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Synthesis of sterically crowded 9-nitrotriptycenes by the Diels–Alder cycloaddition reaction

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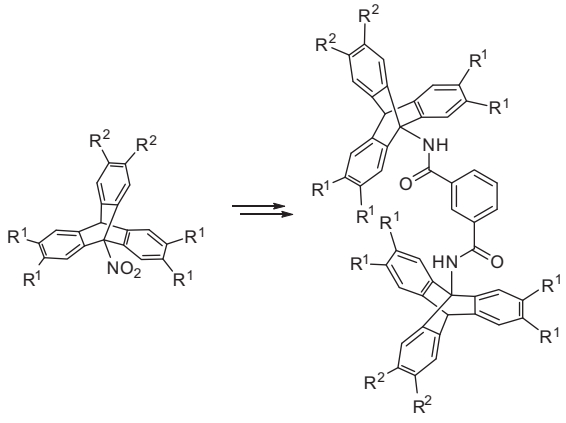
ABSTRACT

The synthesis of novel sterically crowded triptycenes as attractive components for the construction of models for various molecular dynamic studies is reported. 9-Nitrotriptycenes were obtained by the Diels–Alder reactions between 9-nitroanthracene and tetrabromobenzyne as well as 1,4-dichloro-9-nitroanthracene and 2,6-dichlorobenzyne. Interesting regioselectivity relative to the central and terminal rings was observed. Moreover, 1,2,3,4-tetrabromo-9-nitrotriptycene was further functionalized to afford 1,2,3,4-tetrabromotriptycyl-9-ammonium tetrafluoroborate in two-steps. The impact of steric hindrance on the geometry of the molecule was estimated on the basis of single crystal X-ray diffraction data.

Introduction

Triptycene (9,10-dihydro-9,10[1′,2′]-benzenoanthracene) derivatives are an important class of organic compounds due to their structural properties. These compounds have proven to be useful in many areas of chemistry, e.g., in materials and supramolecular chemistry,[1] as molecular rotors, and as models for the study of hindered rotation[2] including non-classical effects on the dynamics of methyl groups.[3] Because of the simple functionalization of the nitro group, nitrotriptycenes and other similar bicyclic nitro compounds are an interesting group of molecules for the construction of models to study hindered rotation (Scheme 1).

However, reports on the synthesis of triptycene derivatives from electron-poor anthracene derivatives are scarce. Reported routes involve the Diels–Alder reaction of 9-nitro,[1e,4a,b,5,6] 9-carbonyl,[4c–h] and 9-nitrile[4b,i,j,5] anthracene derivatives with benzyne[4–6] or alkyl[1e,4a,b,f,h] benzyne derivatives. Examples of the Diels–Alder reaction leading to sterically crowded triptycenes substituted at position 9 by an electron-withdrawing group and by similar groups, e.g., halogens, in the peri positions, are not found in the literature. In such compounds, steric effects exerted by the halogen atoms are easily modelled using quantum chemistry methods. Because the relevant molecular fragments are rigid, extra computational efforts to treat the flexibility issue are spared.



Scheme 1. An example of the application of a 9-nitrotriptycene derivative for the construction of molecular devices executing temperature-controlled rotational and vibrational motions.[1e]

Results and discussion

Reported literature methods for performing the Diels–Alder reaction between electron-deficient anthracenes and benzynes, involve thermal decomposition of the benzyne precursors, added as a suspension.[1e,6] In order to obtain one of the two 9-nitrotriptycene derivatives reported herein, these methods had to be adapted to the specific properties of the precursor. The choice of the counter-anion in the latter was proven critical in this respect. Three side-products of the cycloaddition reactions

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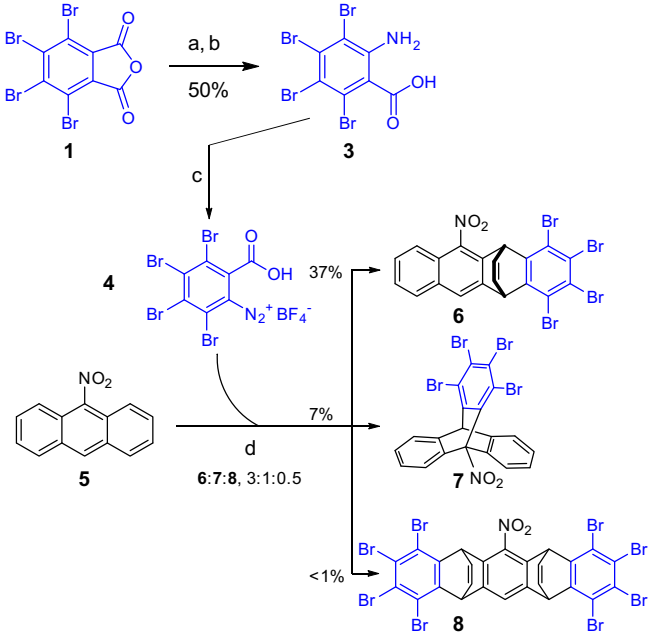
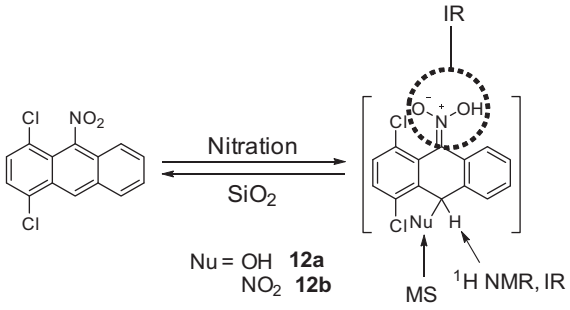
were also identified. Including these, total yields of 62% and 91% were obtained. The considerable yields of the side-products confirm the significance of steric and electronic effects for the regioselectivity of the discussed reaction.

