Unusual Conformational Isomer of 9,10-Dihydro-1,2,3,4,5,6,7,8-octapropylanthracene in Solid State

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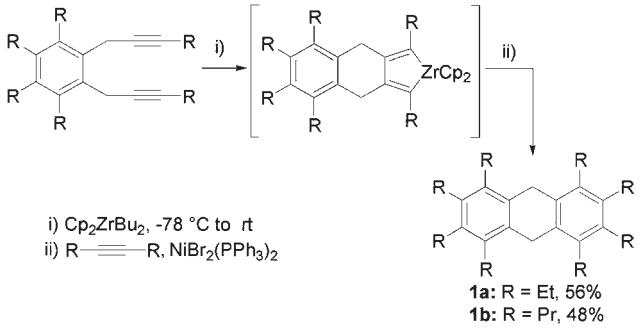
(Received July 5, 2002; CL-020556)

The unusual conformational isomer **1b(2)** of 9,10-dihydro-1,2,3,4,5,6,7,8-octapropylanthracene with three continuous propyl groups up was selectively prepared.

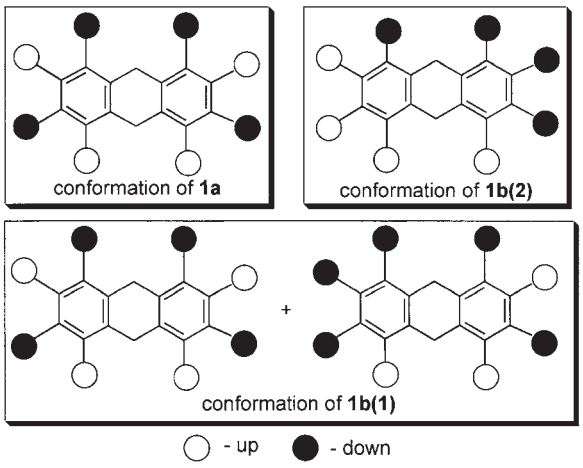
Conformational structures of alkyl groups in the multi alkyl substituted benzene rings in the solid state have been intensively investigated.[1–3] The conformation of the alkyl groups such as up and down based on the benzene ring plane is attractive since the conformational isomers can be distinguished in the solid states. Usually, the substituted benzene rings show the most stable conformation in the solid state and the alkyl groups take alternately up and down conformation.[1–3] Only in special cases with sterical requirement, two alkyl groups next each other were both up or down.[2c–2e] Therefore, it is difficult to prepare with three continuous alkyl groups up or down. In this paper, we would like to report the synthesis of 1,2,3,4,5,6,7,8-octaalkyl-9,10-dihydroanthracenes (**1**) and preparation of the conformational isomer with three continuous propyl groups up or down in 9,10-dihydro-1,2,3,4,5,6,7,8-octapropylanthracene **1b**.

Recently we have developed novel preparative method of variously substituted aromatic rings.[4] 1,2,3,4,5,6,7,8-Octaalkyl-9,10-dihydroanthracenes (**1a**: R = Et; **1b**: R = Pr) were prepared as shown in Scheme 1 using zirconocene complexes.



Scheme 1. Preparation of 1,2,3,4,5,6,7,8-octaalkyl-9,10-dihydroanthracenes.

The structure of 1,2,3,4,5,6,7,8-octaethyl-9,10-dihydroanthracene **1a** was verified by X-ray analysis. As shown in Figure 1,[5] all ethyl groups in **1a** in the aromatic rings were alternately up and down as expected, since the alternate structure is the most stable conformational isomer. It is interesting to note that the X-ray structure of the propyl analogue **1b(1)**, which was crystallized from chloroform/hexane, showed one Pr group among eight Pr groups disordered as shown in Figure 2.[6] This suggests that there are three continuous propyl groups simultaneously up in the crystal.



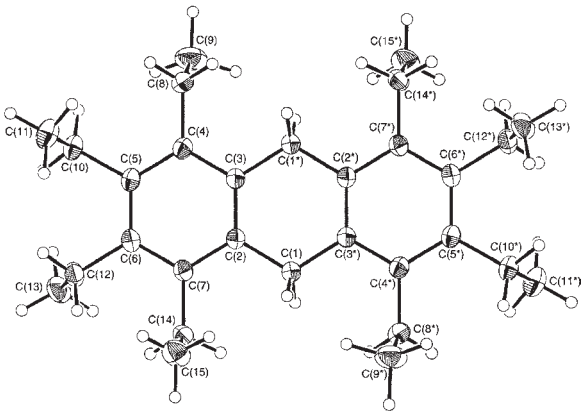


Figure 1. Perspective view of **1a**.

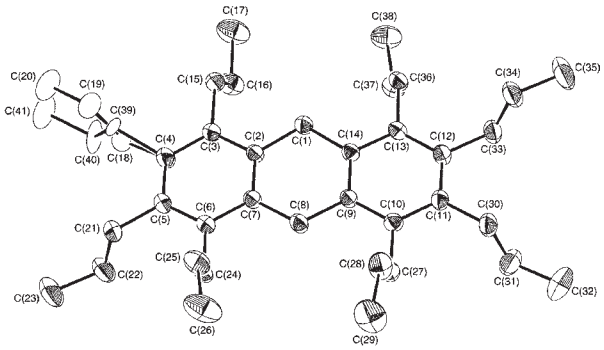


Figure 2. Perspective view of **1b(1)**.

