150 K using mirror monochromated $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro). Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro. The structure was subsequently solved using direct methods, and refined on F2 using the SHELXL 97-2 package (Sheldrick, 1997). All non-hydrogen atoms were refined with anisotropic displacement parameters. All H-atoms bonded to carbon atoms were placed in geometrically optimized positions and refined with an isotropic displacement parameter relative to the attached atoms. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-982212 for **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Table 1: Crystal data and structure refinement for **1**.

Formula	$\text{C}_{22}\text{H}_{18}\text{NPS}$	Z	2
M_r	359.40	ρ_{calcd} [Mg m^{-3}]	1.280
Temp [K]	150(2)	$F(000)$	376
Crystal system	Triclinic	Abs coeff [mm^{-1}]	2.361
Space group	$P-1$	No. of rflns coll.	5835
a [\AA]	9.986(5)	No. of indep rflns	3538
b [\AA]	10.306(5)	R_{int}	0.015
c [\AA]	10.837(5)	No. of params	226
α [$^\circ$]	66.350(5)	$R1$ ($I > 2\sigma(I)$)	0.0436
β [$^\circ$]	72.961(5)	wR2 (all data)	0.1345
γ [$^\circ$]	67.828(5)	$(\Delta/\rho)_{\text{max}}$ [$\text{e.}\text{\AA}^{-3}$]	0.468
V [\AA^3]	932.8(8)	$(\Delta/\rho)_{\text{min}}$ [$\text{e.}\text{\AA}^{-3}$]	-0.364

3. Results and Discussion:

Colorless crystals of **1** were obtained from toluene at 4 °C. Compound **1** crystallizes in the triclinic space group $P-1$. Selected interatomic distances and angles are collected in Table 2. The molecular structure is depicted in Figure 1.

Table 2: Selected bond lengths (\AA) and bond angles (deg.) for **1**

P1–N1	1.6671(17)	\sum angles at N1	360.03
P1–S1	1.9524(11)	C11–P1–C17	104.84(8)
C1–N1	1.419(2)	N1–P1–C11	101.13(8)
P1–C11	1.811(2)	N1–P1–C17	104.84(8)

P1–C17	1.8152(19)	N1–P1–S1	117.52(6)
C1–C2	1.374(3)	S1–P1–C11	113.46(7)
N1–H1	0.8800	S1–P1–C17	111.76(7)
P1–N1–C1	126.23(13)	N1–C1–C10–C9	-0.70(3)
C1–N1–H1	116.90	H1–N1–C1–C10	-3.50(3)
P1–N1–H1	116.90	P1–N1–C1–C10	-176.50(13)

The C-naphthyl skeleton in **1** is almost planar, and the nitrogen atom resides almost in the C-naphthyl plane [$\text{N1-C1-C10-C9} - 0.70(3)^\circ$]. The direction of the P–N bond is virtually perpendicular to the C-naphthyl plane and in the antiperiplanar sector [$\text{P1-N1-C1-C10} - 176.51(13)^\circ$]. On the other hand, the direction of the N–H bond is virtually planar to the C-naphthyl plane and in the synperiplanar sector [$\text{H-N1-C1-C10} - 3.50(3)^\circ$] so that the lone pair at N would be estimated to reside approximately at the borderline between the synclinal and the anticlinal sectors so that Coulomb repulsion of the lone pair is minimized.

The joint effects of Coulomb repulsion and the steric requirements would permit to describe the environment of the phosphorus atom in **1** as a distorted tetrahedral. The smallest value belongs to the N–P– C_{ph} angle and the largest value to the N–P–S angle (*Table 2*).

