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Twisted aromatics, 9-anthryl and 1-pyrenyl terpyridines organize into novel multi-directional 'ladder-like' motifs in the solid state

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Abstract

9-Anthryl and 1-pyrenyl terpyridines (1 and 2, respectively), key precursors for the design of novel fluorescent sensors have been synthesized and characterized by ¹H NMR, mass spectroscopy and X-ray crystallography. Twisted molecular conformations for each 1 and 2 were observed in their single crystal structures. Energy minimization calculations for the 1 and 2 using the semi-empirical AM1 method show that the 'twisted' conformation is intrinsic to these systems. We observe interconnected networks of edge-to-face CH··· π interactions, which appear to be cooperative in nature, in each of the crystal structures. The two twisted molecules, although having differently shaped polyaromatic hydrocarbon substituents, show similar patterns of edge-to-face CH··· π interactions.

The presently described systems comprise of two aromatic surfaces that are almost orthogonal to each other. This twisted or orthogonal nature of the molecules leads to the formation of interesting multi-directional ladder like supramolecular organizations. A combination of edge-to-face and face-to-face packing modes helps to stabilize these motifs. The ladder like architecture in **1** is helical in nature. © 2002 Published by Elsevier Science B.V.

Keywords: X-ray crystallography; Twisted conformations; Polyaromatic systems; CH $\cdots \pi$ and $\pi \cdots \pi$ interactions

1. Introduction

Stable aromatic-aromatic interactions have been classified into two basic types, motifs having either 'face-to-face' (co-facial) or 'edge-to-face' (perpen-

dicular) orientation. Edge-to-face interactions express

In the synthesis of organic solids with controllable packing in their crystalline states, 1 we have earlier

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¹ For some recent examples of development of new structural motifs from organic templates using various structure directing forces see: Refs. [15–18].

themselves, for instance, in determining the arrangement of aromatic molecules both in the gas phase [1,2] and in the solid state [3]. These interactions have biological relevance as they are thought to significantly influence the packing of aromatic side-chain residues in proteins [4]. Moreover, the inclusion of certain edge-to-face interactions in the category of weak hydrogen bonds of the type $CH \cdots \pi$ type has generated considerable recent interest [5–14].

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Table 1 The Crystal data and structure refinement for 1 and 2

Identification code	1	2		
Empirical formula	I CarHarNa	Z Car Hao Na		
Formula weight	409.47	A33 A0		
Temperature	208(2) K	208(2) K		
Wavalangth	0.71073 Å	0.71072 Å		
Crustel system	Monoalinia	0.71075 A		
Space group	$P2_1$	P = 1		
Unit cell dimensions				
$a/\text{\AA}, \alpha/^{\circ}$	6.0474(8)	9.0421(11), 78.971(2)		
$b/\text{\AA}, \beta/^{\circ}$	6.181(2), 102.443(2)	9.9857(12), 89.93		
$c/\text{\AA}, \gamma/^{\circ}$	10.940(2)Å	13.390(2), 66.857(2)		
Volume/Å ³	1045.4(2)	1087.5(2)		
Ζ	2	2		
Density (calculated)/Mg/m ³	1.301	1.324		
Absorption coefficient/mm ⁻¹	0.077	0.079		
F(000)	428	452		
θ range/°	1.91-23.29	1.55-23.28		
Limiting indices	$-6 \le h \le 6, -11 \le k \le 17, -12 \le l \le 12$	$-10 \le h \le 10, -9 \le k \le 11, -11 \le l \le 14$		
Reflections collected	4314	4551		
Independent reflections	2125 [$R(int) = 0.0722$]	3051 [R(int) = 0.0577]		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2		
Data/restraints/parameters	2123/1/289	3046/0/383		
Goodness-of-fit on F^2	1.225	1.304		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0722, wR_2 = 0.1475$	$R_1 = 0.0761, wR_2 = 0.1853$		
Absolute structure parameter	-10(10)			
Largest diff. peak and hole/e $Å^{-3}$	0.212 and -0.247	0.268 and -0.266		

