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2-(4-METHOXY-PHENYL)-1H, 3H-1, 3-DIAZA-2-PHOSPHA-PHENALENE 2-SULFIDE

KodagalaKameswara Rao[1*],Raja. R[2], Thoti Vasantha[3], Ester Antonia Herrera Caro[4],Dámaris Belen Zepeda Zamora[4], Krishna Marlen Alfaro Castro[4], Matías Ignacio Castillo Opazo[4], Rocío Carolina Gallardo Rivera[4], Musali Krishnaiah[5*]

[1]Department of Physics, Sri Venkateswara Arts College, Tirupati 517501, India; [2]Department of Physics, Thiruthangal Nadar College, Chennai-51, India; [3]Sri Venkateswara College, University of Delhi, Dhaula Kuan, South Campus, New Delhi-110021, India; [4]School of Medicine, University of Atacama, Copayapu - 485, Copiapó, Chile, [5]Department of Physics, Sri Venkateswara University, Tirupati 517502, India

[1*]Department of Physics, Sri Venkateswara Arts College, Tirupati 517501, India
[5*]Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

Abstract: In the title compound, $C_{17}H_{15}N_2OPS$, the six membered 1,3-diazaphosphinane ring adopts an envelope conformation with the phosphorus atom at the flap position, as shown in fig.2. The mean planes of the phenyl ring to which methoxy group is attached and the phosphaphenalene form a dihedral angle of 86.6(4)˚. In the crystal, the molecules are linked by weak N-H…O intermolecular hydrogen-bond interactions. In addition, weak C-H…π intermolecular interactions involving the benzene rings at positions 6 and 2 of molecule.

Index Terms: single-crystal X-ray study; phosphaphenalene; sulfide; T = 150 K; mean (C–C) = 0.003 A˚; R factor = 0.036; wR factor = 0.1056; data-to-parameter ratio = 13.9.

Introduction

Lawesson's reagent is widely used for transformation of a carbonyl functional group into a thiocarbonyl (Ozturk et al., 2007). At the same time, the reaction of Lawesson's reagent with compounds having two nucleophilic or one nucleophilic and one electrophilic center may lead to heterocyclic rings incorporating part of Lawesson's reagent. It was shown that Lawesson's reagent reacts with 1,2-naphthoquinone-1-methide precursors to give 1H-naphtho[1,2- e][1,3,2]oxathiaphosphinine 2-sulfide derivatives which are interesting as herbicides (El-Kateb& El-Rahman, 2006; ElKateb et al., 1991; Maigali et al., 2009). However, preparation of 4H-1,3,2-benzoxathiaphosphinine 2-sulfides from salicylic alcohols was not described in literature. The 2-(4-methoxyphenyl)-4H-1,3,2-benzoxathiaphosphinine 2-sulfide was prepared from Lawesson's reagent and o-hydroxybenzyl alcohol in o-xylene at reflux in 35% yield.

I. Experimental

The chemical structure of the compound is shown in **Figure 1**.The title compound was synthesized using a previously

reported procedure (Haribabu et al ., 2020, 2021 & 2022)

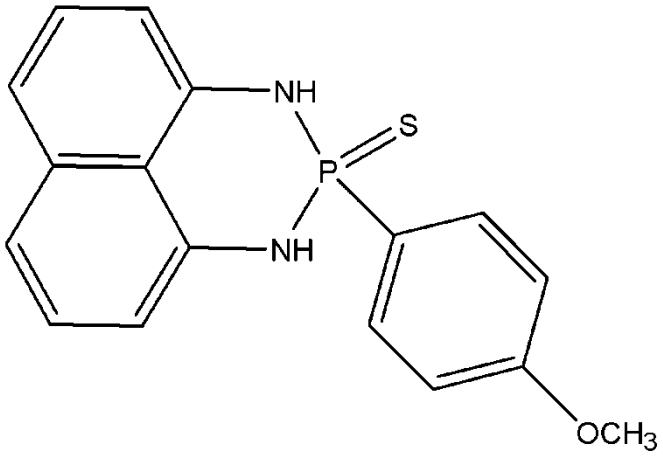

Fig.1. Chemical structure of title compound.

II. Data collection

CrysAlis PRO (Oxford Diffraction, 2010); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: OLEX2 (Dolomanov et al., 2009); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: OLEX2.

III. Refinement

C-bound H-atoms were placed in calculated positions with C–H 0.95 Å for aromatic, 0.99 Å for methylene with $U_{iso}(H) = 1.2U_{eq}(C)$ and 0.98 Å for methyl with $U_{iso}(H) = 1.5U_{eq}(C)$. All H atoms refined as riding.

