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# C–H...N hydrogen bonds mediated solid state structures of 2,2'-*bis* (4-pyridylsulfanylmethyl)-1,1'-biphenyl and 9-(4-pyridylsulfanyl)phenanthrene

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#### 1. Introduction

Design and synthesis of organic and metal-organic assemblies with exotic supramolecular architectures utilizing various noncovalent interactions, in particular, hydrogen bonds, are of current research interest due to the potential applications of these assemblies in the areas of separation technology, catalysis, pharmaceutics, etc. [1-11]. Thus, numerous reports of a myriad of supramolecular assemblies utilizing different types of organic ligands possessing varied functionalities like carboxylates, aza-donor groups etc., are well known in the recent literature [12-15]. However, development of novel supramolecular assemblies is always a challenging, especially choosing co-crystal former with required functional moieties. Since most of the assemblies are generally associated with rigid molecules [16-18], exploration of supramolecular structures through molecules substituted with functional moieties associated with topology, properties, etc., of the conformational flexibility would provide a lot of advantages for tuning the ultimate supramolecular assemblies [19-22]. For this purpose, thio-based pyridylsulfanylmethyl derivatives, with multi-armed tripodal geometry have now used as novel ligands for the evaluation in organic and metal-organic assemblies. In this regard, earlier, we reported [23] a systematic study of coordination assemblies of 1,3,5-tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene, with different mercuric halides. In continuation of our endeavors to prepare such assemblies with other pyridylsulfanyl compounds, 2,2'-bis(4-pyridylsulfanylmethyl)-1,1'-biphenyl and

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#### ABSTRACT

Solid state structure elucidation of sulfanyl ligands, 2,2'-*bis*(4-pyridylsulfanylmethyl)-1,1'-biphenyl,  $L_1$  and 9-(4-pyridylsulfanyl)phenanthrene,  $L_2$  are reported. In the structures  $L_1$  and  $L_2$ , the molecules are self-assembled through C-H...N hydrogen bonds, yielding ensembles of cyclic and helical networks. © 2009 Elsevier B.V. All rights reserved.

9-(4-pyridylsulfanyl)phenanthrene have been prepared. In this process, the native structures of these ligands are found to be not known in the literature, so we carried out structure determination of these pyridylsulfanyl ligands by single crystal X-ray diffraction methods. Herein, we report the salient features of solid state structures of 2,2'-bis(4-pyridylsulfanylmethyl)-1,1'-biphenyl and 9-(4-pyridylsulfanyl)phenanthrene, which form different types of networks in the crystal lattices (see Chart 1).

#### 2. Results and discussion

Refluxing a methanol solution of 2,2'-*bis*(bromomethyl)-1,1'biphenyl with pyridine-4-thiol (also exists as pyridinethione) [24–26] at 35 °C, obtained a product 2,2'-*bis*(4-pyridylsulfanylmethyl)-1,1'-biphenyl but the same reaction mixture refluxing at 80 °C for 48 h, however, gave ligand, 9-(4-pyridylsulfanyl)phenanthrene (Chart 2). Both the compounds upon purification, by recrystallization, gave good quality single crystals, suitable for the structure elucidation by X-ray diffraction methods.

#### 2.1. Structure of 2,2'-bis(4-pyridylsulfanylmethyl)-1,1'-biphenyl, L1

Block type single crystals of  $L_1$  obtained by diffusion of petroleum ether into ethyl acetate, at ambient conditions. X-ray diffraction analysis reveals that  $L_1$  is found to be crystallized into triclinic space group,  $P\bar{1}$ ; unit cell parameters and other pertinent crystallographic details are given in Table 1. In the crystal structure of  $L_1$ , molecules are fully ordered and the asymmetric unit is shown in Fig. 1. The two phenyl moieties of biphenyl core are twisted such that they got arranged almost perpendicular to each other. These

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2,2'-bis(4-pyridylsulfanyl-methyl)-1,1'-biphenyl (L1)



9-(4-pyridylsulfanyl)phenanthrene (L2)

Chart 1.



Chart 2.

Table 1	
Crystallographic data of ligands $L_1$ and $L_2$ .	

	L <sub>1</sub>	L <sub>2</sub>
Formula	C <sub>24</sub> H <sub>20</sub> N <sub>2</sub> S <sub>2</sub>	C <sub>19</sub> H <sub>13</sub> N <sub>1</sub> S <sub>1</sub>
Fw	400.54	287.36
Crystal shape	Blocks	Blocks
Crystal color	Colorless	Colorless
Crystal system	Triclinic	Monoclinic
Space group	ΡĪ	P21
a (Å)	9.337(5)	9.223(4)
b (Å)	9.923(5)	5.517(2)
c (Å)	12.939(6)	14.147(6)
α (deg)	110.52(1)	90
$\beta$ (deg)	94.01(1)	105.20(1)
γ (deg)	113.29(1)	90
V (Å <sup>3</sup> )	1000.5(9)	694.7(5)
Ζ	2	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.330	1.374
T (K)	298	298
Мо-Ка	0.71073	0.71073
$\mu$ (mm <sup>-1</sup> )	0.278	0.224
$2\theta$ range (deg)	46.70	46.74
F (000)	420	300
No. reflns. measured	4232	5846
No. unique reflns. [R (int)]	2844 [0.0349]	2001[0.0466]
No. reflns used	2332	1916
No. parameters	333	185
GOF on $F^2$	1.144	1.214
Flack parameter	-	0.13(14)
$R_1 \left[ I > 2\sigma(I) \right]$	0.0717	0.0506
$wR_2$	0.1595	0.1110



Fig. 1. ORTEP drawing of asymmetric unit in the crystal structure of L1.