exploited hydrogen bonding [19,20] or metal-toligand bonds [21]. We now turn our attention to exploit inter-aromatic stabilizing forces as elements in the structural design [22]. To this end we have chosen two systems, 4'-(9-anthryl)-2,2':6',2"-terpyridine (1) and 4'-(1-pyrenyl)-2,2':6',2"-terpyridine (2), wherein a polyaromatic moiety is directly linked to a terpyridine unit via a C-C single bond. It may be noted that 1 and 2 have a significant degree of conformational flexibility along with considerable aromatic/hetero-aromatic surfaces. Thus they offered interesting possibilities for creating new structures. It also provides an opportunity to explore the link between the shape of the molecular component and the resulting architectures. Also, in view of the increasing demand for the design of ligands and their metal complexes with luminescence properties [23,24], the structural information obtained from 1

and **2** should provide original insights to prepare new family of materials.



2. Experimental

2.1. General

The NMR spectra were recorded on a Bruker AMX 400 MHz and Bruker DRX 500 MHz NMR







Fig. 1. The ORTEP diagrams for (a) 1 and (b) 2 showing the twisted molecular conformations in each of the two cases.

spectrometers. The chemical shifts are reported in parts per million (ppm) downfield relative to standard tetra methyl silane (TMS). The Mass Spectra were recorded on a Jeol Model JMS-DX 303 spectrometer equipped with Jeol JMA-DA Mass Data Station. The mass spectra of the compounds were recorded by a direct inlet system, 70 eV. IR spectra were recorded on a JASCO FT/IR 410 spectrophotometer. 9-Anthryl aldehyde and 1-pyrenyl aldehyde were obtained from Aldrich Chemical Co., and used as received.

2.2. Synthesis

The compounds 1 and 2 were synthesised by a modification of the reported procedure adopted after Krohnke methodology in one step [23-25].

4'-(1-Pyrenyl)-2,2':6',2"-terpyridine (**2**): 1-Pyrenyl aldehyde (1.33 g, 5.8 mmol), 2-acetyl pyridine (1.38 g, 11.4 mmol), acetamide (8.15 g, 138 mmol) and ammonium acetate (6 g, 78 mmol) were taken in an R.B. flask and heated at 180 °C for three hours with stirring. Subsequently, An aqueous solution of 4.8 g

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Table 2 $CH \cdots \pi \text{ Interactions for } 1 \text{ and } 2$

Interaction	Description ^a	d ^b /Å	Dpi ^c /Å	$\alpha^{\rm d}$ /deg.
a	C14H14…ring 5	2.7	2.6	140.5
b	C20H20···ring 1	2.7	2.5	173.4
с	C21H21ring 3	2.8	2.8	145.4
d	C13H13…ring 4	3.2	2.9	135.2
e	C23H23···ring 3B	2.7	2.6	145.6
f	C15H15ring 5B	2.8	2.7	144.0
g	C19H19ring 2B	3.0	2.8	161.3

^a Ring (5), C20.C21.C22.C23.28.C29; ring (1), N1.C1.C2. C3.C4.C5; ring (3), N3.C11.C12.C13.C14.C15; ring (4), C16.C17.C18.C19.C27.C26; ring (3B), N3.C11.C12.C13.C14. C15; ring (2B), N2.C6.C7.C8.C9.C10. ring (5B), C19.C20.C.28. C31.C30.C27.

^b H…i (centroid) distance. The C–H bond lengths normalized to average neutron diffraction value of 1.083 Å.

^c H··· π perpendicular distance.

