Crystal Structure of 1,4,5,8-Tetrapentylanthracene

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The structure of 1,4,5,8-tetrapentylanthracene was determined by X-ray crystallography. The compound crystallizes in a triclinic system and was characterized thus: $P\bar{1}$, $a = 5.350(4)$, $b = 9.580(7)$, $c = 14.946(10)$ Å, $\alpha = 99.685(9)^\circ$, $\beta = 90.243(11)^\circ$, $\gamma = 96.275(15)^\circ$, $V = 750.4(9)$ Å³, and $Z = 1$. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.0915$ with $I > 2\sigma(I)$. The molecule has a crystallographic center of symmetry, and half of the formula unit is independent. The molecular structure takes a semi-chair form.

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Solid-state packing effects play an important role in the performance of electronic and photonic materials.¹ We recently found that the introduction of alkyl side chains onto the anthracene nucleus at the 1-, 4-, 5-, and 8-positions brought about drastic changes in both the packing and solid-state fluorescence properties.² The length of the alkyl side chains affected not only the packing arrangement and the solid-state fluorescence, but also the molecular geometry. Thus, the molecular structures were classified into plane (the ethyl derivative), semi-chair (the propyl derivative), and chair (the hexyl derivative) forms. To investigate the effects of the alkyl side-chain length systematically, investigations on the butyl and pentyl derivatives remained. Herein we report on an X-ray analysis of the pentyl derivative, 1,4,5,8-tetrapentylanthracene.

The title compound was synthesized by our recently reported procedure using 2,5-dipentylfuran, 1,2,4,5-tetrabromobenzene, and *n*-BuLi.² Colorless crystals suitable for X-ray analysis were obtained by slow evaporation of a hexane solution at room temperature. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with Mo- $K\alpha$ ($\lambda = 0.71073$ Å) at 223 K. A structure determination was carried out using the program SIR2004.³ All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97.⁴ H atoms were placed at calculated positions, with C-H distances of 0.94 – 0.98 Å, and treated as riding atoms, with $U_{iso}(H) = 1.2 U_{eq}(C)$ for Csp^2 and CH_2 , and $U_{iso}(H) = 1.5 U_{eq}(C)$ for CH_3 . All calculations were performed using the WinGX

program package.⁵ The crystal and experimental data are summarized in Table 1. Selected bond lengths, angles, and torsion angles are listed in Table 2. An ORTEP drawing and a packing diagram of the title compound are shown in Figs. 2 and 3, respectively.

The molecule possesses a center of symmetry, and half of the formula unit is crystallographically independent (Fig. 2). The anthracene ring is essentially planar with a maximum deviation of 0.008(2) Å for C(1) and C(6). The C-C bond length in the anthracene ring is in the range 1.363(3) – 1.443(3) Å, whose values are similar to those of the other alkyl-substituted

Table 1 Crystal and experimental data

Formula: C ₃₄ H ₅₀	
Formula weight = 458.74	
$T = 223$ K	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 5.350(4)$ Å	$\alpha = 99.685(9)^\circ$
$b = 9.580(7)$ Å	$\beta = 90.243(11)^\circ$
$c = 14.946(10)$ Å	$\gamma = 96.275(15)^\circ$
$V = 750.4(9)$ Å ³	$Z = 1$
$D_x = 1.015$ g cm ⁻³	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073$ Å)	
$\mu(\text{Mo } K\alpha) = 0.056$ mm ⁻¹	$F(0\ 0\ 0) = 254$
Crystal size = $0.50 \times 0.10 \times 0.05$ mm ³	
No. of reflections collected = 6247	
No. of independent reflections = 3635	
θ range for data collection: 2.76 to 28.28°	
Data/Restraints/Parameters = 3635/0/156	
Goodness-of-fit on $F^2 = 1.068$	
R indices [$I > 2\sigma(I)$; 2279]: $R1 = 0.0915$, $wR2 = 0.2452$	
R indices (all data): $R1 = 0.1332$, $wR2 = 0.2860$	
$(\Delta/\sigma)_{\max} = 0.000$	
$(\Delta\rho)_{\max} = 0.424$ e Å ⁻³	$(\Delta\rho)_{\min} = -0.254$ e Å ⁻³
Measurement: Rigaku/MSC Mercury CCD	
Program system: WinGX	
Structure determination: SIR2004	
Refinement: SHELXL97	
CCDC deposition number: 784221

Fig. 1 Chemical diagram of the title compound.

