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Editor's Choice

Synthesis and Crystal Structures of 1,4,8,11-Tetraalkyl-6,13-diphenylpentacenes

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Two 1,4,8,11-tetraalkyl-6,13-diphenylpentacenes were prepared. X-ray analysis revealed that the methyl derivative had a herringbone arrangement with π-overlap, while the propyl derivative had a slipped-parallel structure without π-overlap. The solid-state order reflected UV–vis absorption spectra in the solid state.

Pentacene has attracted much attention as a p-type organic semiconductor, because of the high field-effect transistor (FET) mobilities of its crystals and thin films.[1] However, pentacene is insoluble in common organic solvents, and the development of solution-processing electronic devices is desired. Therefore, a number of soluble pentacene derivatives with substituents have been prepared.[2,3] For instance, Anthony et al. prepared a variety of 6,13-disubstituted pentacenes, whose substituents contained functionalized ethyne units. Interestingly, the substituents controlled the solid-state order that is a significant factor in the performance of FET devices.[3] Nuckolls et al. reported an X-ray crystal structure and a poor hole mobility ($8 \times 10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) of 6,13-diphenylpentacene,[2g] which had first been prepared in 1942.[4] We were impressed particularly by the unique crystal structure, which displayed that the pentacene cores in a column direction were arranged cofacially, although the long molecular axes of nearest neighboring acenes were orthogonal. Additionally, the intermolecular distance between pentacene planes was ca. 5.0 Å.[2g] As a result, there was no π-overlap between pentacene frameworks, but only edge-to-face interactions between phenyl and pentacene rings.

Since it is recognized that the solid-state order can significantly affect charge transport properties as well as intermolecular interactions, the control of stacking arrays of acene moieties is a critical issue for electronic devices. Recently, we prepared a series of alkyl-substituted tetracenes on the terminal benzene rings.[5] We found that the alkyl side chains had abilities to tune both molecular arrangements and photophysical properties in the solid state. To metamorphose the unique stacking pattern of 6,13-diphenylpentacene mentioned above, we introduced alkyl side chains onto the terminal A and E rings in pentacene (Figure 1). We report here the synthesis and crystal structures of 6,13-diphenylpentacene derivatives **1a** and **1b** having methyl and propyl groups, respectively, at the 1-, 4-, 8-, and 11-positions.

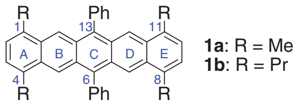
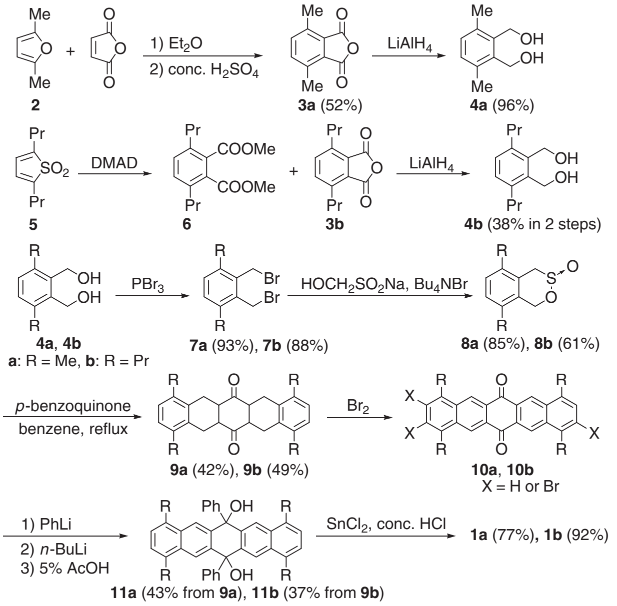


Figure 1. Structures of alkyl-substituted 6,13-diphenylpentacenes.



Scheme 1. Synthesis of pentacecenes **1a** and **1b**.