^d CH···i (centroid) angle.

of NaOH in 9.6 ml water was added to the contents of the R.B. flask and the reaction mixture was heated at 120 °C for a further 2 h without stirring. The reaction mixture was then extracted with CHCl₃ and the crude product chromatographed repeatedly over silica using Petroleum ether-Ethyl acetate. 2 was isolated $(R_{\rm f} = 0.4 \text{ in } 7\% \text{ ethyl acetate in Petroleum ether})$ and further purified by recrystallization using 2:1 CHCl₃-Ethyl acetate. The crystals obtained by this method were analytically pure and were used for X-Ray Crystallography and spectroscopic investigations. ¹H NMR (500 MHz, CDCl₃): δ 7.35-7.39, 2H, m; 7.9-7.94, 2H, m; 8.02-8.28, 9H, m; 8.68-8.7, 2H, m; and 8.74-8.78, 4H, m. LR-MS (EI): M⁺ $(C_{31}H_{19}N_3)^+$: 433; elemental analysis for $C_{31}H_{19}N_3$: calcd: C 85.91, H 4.38, N 9.69; found: C 86.08, H 4.54, N 9.68.

4'-(9-Anthryl)-2,2':6',2"-terpyridine (1): a similar procedure was used except that 9-anthryl aldehyde was used instead of 1-pyrenyl aldehyde. ¹H NMR (400 MHz, CDCl₃): δ 7.3–7.36, 4H, m; 7.44–7.48, 2H, m; 7.69–7.2, 2H, m; 7.89–7.93, 2H, m; 8.05– 8.07, 2H, m; 8.54, 1H, s; 8.6–8.62, 4H, m; and 8.77– 8.79, 2H, m. LR Mass Spectrum: M⁺ (C₂₉H₁₉N₃)⁺: 409; elemental analysis for C₂₉H₁₉N₃·0.4 H₂O: calcd: C 83.59, H 4.78, N 10.08; found: C 83.86, H 4.54, N 9.63.



Fig. 2. The interconnected C-H··· π interactions in the crystal structure of **1** are shown. See Table 2 for details. The interaction 'd' is not shown for the sake of clarity.

2.3. X-ray diffraction studies

X-ray diffraction intensities were measured at room temperature by ϖ scans using a Siemens three-circle diffractometer attached to a CCD area detector and a graphite monochromator for the Mo K α radiation (50 kV, 40 mA). Initially, the unit cell parameters and the orientation matrix of the crystal were determined using \sim 45 reflections from 25 frames collected over a small ϖ scan of 7.5°, sliced at 3.5° interval. A hemisphere of reciprocal space was then collected using the SMART software [26] with the 2θ setting of the detector at 28° . The data reduction was performed using SAINT program [26] and the orientation matrix along with the detector and the cell parameters were refined for every 40 frames on all the measured reflections. The crystal structures were solved by direct methods using the SHELXTL program [27] and refined by full matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in 2 were located by the difference Fourier synthesis and refined isotropically, and in 1 were fixed geometrically and treated as riding. The hydrogen atom positions were then normalized to the average neutron diffraction values [28].

2.4. Energy minimization calculations

GAUSSIAN94 [29] package using the AM1 Hamiltonian [30] was used to perform the semi-empirical A. Gulyani et al. / Journal of Molecular Structure 616 (2002) 103-112



Fig. 3. Orthographic depiction of the C-H··· π interaction 'a' in crystal structure of **1** with (a) showing the side view and (b) showing the top view. Also provided are distances (in Å) between the approaching H and the carbons closest to it.

calculations to optimize the molecular geometry of (1) and (2).

