Preparation and Molecular Arrangement of Novel Pyrenophanes

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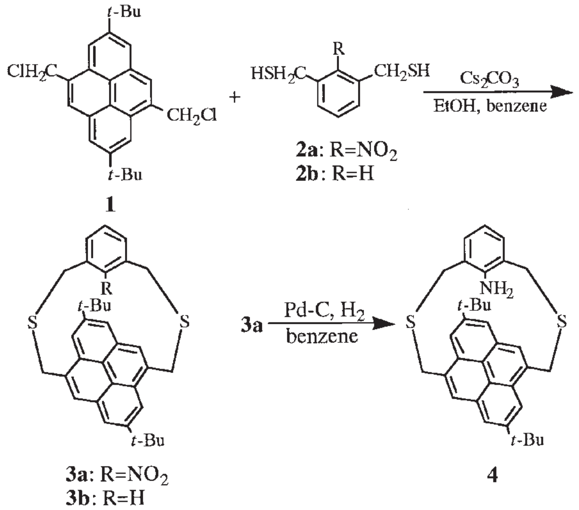
A stack and an offset stack geometrical arrangements based on the columnar structure have been confirmed for the molecular packing of novel pyrenophanes consisting of aniline unit or nitrobenzene unit, respectively, in contrast to a herringbone arrangement identified for the pyrenophane having benzene unit. Such a columnar stack arrangement is probably due to weak intermolecular interaction between the pyrene and the opposite aromatic component.

Small-sized cyclophane compounds can be characterized by aromatic components existing in close proximity each other.[1] By virtue of the π-system, the pyrene framework has been the subject of considerable experimental and theoretical interests. A number of the small-sized cyclophanes[2] consisting of the pyrene unit (pyrenophanes) have been investigated in terms of trans-annular π-electronic interaction of excimer fluorescence and charge-transfer interaction of donor-acceptor systems. During the past two decades intriguing noncovalent forces such as hydrogen-bonding,[3] CH-π interaction[4] and cation-π interaction[5] have been increasingly recognized to be important in chemistry and biochemistry. Inter- and intramolecular weak interactions based on these forces have been studied by our group, employing cyclophane systems as well-defined structures.[6,7] This could allow us to explore the nature of weak interactions involving the π-system of the pyrene component.

Thus, we report here the preparation of novel pyrenophanes having the nitro or the amino group on one aromatic ring and discuss their molecular packings in terms of weak interactions.



Bis(chloromethyl)pyrene **1** was prepared according to the reported method.[8] Cyclization of **1** and mercaptomethyl compound **2a** using Cs_2CO_3 as a base under highly dilute condition afforded the corresponding dithiapyrenophane **3a**[9] in 28% yield. The dithiapyrenophane **3b**[8] was also prepared by the similar method. **3a** was reduced with hydrogen gas in the presence of 10% Pd/C to give the amino compound **4**[10] in 15% yield. The reason for this low yield might be due to the steric hindrance of the pyrene ring for the nitro group.

In the NMR spectrum of **3a** the AB system for the protons of each methylene bridge and six kinds of singlets for the protons of the pyrene unit were observed. These results suggest that **3a** is fixed in an unsymmetrical conformation. On the contrary it has been reported[8] that the NMR spectrum of **3b** shows the pyrene unit as three kinds of singlets and the both methylene bridges as two AB systems, indicating that the benzene ring is fixed perpendicular to the pyrene unit at least in the solution. **4** exhibits NMR patterns very similar to those of **3a**.

The X-ray structural analysis of **3a**[11] is shown in Figure 1. As expected the nitrobenzene unit is almost parallel to the pyrene unit coinciding with the unsymmetrical patterns in the NMR spectrum. The nitro substituent is tilted against the aromatic plane probably due to the steric hindrance of bridging methylene neighboring to the aromatic ring. A similar conformation was obtained for **4**[12] as shown in Figure 2. Interestingly **3b** was also confirmed to assume the conformation similar to that of **3a** contrary to the conformation predicted by its NMR spectrum.

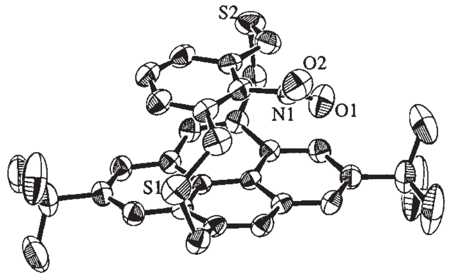


Figure 1. X-ray structure of **3a**.