1a and **1b** were prepared as shown in Scheme 1.[6] First, we thought that the synthesis could be achieved via a reaction of PhLi and 1,4,8,11-tetraalkyl-6,13-pentacenequinones, which was prepared using a method proposed by Hanack et al.[7] Since the key intermediates were 3,6-dialkyl-1,2-bis(bromomethyl)benzenes **7a** and **7b**, we prepared the *o*-xylene-α,α'-diols **4a** and **4b** as precursors. The methyl derivative **4a** was prepared from a Diels–Alder reaction–dehydration sequence between 2,5-dimethylfuran (**2**) and maleic anhydride according to a literature procedure.[8] Although the propyl derivative **4b** could be obtained using the same procedure, the overall yield was poor (<20%) and the procedure was not always suitable for large-scale synthesis. We carried out an improved synthesis of **4b** using first a Diels–Alder reaction–desulfonation sequence between 2,5-dipropylthiophene-1,1-dioxide (**5**) and dimethyl acetylenedicarboxylate (DMAD) at 180 °C, which produced a mixture of phthalate ester **6** and phthalic anhydride **3b**, and subsequently, a $\mathrm{LiAlH_4}$ reduction. The *o*-xylene-α,α'-diols **4a** and **4b** were treated with $\mathrm{PBr_3}$ to give dibromides **7a** and **7b**, respectively. The reaction of **7a** and **7b** with $\mathrm{HOCH_2SO_2Na}$ (rongalite) in the presence of a catalytic amount of $\mathrm{Bu_4NBr}$ provided 1,4-dihydro-2,3-benzooxathiin-3-oxides **8a** and **8b**, which were *o*-quinodimethane synthetic equivalents.[9] Alkyl-substituted octahydropentacenequinones **9a** and **9b** were obtained by heating **8a** and **8b** with 0.4 equiv of *p*-benzoquinone in refluxing benzene. Next, oxidation of **9a** and **9b** with 10 equiv of $\mathrm{Br_2}$ resulted in not only

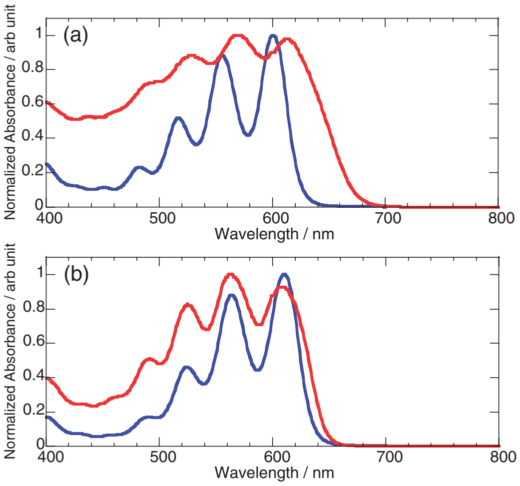


Figure 2. UV–vis absorption (blue in CH_2Cl_2 and red in KBr pellet) spectra of (a) **1a** and (b) **1b**.

dehydration but also bromination,[10] although the treatment of unsubstituted octahydropentacenequinone with Br_2 exclusively produced pentacenequinone.[7] EI-MS of the products showed the molecular ion peaks of monobromo-, dibromo-, and tribromo-pentacenequinones, indicating that the products consisted of a mixture of brominated pentacenequinones, **10a** and **10b**, their compositions, however, could not be defined. We tried reacting the bromide mixture with excess PhLi and *n*-BuLi, expecting nucleophilic addition by PhLi and halogen–lithium exchange by *n*-BuLi. The tandem addition of organolithium reagents was successful in isolating diols **11a** and **11b**.[11] Finally, **11a** and **11b** were reduced by $SnCl_2$ and conc. HCl to pentacenes **1a** and **1b**, respectively.

Both **1a** and **1b** were obtained as dark blue-purple solids. **1b** was soluble in CH_2Cl_2 and toluene and hardly soluble in acetone and hexane, while **1a** was more soluble in common organic solvents. Their solutions were unstable in the presence of both light and air. When the solids were exposed to air under room light, **1b** decomposed to a white solid in a few days; however, **1a** remained dark purple over one month. UV–vis absorption spectra in CH_2Cl_2 and the solid-state absorption (Kubelka–Munk) spectra in diluted KBr pellets of **1a** and **1b** are shown in Figure 2. The absorption spectra, both in solution and in the solid state, displayed structured bands. The absorption spectrum of **1a** in solution was similar to that of **1b**,[12] indicating that the alkyl side chain length hardly affected the pentacene conjugation system. On the other hand, there was a large difference in the solid-state absorption spectrum between **1a** and **1b**. Thus, the absorption maximum peaks of **1a** in the solid state were slightly red-shifted compared to those of **1b**, although the absorption maximum peaks of **1b** in the solid state were analogous to those in the solution.[13] Moreover, it was seen that the absorption edge in the solid state of **1a** was about 680 nm, and that of **1b** was approximately 650 nm. These results suggested that some strong intermolecular interactions between molecules were present in the solid state of **1a**.