3. Results and discussion

Crystallization of 1 and 2 from their respective solutions in CHCl₃-EtOAc (2:1) yielded solids that could be examined by single crystal X-ray diffraction. The crystal structure data for the two compounds are given in Table 1. In monoclinic crystals of 1, there are two molecules in the unit cell in the chiral space group $P2_1$. The ORTEP diagram for **1** is shown in Fig. 1a. A noteworthy feature of this molecule is its highly twisted conformation. The angle between the anthryl ring in 1 and the plane of the central pyridyl ring of the terpyridine moiety about the inter-annular C-C bond is 74.5° (Fig. 1a). The triclinic crystals of 2 crystallize in the Centro symmetric space group P - 1 with two molecules in the unit cell. In 2, the angle between the plane of the pyrenyl ring and that of the central pyridyl ring of the terpyridine moiety is 51.6° (Fig. 1b shows the ORTEP diagram). Thus the twisted molecular conformation is a common feature in both these molecules.

Constable et al. [31] examined the crystal structure of 1-phenyl terpyridine and found that the angle between the phenyl ring and the central pyridyl ring about the interannular C–C bond to be 10.9° . Large



Fig. 4. Orthographic depiction of the $C-H\cdots\pi$ interaction 'b' in crystal structure of **1** with (a) showing the side view and (b) showing the top view. Also provided are distances (in Å) between the approaching H and the carbons closest to it.

deviation from coplanarity about the polyaromaticpyridyl interannular C–C bond observed with 1 and 2 arises largely from the tendency of either molecule to minimize the energetically demanding non-bonded contacts between the 1,8-H's of the anthryl ring in 1 or 10-H of the pyrenyl ring in 2 and those of the central pyridyl ring (3',5'-H's) respectively. There are two contacts that need to be minimized in 1 while there is one such contact in case of 2. This explains the fact that the twist angle is greater in case of 1.

Semi-empirical AM1 calculations were also performed on each of these systems to ascertain their energy-minimized 'gas phase' conformations. As in their crystal structures, the molecules 1 and 2 show twisted conformations in each case. In 1, the angle

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Fig. 5. Orthographic depiction of the C-H··· π interaction 'c' in crystal structure of **1** with (a) showing the side view and (b) showing the top view. Also provided are distances (in Å) between the approaching H and the carbons closest to it.

between the plane of the anthryl ring and the central pyridyl ring is shown to be 67.5° while in **2**, the plane of the pyrenyl ring makes an angle of 55.4° with central pyridyl ring of the terpyridine unit. Thus, the twist angles obtained in the energy minimized conformations are quite comparable to the twist angles revealed from the crystal structure determination of the individual systems. This clearly demonstrates that the presently described systems comprise of two aromatic surfaces that are almost orthogonal to each other and that the twisted conformation is intrinsic to the two molecules.

How do the twisted molecules comprising of two essentially planar components pack in the solid state



Fig. 6. The interconnected $C-H\cdots\pi$ interactions in the crystal structure of **2**. See Table 2 for details.

and determine the nature of interactions that occur? Detailed crystal structure analysis shows the presence of interesting $CH \cdots \pi$ interactions in 1 as listed in Table 2. In two of the contacts a pyridyl H approaches a ring of the anthracene π face while in the other two contacts, an anthryl H approaches a pyridyl ring (Fig. 2). The distances between aromatic H and the 'interacting' π surface observed here are all in the accepted range [5–14] for such type of contact. Two of the contacts can be considered as 'short', viz. interaction 'a', 2.64 Å and interaction 'b', 2.52 Å (Table 2).

The CH··· π interactions observed fall into a pattern of interconnected networks. In the interaction 'a' (Fig. 2), a pyridyl H approaches a π ring belonging to the anthryl moiety of **1**. The π ring that is the acceptor in the CH··· π interaction 'a' happens to be an H donor in the CH··· π interactions 'c' and 'b' (Fig. 2). A consideration of Fig. 2 and Table 2 also shows that the pyridyl ring labeled 'Ring 3' (Table 2) that acts an H donor in interactions 'a' and 'd' acts an H acceptor in the CH··· π interaction 'c'. If one assumes the 'soft' CH··· π interactions can exhibit cooperativity, then interaction 'a' should augment the interactions 'b' and 'c' (Fig. 4a and b).