IV. Structural Commentary

In continuation of our study on organophosphorus compounds, earlier the compound with O and N in the six membered rings has been reported (Babu et al., 2009). Now we are reporting the X-ray crystal analysis of the title compound having two nitrogen atoms in the six membered rings (Fig.2). The methoxy and sulfide group at the meta positions of the benzene group are close to being coplanar with the ring (5.7 (1)° and 4.2 (1)°. The planar phosphaphenalene ring makes an angle of 86.6(4)˚ with the phenyl ring having the methoxy group.The two benzene rings (C1–C6 & C8–C13) and one dimethylbenzene ring (C15– C22) [maximum deviation = 0.0185 (27) Å at atom C19A. Bond lengths (Allen et al., 1987) and angles are within normal ranges and are comparable to related structures (Fun et al., 2011a,b). The compound was synthesized as per the reported literature (Syam Prasad et al., 2008). The P=S bond length [1.9408(5) Å] is

in good agreement with reported structure of (Krishnaiah et al.,2005). Also the P-N bond lengths [1.658(1) Å and 1.656(1) Å] and P-N-C bond angles [124.9(1)˚ and 125.8(1)˚] are comparable. The six membered 1,3-diazaphosphinane ring (P2/N1/C7/C16/C15/N2) adopts envelope form with puckering parameters (Cremer and Pople, 1975) q_2 = 0.298(1)Å, θ = 55.2(3)˚, φ = 11.9(4)˚, having P at flap position.

V. Superamolecular features

In the crystal, molecules are linked by intermolecular bifurcated N-H…S hydrogen bonds (Table 3), generating $R^2_2(8)$ ring motifs and forming infinite chains along b axis (Fig.3).The neighboring molecules form hydrogen bonded dimmers with neighboring molecule via N1…S[3.463(2)Å] and N2-H2…O[3.000(2)Å], which stabilizes the crystal structure. The molecules also have intra molecular hydrogen bonds of C2-H2…S [3.339Å]. In addition, the molecules form infinite one dimensional chain of N-H…O hydrogen bond along b-axis. On the whole, a threedimensional arrangements in the crystal structure consist of neighboring dimers, held together by C—H···O, N-H…O and C—H…π interactions as well as π–π interactions [the shortest centroid-centroid distance is 3.574 (4) Å] (Fig.4).