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Table 2 Selected bond lengths [Å], bond angles [°] and torsion angles [°]

Bond length			
C(1)–C(8)	1.505(3)	C(8)–C(9)	1.525(3)
C(9)–C(10)	1.515(3)	C(10)–C(11)	1.516(3)
C(11)–C(12)	1.518(4)	C(4)–C(13)	1.504(3)
C(13)–C(14)	1.514(4)	C(14)–C(15)	1.536(4)
C(16)–C(17)	1.546(5)		
Bond angle			
C(2)–C(1)–C(8)	122.9(2)	C(1)–C(8)–C(9)	116.8(2)
C(8)–C(9)–C(10)	112.3(2)	C(9)–C(10)–C(11)	114.3(2)
C(10)–C(11)–C(12)	113.3(3)	C(4)–C(13)–C(14)	114.7(2)
C(13)–C(14)–C(15)	111.3(3)	C(14)–C(15)–C(16)	115.4(3)
C(15)–C(16)–C(17)	112.4(4)		
Torsion angle			
C(2)–C(1)–C(8)–C(9)	5.2(3)	C(1)–C(8)–C(9)–C(10)	176.6(2)
C(8)–C(9)–C(10)–C(11)	−178.8(2)	C(9)–C(10)–C(11)–C(12)	179.9(2)
C(3)–C(4)–C(13)–C(14)	99.5(3)	C(4)–C(13)–C(14)–C(15)	177.6(2)
C(13)–C(14)–C(15)–C(16)	175.6(3)	C(14)–C(15)–C(16)–C(17)	−177.5(3)

Fig. 2 ORTEP drawing of the title compound with atom labelling. Symmetry operation: (i) 1−*x*, 1−*y*, 1−*z*.

anthracenes.² All of the pentyl groups take an all-*trans* planar conformation. The bond lengths and bond angles in the alkyl side chains are within the expected ranges (Table 2). Interestingly, a pair of pentyl groups at the 1- and 5-positions takes a coplanar conformation with the anthracene ring [C(2)–C(1)–C(8)–C(9): 5.2(3)°], and another pair of pentyl groups at the 4- and 8-positions extends upward and downward out of the anthracene plane [C(3)–C(4)–C(13)–C(14): 99.5(3)°]. Therefore, this molecular structure was recognized as a semi-chair form, which looks like an intermediate conformer between plane and chair forms similarly to the propyl derivative.²

When viewed down the short molecular axis, the title compound adopts a slipped-parallel pattern, exhibiting a one-dimensional arrangement (Fig. 3). There is no π – π stacking between two nearest-neighbor molecules between (*x*, *y*, *z*) and (*x*+1, *y*, *z*) along the stacking direction. Although the propyl derivative had the same slipped-parallel arrangement without π – π stacking, the crystal packing was different from that of the title compound as follows: The slip distance between the two molecules is 5.35 Å, whose value is smaller than that of the propyl derivative (6.56 Å). In addition, the interplanar distance between the anthracene moieties is 3.48 Å, which is also smaller compared with that of the propyl derivative (3.53 Å). The anthracene rings along the column direction slipped relative to each other along the long molecular axis by 2.44 Å and along the short molecular axis by 3.25 Å. The former parameter was different from that of the propyl derivative (4.54 Å), while the

Fig. 3 Packing diagram viewed down the short molecular axis.

latter parameter was close to that of the propyl derivative (3.16 Å). There are some intermolecular C–H... π interactions [H(8A)...anthracene ring: 2.69 Å, and H(9A)...anthracene ring: 2.87 Å]. The crystal packing is probably stabilized by the combination of intermolecular interactions between alkyl side chains as well as the intermolecular C–H... π interactions.

To examine the influence of crystal packing on the solid-state fluorescence properties, the fluorescence spectrum of the title compound and the absolute quantum yield were measured by a Hamamatsu Photonics PMA11 calibrated optical multichannel analyzer with a solid-state blue laser (λ_{ex} = 377 nm) and a Labsphere IS-040-SF integrating sphere, respectively. The fluorescence maximum was observed at 444 nm, showing a slightly red-shift compared with that of the propyl derivative (436 nm). The title compound exhibited the highest quantum yield in the solid state of 0.92 in the series of 1,4,5,8-tetraalkylanthracenes. Since the propyl derivative had the second-largest quantum yield of 0.85, we concluded that both the molecular structure of the semi-chair form and the crystal packing of the slipped-parallel arrangement without π – π stacking probably led to enhancements of the quantum yields.

Acknowledgments

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