Synthesis of Biphenanthrenyls and Role of C−H···X Noncovalent Interactions in Conformational Control[‡]

Ashoke Sharon,[a] Prakas R. Maulik,[a][‡‡] Champika Vithana,[b] Yuji Ohashi,[b] and Vishnu Ji Ram*[c]

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A convenient synthesis of the 1,2′-biphenanthrenyls **4a–c,f**, 1,3′-biphenanthrenyls **4d,e**, thiabiphenanthrenyl **4g**, the benzo[*h*]chromen-2-ylideneacetonitrile **5a** and the methyl benzo[*h*]chromen-2-ylideneacetate **5b** through carbanion-induced ring transformation of 2*H*-pyran-2-ones **1** or **2** and the 1-naphthalenone **3a** or thiochroman-4-one **3b** separately is described. The structures of the biphenanthrenyls **4b** and **4c** have been confirmed by single-crystal X-ray diffraction. The conformations of **2b**, **4b**, **4c** and **6** have also been studied to establish the role of C–H···X interaction in conformational control.

Introduction

The chemistry of 2*H*-pyran-2-one for the synthesis of unsymmetrical biaryl systems through ring transformation reactions is highly fascinating and has prompted considerable interest not only because of their wide ranging applications[1−3] but also because of their ubiquitous presence in nature.[4]

Biaryls have previously been synthesized by oxidative[5] and reductive[6] coupling reactions of aromatic moieties. Recently, $MoCl_5$ has been successfully used as an oxidative coupling reagent.[7] Palladium-catalyzed cross-coupling between an electrophile C−X (X = Br, I, OTf) and an organometallic species C−M (M = Mg, Zn, Sn, B) has become quite popular for the construction of biaryls[8−9] because of its compatibility with a variety of functional groups and its tolerance of aqueous reaction conditions. In addition to numerous known cross-coupling reactions, Meyers[10] developed an efficient synthesis of unsymmetrical biaryls, through oxazoline-mediated coupling reactions.

A bi(9,10-dihydrophenanthrene) derivative, designated as flavanthrin, was isolated[11] for the first time in 1988 from the orchid *Eria flava*, but the synthesis of this ring system has only been reported recently.[5g] Here, we report an elegant innovative short synthesis of 9,10-dihydrobiphenanthrenyls **4a−f,** 9-thiabiphenanthrenyl **4g** and benzochromen derivatives **5a,b,** where opportunities exist for the synthesis of various structural isomers as a result of different linkages between two phenanthrene moieties and variation in substituents at positions 3 and 4. Experimental work has also been devoted to elucidating the weak noncovalent interaction by X-ray analysis and its implication in controlling the conformation in the solid state.

C−H···O weak interactions are important because they play a major role in controlling disparate chemical phenomena including molecular recognition, stereoselectivity,[12−14] cooperativity with the Lewis acid/Lewis base, interaction for solvation of carbonyl-based CO_2-philes,[15] supramolecular synthons,[16] enhancement of molecular dipoles[17] and crystal packing. The importance of weak hydrogen-bond interactions has long been recognized [18] as these play a significant role in stabilizing the geometry of the molecule by restricting the rotation[19] and in many cases are responsible for conformational changes in the solid state.[20] During the last few years numerous publications have appeared dealing with different aspects of C−H···O and C−H···N interactions.[21] The contribution of C−H···O interactions in aligning the molecules of 1,3,5-trinitrobenzene has been examined and reported by Desiraju et al.[22] Conformational control by weak hydrogen-bond interactions in phosphocin has also been observed by Moore and Avet.[23]

[‡] C.D.R.I. Communication No.: 6295
[a] Molecular & Structural Biology Division, Central Drug Research Institute,
Lucknow, India
[b] Department of Chemistry and Materials Science, Tokyo Institute of Technology,
Tokyo, Japan
[c] Medicinal Chemistry Division, Central Drug Research Institute,
Lucknow, India
Fax: (internat.) + 91-522-2223405
E-mail: vjiram@yahoo.com
[‡‡] For crystallographic queries.

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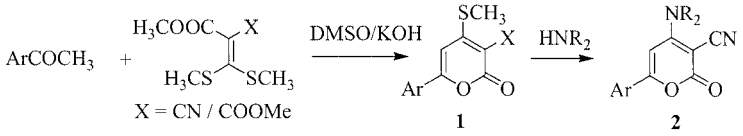
In some cases the energies of intramolecular strong hydrogen bonds amount to several kcal/mol, which is more than the typical rotational barriers and energy differences between molecular conformations. Therefore, strong intramolecular O−H···O/N hydrogen bonding is often a determinant of molecular conformation. In the case of weak hydrogen bonds the situation is very different, as intramolecular C−H···O interactions can hardly compete with conformational and other intramolecular effects. The distance and bond angle alone in C−H···X interactions cannot be the basis for conformational control. Even if such an influence exists it is very difficult to demonstrate, but there are several instances where intramolecular C−H···O/N interactions are operative.