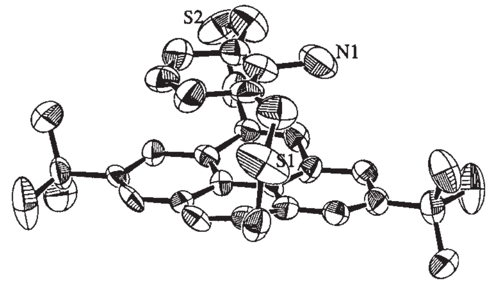


Figure 2. X-ray structure of **4**.

In spite of the similar conformation for **3a**, **3b**, and **4** characterized by the parallel orientation of two aromatic components, quite interestingly the modes of their molecular packings are distinct from each other. Figure 3 shows the molecular packings of **3a** and **4**. The molecular arrangement of **3a** can be considered as laterally shifted overlap which is known as a

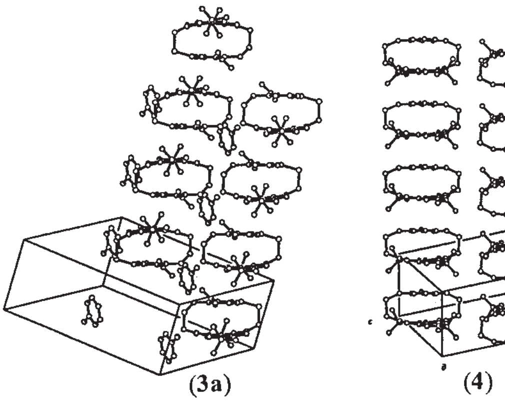


Figure 3. Molecular packings of **3a** and **4**.

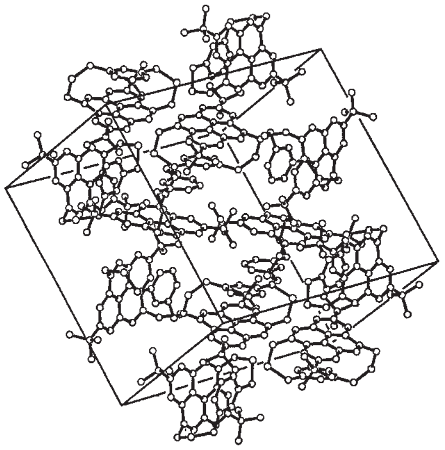
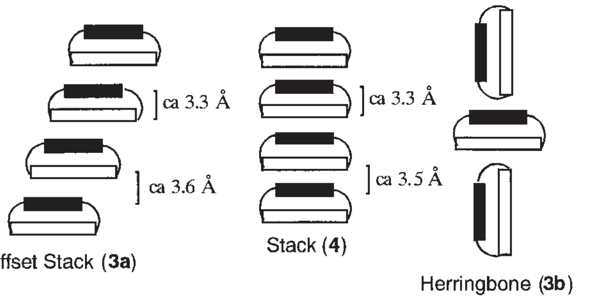


Figure 4. Molecular packing of **3b**.

"offset stacking". And a "stacking" arrangement resulted from face-to-face overlap of molecules was confirmed for **4**. On the contrary the molecules of **3b**[13] assembled into T-shaped "herringbone arrangement" as shown in Figure 4.

In order to clarify the mode of their molecular packings the schematic illustrations of **3a**, **3b**, and **4** were depicted in Scheme 1. It is known[14] that the preponderance of the herringbone arrangement in a very large majority of aromatic hydrocarbons might be attributed to edge-face interactions based on C(δ^-) and H(δ^+) nature. It also might be asserted that van der Waals forces are not solely to determine the packing arrangement, thus, some long-range interactions should be taken into account, which has to be related to the nature of the nitro and the amino group on the aromatic ring.

Concerning **3a** an intermolecular electrostatic interaction between the electron-deficient aromatic ring and electron-rich pyrene unit can be expected to promote the formation of the stacking arrangement with the distance between the molecules of ca. 3.6 Å. The slightly twisted nitro group might well predispose the face-to-face stacking toward inclined offset stacking owing to its steric hindrance. On the other hand, for **4** NH-π hydrogen bonding is supposed to work intermoleculary to prompt the face-to-face stacking. Such a hydrogen bonding is supported by the fact that the wavenumbers of the amino group in **4** observed at 3439 and 3369 cm^{-1} are lower than the corresponding wavenumbers of 3484 and 3400 cm^{-1} in 2,6-dimethylaniline. The distance between the molecules of 3.5 Å also implies attractive forces work in **4**.



Scheme 1. Packing arrangements of pyrenophanes.

