Synthesis and Crystal Structure of 4,5,12,13Tetraaza-Dibenzo[b,k]Chrysene

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Abstract

New synthetic methodology of fused aromatic hydrocarbons with nitrogen heterocyclic of 4,5,12,13-Tetraaza-dibenzo[b,k]chrysene(4) were designed and synthesized by chemical methods. Compound 4 fully characterized by ¹H NMR, ¹³C NMR, EI-mass spectral, elemental and single crystal X-ray analysis. Molecules of 4 are completely planar and form face-to-face π -stacking. Shortest distances between fused rings of π - π interactions are 3.346 Å. Compound (4) is a potential candidate for high mobility single crystal organic field effect transistors (OFET's).

Keywords: 4,5,12,13-Tetraaza-dibenzo[b,k]chrysene, heterocyclic aromatic hydrocarbons, organic semiconductors, crystal structure

1 Introduction

The importance and performance of organic electronic devices have both increased significantly over the last 30 years, evolving from a field with great promise for new materials and applications to a real industry with a few commercial products on the market. Broader acceptance of organic semiconductors will hinge on the development of materials with competitive properties and superior processability, yielding high-performance devices from a significantly less expensive fabrication process. Polycyclic and heterocyclic aromatic hydrocarbons and their derivatives are used for active layer of n- and p-channel organic field-effect transistors (OFETs), because they can realize a high mobility.¹ Most of the research has been performed on thin film transistors (TFTs)1b ,because of the majority of unsubstituted conjugated organic oligomers crystallize into a herringbone structure. In this packing motif, molecules minimize π -orbital repulsion adopting an edge-to-face by arrangement forming a two-dimensional layer and gives better polycrystalline films. The highest charge carrier mobility has been achieved with pentacene, which has been used as benchmark semiconductor materials and led organic semiconductors with a mobility over 1 cm²/Vs.² Though pentacene has adequate

charge transfer properties, it is subject to rapid degradation in ambient conditions, and it is virtually insoluble even in hot aromatic solvents.3 Additionally, herringbone packing of pentacene molecules in the solid state does not provide for optimal intermolecular π -orbital overlap, which is a critical factor impacting the intrinsic carrier mobility.4 Recently organic single crystals are used as the ideal tool for the exploration of charge transport in organic materials.⁵ Research on the single crystal FETs has been increasing due to their development and advantages in studying the intrinsic carrier transport properties of organic semiconductors by avoiding the extrinsic effects of grain boundaries, molecular disorder and concentration of charge traps is minimized.6 Among the single crystal FETs rubrene single crystal yielding high performance with charge carrier mobility up to 20 cm²/Vs.⁷

Quantum mechanical calculations have predicted that high mobility in OFETs can be obtained when conjugated molecules have strong interactions with neighboring molecules to maximize the overlap of π molecular orbitals.8,9 In addition, Curtis and co-workers have recently made a structural analysis on some common organic semiconductors, discussing the correlation between solid-state packing and transport.¹⁰ Theoretically speaking,

a co facial π stacking structure is expected to provide more efficient orbital overlap and thereby facilitate carrier transport. Several oligomers that have been shown to adopt a cofacial packing arrangement include fused ring oligomers, ^{11, 12} oligomers containing bulky substituents, ¹³ and oligomers incorporating both electron-rich and electron-deficient aryl rings.^{14, 15} The device data from these oligomers is quite promising as compared with analogs that adopt a herringbone structure, but further investigations are needed to demonstrate conclusively those face-to-face π -stacking results in higher charge mobility.



Figure1. Chemical formula of 4,5,12,13-Tetraazadibenzo[b,k]chrysene

In this paper we report the synthesis and crystal structure of new poly nuclear heterocyclic aromatic hydrocarbon of 4,5,12,13-Tetraaza-dibenzo[b,k]chrysene(4), as a potential candidate for single crystal field effect transistors and high mobility in OFETs can be obtained because of conjugated molecules have strong interactions with neighboring molecules and exhibits the face-to-face π - stacking molecular packing.