Results and Discussion

Synthesis: This paper describes a direct approach to the synthesis of biphenanthrenyls **4a−f,** 9-thiabiphenanthrenyl **4g** and benzochromen derivatives **5a,b** through base-catalyzed ring transformation of 2*H*-pyran-2-one **2a−e** (Scheme 1) and 2-oxo-2*H*-pyran-3-carboxylate **1c** by a carbanion, generated in situ from 1-naphthalenone (**3a**) and benzothiochroman-4-one (**3b**). The topography of 2*H*-pyran-2-ones **1** and **2** revealed the presence of three electrophilic centers C-2, C-4 and C-6 the last of which is susceptible to nucleophilic attack. The difference in the electron densities of the various carbon centers has been exploited for ring-transformation reactions by different carbanions. The synthesis of biphenanthrenyls is a one-pot reaction in which an equimolar mixture of 2*H*-pyran-2-one **1** or **2** and **3** in the presence of powdered KOH in dry DMF under an inert atmosphere was stirred for 30 h, thereafter poured onto ice water and neutralized to pH 7 by 10% HCl. After purification on a silica-gel column biphenanthrenyls **4a−f**, and the 9-thiabiphenanthrenyl **4g** were obtained as major products. Only in two cases were benzochromen derivative **5a** and **5b** also isolated as a mixture of (*E*) and (*Z*) isomers in addition to **4a** and **4f** from the reaction of **2a** and **1c** with **3a**, respectively. Though the isomeric mixture of (*E*) and (*Z*) isomers could not be separated they were readily distinguished by proton NMR on the basis of NOE experiments. Signals of **5a** at δ = 4.29 ppm and δ = 6.36 ppm showed 12% NOE confirming that it was the (*Z*) isomer, while no change in the peak intensity of either of the signals at δ = 4.63 and δ = 6.83 after irradiation identified the (*E*) isomer. Similarly the (*E*) and (*Z*) isomers of **5b** were assigned by NOE. This reaction was further generalized through ring transformation of 2*H*-pyran-2-one **1c** by 1-naphthalenone (**3**) which provided the corresponding hydroxy biphenanthrenyl derivative **4f** in lieu of methyl 3-methylsulfanyl-9,10-dihydro-1,2′-biphenanthrenyl-4-carboxylate owing to nucleophilic displacement of methylsulfanyl substituents by a hydroxy group during the reaction. The ring transformation of **2c** was also carried out using thiochroman-4-one as a source of carbanion, which ultimately provided a ring-transformed product, 9-thiabiphenanthrenyl **4g** in 30% yield. Thus, this reaction opens a new avenue for the general synthesis of highly functionalized biphenanthrenyls.

The formation of two products **4** and **5** from the reaction of **1** or **2** and 1-naphthalenone (**3**) is possibly due to different reaction paths. The initial step in this reaction is possibly attack of a carbanion generated from ketone **3** by alkali at C-6 of the 2*H*-pyran-2-one. The intermediate thus formed can then follow either of the two paths A and B (Scheme 2). In the formation of product **4**, the reaction possibly proceeds through path A with attack of the carbanion intermediate on the carbonyl carbon to yield a cyclic intermediate which finally yields the desired product **4,** liberating carbon dioxide and water, while in the formation of benzo[*h*]chromen derivatives **5a,b**, the reaction possibly follows path B. In this reaction CO_2 is liberated from the carbanion intermediate in the second step, followed by cyclization involving the carbonyl oxygen and C-4 carbon of the 2*H*-pyran-2-one **1** or **2** with elimination of methyl mercaptan or a secondary amine. All the synthesized compounds were characterized by spectroscopic and elemental analyses. The structure of biphenanthrenyls **4b, 4c**, and 2*H*-pyran-2-one **2b** were confirmed by X-ray diffraction.[24]

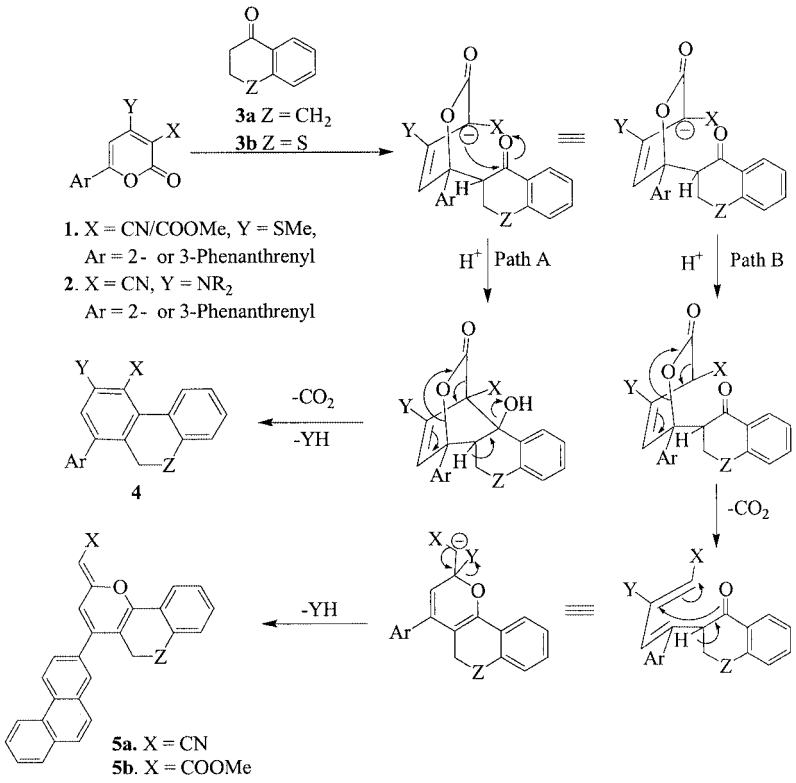
X-ray Structural Analysis: The structure of compound **4b** was confirmed by single-crystal X-ray diffraction. The structural studies of **4b** provided evidence for the existence of two rotameric conformations in the solid state. During the course of our crystallographic analysis, we faced the interesting problem of assigning the identity of the rotamers, which arise because of free rotation around the single



1	Ar	X
1a	2-Phenanthrenyl	CN
1b	3-Phenanthrenyl	CN
1c	2-Phenanthrenyl	$COOCH_3$

2	Ar	NR_2
2a	2-Phenanthrenyl	1-Pyrrolidinyl
2b	2-Phenanthrenyl	1-Piperidinyl
2c	2-Phenanthrenyl	4-Methyl-1-piperidinyl
2d	3-Phenanthrenyl	1-Pyrrolidinyl
2e	3-Phenanthrenyl	1-Piperidinyl

