Rapid access to triptycene-like naphthopleiadenes for use in supramolecular and materials chemistry

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Abstract

Triptycene derivatives are used extensively in supramolecular and materials chemistry, however, most are prepared using a multi-step synthesis that involves the generation of a benzyne intermediate, which hinders scale-up. Inspired by the ease of resorcinarene synthesis, we report the rapid and efficient preparation of triptycene-like 1,6,2',7'-tetrahydroxynaphthopleiadene directly from 2,7-dihydroxynaphthalene and phthalaldehyde. Structural characterisation confirms the novel bridged bicyclic framework, within which the planes of the single benzene ring and two naphthalene units are fixed at an angle of ~120° relative to each other. Several simple variations of aromatic 1,2-dialdehydes and 2,7-disubstituted naphthalenes also provided triptycene-like products. The low cost of the precursors and undemanding reaction conditions allows for rapid multigram synthesis of 1,6,2',7'-tetrahydroxynaphthopleiadene with product isolation by simple filtration. The potential for its use in supramolecular and polymer chemistry was demonstrated by the preparation of a very rigid novel cavitand, a microporous network polymer, and a solution-processable polymer of Intrinsic microporosity.

Introduction

Triptycene is a bridged bicyclic hydrocarbon composed of three benzene rings fused to two sp^3 hybridised carbon bridgeheads (Fig. 1).[1] The symmetry and rigidity of triptycene results in its derivatives being used extensively in supramolecular[2] and materials chemistry.[3] For example, triptycenes are key components in molecular machines (such as gears,[4] brakes[5], rotors[6]), crystal engineering,[7] macrocycles,[2d,8] cages,[9] optoelectronic materials,[10] self-assembling monolayers at interfaces,[11] and ligands for metal catalysts.[12] The shape of triptycene, with the plane of the three benzene rings placed at an angle of 120° relative to each other, is particularly attractive for providing the vertices within ordered porous materials such as 2D honeycomb-like polymers,[13] molecular crystals,[14] nanotubes,[15] Covalent Organic Frameworks[16], and Metal Organic Frameworks.[6,17] However, our long-term interest in triptycene derivatives has been in their use as monomers for making *amorphous* Polymers of Intrinsic Microporosity (PIMs),[18] an interest which is shared with several other research groups.[19] PIMs exploit the rigidity[20] of triptycene and the internal molecular free volume (IMFV)[21] that originates from its concavities (Fig. 1). Triptycene-derived PIMs have great potential for making high performance gas separation membranes.[22] Indeed, data from these polymers define the current upper bounds for the trade-off between permeability and selectivity for the separation of several important gas pairs,[23] including those of interest for post combustion carbon capture and natural gas purification.[24]

The many different triptycene derivatives used for the diverse applications listed above all require a multi-step synthesis, which often requires laborious chromatographic purification of intermediates and product.[25] Despite some newly developed methods,[26] triptycenes are still predominantly prepared by the Diels-Alder reaction between an anthracene and a reactive benzyne intermediate.[27] It should be noted that even the parent hydrocarbon is an expensive starting material, presumably due to the inherent difficulties and danger in scaling-up reactions involving benzyne.[28] Frustrated by the time-consuming preparation of triptycene monomers for making PIMs, we are currently developing methods for their rapid synthesis that are compatible with the large scale development of materials.

