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Efficient synthesis and conformational investigations of cis-pentacenediols

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Abstract
Diisobutylaluminum hydride is utilized to reduce pentacene-6,13-diones to the corresponding diols, useful precursors to functionalized pentacenes. This pathway is mild and efficient, and produces the cis-diols as major products. Further, we found the cis-diols adopt endo conformation, which cannot flip to the exo conformation under ambient conditions. Due to the cis and endo orientation, the cis-diols can be potential bidentates in catalysis, molecular propellers, and optoelectronic devices.

Keywords: Pentacene, Pentacenediol, Reduction of pentacenedione, Diisobutylaluminum hydride, Low-temperature NMR

Pentacene, the work horse in the field of organic field-effect transistors, is prepared from pentacene-6,13-dione via two pathways, either a one-step reaction with Al-Hg amalgam,1,2 or by a stepwise conversion involving metal hydride reduction to 6,13-dihydropentacene-6,13-diol, followed by aromatization with tin chloride.3,4 Because of the health and environmental risks involved in the use of mercury, the former methodology has almost been phased out in industry, and is only occasionally executed in research labs. Compared with the former, the latter proceeds in a reproducible and clean fashion, and hence is dominant in the literatures. Metal hydrides, such as, KBH4, NaBH4, and LiAlH4, are able to deliver good results with pentacene-6,13-dione;3,5 however, they fail to reduce 2,3-dibromopentacene-6,13-dione, a useful intermediate in the synthesis of functionalized pentacenes.5,6 Herein we report diisobutylaluminum hydride (DIBAH) as a useful reagent for reduction of pentacenediones. Easily handled DIBAH is mild, and very useful in reducing carbonyl functionality.7–10 but its application with pentacene-6,13-dione has not been investigated so far. As discussed later, this methodology delivers the cis-diol as the major product, and therefore the cis-diol can be separated as a pure isomer (Scheme 1). In view of the two hydroxyls’ specific orientation and the two flanking naphthyl moieties, we envision the cis-diols as useful bidentates to coordinate with suitable centers, and thus to have potential applications in catalysis, molecular propellers, and/or optoelectronic devices.

Our efforts to reduce 2,3-dibromopentacene-6,13-dione with metal hydride revealed that neither NaBH4 nor LiAlH4 was effective, even at elevated temperatures, but DIBAH readily realized this.11,12 We attribute this to the excellent solubility of DIBAH. In contrast, it has been reported that a successful reduction of the unsaturated pentacene-6,13-dione needs a stepwise addition of KBH4 over a period of 10-days.3 Very likely, the metal hydrides suffered because of their poor solubility in the system.

In order to better understand the reactivity of DIBAH within this system, we further investigated the reduction of the unsubstituted pentacene-6,13-dione as a model substrate. Compared with literatures,5,9–11 our procedure with DIBAH offers conveniences in handling and stoichiometric addition. Furthermore, it is mild and efficient—in less than 2 h, and at rt, the reaction is complete, producing an approximately 2:1 mixture of the cis and trans isomers of 6,13-dihydropentacene-6,13-diol with good yield (the major product was assigned based on a previous report).12 Very likely, the metal hydrides suffered because of their poor solubility in the system.

The
gin can date back to the mono-adduct D, which adopts a puckered conformation along its 6 and 13 carbons with a dihedral angle being 160°. As a result of this conformation, the second hydride is delivered from the \textit{exo} face to furnish the \textit{endo} alcohol. In fact, our calculation suggests an energy difference of 0.13 eV between the second transition states. Hence the \textit{cis} isomer is a dominant product.