2.2. Structure of 9-(4-pyridylsulfanyl)phenanthrene, L2

Compound  $L_2$  crystallizes in a non-centrosymmetric and chiral space group ( $P2_1$ ), unlike  $L_1$ . The salient features of the crystal structure parameters are given in Table 1. In the crystal structure of  $L_2$ , the pyridyl moiety exists like a pendant group on the phenanthrene moiety, as shown in Fig. 3. Further, in accordance with the chiral space group arrangement, the molecules in the crystal structure of  $L_2$ , self-assembled through C–H...N hydrogen bonds (H...N, 2.64 Å) into right-handed helical pattern. The hydrogen bonds are formed between pyridyl N atom and –CH group of the phenanthrene group, as shown in Fig. 4.

molecules interact with the surrounding ones through C–H. . .N hydrogen bonds (H. . .N, 2.46 Å).

However, in the structure of  $L_1$ , the hydrogen bonds are formed between pyridyl N atoms and –CH group of pyridyl moieties. Thus, cyclic networks of dimers are present in the crystal structure of  $L_1$ as shown in Fig. 2a. Such dimeric units are further held together through C–H...N bonds (H...N, 2.69 Å) using methylene hydrogen atoms and pyridyl N atoms constituting a bracelet network, as shown in Fig. 2b.



Fig. 2. (a) Dimers of molecules of L<sub>1</sub> formed through C-H...N hydrogen bonds. (b) Packing of cyclic moieties in the extended structure, within the crystal lattice L<sub>1</sub>.



Fig. 3. ORETP drawing of the asymmetric unit in the crystal structure of L<sub>2</sub>.

The structures of both  $L_1$  and  $L_2$  indeed signify the effectiveness of weak hydrogen bonds like C–H...N towards stabilizing the molecular aggregation in the solid state. Also the cyclic network observed in  $L_1$ , could be evaluated for the possible incorporation of guest species by increasing the dimensions of the empty space through co-crystallization of it with appropriate receptors.

#### 3. Conclusion

We have reported two solid structures of the pyridylsulfanyl compounds  $L_1$  and  $L_2$ , mediated by C–H...N hydrogen bonds with different topological arrangement, in the form of cyclic and helical networks.

#### 4. Experimental

#### 4.1. Synthesis of 2,2'-bis(4-pyridylsulfanylmethyl)-1,1'-biphenyl, L1

Pyridine-4-thiol (222 mg, 2 mmol) and KOH (560 mg, 10 mmol) were stirred in methanol at 0 °C. To the above mixture 2,2'-*bis*(bro-momethyl)-1,1'-biphenyl (340 mg, 1 mmol) was added slowly and stirred for about 24 h at room temperature. The mixture was poured into ice-cold water, filtered the crude product and pure product was separated by column chromatography to give pure colorless microcrystalline solid. Yield: 75%, melting point: 137–139 °C. Crystals of L<sub>1</sub>, suitable for single crystal X-ray diffraction, were obtained by diffusion of petroleum ether into a solution of ethyl acetate.

#### 4.2. Synthesis of 9-(4-pyridylsulfanyl)phenanthrene, L2

The same procedure, as that of the preparation of ligand  $L_1$ , was followed for the preparation of  $L_2$  as well except that the mixture was refluxed at 80 °C. The solution was poured into ice-cold water, filtered the crude product and separated by column chromatography to give pure colorless microcrystalline solid. Yield: 70%, melting point: 185–187 °C. Single crystals of  $L_2$  suitable for X-ray diffraction were obtained from chloroform solution after 2 days.

#### 4.3. Crystal structure determination

Good quality single crystals of  $L_1$  and  $L_2$ , grown as described above were carefully chosen with the aid of polarized optical microscope and glued to glass fiber to mount on an X-ray diffractometer goniometer equipped with CCD area detector [27]. The data collection proceeded without any complication and processed using the Bruker suite of software. The structures were determined and refined using SHLEXTL suite of programmes, and absorption



Fig. 4. (left) Hydrogen bonds between the adjacent molecules in a helix formed in the crystals of L<sub>2</sub>. (right) Representation of a typical helical arrangement.

corrections were made on all the crystals using SADABS [28]. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in the calculated positions. The structural parameters were given in Table 1. All the intra and intermolecular distances were computed using PLATON [29] software. The packing diagrams were generated by using DIAMOND version 3.1f [30].

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