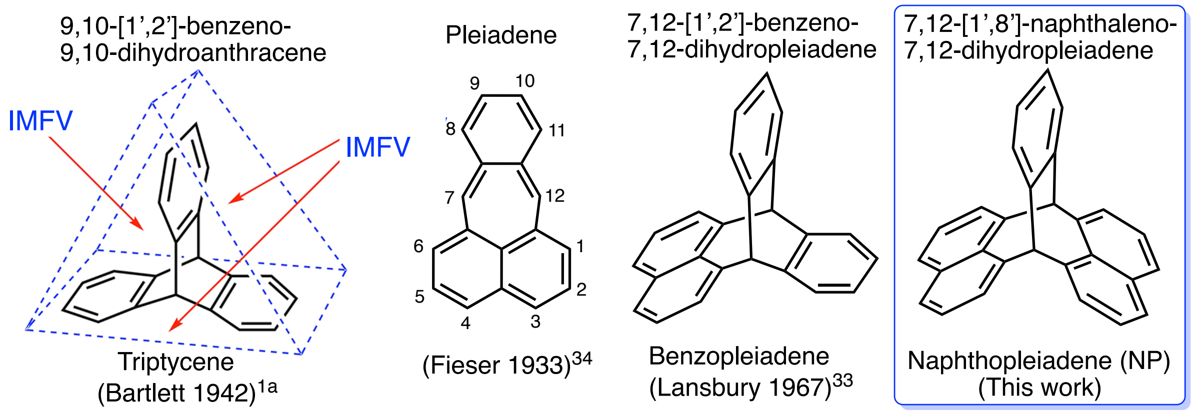

Fig. 1. The structure and nomenclature of triptycene, pleiadene and the two triptycene-like frameworks obtained from fusing phenylene or naphthalene, via *peri*-carbons, to the 7,12 sites of pleiadene. The intramolecular free volume (IMFV)[21] is shown for triptycene and is clearly greater for naphthopleiadene.

Here we report the simple one-step synthesis of a triptycene-like compound, which has a novel bridged bicyclic framework composed of a single benzene and two naphthalene units fused to two carbon bridging atoms, for which we propose the name naphthopleiadene (NP, Fig. 1). The readily prepared derivative NP **1** (Fig. 2) contains in-built hydroxyl functionality that is useful for further synthetic elaboration, as demonstrated by the synthesis of a very rigid novel cavitand, a microporous network polymer and a solution-processable PIM (Fig. 3).

Results and discussion

Acid-mediated reactions between aldehydes and electron-rich aromatic compounds, similar to those used for the efficient assembly of resorcinarenes (Fig. 3a),[29] were considered for the synthesis of triptycene derivatives. Naïvely, it was anticipated that these could be formed from the double addition of an appropriate aromatic compound to phthalaldehyde, however, literature reports of such reactions with benzene derivatives present no evidence of any triptycene product.[30] Instead, 9-phenyl anthracenes are produced *via* a carbocation contained within a six-membered ring, from which the loss of a proton enables the efficient formation of the extended aromatic system (Fig. 2a). Nevertheless, it was reasoned that a triptycene-like product may be formed if the reaction pathway to 9-phenylanthracene could be avoided. For example, the double addition of 2,7-dihydroxynaphthalene to phthalaldehyde was anticipated to form a carbocation intermediate contained within a seven-membered ring, which would not be compatible with aromatization (Fig. 2b).