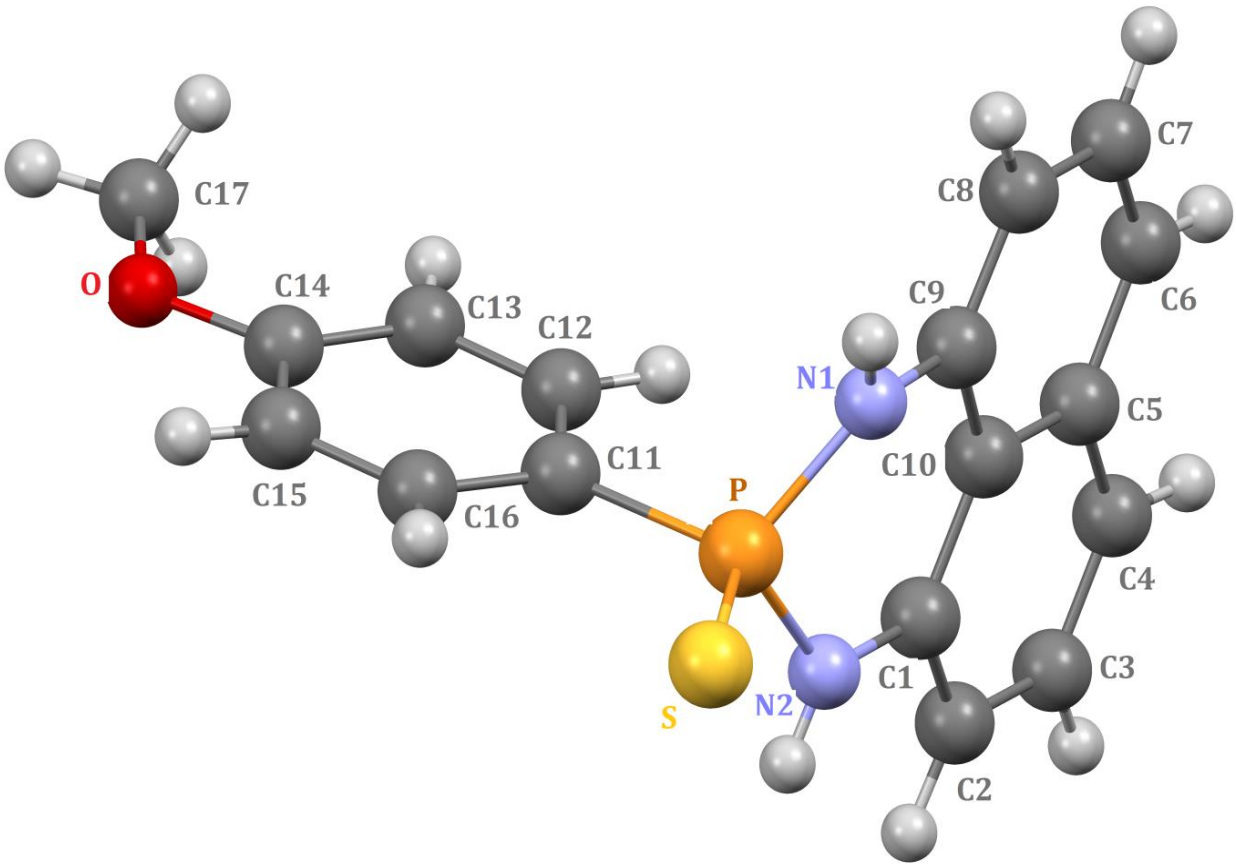

Figure: 2 ORTEP-3 (Farrugia, 1997) plot of molecular structure of the title compound showing the atom-numbering scheme. Thermal displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

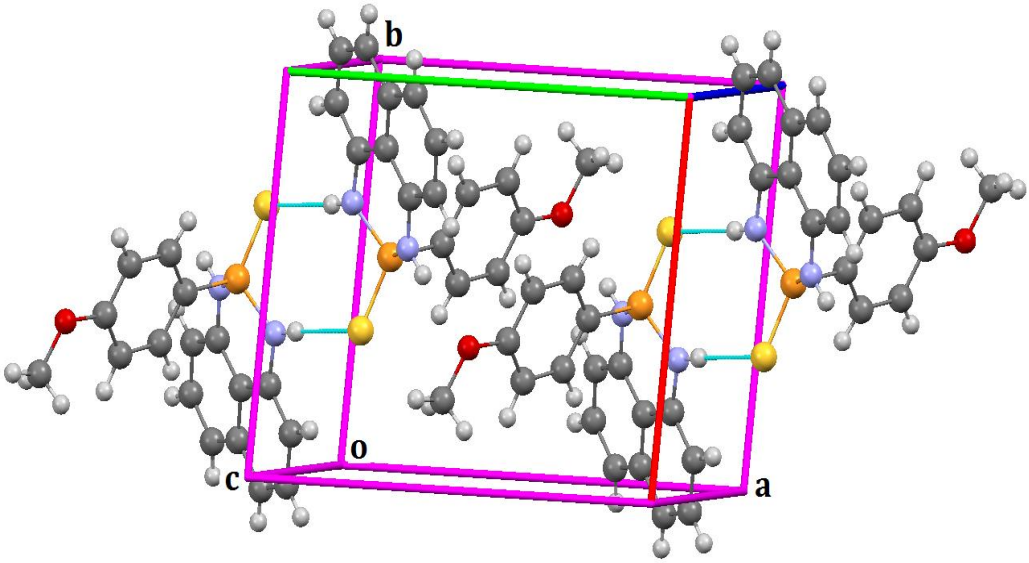

Fig.3. Title of the compound packing of the molecules dimmer enclosing *via* N-H….S Hydrogen bond, showing the $R^2_2(8)$ ring motif.

