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Synthesis and thermolysis of a Diels–Alder adduct of pentacene and thiophosgene

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Abstract—Pentacene has excellent semi-conducting properties but its practical use in organic thin film transistors (OTFTs) gives rise to a lot of problems caused by its sensitivity to oxygen and its very low solubility. In order to solve the problems involved in the use of pentacene, we have synthesized a Diels–Alder adduct of pentacene with thiophosgene.

1. Introduction

During the last few years, the development of organic thin film transistors (OTFTs) has attracted much interest. The production of OTFTs has been studied because organic molecules offer the opportunity of deposition over large surface areas and are compatible with flexible plastic substrates. A number of organic compounds have been proposed for use in light-emitting diodes, field-effect transistors and photovoltaic cells.[1] Pentacene, which is commercially available but expensive, has shown good field effect mobilities on vacuum-deposition.[2] However, pentacene has some drawbacks. Firstly, its poor solubility necessitates the use of vacuum systems for deposition. Secondly, pentacene is very sensitive to oxidation leading to rapid degradation of the material unless manipulated under rigorous exclusion of oxygen.

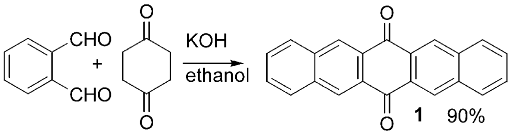
One can overcome these problems by preparing a precursor of pentacene by Diels–Alder reaction. Such a precursor is soluble and can be reconverted to pentacene by a retro-Diels–Alder reaction. Because of the solubility and the stability of the precursor, simple methods like spincoating can be used for deposition and the product can be conveniently stored and handled. This pathway was first proposed by Mullen and Herwig.[3] His product however displayed a relative high conversion temperature (200 °C) and required a multistep synthesis.

2. Results and discussion

In order to prepare the Diels–Alder adduct of pentacene, we first looked for a suitable way to prepare our starting material, pentacene itself. The most widespread method to prepare pentacene was first described by Bruckner and Tomasz[4] in 1961. Firstly, pentacenequinone (**1**) is prepared by condensation of *o*-phthalaldehyde and 1,4-cyclohexanedione (Scheme 1). This is a high yielding reaction and the starting materials are cheap and readily available.

Secondly, the pentacenequinone can be reduced to pentacene (**4**) with Al-amalgam. Because of the health and environmental risks involved in the use of mercury, we have been looking for an alternative reduction process of the quinone **1**, proceeding in a reproducible and clean way. $LiAlH_4$ was found to give the best results (Scheme 2).[5]

When we have a closer look at the reaction sequence, we see that there are two successive steps needed to obtain



Scheme 1.

Keywords: Pentacene; OTFTs; Diels–Alder adduct; Thiophosgene.

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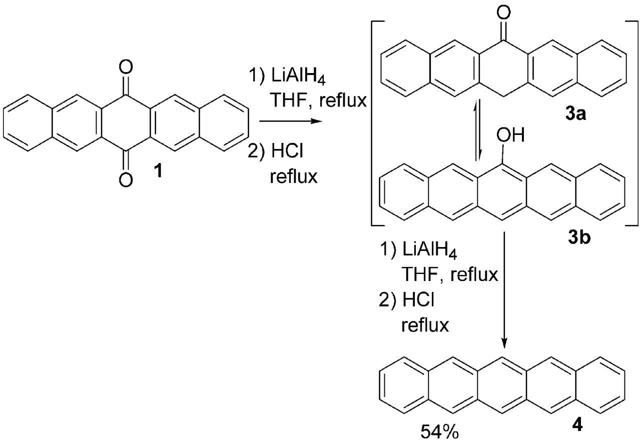
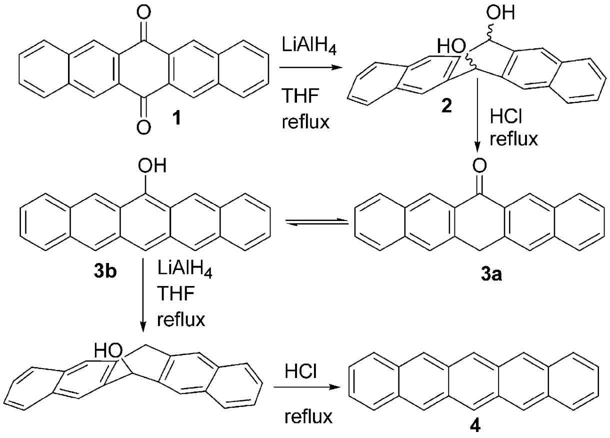
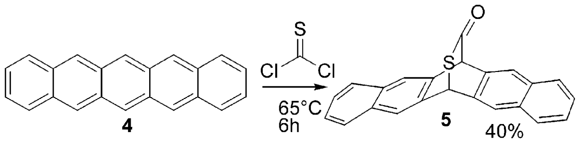


Scheme 2.



Scheme 3.