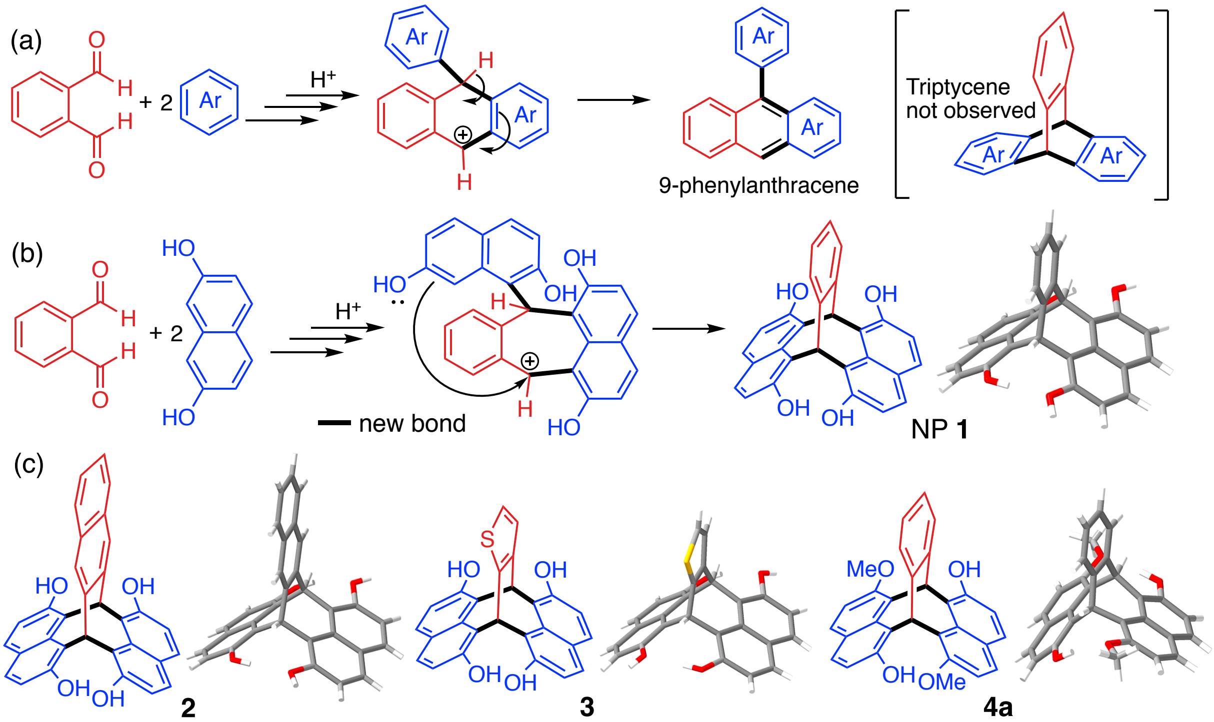

Fig. 2. Proposed partial mechanisms for (a) formation of 9-phenylanthracenes from the reaction between phthalaldehyde and benzene derivatives (Ar) and (b) the reaction between phthalaldehyde and 2,7-dihydroxynaphthalene to give naphthopleiadene **1,** via an intermediate containing a seven-membered ring which cannot aromatise via loss of proton. (c) The structures of triptycene-like compounds **2**, **3** and **4a**.

Using reaction conditions optimised for the synthesis of resorcinarenes (Fig. 3a),[31] heating an acidified ethanol solution of a 2:1 mole ratio of 2,7-dihydroxynaphthalene and phthalaldehyde rapidly produced a solid. Intriguingly, ^{1}H and ^{13}C NMR analysis showed that a highly symmetric product was obtained in high purity. A single crystal x-ray diffraction study confirmed the formation of a novel bridged bicyclic framework with two *sp*^{3} hybridised bridging carbons, to which are fused a single benzene ring and two naphthalene units, the latter at their *peri*-(1,8)-positions. Like triptycene, the planes of the three fused aromatic units are fixed at an angle of ~120° relative to each other (Fig. 2b). The related triptycene-like framework, consisting of two benzene rings and a single naphthalene unit, was reported in 1967.[32] This bridged bicyclic compound was considered a derivative of the unsaturated hydrocarbon *pleiadene*,[33] for which the seven-membered ring evoked the Pleiades of Greek mythology, therefore, it was named 7,12-(1',2'-benzeno)-7,12-dihydropleiadene (Fig. 1). Using the same IUPAC endorsed nomenclature,[34] we suggest the systematic name of 7,12-(1',8'-naphthaleno)-7,12-dihydropleiadene, simplified to naphthopleiadene (NP), for the parent hydrocarbon of the novel bridged bicyclic framework (Fig. 1).