The cycloaddition reaction between 9-nitroanthracene **5** and tetrabromobenzyne was performed via generation of the latter by thermal decomposition of 2-carboxytetrabromodiazonium tetrafluoroborate **4** (Scheme 2). Three cycloadducts, **6**, **7** and **8**, in a ratio of 3:1:0.5, respectively, were obtained, as determined by NMR spectroscopy (91% conversion). This regioselectivity was postulated to be caused by a steric interaction between the halogen substituent of the aryne derivatives and the nitro group of 9-nitroanthracene and/or the lower reactivity of the central ring of the anthracene system.

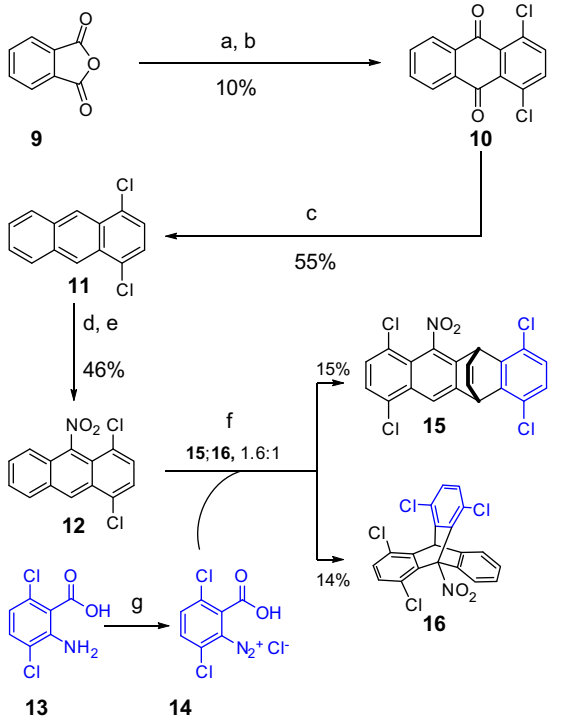
Nitrotriptycene **16** was obtained via the cycloaddition reaction between 1,4-dichloro-9-nitroanthracene **12** and 3,6-dichloro-2-carboxybenzenodiazonium chloride **14** as the benzyne precursor (Scheme 4). Compound **12** was obtained via a four-step synthesis. The $AlCl_3$ catalysed Friedel–Crafts reaction of phthalic anhydride **9** with 1,4-dichlorobenzene yielded the corresponding keto-acid which was treated with concentrated sulfuric acid to afford 1,4-dichloroanthraquinone **10**. After reduction under basic conditions according to a literature procedure,[10] 1,4-dichloroanthracene **11** was obtained in 55% yield. The synthesis of **12** was troublesome, due to the high reactivity of 1,4-dichloro-9-nitroanthracene towards the oxidising reagent. In the nitration reaction of **11** with HNO_3/H_2SO_4 in acetic acid only 1,4-dichloroanthraquinone was observed, which was consistent with literature reports.[11] Compound **12** could be obtained in low yields (8%) under milder conditions (1,2-dichloroethane/35% HNO_3 aq, 60 °C), despite complete conversion. A satisfactory yield was achieved using nitrogen oxide as the nitration reagent. However, in the ^1H NMR spectra of the crude reaction mixture (ESI) the characteristic signals of product **12** could not be identified. Instead, two strong singlets at 7.13 and 6.93 ppm were observed. In the MS (ESI) spectra, two signals at $m/z = 332.1$ and 360.4 (M+Na) were present. In the IR spectra, two characteristic absorptions at 2961–2853 cm^{-1} and



Scheme 2. Synthesis of **6**, **7** and **8**. Reagents and conditions: (a)[7] $NH_{3\ aq}$, DMSO, rt.; (b) $Br_2/NaOH_{aq}$, 0–80 °C, (c)[8] *iso*-pentyl nitrite, Et_2O, $HBF_{4\ aq}$, 0 °C; (d) 1,2-dichloroethane, reflux. For **8** only one stereoisomer was obtained, however, its stereochemistry (*cis* or *trans*) could not be determined.