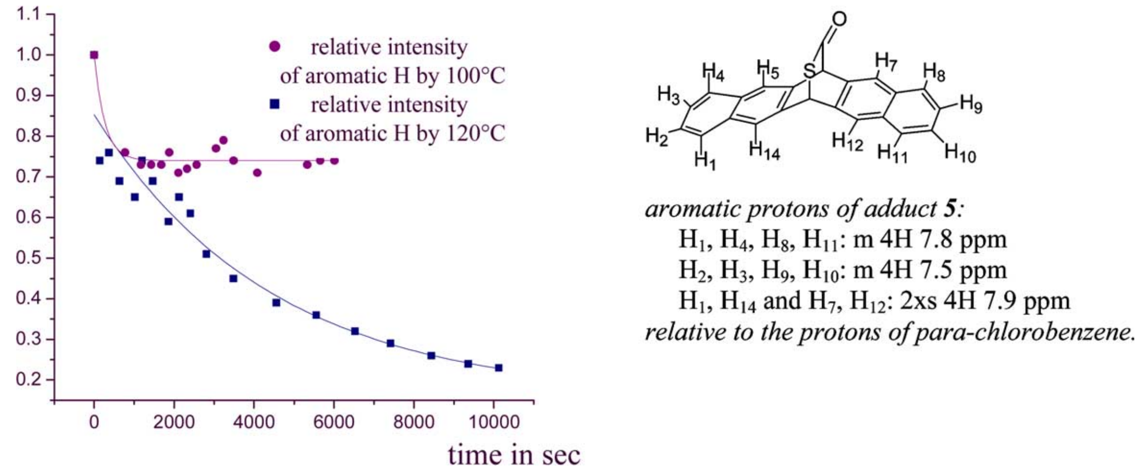
the pentacene, each consisting of a reduction followed by elimination of water (Scheme 3). We studied this sequence in detail and observed the formation of the products **2** and **3a**–**b**.[6] Thus, first the two carbonyl groups of **1** are reduced to alcohols. Upon acidification, water is expelled from diol **2**, affording **3a**–**b**. Diol **2** could be isolated as a mixture of *cis*- and *trans*-isomers when the reduction reaction was worked up carefully only with acetic acid. Ketone **3a** is formed together with the corresponding enol 6-hydroxypentacene (**3b**). The latter is insoluble and can not be characterized with NMR-spectroscopy. However, we suspect its existence because in the mass spectra, the same *m*/*z* value was observed for the molecular ion of the soluble yellow ketone **3a** and a purple, highly insoluble residue from the same reaction mixture. The second reduction step, that was carried out on the crude mixture containing **3a** and **3b**, gave pentacene. The amount of pentacene obtained is larger than the amount of **3a** that can be isolated after the first step, indicating that **3b** is present and can be reduced, probably after tautomerisation to **3a**.



Scheme 4.

To circumvent the purification problems associated with pentacene, a soluble Diels–Alder adduct has been prepared and purified. After deposition by spincoating, the adduct can be converted to pentacene by inducing a retro-Diels–Alder reaction by heating the sample. We made a Diels–Alder adduct in one step by reacting pentacene with readily available thiophosgene (Scheme 4).[7] After trying several conditions, the best results were obtained using thiophosgene as a solvent while heating at 65 °C. The primary Diels–Alder adduct could not be isolated. All attempts resulted in the formation of the hydrolysed derivative.

During the completion of our studies, another Diels–Alder adduct for the use in transistors, which has been made in one step from pentacene and *N*-sulfinylacetamide, has been reported.[8]



aromatic protons of adduct ***5****:*
H$_1$, H$_4$, H$_8$, H$_{11}$: m 4H 7.8 ppm
H$_2$, H$_3$, H$_9$, H$_{10}$: m 4H 7.5 ppm
H$_1$, H$_{14}$ and H$_7$, H$_{12}$: 2xs 4H 7.9 ppm
relative to the protons of para-chlorobenzene.

Figure 1. Investigation of the retro-Diels–Alder reaction of product **5** by ^{1}H NMR-spectroscopy in deuterated tetrachloroethane with *para*-dichlorobenzene as an internal standard.

The thermolysis of adduct **5** was studied by ^{1}H NMR spectroscopy. At 100 °C, the reaction reaches an equilibrium at a conversion of 25%. However, the retro-Diels–Alder reaction reached a 75% conversion after approximately 3 h at 120 °C (Fig. 1).

3. Conclusions

We can conclude that we found a new, environmentally friendlier method to reduce pentacenequinone to pentacene. A Diels–Alder adduct with thiophosgene and pentacene was prepared and thermolysis to regenerate pentacene was found possible at temperatures exceeding 120 °C.