Optimisation of the reaction conditions for the synthesis of 1,6,2',7'-tetrahydroxynaphthopleiadene (NP **1**) indicated that only a few drops of conc. HCl are required and that simple alcohols perform best as solvents (SI Table 1). NP **1** was produced as a white product directly in good yield (~70%, first crop) and required no further purification except for the removal of included alcohol in a drying oven. Additional product (~20%, second crop) can be obtained by work-up of the filtrate and recrystallisation. Remarkably, the maximum yield is produced within only a few minutes after heating to reflux. Alternatively, similar yield and purity of product was obtained at ambient temperature, but the reaction took longer to complete (~24 h). The low cost of the precursors and undemanding reaction conditions allows for large-scale synthesis with, for example, 70 g of NP **1** being obtained easily (Table 1). Water as reaction solvent gave a good crude yield but the resulting solid contained a purple impurity and required recrystallisation from ethanol, therefore, negating any potential benefits from its use.

Replacement of phthalaldehyde in the reaction with 2,3-napthalenedialdehyde or 1,2-thiophenedialdehyde also provided triptycene-like products **2** and **3**, respectively (Fig. 2). Similarly, 2-hydroxy-7-methoxynapthalene reacts with phthalaldehyde to give a mixture of the isomeric products 1,7'-dihydroxy-6,2'-dimethoxy-naphthopleiadene (**4a**) and 1,2'-dihydroxy-6,7'-dimethoxy-naphthopleiadene (**4b**), which could be separated by using the relatively poor solubility of the former in acetone. The same reaction conditions using 2,7-dimethoxnaphthalene and phthalaldehyde failed to provide 1,6,2',7'-tetramethoxynaphthopleiadene (**5**). However, by adapting an efficient preparation of methoxy-substituted triphenylmethanes,[35] using $BF_3.OEt_2$ in dichloromethane, NP **5** was obtained in moderate yield with its structure confirmed by single crystal XRD analysis.