It was important to ascertain the geometry of these interconnected edge-to-face interactions, and the results have been shown through orthographic depiction of the individual $CH \cdots \pi$ interactions. Fig. 3a and b show the side and top view, respectively, of the

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Fig. 7. Orthographic depiction of the C-H··· π interaction 'e' in crystal structure of **2** with (a) showing the side view and (b) showing the top view. Also provided are distances (in Å) between the approaching H and the carbons closest to it.

CH··· π interaction 'a'. The figure also shows the distance of the interacting H from the π carbons with which it makes the closest contacts. Fig. 3a and b clearly show that the H in the CH··· π interaction 'a' is close to one edge of the π face. It is positioned closest to π carbons C21 and C22, with the angle C14H14···C22 being 169.5°. In turn, C21 acts as a CH··· π donor in interaction 'c'. Also, a proximal π carbon C20 also acts as a CH··· π donor. Thus, there appears to be directionality in this interaction that suggests that these interconnected interactions are cooperative in nature. This apparent cooperativity is also in evidence in Fig. 5 that shows the side (Fig. 5a) and top (Fig. 5b) view of interaction 'c'. The



Fig. 8. Orthographic depiction of the C-H··· π interaction 'f' in crystal structure of **2** with (a) showing the side view and (b) showing the top view. Also provided are distances (in Å) between the approaching H and the carbons closest to it.

geometry of interaction is such that H21 makes close contacts with carbons C14 and C15. The angles involved in the interaction C21H21···C14, 143.6° and C21H21···C15, 169.3° again provide evidence that the contacts are directional. The π carbon C14 in turn acts as a donor in interaction 'a'. Taken together, the orthographic views of the CH··· π interactions clearly bring forth a common feature of the geometry of the interactions. These interactions are such that H makes close contacts with one or two of the ring carbons and



Fig. 9. Orthographic depiction of the C-H··· π interaction 'g' in crystal structure of **2** with (a) showing the side view and (b) showing the top view. Also provided are distances (in Å) between the approaching H and the carbons closest to it.

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Fig. 10. The ladder-like arrangements shown for 2 involving two face-to-face interacting pyrene moieties. The 'pyrene sandwich dimer' like unit forms the rung of the ladder.

is generally directed towards the edge of the π face that is involved in propagating other CH··· π interactions, suggesting cooperativity.

Multiple interconnected CH··· π interactions are also seen in the crystalline state of **2** (Table 2, Fig. 6). The two short contacts 'e' and 'f' are in the range of ~ 2.6 Å. Fig. 6 clearly shows π units involved as both as donor and acceptor in the interconnected edge-to-face interactions. The pyridyl ring that is an acceptor in the interaction 'e' is a donor in interaction 'f'. Similarly, the ring unit 'Ring 5B' (See Table 2) that is the acceptor in interaction 'f' is a donor in interaction 'g'.

The orthographic projections (top and side views) again shed light on the geometry of the interactions. Fig. 7a and b shows C23H23 making close contacts with one side of the π surface (C15 and C14) of the proximal pyridyl ring (interaction 'e'). The CH bond is directed towards C15 (The angle C23H23…C15 is 172.4°). In turn, C15H15 interacts with pyrenyl π carbons in interaction 'g' (Fig. 8a and b). Thus C15 is strongly involved as a donor and acceptor of the CH… π interaction. Fig. 8 provides further evidence in this regard. C15H15 makes close contact with C27 and is directed towards the adjacent C19 in interaction 'g' (the angle C15H15…C19 being 170.9). C19 acts



Fig. 11. Another ladder-like arrangement in the crystal structure of **2**. Here, face-to-face interacting pyridyl units constitute the rung of the ladder.

as a donor in interaction 'f' (Fig. 9 provides the orthographic depiction for interaction 'f').