2 Experimental Section

All starting materials were purchased from Aldrich, TCI and Across. 1H NMR spectra were recorded with Bruker AMX 500, proton chemical shifts (δ) are reported in ppm relative to the methine singlet at 7.24 ppm for the residual CHCl3 in the deuteriochloroform. EImass spectra were obtained with a JMS-700 double focusing mass spectrometer (JEOL), elemental analysis were done by FlashEA 1112 Series CHNS-O Analyzer. To investigate the molecular structure and intermolecular interactions in the solid state, we performed single-crystal structure analysis using Bruker X8APEX X-ray diffractometer with Mo Ka radiation (λ = 0.71073 Å). The data were collected at 150.0(2) K and the structure was solved by SHELXS-97 program.16

2-bromo-3-(1,3-dioxolan-2-yl)pyridine(1). The 0.02 mol(3.72g) of 2-bromonicotinaldehyde, 0.08 mol(4.96g) of ethylene qlycol, 0.5g of p-TsOH and 150 ml of benzene were placed in a round bottomed flask equipped with stirrer and Dean-Stark adapter connected to a reflux condenser. The mixture stirred and refluxed until all reaction water was collected in the adapter (11 h.). The reaction mixture was then cooled to room temperature and washed once with 100ml Na₂CO₃ solution(2 %) and twice with 50 ml portions of water. The organic layer was separated and dried over anhydrous MgSO4 . The solvent was evaporated in vacuo, and to give 4.37 g, 95 % yield of 2-bromo-3-(1,3dioxolan-2-yl)pyridine as a white crystals.

¹H NMR (400 MHz , CDCl₃) , δ = 8.351-8.334(dd, 1H , J= 2.0 Hz , J= 2.1 Hz,) ; 7.874-7.851(dd, 1H, J= 2.05 Hz , J= 2.1 Hz) ; 7.296-7.264(dddd, 1H, J= 0.4 Hz , J= 0.28 Hz, J= 0.4 Hz , J= 0.3 Hz) ; 6.008 (s, 1H); 4.132-4.057(m, 4H).

N¹,N⁵-bis(3-(1,3-dioxolan-2-yl)pyridin-2yl)naphthalene-1,5-diamine(2).

5.6 g (24 mmol) of compound 1, 1.93 g (12 mmol) of naphthalene-1,5-diamine, 2.88 g (30 mmol) of t-BuONa, 280 mg of Pd2(dBu)3, 250 mg of dppp , 100 ml of dry benzene were placed in a round bottomed flask equipped with stirrer and reflux condenser. The mixture was stirred and refluxed until the starting aldehyde has been completely used(TLC). Then the reaction mixture was cooled to room temperature, 100 ml water was added and organic compound extracted with dichloromethane. After drying and evaporation crude product was purified by column chromatography on a silica gel, using CH₂Cl₂-Acetone(10:1), to give 4.22 g (76 %) of compound 2 as a light yellow solid. ¹H NMR (500 MHz , CDCl₃), δ = 8.192-8.178 (dd, 2H , J= 1.8 Hz , J= 1.84 Hz,) ; 8.112- 8.097 (d, 4H, J= 7.5 Hz); 7.713-7.696 (d, 2H, J= 8.4 Hz); 7.665-7.646 (dd, 2H , J= 1.75 Hz , J= 1.82 Hz); 7.496-7.464 (t, 2H, J = 8 Hz); 6.764-6.739 (dd, 2H, J= 4.92 Hz, J= 4.96 Hz); 5.914 (s, 2H); 4.226-4.13 (m, 8H).

2-(naphtho[1,2-b][1,8]naphthyridin-4-

ylamino)nicotinaldehyde (3). 1ml H₂SO₄ was added dropwise to a stirred solution of 2.28 g (5 mmol) of compound **2** in 10 ml of glacial acetic CBÜ Fen Bil. Dergi., Cilt 11, Sayı 3, 339-344 s 344

acid and stirred for 1 h at 100 °C, then cooled to room temperature. Reaction mixture was poured into the ice cooled water and NH4OH was added with vigorous stirred until pH=8. The solid was filtered off, washed with water, ethanol, EA, and hexane, to gave 1.66 g (95 %) of pure 2-(naphtho[1,2-b][1,8]naphthyridin-4ylamino)nicotinaldehyde as a yellow solid. 1H NMR (300 MHz , CDCl₃), δ= 10.775 (s, 1H); 10.012 (s, 1H); 9.586-9.559 (d, 1H, J= 8.1 Hz); 9.290-9.270 (dd, 1H , J= 2.1 Hz , J= 2.1 Hz,); 8.688 (s, 1H); 8.406-8.344 (m, 3H); 8.093-8.062 (d, 1H, J= 9.3Hz); 7.968-7.936(dd, 1H , J= 2.1 Hz , J= 2.1 Hz,); 7.848-7.786(m, 2H); 7.552-7.511 (dd, 1H, J= 4.2 Hz , J= 4.2 Hz); 6.886-6.845 (dd, 2H , J= 4.8 Hz, J= 4.8 Hz).