Scheme 1. Formation of pyran-2-one **1** or **2** by the reaction of aromatic ketone and ketene dithioacetal. While **2** from the reaction of **1** and sec. amine



4	Ar	X	Y	Z
4a	2-Phenanthrenyl	CN	1-Pyrrolidinyl	CH_2
4b	2-Phenanthrenyl	CN	1-Piperidinyl	CH_2
4c	2-Phenanthrenyl	CN	4-Methyl-1-piperidinyl	CH_2
4d	3-Phenanthrenyl	CN	1-Pyrrolidinyl	CH_2
4e	3-Phenanthrenyl	CN	1-Piperidinyl	CH_2
4f	2-Phenanthrenyl	COOMe	Hydroxy	CH_2
4g	2-Phenanthrenyl	CN	4-Methyl-1-piperidinyl	S

Scheme 2. Formation of the biphenanthrenyls **4** and **5** by the ring-transformation reaction of pyran-2-one **1** or **2**

bond between biaryl systems. There is positional disorder at two carbon atoms of the middle ring of phenanthrene and each of them can be resolved into two positions C33 into C33A and C33B; C34 into C34A and C34B with 0.5 occupancy for each atom (Figure 1). This clearly provides evidence for the coexistence of two rotamers due to rotation along the C23−C4 bond (Figure 1). The phenanthrene ring is twisted by 45.8(1)° from ring B (Scheme 3). During this study we became interested in exploring the rotameric condition and its restriction mediated through C−H···X intramolecular interactions.

The only known geometrical values may not be very helpful in predicting the intramolecular C−H···X interaction. Proper angular ranges for intramolecular C−H···X hydrogen bonds have not yet been established and the present situation is confusing. Quite a number of short intramolecular C−H···O contacts that are claimed to be hydrogen bonds in the literature do not pass muster on closer inspection and should be characterized as "forced con-

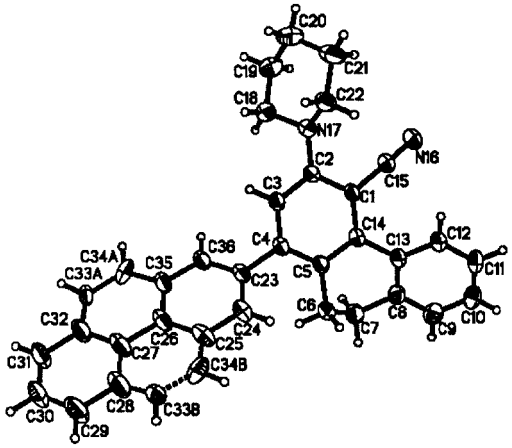
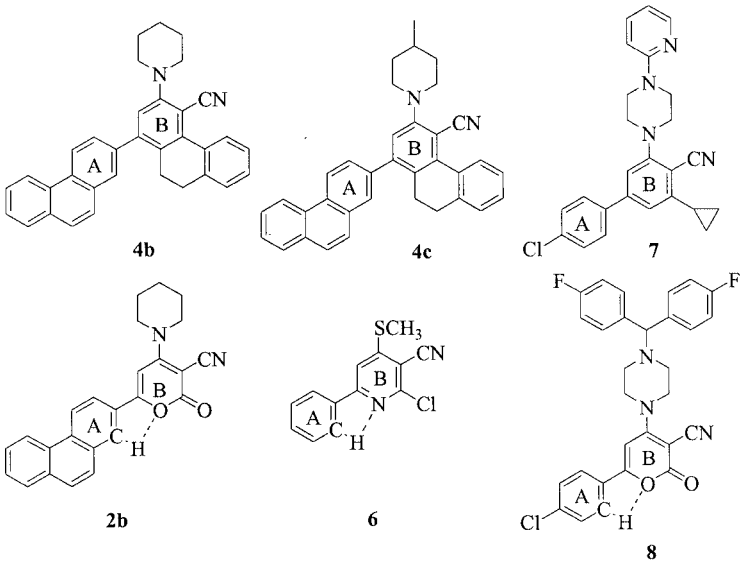


Figure 1. ORTEP diagram showing the X-ray structure of the phenanthrenyls **4b**



Scheme 3

tacts''.[21] In general, independent supporting evidence is necessary before an intramolecular C−H···O contact can be considered to be a hydrogen bond. Here we have the interesting examples of compounds **4b, 4c** and **7** (Scheme 3) which have a non-planar conformation, while **2b, 6** and **8** (Scheme 3) show a planar conformation, indicating the role of weak intramolecular hydrogen bond in conformational control.

For a better understanding of the rotameric status, we also determined the crystal structure of compound **4c** (Figure 2) by X-ray diffraction. In the case of **4c**, where a methyl group is substituted at position 4 of the piperidine ring, only one rotamer exists in the solid state as evident from crystal data. Surprisingly, the presence of this remote methyl group alters the solid-state packing pattern, which leads to a lower cavity volume around the phenanthrene ring as shown in the cavity diagram (Figure 3).[24,25] The cavity volume of molecule **4b** is 84.5 Å^3 (Figure 4), while that of **4c** is only 59.6 Å^3.[25] Thus the cavity volume around the phenanthrenyl of **4b** is enough to accommodate the disordered two rotamers, while in the case of **4c** this is not possible owing to the shape and size of the cavity. X-ray analysis of **4c** revealed the presence of a single rotamer, and the torsion angle in the biaryl (ring A & ring B, Scheme 3) is 39.6(1)° (Figure 2). These results suggest the presence of a high degree of freedom of rotation and non-planar con-