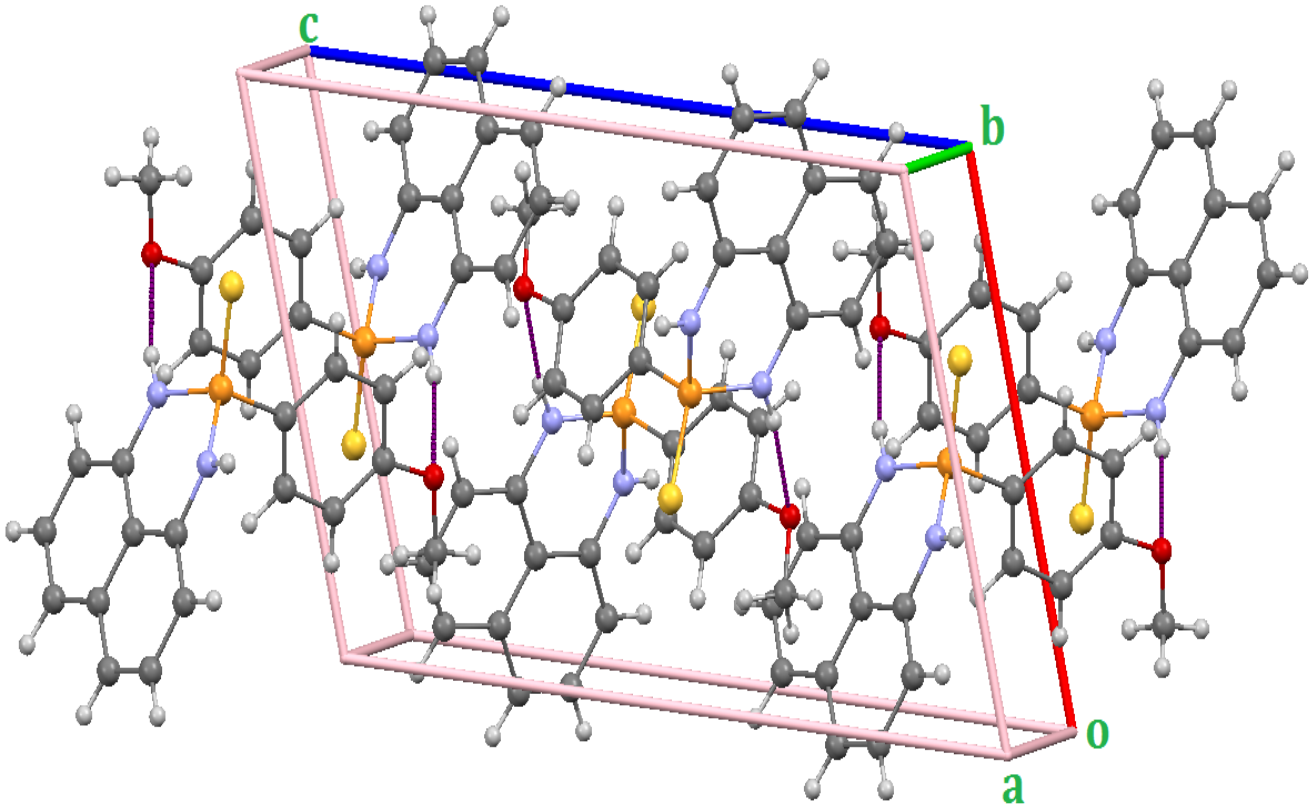

Fig.4. Title of the compound packing of the molecule in the unit cell, viewed down 'a'-axis

VI. Table 1

Selected Bond length and Bond angles (Å, °)

Atom		Length(Å)	Atom	Angles(°)
S	P	1.90407(6)	S-P-N1	114.91(5)
P	N1	1.6577(15)	N1-P-N2	99.25(6)
P	N2	1.6558(12)	C14-O-C17	118.06(15)
P	C11	1.7987(15)	N2-C1-C2	119.67(14)
O	C14	1.368(2)	C1-C2-C3	119.85(16)
O	C17	1.430(3)	C4-C5-C6	122.18(15)
N1	C9	1.397(2)	C5-C6-C7	120.50(17)
N2	C1	1.4027(19)	N1-C9-C8	120.47(14)
C1	C2	1.377(2)	C1-C10-C5	118.71(13)
C1	C10	1.420(2)	P-C11-C12	120.09(11)
C2	C3	1.402(2)	C11-C12-C13	121.60(16)

VII. Table: 2 Crystal Data and Details of the Structure Determination

Crystal data	Title of the Compound
Empirical formula	C17 H15 N2 O P S
Formula weight	326.34
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 10.0947 (6) Å α= 90°
	b = 11.1761 (7) Å β= 109.231 (1)°
	c = 14.6633 (9) Å γ= 90°
Volume	1561.99 (17) $Å^3$
Z	4
Density (calculated)	1.3877g/cc
Absorption coefficient	3.12 mm^{-1}
F(000)	680
Crystal size	0.18 x 0.24 x 0.30 mm^3
Theta range for data collection	2.1 to 28.2°.
Index ranges	-11<=h<=12, -14<=k<=13, -18<=l<=11
Reflections collected	9065
Independent reflections	3516[R(int) = 0.017]
Completeness to theta = 25.00°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9524 and 0.4826
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3516/ 0 / 248
Goodness-of-fit on F2	1.07
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.1056
R indices (all data)	R1 = 0.0869, wR2 = 0.1670
Largest diff. peak and hole	0.35 and -0.35 e.$Å^{-3}$

VIII. Table 3

Hydrogen-bond geometry for title Compound (Å, °).

D-H…A	D-H	H…A	D…A	D-H…A
N2-H2…O^{i}	0.82	2.19	3.0015	170
N1-H1…S^{ii}	0.85	2.61	3.4633	177

Symmetry Code: (i) 1-x, 1-y, -z
(ii) 1-x, -y, -z

IX. ACKNOWLEDGMENT

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X. References

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