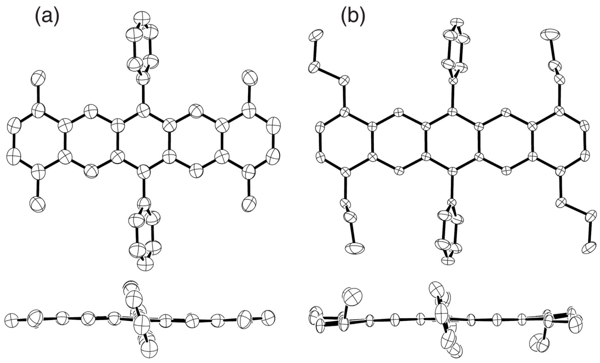


Figure 3. Molecular structures of (a) **1a** and (b) **1b**.

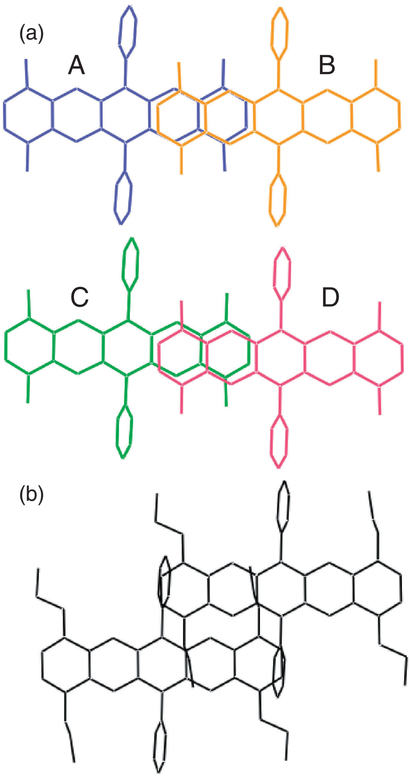


Figure 4. Stacking patterns of neighboring molecules of (a) **1a** and (b) **1b**. Each colored molecule represents a crystallographically independent unit.

To examine the effect of alkyl side chain groups on the molecular order in the solid state, X-ray analysis was performed.[14] Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene in the dark. Molecular structures, stacking patterns of two nearest neighboring molecules, and packing diagrams are shown in Figures 3–5. The crystal systems were monoclinic space group $C2/c$ with $Z = 16$ for **1a**, and triclinic space group $P\bar{1}$ with $Z = 1$ for **1b**. Molecules **1a** and **1b** each possess a center of symmetry, and halves of their formula units are crystallographically asymmetric. Interestingly, **1a** has four independent halves of the formula unit, which are similar to each other in the unit cell. All the pentacene rings are almost planar (Figure 3), and the average of the dihedral angles between the planes of benzene and pentacene in **1a** is 72.3°. On the other hand, the dihedral angle between the planes of benzene and pentacene in **1b** is 78.0°. The propyl groups have unique structural characters. Thus, a pair of propyl

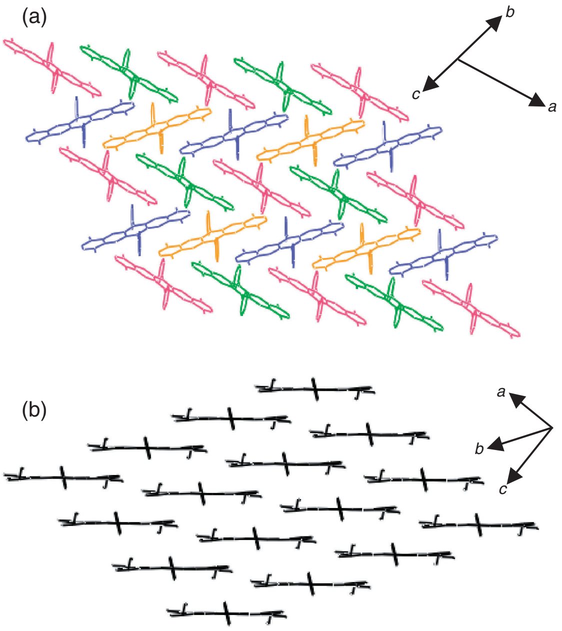


Figure 5. Packing diagrams of (a) **1a** and (b) **1b**.

