A One-Step Synthesis of a Poly(iptycene) through an Unusual Diels–Alder Cyclization/Dechlorination of Tetrachloropentacene

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There is a continuous interest in polycyclic aromatic compounds mostly as materials for optoelectronic applications (LED, FET, photovoltaics, etc.), but also as building blocks in construction of supramolecular systems such as fullerenes, nanotubes, and triptycenes (tribenzo[2.2.2]bicyclohexadiene, Tr).1 In the latter, the intramolecular cavities allow for strong, noncovalent binding to suitably sized species, which can be used in sensing of, e.g., nitric oxide.2 Even more specific cavities have been synthesized with dendritic molecules, “superiptycenes”, containing up to nine Tr units connected by rigid benzene rings.3 Recently, the special geometry of Tr was recognized as a way to control the supramolecular architecture in liquid crystals and polymer matrices.4 Several polymers incorporating iptycene moieties, connected by (phenylene ethynylene) or (phenylene vinylene) units, have been synthesized and shown to possess improved order and electronic properties.5 To the best of our knowledge, there was only one preliminary report on polymers incorporating triptycene as the only repeating unit.5b In principle, it can be constructed via [4 + 2] cycloaddition of dienes and dienophiles

Figure 1. Thermal gravimetric analysis monitoring of the thermal decomposition of Cl4Pn.

Figure 2. UV–vis–NIR spectra of thin films of Cl4Pn and its pyrolysis products, PP1 and PP2.

Figure 3. (a) CP and (b) NQS MAS 13C NMR spectra of PP1.
the absence of oligomer molecular fragments in the mass spectra, and the elemental analysis showing precise loss of two chlorine atoms suggest a polymerization rather than a short-length oligomerization. At higher temperatures, it is unlikely to have a selective polymerization direction; i.e., an initial “dimer” may act as both a diene and a dienophile. Consequently, hyperbranching polymerization, competing with linear chain growth, should give an extended 2D structure of poly(iptycene).

Loss of the two residual chlorine atoms above 600 °C is accompanied by gradual dehydrogenation (as evidenced by elemental analysis), resulting in a highly conducting material (pressed pellet elemental analysis), resulting in a highly conducting material (pressed pellet), accompanied by gradual dehydrogenation (as evidenced by elemental analysis). (i) The FT-IR spectrum of PP2 indicates a smooth surface and does not provide enough information to distinguish it from glassy carbon.

To shed light on this unusual transformation of Cl₄Pn to poly(iptycene) PP1, we performed DFT (B3LYP) calculations using the 6-31G(d) basis set. Our first hypothesis was dechlorination of Cl₄Pn to give a benzyne species which could be trapped in a DA reaction with another Cl₄Pn molecule, which, however, had to be discarded due to extremely high energy requirements (111.7 kcal/mol for elimination of Cl₂ from Cl₄Pn, similar to 111.3 kcal/mol for elimination of Cl₂ from 2,3-dichloronaphthalene). An alternative mechanism included a DA reaction between the peripheral double bond (C₂=C₃) of Cl₄Pn itself (acting as dienophile) and the central ring of another Cl₄Pn molecule (acting as diene). The [4 + 2] cycloaddition product is expected, at the reaction temperature, to dechlorinate readily, due to aromatization resulting in an iptycene structure. The calculated activation energy of the concerted DA addition, keeping C₃ symmetry, is 64.7 kcal/mol. The frequency analysis indicated a second-order saddle point. Indeed, when the wave function was allowed to become unrestricted and symmetry constraints were released, calculation of the asymmetric reaction mechanism through a formation of a biradical, rotation, and finally cyclization showed its preference versus the concerted mechanism by 13.8 kcal/mol (for unsubstituted pentacene), leading to an overall activation barrier of ca. 50 kcal/mol, very reasonable for a reaction occurring at 400 °C. A DA adduct involving the second benzene ring as a diene is higher by 4.2 kcal/mol, which should result in ~3% of this byproduct. Once the pentacene has undergone cycoaddition, the terminal double bond loses its dienophilicity (calculations show that naphthalene has a higher activation energy, by 5.8 kcal/mol, toward cycloaddition with pentacene than pentacene itself). The overall reaction of the dechlorinating “dimerization” of Cl₄Pn is endothermic by 12.3 kcal/mol. To our knowledge, this is the first example of (i) a DA reaction between two acene molecules and (ii) the asymmetric biradical DA reaction mechanism for symmetric reagents. The mechanism of this unusual reaction will be discussed in detail in a forthcoming paper.

To conclude, we have discovered the first reaction of a substituted pentacene molecule as a dienophile. A surprisingly clean DA self-coupling of Cl₄Pn leads to a novel ladder polymer, poly(iptycene), which can be converted to a conducting carbon at relatively low temperature (600°–900 °C). Theoretical calculations of the former reaction suggest a biradical asymmetric mechanism, despite highly symmetric reactants.

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Supporting Information Available: Experimental details for synthesis of Cl₄Pn, PP1, and PP2, their characterization, and DFT calculations; DSC, FTIR, ESR, and ¹³C NMR solid-state spectra of Cl₄Pn, SEM micrograph of the product PP2; schemes of the calculated reaction pathway (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(7) The only relevant report describes an intramolecular [4 + 2] cyclization of 1,2-bis(1,5-dichloroarylethenyl) where a 1,2-double bond of one anthracene moiety acts as a dienophile toward the 9,10 diene of another: Becker, H.-D.; Anderson, K. Tetrahedron Lett. 1983, 24, 3273–3276.
(9) Bao, Z. Personal communication.
(10) For details, see Supporting Information.
(12) Presumably, the ESR signal shall be attributed to the intermediate and/or side reaction radical species.
(14) The calculated C2=C₃ bond in Cl₄Pn (1.442 Å) is relatively long, relatively weaker, and hence more reactive.