Scheme 3. Proposed transient structures observed in the nitration reaction with nitrogen oxide.



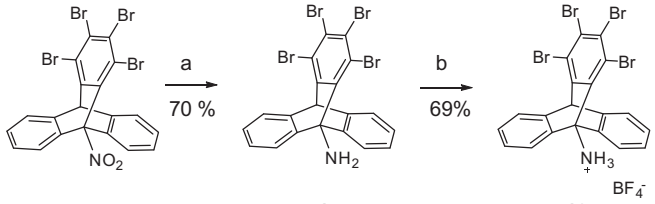
Scheme 4. Synthesis of 1,4-dichloro-9-nitroanthracene and the cycloaddition reaction with 2,5-dichlorobenzyne. Reagents and conditions: (a)[9] 1,4-Dichlorobenzene, $AlCl_3$, 120 °C; (b) H_2SO_4, 100 °C; (c)[10] Zn, NH_3/H_2O, 0–75 °C, (d) dichloromethane, N_2O_5, rt, (e) SiO_2; (f) 1,2-dichloroethane, reflux, (g)[1e] *iso*-pentyl nitrite, EtOH, HCl_{aq}, 0 °C, Et_2O.

1557 cm^{-1} were observed. The above NMR, MS and IR data were consistent with the transient structures **12a** and **12b** (Scheme 3). During the course of purification by silica gel chromatography, these must have been converted into compound **12**, which was finally isolated in 46% yield.

In the next step, the cycloaddition reaction between **12** and **14** was carried out. Two cycloadducts were observed, **16** and **15** in a ratio of 1:1.6, respectively, as determined by NMR spectroscopy (62% conversion).

A suitable single crystal for X-ray diffraction measurements on the sterically crowded triptycenes was obtained for the ammonium salt **18**, obtained by functionalization of compound **7** (Scheme 5).

Compound **18** (Fig. 1) crystallizes in the orthorhombic $P\,2_1\,2_1\,2_1$ space group. The position of the NH_3 group and specific interactions shows the influence of the hindered environment on this group. The ammonium protons may form so called blue-shifting hydrogen bonds with the bromine atom (Fig. 1), by analogy with



Scheme 5. Synthesis of 1,2,3,4-tetrabromotriptycyl-9-ammonium tetrafluoroborate. Reagents and conditions: (a) $SnCl_2$/HCl, propionic acid, reflux; (b) $HBF_4{\cdot}Et_2O$, CH_2Cl_2, rt.

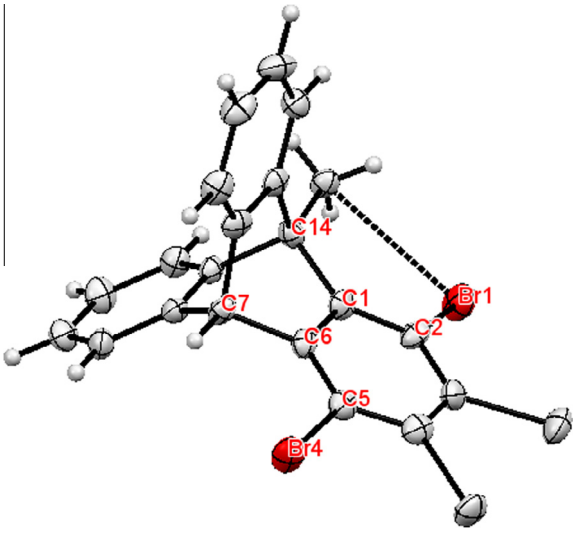


Figure 1. Single crystal X-ray structure (ORTEP) of compound **18**.

the methyl protons in the methyl analogue of **18**.[12] Br1 was bent out of the plane of the ring. This appears to be the most significant manifestation of the steric hindrance in **18**. Namely, the torsion angle in the sequence Br1-C2-C1-C14 amounts to −14.1 deg, for comparison, in the Br4-C5-C6-C7 arrangement the torsion angle was only 1.31 deg.

Conclusion

In summary, the synthesis of new sterically crowded bicyclic compounds via cycloaddition reactions between deactivated anthracene systems and substituted arynes was described. Functionalization of one of the newly obtained compounds was carried out yielding 1,2,3,4-tetrabromotriptycyl-9-ammonium tetrafluoroborate, an ammonium salt with the ammonium group placed in extremely crowded environment. Some steric hindrance effects in the latter compound were discussed on the basis of its single crystal X-ray structure.

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Supplementary data

Supplementary data (general procedures, experimental procedures and compound characterization: ^{1}H NMR, ^{13}C NMR and mass spectra of compounds **3**–**17**. ^{1}H NMR, ^{19}F NMR and single crystal X-ray data for compound **18** (CCDC 1448445). ^{1}H NMR spectra of the cycloaddition reactions. ^{1}H NMR and IR spectra of the nitration reaction) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.10.041.

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