Our careful assignment of the $^1$H NMR spectra of 6,13-dihydropentacene-6,13-diol leads to another finding that differs from a previous report.\textsuperscript{4} The \textit{cis}-diole is expected to have five peaks in the $^1$H NMR spectrum: three signals for aromatic hydrogens, one for the carbinol CH, and another one for the hydroxyl groups. And the expected relative integration ratio should be 4:4:4:2:2. In various deuterated solvents such as THF-$d_8$, CDCl$_3$, acetone-$d_6$, and DMSO-$d_6$, we found that the three aromatic hydrogen peaks are in good agreement with the literature, but a difference arose in the assignments for the carbinol CH and the OH groups. For example in acetone-$d_6$, these two very peaks for \textit{cis} isomer are at 5.91 and 5.67 ppm, respectively. As shown in Figure 1, the \textit{cis} isomer is predicted to adopt the \textit{endo} conformation. The disparity between our observations and that reported led us to investigate whether the pentacene-diol could exist as both \textit{endo}- and \textit{exo}-conformers and how easily these could interconvert. To answer these questions, we performed a series of NMR experiments on the \textit{cis} isomer at varying temperatures at 600 MHz. In $^1$H NMR, all peaks kept their chemical shift with varying temperatures, except one, the hydroxylic hydrogen, which migrated dramatically from 5.67 ppm at 298 K to 6.44 ppm at 205 K (Figure 3). However, no change was observed in the $^{13}$C spectra over the same temperature range, suggesting the $^1$H signal change for the OH is not associated with major conformational changes in the dihydropentacene skeleton. We suspect the change is probably due to the temperature-dependent geometry of hydrogen-bonding.\textsuperscript{17} As we did not observe the CH peak resolving into two peaks at a low temperature of 205 K, it could be either that at 205 K, the isomeric flip is too fast for the NMR window to detect or that only \textit{endocis} isomer exists and no flipping occurs at all. Our verdict favors the latter one. As shown in Scheme 1, the \textit{endocis} isomer can be viewed as a boat conformation of cyclohexane with 4 sp2 carbons on sides. Consequently, flipping between \textit{exo} and \textit{endo} conformations, if any, probably involves extreme energy. Collectively, our results suggest that the...
DIBAH reduction of pentacenediones selectively furnishes the cis-6,13-diol as a single major conformer displaying only one carbinol CH peak in $^1$H NMR.

In summary, DIBAH is effective at converting pentacene-6,13-diones into 6,13-dihydropentacene-6,13-diols. This trans-formation proceeds with good selectivity for production of the cis-isomer, which can be isolated in pure form. Considering the specific orientation of hydroxyl functionality and the two rigid conjugated flanks, we foresee that the cis-diol isomer will possibly find applications in catalysis, molecular propellers, and optoelectronic devices. This pathway is likely to be applicable as a means of reducing other functionalized pentacenediones, and we are now actively pursuing in that direction.

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References and notes

11. Synthesis of 6,13-dihydro-pentacene-6,13-diol: To a suspension of pentacene-6,13-dione (308.3 mg, 1 mmol) in anhydrous THF (30 mL) was added dropwise DIBAH in toluene (1.5 M, 2 mL). The reaction mixture was then stirred at rt for 2 h, followed by addition of saturated aqueous Rochelle’s salt solution (25 mL). The resulting mixture was stirred at rt for another 2 h. Filtration and copious washing with distilled water and CH$_2$Cl$_2$ gave an orange solid (250 mg, 80%). NMR confirmed this orange solid is a mixture of cis-6,13-dihydronitracene-6,13-diol ($^1$H NMR, cis/trans, 2:1). HRFAB: calcd for C$_{22}$H$_{16}$O$_2$: 312.1151; found 312.1140.