groups at the 1- and 8-positions takes a coplanar conformation with the pentacene ring and another pair of propyl groups at the 4- and 11-positions extends upward and downward out of the pentacene plane. These conformations of propyl groups were the same as those in other oligoacenes.[5b,15]

The stacking patterns of **1a** and **1b** are essentially different, not only from that of 6,13-diphenylpentacene but also from each other (Figure 4). Obviously, there is π-overlap only for **1a**. Both the propyl and phenyl groups in **1b** are located over the pentacene ring. In contranst, neither the methyl nor phenyl groups in **1a** are located over the pentacene ring. The interplanar distances between pentacene rings are 3.46 Å (molecules A and B) and 3.52 Å (molecules C and D) for **1a**, and 3.51 Å for **1b**. The slip distances along the long molecular axis are 6.56 Å (molecules A and B) and 7.68 Å (molecules C and D) for **1a**, and 8.93 Å for **1b**. Additionally, the slip distances along the short molecular axis are 0.11 Å (molecules A and B) and 0.42 Å (molecules C and D) for **1a**, and 3.50 Å for **1b**. Thus, **1a** exhibits two kinds of π-overlap stacking patterns that slightly slipped along the molecular short axis. This can probably be ascribed to the red shift of the absorption spectrum of **1a** in the solid state.

The packing patterns of **1a** and **1b** are also completely different from that of 6,13-diphenylpentacene, as well as from each other (Figure 5). Molecule **1a** is stacked in a herringbone structure, in which a pair of molecules, A and B, and another pair of molecules, C and D, form respective stacks along the diagonal direction between the axes *a* and *b*. The average of the interplanar tilt angles between pentacene cores in two adjacent columns is 48.4°. Within the columns, there are edge-to-face interactions between the edge of the phenyl group in one column and the face of the pentacene in another column. On the other hand, the pentacene rings in **1b** adopt a slipped-parallel arrangement. The molecular order of **1a** may increase charge mobilities compared with 6,13-diphenylpentacene. Their applicability to FET device fabrication is under investigation.

In conclusion, we prepared 6,13-diphenylpentacene derivatives having alkyl side chains on the terminal benzene rings in pentacene. The presence of the alkyl groups at the *peri*-positions of the pentacene dramatically changed the packing pattern of 6,13-diphenylpentacene. The methyl derivative **1a** took the herringbone structure with π-overlap. In contrast, the propyl derivative **1b** had the slipped-parallel arrangement without π-overlap. The difference in stacking pattern was considered to be caused by the difference in solid-state absorption.

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10 Oxidation with DDQ did not proceed.

11 Usage of only PhLi produced a mixture of brominated diols.

12 Absorption maximum peaks in CH_2Cl_2; **1a**: 517, 557, and 601 nm; **1b**: 524, 564, and 610 nm.

13 Absorption maximum peaks in KBr pellet; **1a**: 536, 569, and 613 nm; **1b**: 525, 563, and 608 nm.

14 Crystal data for **1a**: $C_{38}H_{30}$, $M_r = 486.62$, $T = 203$ K, monoclinic, space group $C2/c$, $a = 29.249(2)$, $b = 17.048(1)$, $c = 24.879(2)$ Å, $\beta = 120.662(1)°$, $V = 10671.2(13)$ Å^3, $Z = 16$, $D_{\text{calcd}} = 1.212$ g cm^{-3}, 50356 reflections measured, 12160 unique, 686 parameters refined, GOF = 0.912, $R_1 = 0.090$ [$I > 2\sigma(I)$], $wR = 0.359$ (all data). CCDC-778535. Crystal data for **1b**: $C_{46}H_{46}$, $M_r = 598.83$, $T = 223$ K, triclinic, space group $P\bar{1}$, $a = 8.767(4)$, $b = 10.208(4)$, $c = 11.400(5)$ Å, $\alpha = 64.00(2)$, $\beta = 73.12(2)$, $\gamma = 73.54(2)°$, $V = 862.9(6)$ Å^3, $Z = 1$, $D_{\text{calcd}} = 1.152$ g cm^{-3}, 6697 reflections measured, 3780 unique, 210 parameters refined, GOF = 1.101, $R_1 = 0.079$ [$I > 2\sigma(I)$], $wR = 0.223$ (all data). CCDC-778536.

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