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References and notes

1. Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359–369.
2. Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Trans. Electron Dev.* **1997**, *44*, 1325–1331.
3. Herwig, P. T.; Müllen, K. *Adv. Mat.* **1998**, *11*, 480–483.
4. Bruckner, V.; Tomasz, J. *Acta. Chim. Hung.* **1961**, *28*, 405–408.
5. *Synthesis of pentacene* (**4**): $LiAlH_4$ (0.98 g, 25 mmol) was added to a ice-cooled suspension of pentacenequinone (2.0 g, 6.5 mmol) in dry THF (100 mL) under argon atmosphere. The suspension was refluxed for 30 min. The mixture was cooled to room temperature and HCl (6 M, 60 mL) was added under cooling with ice. The mixture was then refluxed for another 3 h. The residue was filtered, washed with water (2 × 30 mL), dichloromethane (2 × 30 mL), MeOH (2 × 30 mL) and diethyl ether (2 × 30 mL) and after drying again treated with $LiAlH_4$ (0.98 g, 25 mmol). The same procedure was repeated. The pure pentacene was filtered and washed with water (2 × 30 mL), dichloromethane (2 × 30 mL), MeOH (2 × 30 mL) and diethyl ether (2 × 30 mL). After drying in vacuo, pentacene was obtained in 54% yield.Melting point: >300 °C (dec); Mass Spectrum (MH^+): *m/z* 279. The spectral characteristics (UV–vis) are in agreement with the literature.[9]
6. *Synthesis of 6,13-dihydropentacene-6,13-diol* (**2**): To a suspension of pentacenequinone (2.0 g, 6.5 mmol) in dry THF (100 mL) was added $NaBH_4$ (1.06 g, 29 mmol). After refluxing the mixture overnight, it was acidified with acetic acid while cooling with ice. After extraction with dichloromethane (200 mL), drying over $MgSO_4$ and evaporation in vacuo, the product was isolated by column chromatography of the residue on silica gel using CH_2Cl_2/EtOAc (95:5). The diol was obtained in 51% yield as a mixture of the *cis*- and *trans*-isomers (35:65). Melting point: 171 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ *trans*-isomer 5.8, 6.6 (2 × d H6, H13), 7.5 (m H2, H3, H9, H10), 7.9 (m H1, H4, H8, H11), 8.1 (s H5, H7, H12, H14); δ *cis*-isomer 6.0, 6.1 (d, d H6, H13); ^{13}C NMR (75 MHz, $CDCl_3$) δ 60.4, 125.0, 126.4, 127.9, 133.0, 136.9; mass spectrum (MH+): *m/z* 313. Synthesis of 6,13-*Dihydropentacen*-6-*one* (**3**): $NaBH_4$ (0.5 g, 14.5 mmol) was added to an ice-cooled suspension of pentacenequinone (1.0 g, 3.3 mmol) in dry THF (50 mL) under argon atmosphere. The suspension was heated at reflux overnight. The mixture was cooled to room temperature and HCl (6 M, 30 mL) was added under cooling with ice. The mixture was then heated at reflux for another 3 h. The residue was filtered, washed with water (2 × 30 mL) and dichloromethane (2 × 50 mL). The filtrate was taken aside and the two layers were separated. The organic layer was washed with water (3 × 50 mL), dried over $MgSO_4$ and evaporated in vacuo. After column chromatography on silica gel using petroleum ether/CH_2Cl_2/EtOAc (55:40:5), 6,13-dihydropentacen-6-one was isolated in 11% yield.
   Melting point: 274 °C (Clar, E., *Chem. Ber.*, **1949**, *82*, 495–514); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.7 (s 2 × H13), 7.5 (t H2, H10), 7.6 (t H3, H9), 7.9 (d H1, H11), 8.0 (s H12, H14), 8.1 (d H4, H8), 9.1 (s H5, H7); ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.6, 126.1, 126.7, 127.1, 128.6, 129.4, 129.9, 130.3, 131.9, 135.6, 185.4; mass spectrum (MH^+): *m/z* 295.
7. *Synthesis of Diels–Alder adduct* (**5**): A suspension of pentacene (0.46 g, 1.6 mmol) in thiophosgene (2 mL) was heated at 65 °C for 6 h. After cooling to room temperature, dichloromethane (2 mL) was added to the reaction mixture and the unreacted pentacene was removed by filtration. The filtrate was evaporated. Then toluene (2 × 40 mL) was added and again evaporated in order to remove all thiophosgene. The product was purified by column chromatography on silica gel using CH_2Cl_2/petroleum ether (50:50). The white adduct was obtained in 40% yield.
   Melting point:/decomposition starting at 100 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.5 (s, H13), 5.8 (s H6), 7.5 (m H2, H3, H9, H10), 7.8 (m H1, H4, H8, H11), 7.9 (2 × s H5, H7 and H12, H14); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.8, 125.2, 126.7, 126.8, 127.8, 127.9, 132.3, 132.6, 134.4, 137.7; Mass spectrum (MH^+): *m/z* 339.
8. (a) Afzali-Ardakani, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812–8813; (b) Afzali-Ardakani, A.; Dimitrakopoulos, C. D.; Graham, T. O. *Adv. Mater.* **2003**, *24*, 2066.
9. Goodings, E. P.; Mitchard, D. A.; Owen, G. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1310–1314.