Thus, a common feature of the CH··· π interactions in the two crystal structures is that interactions are directional in nature so as to exemplify the apparent cooperativity. The CH units are close to and directed towards π carbons that are involved as donors in other edge-to-face interactions. Cooperativity [10,11] in an interconnected network of CH··· π interactions has been earlier noted for acetylenic systems [11] and it is believed that if a unit behaves both as donor and acceptor in the CH··· π interaction, the net stabilization is more than the sum of the isolated interactions.

In the context of the observations regarding multiple $CH \cdots \pi$ interactions, it is noteworthy that anthracene and pyrene show different packing behavior in their crystal structures. Anthracene shows a 'herringbone-structure' while pyrene packs in the 'sandwich-herringbone' arrangement with strong co-facial interaction [3]. The molecules 1 and 2 having twisted geometries, although having differently





Fig. 12. Multi-directional ladder-like architecture for **1**. A partial overlap of two anthracene units is shown leading to a 'step-ladder arrangement'. Also illustrated is the overlap of two pyridyl rings leading to a ladder of a different directionality.

shaped polyaromatic hydrocarbon moieties, show similar patterns of edge-to-face $CH \cdots \pi$ interactions.

The crystal structures show interesting supramolecular architectures. Fig. 10a shows a ladder type arrangement in the crystal structure of 2, where each rung of the ladder happens to be a 'pyrene sandwich dimer'! The twisted molecular conformation leads to such an arrangement. Faceto-face $(\pi \cdots \pi)$ interaction between two pyrene moieties (face to face distance, ~ 3.9 Å) is the 'glue' that helps make the 'sandwich' rung while the edge-to-face $CH \cdots \pi$ interactions hold the architecture together. Interestingly, there is not just one type of ladder, but two. Fig. 11 reveals another ladder like arrangement in 2, where two pairs of pyridyl rings overlapping each other constitute the rung of the ladder (distance between the ring centroids, 3.7 Å). In each of these overlaps, a central pyridyl ring of the terpyridine unit interacts with a peripheral pyridyl ring of another terpyridine unit. Here, again it may be emphasized that the $CH \cdots \pi$ interactions hold the

architecture together. Thus, the crystal structure of 2 can be said to have a 'bi-directional twin ladder' arrangement. Geometrical considerations would necessitate the presence of bi-directional ladders if an orthogonal system comprising two essentially planar components packs itself. The periodicity of the 'ladder-like' arrangement is determined by the 'twist' angle between the two planes and the nature of interactions between the planes.

A multi-directional ladder arrangement is observed with **1** as well. However, as the shape and nature of the polyaromatic substituent differs, significant differences from **2** are indeed observed. Fig. 12 shows the 'step-ladder' arrangement where the pyridyl-pyridyl overlap (contact distance of 3.9 Å) forms the rung of the ladder. Also seen in the figure are interactions where a part of the anthracene moiety overlaps with a different part of another anthracene unit (contact distance of 3.6 Å) giving a step-ladder of a different directionality. This is unlike the 'sandwich dimer' type arrangement for overlap involving two pyrene units that is observed in **2**. The ladder like arrangement in **1** is helical in nature.

4. Concluding remarks

We have shown the crystal structures of two 'twisted' or 'orthogonal' molecular systems, 1 and 2. Semi-empirical AM1 calculations have shown the twisted molecular conformation is intrinsic to the systems. Interconnected networks of cooperative $CH \cdot \cdot \cdot \pi$ interactions exist in the crystal structures of these molecules. Simple-minded geometrical constraints can be used to rationalize the presence of ladder-like arrangements in each of the crystal structure of the two twisted molecules. Thus such orthogonal or twisted aromatic molecules may lead to the development of novel ladder like motifs with varying periodicity. A combination of edge-to-face and face-to-face interactions in each of the two cases helps stabilize the multi-directional ladder-like supramolecular [32,33] scaffolds. Efforts are now underway to utilize these orthogonal systems for the preparation of metal-mediated crystalline coordination polymers.

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