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

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Abstract: In the title compound, \( C_{17}H_{15}N_{2}OPS \), 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; \( T = 150 \text{ K} \); mean (C–C) = 0.003 \( \text{Å} \); \( R \) 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-benzoaxathiaphosphinine 2-sulfides from salicylic alcohols was not described in literature. The 2-(4-methoxyphenyl)-4H-1,3,2-benzoaxathiaphosphinine 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).

![Chemical structure of title compound](image)

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) \( q_2 = 0.298(1) \text{Å}, \theta = 55.2(3)^\circ, \phi = 11.9(4)^\circ \), 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 \( R^2(8) \) 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$^2_{21}(8)$ ring motif.

Fig. 4. Title of the compound packing of the molecule in the unit cell, viewed down 'a'-axis.
VI. Table 1

<table>
<thead>
<tr>
<th>Atom</th>
<th>Length(Å)</th>
<th>Atom</th>
<th>Length(Å)</th>
<th>Atom</th>
<th>Length(Å)</th>
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<td>S</td>
<td>1.90407(6)</td>
<td>P-N1</td>
<td>1.6577(15)</td>
<td>S</td>
<td>1.6558(12)</td>
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<tr>
<td>P</td>
<td>1.6558(12)</td>
<td>C14</td>
<td>1.7987(15)</td>
<td>N1</td>
<td>1.430(3)</td>
</tr>
<tr>
<td>O</td>
<td>1.368(2)</td>
<td>C14</td>
<td>1.430(3)</td>
<td>N2</td>
<td>1.397(2)</td>
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<tr>
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<td>1.397(2)</td>
<td>C11</td>
<td>1.4027(19)</td>
<td>C1</td>
<td>1.377(2)</td>
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<tr>
<td>C11</td>
<td>1.377(2)</td>
<td>C1</td>
<td>1.420(2)</td>
<td>C11</td>
<td>1.7987(15)</td>
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<tr>
<td>C12</td>
<td>1.420(2)</td>
<td>C1</td>
<td>1.402(2)</td>
<td>C12</td>
<td>1.7987(15)</td>
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<tr>
<td>C12</td>
<td>1.402(2)</td>
<td>C1</td>
<td>1.420(2)</td>
<td>C12</td>
<td>1.7987(15)</td>
</tr>
</tbody>
</table>

Selected Bond length and Bond angles (Å, °)

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

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>Title of the Compound</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C17 H15 N2 O P S</td>
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<td>Temperature</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
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</tr>
<tr>
<td>Space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.0947 (6) Å, α = 90°</td>
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<tr>
<td></td>
<td>b = 11.1761 (7) Å, β = 109.231 (1)°</td>
</tr>
<tr>
<td></td>
<td>c = 14.6633 (9) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1561.99 (17) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
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<tr>
<td>Density (calculated)</td>
<td>1.3877g/cc</td>
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<td>Absorption coefficient</td>
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<td>680</td>
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<td>Crystal size</td>
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<tr>
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<tr>
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<tr>
<td>Independent reflections</td>
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<td>Completeness to theta = 25.00°</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0869, wR2 = 0.1670</td>
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<td>Largest diff. peak and hole</td>
<td>0.35 and -0.35 e.Å⁻³</td>
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VIII. Table 3

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

<table>
<thead>
<tr>
<th>D-H…A</th>
<th>D-H</th>
<th>H…A</th>
<th>D…A</th>
<th>D-H…A</th>
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</thead>
<tbody>
<tr>
<td>N2-H2…O&lt;sup&gt;i&lt;/sup&gt;</td>
<td>0.82</td>
<td>2.19</td>
<td>3.0015</td>
<td>170</td>
</tr>
<tr>
<td>N1-H1…S&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.61</td>
<td>3.4633</td>
<td>177</td>
</tr>
</tbody>
</table>

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

IX. ACKNOWLEDGMENT

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X. References