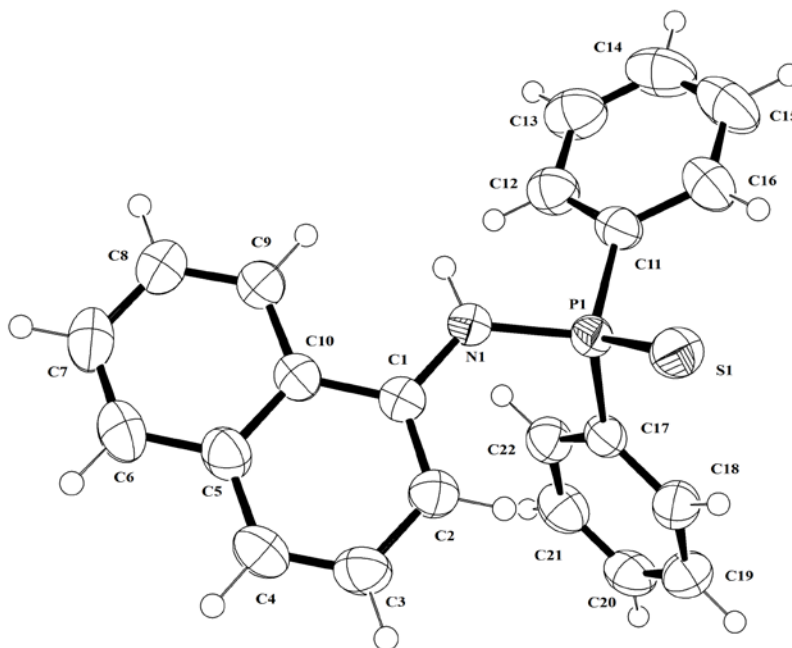


Figure 1: An *ORTEP* view of **1**, showing 50% probability displacement ellipsoids and arbitrary spheres for the hydrogen atoms.

The P=S bond length in **1** [1.9524(11) Å] being longer than those observed for the P=S bond length in 1,2-C₂H₄-{NHPh₂(S)}₂ [1.936(3) and 1.943(2) Å] (**2**), 1,8-C₁₀H₆-{NHPh₂P(S)}₂ [1.951(4) and 1.952(4) Å] (**3**) (Ly, 1997), and similar to those of 1,4-C₆H₄-{CH₂NHPh₂P(S)}₂ [1.9523(11) and 1.9568(11) Å] (**4**) (Salwin, 2004). and 2,6-Me₂C₆H₃-{NHPh₂P(S)} [1.9516(8) Å] (**5**) (Naktode, 2012).

The P–N bond length [1.671(17) Å] is slightly longer than those observed for **2** [1.649(5) and 1.654(5) Å], **3** [1.659(7) and 1.655(7) Å], **4** [1.654(3) and 1.661(2) Å], and **5** [1.662(2) Å]. The P–C_{ph} bond lengths [1.811(2), 1.8152 (19) Å] in **1** were within the ranges reported for those in **2–5**.

The P–N bond length is significantly shorter in this P(V) compound compared to the P(III) compounds Ph₂PNHNHpy [1.709(7) Å] (Salwin, 2003), and Ph₂PNH(C₁₀H₆)₂NHPh₂ [1.7043(19) Å] ((Ly, 1997)) which suggests antibonding π -character in the P–N linkage.

The X-ray crystal structure of **1** (*Figure 1, Table 2*) shows a trigonal-planar three-coordinate nitrogen atom (angle sum at nitrogen 360.03°).

The N–P–S bond angle [117.25(6)°] (*Table 2*) is smaller than those observed for **2** [119.1(2) and 118.3(2)°], and larger than those observed for **3** [Av. 115.9°], **4** [Av. 116.54°], and **5** [111.65(10)°].

The aromatic rings in **1** as expected have usual bond lengths and angles.

4. Conclusion

In conclusion, we have shown the crystal structure determination for *N*-(naphthalene-1-yl)-*P,P*-diphenylphosphinothioic amide (**1**). In the solid structure, the compound **1** shows a trigonal-planar three-coordinate nitrogen atom and a distorted tetrahedral environment around the phosphorus atom.

5. Acknowledgment

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References:

- H. T. Al-Masri, A. H. Emwas, Z. A. Al-Talla, M. H. Alkordi, *Phosphorus Phosphorus, Sulfur, Silicon Relat. Elem.* 187 (2012) 1082.
- H. T. Al-Masri, *Synth. React. Inorg., Met.-Org. Chem.* 43 (2013) 102.
- H. T. Al-Masri, *Z. Anorg. Allg. Chem.* 638 (2012) 1012.
- H. T. Al-Masri, B. M. Mohamed, Z. Moussa, M. H. Alkordi, *Helv. Chim. Acta* 96 (2013) 738.
- J. Gopalakrishnan, *Appl. Organomet. Chem.* 23 (2009) 291.

- Z. Fei, P. J. Dyson, *Coord. Chem. Rev.* 249 (2005) 2056.
- P. Kafarski, P. Mastalerz, *Aminophosphonates. Beitr. Wirkstoffforsch.* 21 (1984) 1.
- D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, third ed., Pergamon, New York, (1988).
- CrysAlisPro* (Version 1.171.31.7.), Agilent Technologies.
- G. M. Sheldrick, *SHELX97 (Release 97–2), Programs for Crystal Structure Analysis*, University of Göttingen, Germany, (1997).
- T. Q. Ly, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* (1997) 1611.
- A. M. Z. Salwin, J. Wheatly, J. D. Woollins, *Polyhedron* 23 (2004) 2569.
- K. Naktode, R. K. Kottalanka and T. K. Panda, *New J. Chem.* 36 (2012) 2280.
- A. M. Z. Salwin, J. Wheatly, M. V. Wheatly, J. D. Woollins, *Polyhedron* 22 (2003) 1397.