4,5,12,13-Tetraaza-dibenzo[b,k]chrysene(4).

1ml H_2SO_4 was added dropwise to a stirred solution of 1.60 g of 2-(naphtho[1,2-b][1,8]naphthyridin-4-ylamino)nicotin-

aldehyde in 30 ml of glacial acetic. The mixture was refluxed for 24 h and then cooled to room temperature. Reaction mixture was poured into the ice cooled water and NH4OH was added with vigorous stirred until pH=8. The solid was filtered off, washed with water, ethanol, EA, and hexane, to gave 1.4 g (92 %) of pure 4,5,12,13-Tetraaza-dibenzo[b,k]chrysene as a yellow solid. An analytical sample was prepared by vacuum sublimation at 320 °C (10-5 Torr). ¹H NMR (300 MHz , CDCl₃), δ= 9.852-9.822(d, 2H, J= 9 Hz); 9.376-9.356(dd, 2H, J= 2.1 Hz, J= 2.1 Hz); 8.959(s, 2H); 8.524-8.489(dd, 2H, J= 2.1 Hz, J= 2.1 Hz); 8.288-8.257(d, 2H, J= 9.3 Hz); 7.624-7.584(dd, 2H, J= 3.9 Hz, J= 3.9 Hz). MS (EI, 70 eV) 332.1 (M⁺, 100 %), Anal.calc C, 79.50 %; H, 3.64 %; N, 16.86 % Found: C, 79.35 %; H, 3.49 %; N, 16.47 %

3 Results and Discussion

Synthesis. Scheme **1** shows synthetic route of compound **4**. Reaction of commersially available 2-bromonicotinaldehyde with ethylene glicol and *p*-TsOH in benzene yielded the 2-bromo-3-(1,3-dioxolan-2-yl)pyridine (**1**) in

95 % yield. Condensation of compound **1** with naphthalene-1,5-diamine in the presence of $Pd_2(dBu)_3$ catalyst gave in 76 % yield of N^1,N^5 -bis(3-(1,3-dioxolan-2-yl)pyridin-2-yl) naphthalene-1,5-diamine (**2**).



Scheme1. Synthetic scheme of 4,5,12,13-Tetraaza-dibenzo[b,k]chrysene.

By cyclization reaction of **2** in acetic acid in the presence of catalytic amount of H₂SO₄ during 1 hours at 100 °C was obtained 2-(naphtho[1,2-b][1,8]naphthyridin-4-ylamino)nicotinaldehyde (3) in 95% yield. But when cyclization reaction was used for 24 hours at 100 °C target compound of 4,5,12,13-Tetraaza-dibenzo [b,k]chrysene were found in 95% yield. Compound **4** characterized by ¹H NMR, ¹³C NMR, mass and elemental analysis.

Crystal structure. In the range of $\sim 0.7 - 1.0$ cm long and ~ 0.10 - 0.06 mm wide needle like vellow single-crystals of 4,5,12,13-Tetraazadibenzo [b,k]chrysene were grown by vacuum sublimation at 320 °C (10-5 Torr). Single-crystal X-ray analyses revealed molecules of 4 are completely planar and form face-to-face π stacking along the a-axis, which is the shortest axis (Figure 3a). The direction of the long axis of the needle-like single-crystal was confirmed by X-ray structure analysis. The crystal data for compound 4 are listed in Table 1 and the selected bond lengths and angles are listed in Table 2. The crystal structure of 4 shows that, the molecule is unsymmetric, the disorder in the X-ray structure leads to two possible motifs, in which nitrogen atoms of N4AA ,N5AA and N4BB,N5BB are located in the opposite side of molecules(Figure2) and exhibit antiparallel packing.