In order to obtain the different type of crystals of **1b**, we carried out recrystallization from various kinds of solvents. And interestingly, the powder X-ray spectrum of **1b** crystallized from THF showed that a different type of crystals **1b(2)** was selectively formed. To our surprise, the X-ray analysis of **1b(2)** indicated that three continuous propyl groups were simultaneously up or down in both aromatic rings as shown in Figure 3.[7]

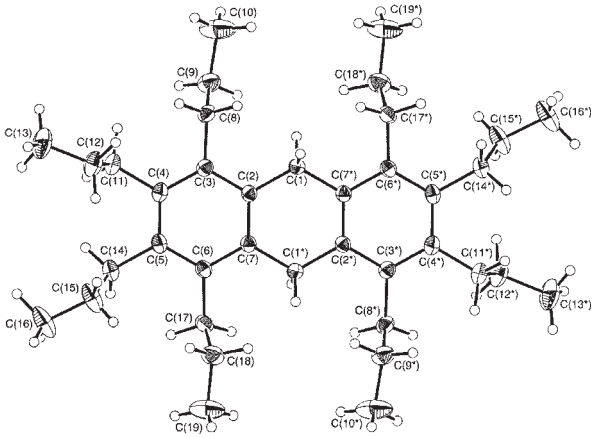


Figure 3. Perspective view of **1b(2)**.

It is unusual that the unstable conformational isomer **1b(2)** was formed by crystallization from THF selectively, though Pr group is considered to have similar character with Et groups in the hexa-substituted benzene.[8] However, the distances between molecules in **1a** and **1b(2)** were different and also crystal packings in a unit cell were distinct as shown in Figure 4 and 5. The distances between two molecular planes of **1a** and **1b(2)** were 4.89 Å and 3.60 Å, respectively. The molecules in **1b(2)** are stacked well and the intermolecular interaction in **1b(2)** seems to be stronger than that in **1a**. This unusual conformational isomer is stabilized by the intermolecular interaction in the crystal packing. The conformational isomer of **1b(2)** with three alkyl groups simultaneously up or down is unprecedented.

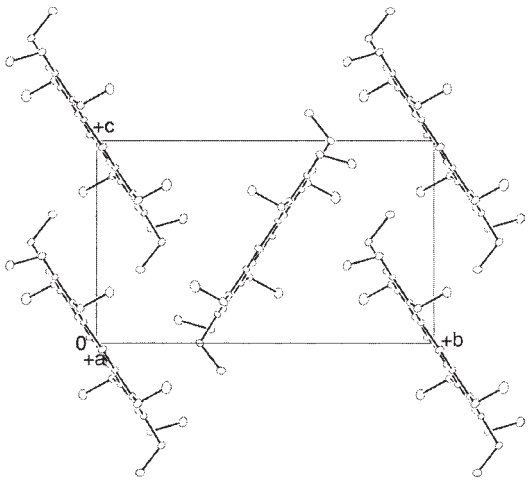


Figure 4. Crystal packing of **1a** in the unit cell.

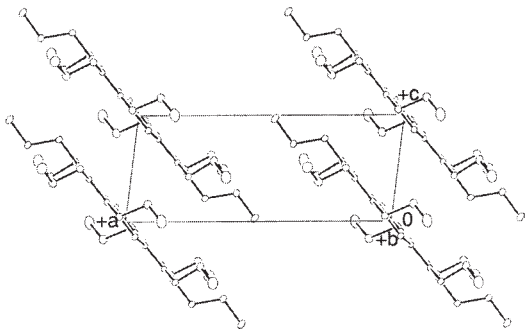


Figure 5. Crystal packing of **1b(2)** in the unit cell.

References and Notes

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5 Crystal data for **1a**: $C_{30}H_{44}$ $M_w = 404.68$, monoclinic, $P2_1/c$, $a = 9.6071$ Å, $b = 14.7192$ Å, $c = 8.8556$ Å, $\beta = 95.375°$, $V = 1246.8$ Å^3, $Z = 2$, $D_{calcd} = 1.078$ g cm^{-3}, $T = 298$ K, Cu Kα, A total of 2632 reflections were measured in which 2366 were independent ($R_{int} = 0.007$). $R = 0.049$, and $R_w = 0.072$ for 2022 observed reflections with $I > 2\sigma(I)$.

6 Crystal data for **1b(1)**: Mp 131.3–143.9 °C, $C_{38}H_{60}$ $M_w = 516.89$, triclinic, $P\bar{1}$, $a = 13.010$ Å, $b = 15.713$ Å, $c = 9.3455$ Å, $\alpha = 93.390°$, $\beta = 107.272°$, $\gamma = 104.390°$, $V = 1748.7$ Å^3, $Z = 2$, $D_{calcd} = 0.982$ g cm^{-3}, $T = 298$ K, Cu Kα, A total of 7292 reflections were measured in which 6604 were independent ($R_{int} = 0.011$). $R = 0.069$, and $R_w = 0.098$ for 3736 observed reflections with $I > 2\sigma(I)$.

7 Crystal data for **1b(2)**: Mp 128.8–130.1 °C, $C_{38}H_{60}$ $M_w = 516.89$, triclinic, $P\bar{1}$, $a = 12.922$ Å, $b = 13.281$ Å, $c = 5.0635$ Å, $\alpha = 92.308°$, $\beta = 96.426°$, $\gamma = 104.823°$, $V = 832.6$ Å^3, $Z = 1$, $D_{calcd} = 1.031$ g cm^{-3}, $T = 298$ K, Cu Kα, A total of 3634 reflections were measured. $R = 0.050$, and $R_w = 0.073$ for 2537 observed reflections with $I > 2\sigma(I)$.

8 The conformation of alkyl groups in hexaethylbenzene and hexapropylbenzene has been recognized to be remarkably similar, G. Hunter, T. J. R. Weakly, and W. Weissensteiner, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 1633.