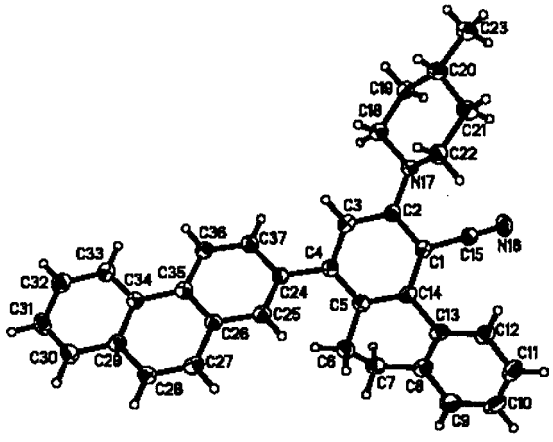


Figure 2. ORTEP diagram showing the X-ray structure of phenanthrenyls **4c**

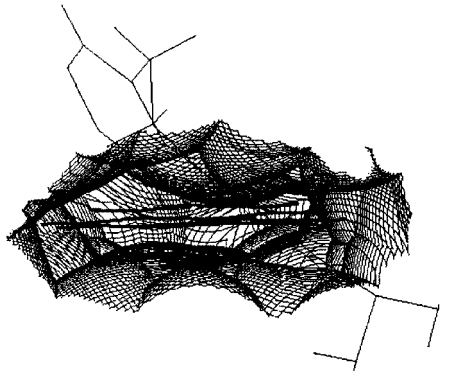


Figure 3. Cavity diagram showing volume (59.6 Å^3) around phenanthrenyl of compound **4c**

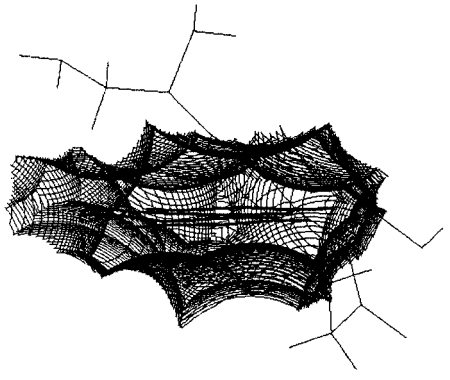


Figure 4. Cavity diagram showing volume (84.5 Å^3) around phenanthrenyl of compound **4b**

Table 1. X-ray geometrical data for C−H···X intramolecular weak hydrogen bond

	Twisting angle[a] (°)	<DHA (°)[b]	D−A (Å)[b]	H−A (Å)[b]	Conformation along ring A & B
2b	9.9 (1)	102.2	2.65	2.30	planar
6	16.5 (2) & 3.1 (1)	100.6 & 101.7	2.77 & 2.78	2.44 & 2.44	planar
8	5.8 (1)	101.4	2.708(4)	2.37	planar
4b	45.8 (1)	Absence of C−H···X (D−H···A) non-covalent interaction			non-planar
4c	39.6 (1)				non-planar
7	36.6 (1) & 38.1 (1)				non-planar

[a] Torsion angle between ring A and ring B (Scheme 3).[b] Highlighted C−H···X (D−H···A) bond (Scheme 3).

formation between biaryl systems. Recently it has been reported that aryl rotation is responsible for spectral changes and rotation affected by space interaction (Polar-π interaction).[26] In order to study the rotational barrier, we carried out X-ray analysis of compound **2b**.[24]

This molecule has two advantages: (i) the size of one of the aryl groups is as bulky as in **4b** and **4c**, (ii) the "O" atoms in the pyran ring may effectively participate in intramolecular C−H···O interactions. The structure of **2b** (Figure 5), as determined by X-ray analysis, demonstrates the presence of intramolecular C−H···O contacts, which are confirmed by its planar conformation. Simultaneously the torsion angle around the single bond is less than 10°, which indicates a rotational barrier. Another compound (**6**[27] Scheme 3) containing a phenyl-pyridine system was also studied through X-ray diffraction.[24] As we expected, C−H···N interaction is evident in this molecule. Interestingly we found 16.5° and 3.1° rotamers in one asymmetric unit. The X-ray structure (Figure 6) has shown the nearly planar conformation for rings A and B, due to the presence of the highlighted C−H···X noncovalent interactions (Scheme 3). To obtain more evidence in favour of this prediction, we reviewed our previous work, in which we have reported only the structural characterization for **7** and **8** (Scheme 3) by X-ray diffraction.[28] The X-ray structure of **7** shows (Figure 7) the presence of two rotamers (36.6° and 38.1°) in an asymmetric unit, indicating a nonplanar conformation between ring A and ring B, while compound **8** (Figure 8) shows only planar conformation and a single rotamer (5.8°) in an asymmetric unit, owing to the presence of C−H···O interactions (Scheme 3). Here, we have described the presence of a noncovalent C−H···X bond, responsible for the rotational barrier. Our experimental observations are summarized in Table 1.