Careful purification of this mixture one time with column chromatography (eluent: Hex/EtOAc, 4:1) resulted in pure cis-6,13-dihydronicene-6,13-diol (75 mg, 24%). Mp, 230 °C (decomp.).$^1$H NMR (400 MHz, acetone-$d_6$): 8.82 (4H, s), 7.94 (4H, m), 7.48 (4H, m), 5.91 (2H, d, $J = 6.8$ Hz), 5.64 (2H, d, $J = 7.0$ Hz); $^{13}$C NMR (100 MHz, acetone-$d_6$): 139.2, 133.6, 128.7, 126.6, 122.9, 68.4; $^1$H NMR (400 MHz,
THF-$d_8$): 8.17 (4H, s), 7.87 (4H, m), 7.40 (4H, m), 5.77 (2H, d, $J = 7.5$ Hz), 5.59 (2H, d, $J = 7.8$ Hz); $^{13}$C NMR (100 MHz, THF-$d_8$): 139.4, 133.7, 128.5, 126.2, 122.4, 69.2. $^1$H NMR (400 MHz, CDCl$_3$): 8.08 (4H, s), 7.90 (4H, m), 7.53 (4H, m), 5.90 (2H, d, $J = 7.1$ Hz), 3.30 (2H, d, $J = 7.1$ Hz); HRFAB: calcd for C$_{22}$H$_{16}$O$_2$, 312.1151; found 312.1165.

Trans-6,13-dihydropentacene-6,13-diol: NMR spectra were obtained via spectrum subtraction. $^1$H NMR (400 MHz, acetone-$d_6$): 8.10 (4H, s), 7.89 (4H, m), 7.45 (4H, m), 6.15 (2H, m), 5.08 (2H, m); $^{13}$C NMR (100 MHz, acetone-$d_6$): 139.3, 133.8, 128.5, 126.7, 125.2, 70.5; $^1$H NMR (400 MHz, CDCl$_3$): 8.14 (4H, s), 7.91 (4H, m), 7.52 (4H, m), 6.22 (2H, d, $J = 5.8$ Hz), 2.28 (2H, d, $J = 5.8$ Hz).

12. Synthesis of 2,3-dibromo-6,13-dihydropentacene-6,13-diol: 2,3-dibromopentacene-6,13-dione (116 mg, 0.25 mmol) was used to prepare the target molecule, following a similar procedure as described in Note 11. Filtration and copious washing with distilled water and CH$_2$Cl$_2$ gave an orange solid. The solid was stirred with THF (20 mL) and the resulting suspension was filtered. Addition of CH$_2$Cl$_2$ (20 mL) to this THF filtrate resulted in an orange solid ($cis$, 30 mg, 25%). Further chromatographic purification on the residue failed to separate the trans-isomer due to its very limited solubility. $^1$H NMR (400 MHz, THF-$d_8$): 8.31 (2H, s), 8.17 (s, 2H), 8.15 (s, 2H), 7.88 (m, 2H), 7.41 (m, 2H), 5.77–5.72 (m, 2H); $^{13}$C NMR (100 MHz, THF-$d_8$): 141.6, 138.9, 133.8, 133.5, 133.2, 128.6, 126.4, 122.5, 121.9, 121.5, 69.1, HRFAB: calcd for C$_{22}$H$_{10}$Br$_2$O$_2$, 467.9361; found 467.8355.

13. Experimental details in theoretical calculation: The reaction pathway is investigated using the density functional theory (DFT) method. The B3LYP exchange-correlation functional is used. The C, H, Al, and O atoms are treated with the 6-31g (d,p) basis set. All minima and transition states are confirmed via harmonic vibrational frequency calculations. All calculations are performed using the GAUSSIAN 03 software package.


Supplementary data follows.
Supporting Information for:

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Figure S2: $^{13}$CNMR of cis-6,13-dihydropentacene-6,13-diol (100 MHz, acetone-$d_6$)
Figure S3: $^1$HNMR of mixture of trans and cis-6,13-dihydroptacene-6,13-diol (400 MHz, acetone-$d_6$) after D$_2$O exchange, where OH peak does not show up
Figure S4: $^{13}$C NMR of mixture of trans and cis-6,13-dihdropentacene-6,13-diol (100 MHz, acetone-$d_6$)
Figure S5: $^1$HNMR of cis-2,3-dibromo-6,13-dihydropentacene-6,13-diol (400 MHz, THF-$d_8$). The insert is the NMR after $D_2O$ exchange, where the hydroxylic hydrogen peak is absent.
Figure S6: $^{13}$CNMR of cis-2,3-dibromo-6,13-dihydropentacene-6,13-diol (100 MHz, THF-$d_8$)