Table 1. Crystal data of 4

Empirical formula C22 H12 N4					
	impirical formula C22 H12 N4		Absorption coefficient mm ⁻¹ 0.093		
Formula weight	332.36		F(000) 344		
Temperature	150(2) K		Crystal size, mm 0.75 x 0.10 x 0.05		
Wavelength	0.71073 A		Theta range for data collection 2.05 to 27.50°		
Crystal system	Triclinic		Reflections collected 8288		
Space group P-1		Independent reflections 3273 [R _{in} = 0.0434]			
Unit cell dimensions: a/Å	3.7511(2)		Completeness to	theta =	27.50° 98.4 %
b/ Å	11.8372(5)		Max. and min. tr	ansmissic	on 0.990 and 0.918
c/ Å	16.6606(9)		Data / restraints	/ paramet	ers 3273 / 0 / 235
$\alpha ^{\circ}$	93.814(2)		GOF		1 071
β⊚° 94.941(3)			Final R indices [I>2sigma(I) R1 = 0.0631.		
0000000000000000000000000000000000000	000000000000000000000000000000000000000	o/°	i mai remaiees [i	> 20151110(1	wR2 = 0.1619
98.645(3)			R indices (all dat	· 2)	R1 = 0.1098
Volumo Å 3	776 77(6)		R marces (an dat	<i>a</i>)	R1 = 0.1000,
	20.27(0)				WK2 = 0.1855
2	2				
Density (calculated) Mg/m ³	1.520				
Table 2. Bond lengths [Å] and angles [°] for 4.					
C(1A)-C(2A)	1.359(3)	C(8B)-C(9B)		1.388(3)	C(13A)#1-C(13A)-C(6A)#1
C(1A)-C(9A)	1.422(3)	C(8B)-H(8B)	C	0.9500	C(13A)#1-C(13A)-C(12A)
C(1A)-H(1A)	0.9500	C(9B)-C(10B)		1.432(3)	C(6A)#1-C(13A)-C(12A)
C(2A)-C(3A)	1.416(3)	C(11B)-C(12B)		1.439(3)	C(2B)-C(1B)-C(9B)
C(2A)-H(2A)	0.9500	C(12B)-C(13B)		1 453(3)	C(2B)-C(1B)-H(1B)
C(3A)-N(4A)	1 315(3)	C(13B)-C(13B)#2		1.390(4)	C(9B)-C(1B)-H(1B)
C(3A)-H(3A)	0.9500	C(13B)-C(6B)#2		1.370(4) 1.437(3)	C(1B)-C(2B)-C(3B)
N(4A) C(10A)	1 376(3)	C(2A) C(1A) C(9)	(A)	1.407(0) 118 5(2)	C(1B) C(2B) H(2B)
N(4A) - C(10A)	1.370(3) 1.248(2)	C(2A) - C(1A) - U(1A)		110.3(2) 120.7	C(1D)- $C(2D)$ - $H(2D)$
N(5A) - C(12A)	1.340(3) 1.251(2)	C(2A)-C(1A)-11(1)	IA)	120.7	N(4P) C(2P) C(2P)
N(5A)-C(10A)	1.351(3)	C(9A)- $C(1A)$ - $H(1)$	IA)	120.7	N(4D)-C(3D)-C(2D)
C(6A) - C(7A)	1.351(3)	C(1A)-C(2A)-C(3)	SA)	118.8(2)	N(4B)-C(3B)-H(3B)
C(6A)-C(13A)#1	1.434(3)	C(IA)-C(2A)-H(2	2A)	120.6	C(2B)-C(3B)-H(3B)
C(6A)-H(6A)	0.9500	C(3A)-C(2A)-H(2A)		120.6	C(3B)-N(4B)-C(10B)
C(7A)-C(11A)	1.433(3)	N(4A)-C(3A)-C(2A)		125.2(2)	C(12B)-N(5B)-C(10B)
C(7A)-H(7A)	0.9500	N(4A)-C(3A)-H(3A)		117.4	C(7B)-C(6B)-C(13B)#2
C(8A)-C(11A)	1.381(3)	C(2A)-C(3A)-H(3A)		117.4	C(7B)-C(6B)-H(6B)
C(8A)-C(9A)	1.394(3)	C(3A)-N(4A)-C(10A)		117.0(2)	C(13B)#2-C(6B)-H(6B)
C(8A)-H(8A)	0.9500	C(12A)-N(5A)-C(10A)		7.30(19)	C(6B)-C(7B)-C(11B)
C(9A)-C(10A)	1.428(3)	C(7A)-C(6A)-C(13A)#1		120.8(2)	C(6B)-C(7B)-H(7B)
C(11A)-C(12A)	1.438(3)	C(7A)-C(6A)-H(6A)		119.6	C(11B)-C(7B)-H(7B)
C(12A)-C(13A)	1.452(3)	C(13A)#1-C(6A)-H(6A)		119.6	C(11B)-C(8B)-C(9B)
C(13A)-C(13A)#1	1.397(4)	C(6A)-C(7A)-C(1	1A)	121.6(2)	C(11B)-C(8B)-H(8B)
C(13A)-C(6A)#1	1.434(3)	C(6A)-C(7A)-H(7	7A)	119.2	C(9B)-C(8B)-H(8B)
C(1B)-C(2B)	1.355(3)	C(11A)-C(7A)-H	(7A)	119.2	C(8B)-C(9B)-C(1B)
C(1B)-C(9B)	1.423(3)	C(11A)-C(8A)-C((9A)	119.6(2)	C(8B)-C(9B)-C(10B)
C(1B)-H(1B)	0.9500	C(11A)-C(8A)-H	(8A)	120.2	C(1B)-C(9B)-C(10B)
C(2B)-C(3B)	1.417(3)	C(9A)-C(8A)-H(8	3A)	120.2	N(5B)-C(10B)-N(4B)
C(2B)-H(2B)	0.9500	C(8A)-C(9A)-C(1	A)	123.0(2)	N(5B)-C(10B)-C(9B)
C(3B)-N(4B)	1.319(3)	C(8A)-C(9A)-C(1	.0A)	118.3(2)	N(4B)-C(10B)-C(9B)
C(3B)-H(3B)	0.9500	C(1A)-C(9A)-C(1	.0A)	118.8(2)	C(8B)-C(11B)-C(7B)
N(4B)-C(10B)	1.372(3)	N(5A)-C(10A)-N	(4A)	115.2(2)	C(8B)-C(11B)-C(12B)
N(5B)-C(12B)	1.344(3)	N(5A)-C(10A)-C	(9A)	123.3(2)	C(7B)-C(11B)-C(12B)
N(5B)-C(10B)	1.349(3)	N(4A)-C(10A)-C	(9A)	121.5(2)	N(5B)-C(12B)-C(11B)
C(6B)-C(7B)	1.349(3)	C(8A)-C(11A)-C((7A)	122.9(2)	N(5B)-C(12B)-C(13B)
C(6B)-C(13B)#2	1.37(3)	C(8A)-C(11A)-C((12A)	1184(2)	C(11B)-C(12B)-C(13B)
C(6B)-H(6B)	0.9500	C(7A) - C(11A) - C(1A) -	(12A)	118 8(2)	C(13B)#2- $C(13B)$ - $C(6B)$ #2
C(7B)- $C(11B)$	1 429(3)	N(5A)-C(12A)-C	(11A)	1231(2)	C(13B)#2- $C(13B)$ - $C(12B)$
C(7B)-H(7B)	0.9500	N(5A) - C(12A) - C(12A)	(13A)	117 8(2)	C(6B)#2- $C(13B)$ - $C(12B)$
C(8B)-C(11B)	1.387(3)	C(11A)-C(12A)-C	C(13A)	119.1(2)	