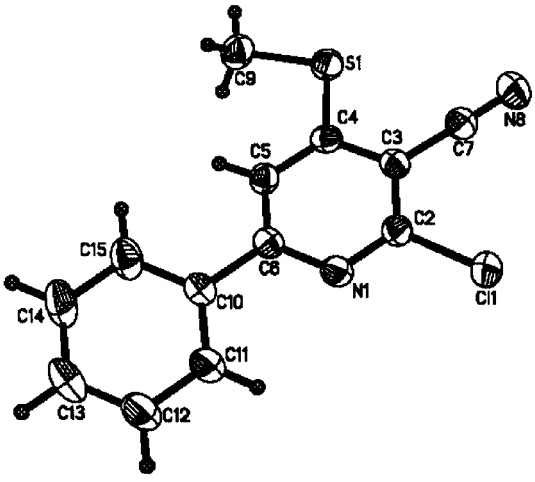


Figure 6. ORTEP diagram showing the X-ray structure of pyridine **6**

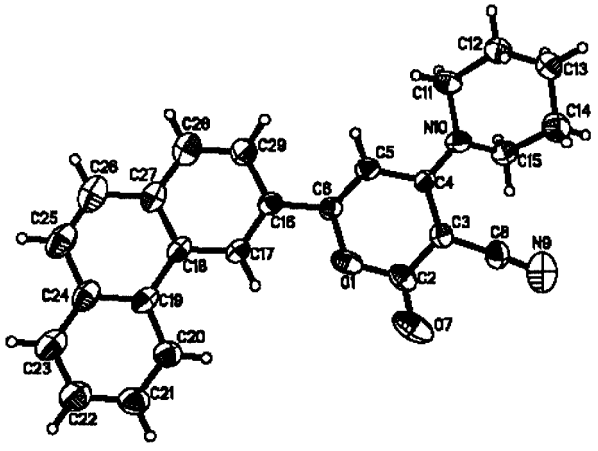


Figure 5. ORTEP diagram showing the X-ray structure of phenanthrenyls **2b**

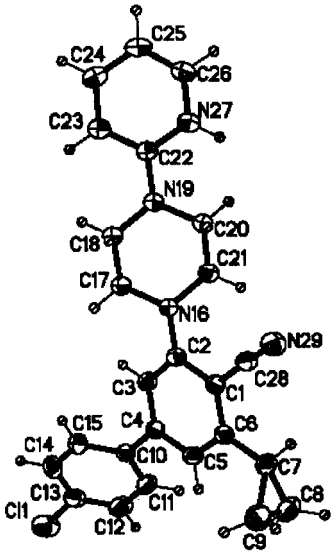


Figure 7. ORTEP diagram showing the X-ray structure of biaryl **7**

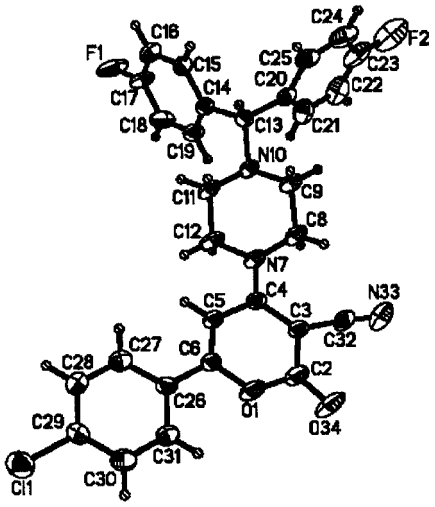


Figure 8. ORTEP diagram showing the X-ray structure of 2*H*-pyran-2-one **8**

Based on experimental observations it can be concluded that C−H···X weak H-bonding is an important factor in restricting rotameric conformation. Thus, the solid-state planar conformation in biaryl systems may result from the presence of C−H···X interactions.

Experimental Section

General: Melting points were determined with a Büchi 510 apparatus and are uncorrected. The reagent grade reaction solvents such as DMSO and DMF were further dried by distillation over calcium hydride. 2-Acetylphenanthrene, 3-acetylphenanthrene, thiochroman-4-one, 4-methylpiperidine, etc. were purchased from Aldrich. 2-Substituted 3,3-bis(methylsulfanyl)acrylate was prepared by a literature procedure[29] for the synthesis of **1**. TLC was performed on precoated silica-gel plastic plates and visualized by UV irradiation, exposure to iodine vapor, or spraying with $KMnO_4$ solution. IR spectra of liquid samples were run neat, and spectra of solids were obtained using KBr pellets. ^{1}H NMR spectra were recorded at 200 and 300 MHz in $CDCl_3$ with tetramethylsilane as internal reference. Chemical shifts and coupling constants (*J*) are reported in δ (ppm) and in Hz, respectively. Mass spectra were collected with a FAB Mass Spectrometer SX-102, JEOL (Japan) data system-6000. Elemental analyses (C, H, and N), including other analyses mentioned above were performed at SAIC, Central Drug Research Institute, Lucknow, India.

General Method for the Synthesis of 4-Methylsulfanyl-2-oxo-6-phenanthrenyl-2*H*-pyran-3-carbonitrile/carboxylate (1): This compound was prepared by stirring a mixture of 2 or 3-acetylphenanthrene (220 mg, 1 mmol), methyl 2-cyano/methoxycarbonyl-3,3-bis(methylsulfanyl)acrylate[29] (1 mmol) and powdered KOH (84 mg, 1.5 mmol) in DMSO (10 mL) for 8−10 h at ambient temperature until TLC showed that the starting materials had disappeared completely. The reaction mixture was poured into ice-water and stirred for 2 h. The solid thus obtained was filtered and washed with water (25 mL) and methanol (25 mL) and finally crystallized from a DMSO/methanol mixture.

4-Methylsulfanyl-2-oxo-(6-phenanthren-2-yl)-2*H*-pyran-3-carbonitrile (1a): Yield (275 mg, 80%), m.p. > 250 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.68 (s, 3 H), 7.72 (s, 1 H), 7.89−8.46 (m, 7 H), 9.16−9.20 (d, *J* = 7.8 Hz, 1 H), 9.39 (s, 1 H) ppm. IR (KBr): ṽ = 2210.5 cm^{-1}. FAB MS: found 344 [M$^+$ + 1]. $C_{21}H_{13}NOS_2$ (343.07): calcd. C 73.45, H 3.82, N 4.08, S, 9.34; found C 73.52, H 3.91, N 4.12, S 9.44.

4-Methylsulfanyl-2-oxo-6-(phenanthren-3-yl)-2*H*-pyran-3-carbonitrile (1b): Yield (281 mg, 82%), m.p. > 250 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.70 (s, 3 H), 7.73 (s, 1 H), 7.91−8.48 (m, 7 H), 9.20−9.24 (d, *J* = 7.8 Hz, 1 H), 9.59 (s, 1 H) ppm. IR (KBr): ṽ = 2214.4 cm^{-1}. FAB MS: found 344 [M$^+$ + 1]. $C_{21}H_{13}NOS_2$ (343.07): calcd. C 73.45, H 3.82, N 4.08, S, 9.34; found C 73.59, H 3.90, N 4.12, S 9.48.