These results obtained here therefore elucidate that the small-sized cyclophane system could provide unique facet in crystal engineering.

References and Notes

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9 Spectral data for **3a**. mp 260–262 °C (pale yellow prisms). ^{1}H NMR ($CDCl_3$, ppm): 1.62 (s, 9H); 1.63 (s, 9H); 2.93 (d, $J = 17.9$ Hz, 1H); 3.02 (d, $J = 17.9$ Hz, 1H); 3.08 (d, $J = 17.4$ Hz, 1H); 3.20 (d, $J = 17.4$ Hz, 1H); 4.13 (d, $J = 12.3$ Hz, 1H); 4.31 (d, $J = 12.5$ Hz, 1H); 4.69 (d, $J = 12.5$ Hz, 1H); 5.10 (d, $J = 12.3$ Hz, 1H); 6.14 (t, $J = 7.7$ Hz, 1H); 6.47 (d, $J = 7.7$ Hz, 1H); 7.06 (d, $J = 7.7$ Hz, 1H); 7.74 (s, 1H) 7.83 (s, 1H); 7.84 (s, 1H); 8.16 (s, 1H); 8.25 (s, 1H); 8.33 (s, 1H). MS-EI, m/z :553 (M^+).

10 Spectral data for **4**. mp 293–295 °C (colorless prisms). ^{1}H NMR ($CDCl_3$, ppm): 1.59 (s, 9H); 1.61 (s, 9H); 2.57 (d, $J = 16.8$ Hz, 1H); 2.75 (d, $J = 16.3$ Hz, 1H); 2.89 (d, $J = 16.3$ Hz, 1H); 2.90 (d, $J = 16.8$ Hz, 1H); 4.17 (d, $J = 12.6$ Hz, 1H); 4.31 (d, $J = 12.2$ Hz, 1H); 4.78 (d, $J = 12.2$ Hz, 1H); 5.08 (d, $J = 12.6$ Hz, 1H); 5.57 (t, $J = 7.6$ Hz, 1H); 6.19 (d, $J = 7.6$ Hz, 1H); 6.66 (d, $J = 7.6$ Hz, 1H); 7.74 (s, 1H) 7.77 (s, 1H); 7.82 (s, 1H); 8.12 (s, 1H); 8.30 (s, 1H); 8.38 (s, 1H). MS-EI, m/z: 523 (M^+).

11 Crystal Data for **3a**·toluene (recrystallized from toluene): $C_{41}H_{43}NO_2S_2$, M = 645.92, triclinic, space group P-1 (#2), $a = 15.906(4)$, $b = 16.662(5)$, $c = 7.0454(7)$ Å, $\alpha = 94.895(8)^\circ$, $\beta = 101.25(1)^\circ$, $\gamma = 107.00(1)^\circ$, $V = 1731.1(5)$ Å^3, $Z = 2$, $D_{calc} = 1.239$ g/cm^3, μ(CuKα) = 1.54 cm^{-1}, Rigaku AFC7R diffractometer, $R_1 = 0.0621$ (for 5656 reflections with $I > 3.0\sigma(I)$), $_wR_2 = 0.1423$ (for all data (6208 reflections)).

12 Crystal Data for **4** (recrystallized from CH_2Cl_2-MeOH): $C_{34}H_{37}NS_2$, M = 523.79, triclinic, space group P1 (#1), $a = 14.547(4)$, $b = 6.8097(9)$, $c = 16.174(3)$ Å, $\alpha = 94.895(8)^\circ$, $\beta = 101.25(1)^\circ$, $\gamma = 103.35(2)^\circ$, $V = 1399.4(5)$ Å^3, $Z = 2$, $D_{calc} = 1.243$ g/cm^3, μ(CuKα) = 1.54 cm^{-1}, Rigaku AFC7R diffractometer, $R_1 = 0.0842$ (for 3941 reflections with $I > 2.0\sigma(I)$), $_wR_2 = 0.1423$ (for all data (4651 reflections)).

13 Crystal Data for **3b** (recrystallized from $CHCl_3$-hexane): $C_{34}H_{36}S_2$, M = 508.78, orthohombic, space group Pbcn (#60), $a = 24.181(3)$, $b = 18.347(5)$, $c = 12.691(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 5630(4)$ Å^3, $Z = 8$, $D_{calc} = 1.200$ g/cm^3, μ(MoKα) = 0.7107 cm^{-1}, Rigaku AFC7R diffractometer, $R_1 = 0.0487$ (for 3760 reflections with $I > 3.0\sigma(I)$), $_wR_2 = 0.1348$ (for all data (6473 reflections)).

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