(a)Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z; (b) Label B represents nonsymmetric related

positions (disordered positions).



Figure 2. The molecular structure of 4,5,12,13-Tetraaza-dibenzo [b,k]chrysene, thermal ellipsoids drawn at the 50 % probability level.



Figure 3. (a) Face to face π - π - stacking along the a axis,(b)short distances between fused rings of **4**

Introduction of strongly electron-withdrawing nitrogen atoms to both end four benzene rings dibenzochrysene of molecules changed herringbone packing to face to face π - π stacking structure of 4. Shortest distances between fused rings of π - π interactions are 3.346 Å (Figure 3b), well within the van der Waals radius of the carbon atoms (3.4 Å). This series of molecules constitutes a unique approach to inducing face-to-face interaction in organic semiconductors by exploiting electronic, rather than steric, interactions. Compound **4** as a potential candidate for single crystal field effect transistors and high mobility in OFETs can be obtained because of conjugated molecules have strong interactions with neighboring molecules. As a result in this study we introduce new synthetic methodology of fused aromatic hydrocarbons with nitrogen heterocyclic 4,5,12,13-Tetraazadibenzo[b,k]chrysene (4), where the nitrogen's are replaced of carbon atoms to maximize the electronic coupling between semiconducting molecules and to enhance stability, solubility and processability.

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