Methyl 4-Methylsulfanyl-2-oxo-6-(phenanthren-2-yl)-2*H*-pyran-3-carboxylate (1c): Yield (282 mg, 75%), m.p. > 250 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.73 (s, 3 H), 3.76 (s, 3 H), 7.75 (s, 1 H), 7.94−8.52 (m, 7 H), 9.23−9.27 (d, *J* = 7.8 Hz, 1 H), 9.61 (s, 1 H) ppm. IR (KBr): ṽ = 1713.5 cm^{-1}. FAB MS: found 377 [M$^+$ + 1]. $C_{22}H_{16}O_4S$ (376.08): calcd. C 70.20, H 4.28, S 8.52; found C 70.35, H 4.32, S 8.65.

General Method for the Synthesis of 6-Phenanthrenyl-4-amino-2*H*-pyran-3-carbonitrile (2): A mixture of 4-methylsulfanyl-2-oxo-6-phenanthrenyl-2*H*-pyran-3-carbonitrile (**1a** or **1b**) (344 mg, 1 mmol) and secondary amine (1.5 mmol) was refluxed in methanol (10 mL) for 8−10 h until TLC showed that all the starting materials had disappeared. The reaction mixture was concentrated under reduced pressure at 40−45 °C. The crude solid thus obtained was washed with water (10 mL), followed by ethanol (10 mL). Finally it was purified by silica-gel column chromatography using 1% methanol in chloroform as eluent.

2-Oxo-6-(phenanthren-2-yl)-4-(pyrrolidin-1-yl)-2*H*-pyran-3-carbonitrile (2a): Yield (288 mg, 79%), m.p. > 250 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.00 (br. s, 4 H), 3.83−4.03 (m, 4 H), 7.11 (s, 1 H), 7.73−7.86 (m, 2 H), 7.89−8.06 (m, 3 H), 8.16 (s, 2 H), 8.99−9.02 (m, 1 H), 9.29 (s, 1 H) ppm. IR (KBr): ṽ = 2199.4 (s) cm^{-1}. FAB MS: found 367 [M$^+$ + 1]. $C_{24}H_{18}N_2O_2$ (366.14): calcd. C 78.67, H 4.95, N 7.65; found C 78.68, H 4.97, N 7.69.

2-Oxo-6-(phenanthren-2-yl)-4-(piperidin-1-yl)-2*H*-pyran-3-carbonitrile (2b): Yield (319 mg, 84%), m.p. > 250 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.75 (br. s, 6 H), 3.97 (br. s, 4 H), 7.31 (s, 1 H), 7.68−7.80 (m, 2 H), 7.91−8.07 (m, 3 H), 8.12−8.20 (m, 2 H), 8.98−9.00 (d, *J* = 8.4 Hz, 1 H), 9.29 (s, 1 H) ppm. IR (KBr): ṽ = 2212.0 (s) cm^{-1}. FAB MS: found 381 [M$^+$ + 1]. $C_{25}H_{20}N_2O_2$ (380.14): calcd. C 78.93, H 5.30, N 7.36; found C 78.97, H 5.28, N 7.30.

4-(4-Methylpiperidin-1-yl)-2-oxo-6-(phenanthren-2-yl)-2*H*-pyran-3-carbonitrile (2c): Yield (353 mg, 89.5%), m.p. > 250 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.96−0.98 (d, *J* = 5.7 Hz, 3 H), 1.86 (m, 1 H), 3.3−3.45 (m, 4 H), 4.51−4.56 (m, 4 H), 7.28 (s, 1 H), 7.70−7.78 (m, 2 H), 7.96−8.05 (m, 3 H), 8.28−8.31 (d, *J* = 9.0 Hz, 1 H), 8.62 (s, 1 H), 8.91−9.03 (m, 2 H) ppm. IR (KBr): ṽ = 2211.0 (s) cm^{-1}. FAB MS: found 395 [M$^+$ + 1]. $C_{26}H_{22}N_2O_2$ (394.17): calcd. C 79.16, H 5.62, N 7.10; found C 79.12, H 5.52, N 7.11.

2-Oxo-6-(phenanthren-3-yl)-4-(pyrrolidin-1-yl)-2*H*-pyran-3-carbonitrile (2d): Yield (307 mg, 84%), m.p. > 250 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.07 (br. s, 4 H), 3.81−4.01 (m, 4 H), 7.08 (s, 1 H), 7.71−7.85 (m, 2 H), 7.87−8.04 (m, 3 H), 8.13 (s, 2 H), 8.98−9.01 (m, 1 H), 9.28 (s, 1 H) ppm. IR (KBr): ṽ = 2199.7 (s) cm^{-1}. FAB MS: found 367 [M$^+$ + 1]. $C_{24}H_{18}N_2O_2$ (366.14): calcd. C 78.67, H 4.95, N 7.65; found C 78.61, H 4.94, N 7.67.

2-Oxo-6-(phenanthren-3-yl)-4-(piperidin-1-yl)-2*H*-pyran-3-carbonitrile (2e): Yield (323 mg, 85%), m.p. > 250 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.74 (br. s, 6 H), 3.95 (br. s, 4 H), 7.34 (s, 1 H), 7.70−7.82 (m, 2 H), 7.90−8.06 (m, 3 H), 8.13−8.21 (m, 2 H), 8.99−9.01 (d, *J* = 8.4 Hz, 1 H), 9.29 (s, 1 H) ppm. IR (KBr): ṽ = 2202.5 (s) cm^{-1}. FAB MS: found 381 [M$^+$ + 1]. $C_{25}H_{20}N_2O_2$ (380.14): calcd. C 78.93, H 5.30, N 7.36; found C 79.00, H 5.31, N 7.36.

General Method for the Synthesis of 9,10-Dihydrobiphenanthrenyls and Hetero-biphenanthrenyls (4, 5): A mixture of **1** or **2** (1 mmol) and ketone **3** (1 mmol) was stirred with powdered KOH (1.5 mmol) in dry DMF (10 mL) for 30 h under an inert atmosphere. The reaction mixture was poured into ice-water and the solution was neutralized with 10% HCl. The precipitate obtained was filtered, washed with distilled water and purified by column chromatography using hexane/chloroform (1:2) mixture as eluent.

3-(Pyrrolidin-1-yl)-9,10-dihydro-1,2′-biphenanthrenyl-4-carbonitrile (4a): Yield (108 mg, 24%), m.p. 208−210 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.03 (t, *J* = 6.4 Hz, 4 H), 2.65 (br. s, 4 H), 3.66 (t, *J* = 6.2 Hz, 4 H), 6.78 (s, 1 H), 7.25−7.35 (m, 4 H), 7.59−7.91 (m, 6 H), 8.22 (d, *J* = 7.2 Hz, 1 H), 8.72−8.76 (m, 2 H) ppm. IR (KBr): ṽ = 2200 (s) cm^{-1}. FAB MS: found 451 [M$^+$ + 1]. $C_{33}H_{26}N_2$ (450.21): calcd. C 87.97, H 5.82, N 6.22; found C 87.93, H 5.86, N 6.18.

3-(Piperidin-1-yl)-9,10-dihydro-1,2′-biphenanthrenyl-4-carbonitrile (4b): Yield (189 mg, 39%), m.p. 200−202 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.58−1.64 (m, 2 H), 1.84 (t, *J* = 5.0 Hz, 4 H), 2.69 (br. s, 4 H), 3.25 (t, *J* = 5.0 Hz, 4 H), 7.03 (s, 1 H), 7.27−7.40 (m, 4 H), 7.59−7.95 (m, 6 H), 8.30 (d, *J* = 7.6 Hz, 1 H), 8.70−8.78 (m, 2 H) ppm. IR (KBr): ṽ = 2200 (s) cm^{-1}. FAB MS: found 465 [M$^+$ + 1]. $C_{34}H_{28}N_2$ (464.23): calcd. C 87.90, H 6.07, N 6.03; found C 87.93, H 5.96, N 6.10.

3-(4-Methylpiperidin-1-yl)-9,10-dihydro-1,2′-biphenanthrenyl-4-carbonitrile (4c): Yield (201 mg, 42%), m.p. 208−210 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.01−1.03 (d, *J* = 5.1 Hz, 3 H), 1.61−1.78 (m, 5 H), 2.69 (br. s, 4 H), 2.75−3.05 (m, 2 H), 3.63−3.68 (m, 2 H), 7.03 (s, 1 H), 7.25−7.91 (m, 10 H), 8.28−8.31 (d, *J* = 7.8 Hz, 1 H), 8.73−8.77 (t, *J* = 8.3 Hz, 2 H) ppm. IR (KBr): ṽ = 2210 (s) cm^{-1}. FAB MS: found 479 [M$^+$ + 1]. $C_{35}H_{30}N_2$ (478.24): calcd. C 87.83, H 6.32, N 5.85; found C 87.87, H 6.39, N 5.87.

3-(Pyrrolidin-1-yl)-9,10-dihydro-1,3′-biphenanthrenyl-4-carbonitrile (4d): Yield (153 mg, 34%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.03 (t, *J* = 6.3 Hz, 4 H), 2.68 (br. s, 4 H), 3.67 (t, *J* = 6.2 Hz, 4 H), 6.78 (s, 1 H), 7.25−7.39 (m, 4 H), 7.54−7.97 (m, 6 H), 8.23 (d, *J* = 7.3 Hz, 1 H), 8.64−8.67 (m, 2 H) ppm. IR (KBr): ṽ = 2210 (s) cm^{-1}. FAB MS: found 451 [M$^+$ + 1]. $C_{33}H_{26}N_2$ (450.21): calcd. C 87.97, H 5.82, N 6.22; found C 87.94, H 5.86, N 6.19.

3-(Piperidin-1-yl)-9,10-dihydro-1,3′-biphenanthrenyl-4-carbonitrile (4e): Yield (162.5 mg, 35%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.61−1.64 (m, 2 H), 1.75−1.84 (t, *J* = 5.0 Hz, 4 H), 2.69 (br. s, 4 H), 3.25 (t, *J* = 5.0 Hz, 4 H), 7.05 (s, 1 H), 7.26−7.41 (m, 4 H), 7.53−7.99 (m, 6 H), 8.30 (d, *J* = 7.3 Hz, 1 H), 8.63−8.67 (m, 2 H) ppm. IR (KBr): ṽ = 2200 (s) cm^{-1}. FAB MS: found 465 [M$^+$ + 1]. $C_{34}H_{28}N_2$ (464.23): calcd. C 87.90, H 6.07, N 6.03; found C 87.91, H 5.96, N 6.11.

Methyl 3-Hydroxy-9,10-dihydro-1,2′-biphenanthrenyl-4-acetate (4f): Yield (129 mg, 30%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.70 (br. s, 4 H), 3.70 (s, 3 H), 7.04 (s, 1 H), 7.21−7.25 (m, 4 H), 7.60−7.90 (m, 7 H), 8.69−8.75 (m, 2 H) ppm. IR (KBr): ṽ = 1596.6 (s) cm^{-1}. FAB MS: found 431 [M$^+$ + 1]. $C_{30}H_{22}O_3$ (430.16): calcd. C 83.70, H 5.15; found C 83.74, H 5.18.

3-(4-Methylpiperidin-1-yl)-1-(phenanthren-2-yl)-10*H*-9-thia-phenanthrene-4-carbonitrile (4g): Yield (150 mg, 30%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00−1.03 (d, *J* = 4.5 Hz, 3 H), 1.54−1.77 (m, 5 H), 2.87 (br. s, 2 H), 3.63−3.69 (m, 4 H), 7.06 (s, 1 H), 7.32−7.91 (m, 10 H), 8.18−8.20 (m, 1 H), 8.70−8.80 (m, 2 H) ppm. IR (KBr): ṽ = 2211.5 (s) cm^{-1}. FAB MS: found 497 [M$^+$ + 1]. $C_{34}H_{28}N_2S$ (496.2): calcd. C 82.22, H 5.68, N 5.64; found C 82.26, H 5.62, N 5.66.

(*E*)- and (*Z*)-{4-(Phenanthren-2-yl)-5,6-dihydrobenzo[*h*]chromen-2-ylidene}acetonitrile (5a): Yield (127 mg, 32%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.59−2.63 (m, 2 H), 2.79−2.86 (m, 2 H), 4.29 [s, 1 H, CH, (*Z*)-isomer], 4.63 [s, 1 H, CH, (*E*)-isomer], 6.36 [s, 1 H, (*Z*)-isomer], 6.83 [s, 1 H, (*E*)-isomer], 7.20−7.95 (m, 11 H), 8.68−8.76 (m, 2 H) ppm. IR (KBr): ṽ = 2211 (s) cm^{-1}. FAB MS: found 398 **[M$^+$ + 1]**. $C_{29}H_{19}NO$ (397.15): calcd. C 87.63, H 4.82; found C 87.64, H 4.86.

Methyl (*E*)- and (*Z*)-{4-(Phenanthren-2-yl)-5,6-dihydrobenzo[*h*]chromen-2-ylidene}acetate (5b): Yield (147 mg, 34%), ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.61−2.65 (m, 2 H), 2.78−2.82 (m, 2 H), 3.69 (s, 3 H), 4.99 [s, 1 H, CH, (*Z*)-isomer], 5.38 [s, 1 H, CH, (*E*)-isomer], 6.32 [s, 1 H, CH, (*Z*)-isomer], 7.18−7.34 (m, 4 H), 7.57−7.90 (m, 8 H), 8.69−8.74 (m, 2 H) ppm. IR (KBr): ṽ = 1588 (s) cm^{-1}. FAB MS: found 431 [M$^+$ + 1]. $C_{30}H_{22}O_3$ (430.16): calcd. C 83.70, H 5.15; found C 83.64, H 5.16.

X-ray Single-Crystal Analysis: A single crystal of lactone **2b** was prepared from chloroform while bi(phenanthrenyls) **4b**, **4c** and pyridine derivative **6** were grown from acetone solution by slow evaporation. Unit cell determination and intensity data collection (2θ = 50°) were performed with a Bruker P4 diffractometer at 293(2) K. The structures were solved by direct methods and refined[24] by full-matrix least-squares on F^2 in the anisotropic approximation for all non-hydrogen atoms.

Crystal Data of 2b: $C_{25}H_{20}N_2O_2$, *M* = 380.43, monoclinic, $P2_1/c$, *a* = 10.853(1), *b* = 10.043(1), *c* = 17.499(2) Å, β = 93.34(1), *V* = 1904.1 Å^3, *Z* = 4, $D_{calcd.}$ = 1.327 g·cm^{-1}, μ (Mo-K_α) = 0.07 mm^{-1}, *F*(000) = 800.0, colorless rectangular crystal, size 0.30 × 0.25 × 0.125 mm, 3848 reflections measured (2870 unique), R_w = 0.13, conventional *R* = 0.0552 on *F* values of 1484 reflections with $I > 2\sigma(I)$, *S* = 0.999 for all data and 262 parameters.

Crystal Data of 4b: $C_{34}H_{28}N_2$, *M* = 464.64, monoclinic, $P2_1/c$, *a* = 13.480(2), *b* = 18.332(2), *c* = 10.167(1) Å, β = 91.519(10), *V* = 2511.54 Å^3, *Z* = 4, $D_{calcd.}$ = 1.223 g cm^{-1}, μ (Mo-K_α) = 0.07 mm^{-1}, *F*(000) = 976.0, colorless rectangular crystal, size 0.42 × 0.30 × 0.20 mm, 6849 reflections measured (5491 unique), R_w = 0.17, conventional *R* = 0.0607 on *F* values of 2826 reflections with $I > 2\sigma(I)$, *S* = 1.024 for all data and 342 parameters.

Crystal Data of 4c: $C_{35}H_{30}N_2$, *M* = 478.61, orthorhombic, *Pbca*, *a* = 22.882(3), *b* = 7.731(1), *c* = 28.735(3) Å, *V* = 5083.24 Å^3, *Z* = 8, $D_{calcd.}$ = 1.251 g·cm^{-1}, μ (Mo-K_α) = 0.07 mm^{-1}, *F*(000) = 2032.0, colorless rectangular crystal, size 0.325 × 0.20 × 0.15 mm, 5690 reflections measured (4375 unique), R_w = 0.26, conventional *R* = 0.0860 on *F* values of 2075 reflections with $I > 2\sigma(I)$, *S* = 1.013 for all data and 335 parameters.

Crystal Data of 6: $C_{13}H_9Cl_1N_2S_1$, *M* = 260.73, triclinic, $P\bar{1}$, *a* = 7.644(1), *b* = 12.712(1), *c* = 13.244(1) Å, α = 81.760002, β = 78.290001, γ = 78.180000, *V* = 1226.5(2) Å^3, *Z* = 4, $D_{calcd.}$ = 2.824 g·cm^{-1}, μ (Mo-K_α) = 0.07 mm^{-1}, *F*(000) = 1072.0, colorless

rectangular crystal, size 0.275 × 0.25 × 0.175 mm, 5124 reflections measured (4193 unique), $R_w = 0.124$, conventional $R = 0.049$ on F values of 2977 reflections with $I > 2\sigma(I)$, $S = 1.042$ for all data and 310 parameters.

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