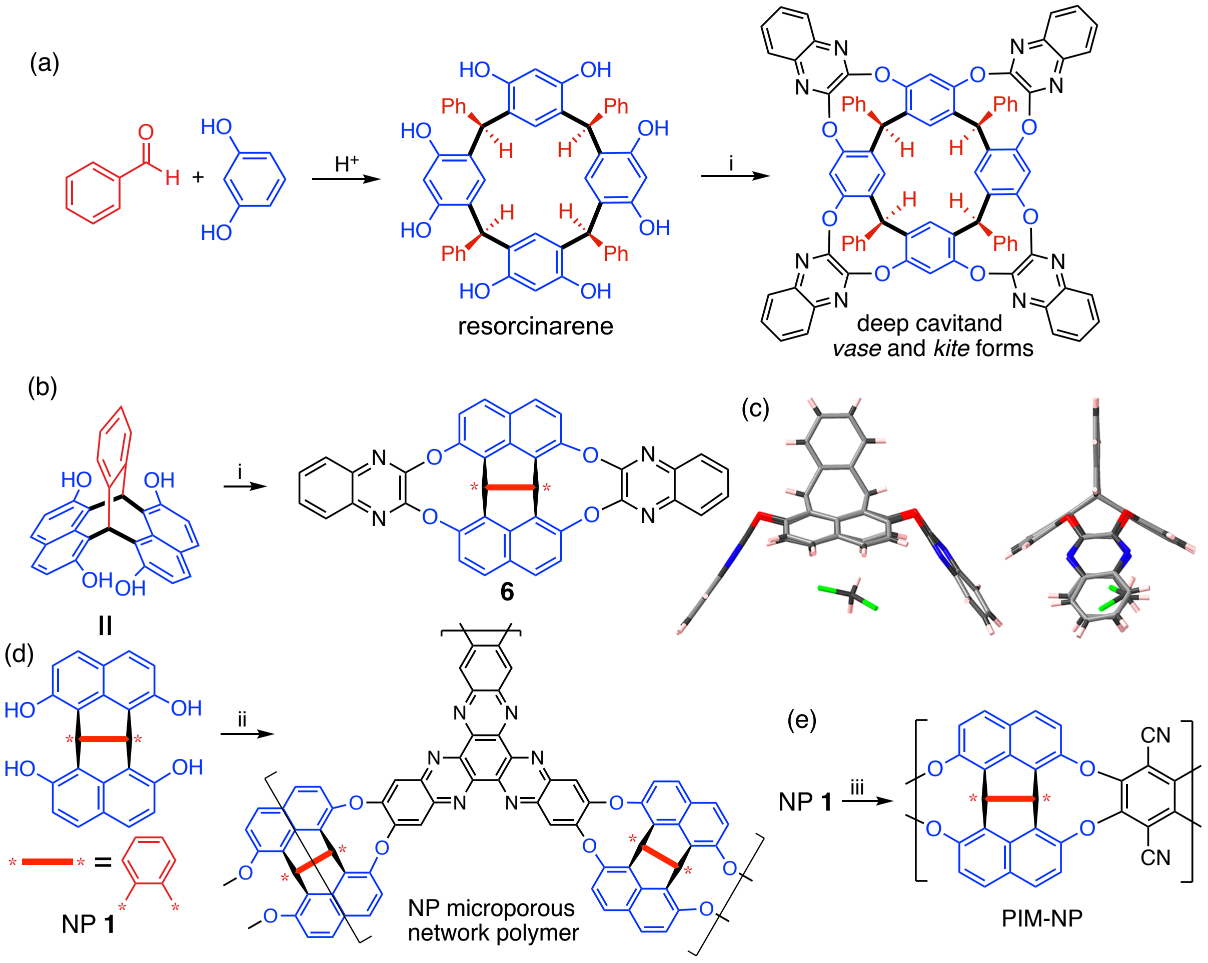

Fig. 2. (a) Synthesis of the rigid cavitand NP **6**. i. 2,3-dichloroquinoxaline, K_2CO_3, DMF, 80 °C, 48 h. (b) Two view of the XRD structure of NP **6** showing the included CH_2Cl_2 molecule. (c) ii. 2,3,8,9,14,15-Hexafluoro-5,6,11,12,17,18-hexaazatrinaphthylene, K_2CO_3, DMF, 120 °C, 48 h. (d) 2,3,5,6-Tetrafluoroterephthalonitrile, K_2CO_3, DMF, 30-120 °C, 160 h.

The structure of NP **1**, with a short distance between adjacent hydroxyl groups (O to O distance = 2.74 Å), suggested a similar reactivity to that of the resorcinarenes, for which Cram demonstrated deep cavitand formation using the efficient reaction with 2,3-dichloroquinoxaline (Fig. 3a).[36] Similarly, the reaction between NP **1** and 2,3-dichloroquinoxaline proceeds in very high yield to give **6** with the formation of two nine-membered tribenzo-1,4-dioxonine rings (Fig. 3b). A single crystal XRD analysis of **6** shows a symmetrical cavitand-like structure that contains a single molecule of dichloromethane held within the cavity (Fig. 3c). Unlike Cram's deep cavitands, which exists in rapidly exchanging *vase* and *kite* conformers,[29b,37] the structure of **6** appears fully fixed by the NP framework. Indeed, simple molecular mechanical modelling suggest that the conformer produce by the inversion of a single tribenzo-1,4-dioxonine ring is ~60 kJ mol^{-1} higher in energy due to the steric effect of the NP bridgehead hydrogen (SI Fig. 1).

The highly efficient formation of the tribenzo-1,4-dioxonine unit, demonstrated by the synthesis of cavitand **6**, suggested that polymers may also be prepared by similar aromatic nucleophilic substitution reactions. Hence, the synthesis of both a network and a non-network polymer was attempted by the reactions between NP **1** and 2,3,8,9,14,15-hexafluoro-5,6,11,12,17,18-hexaazatrinaphthylene[38] or 2,3,5,6-tetrafluorophthalonitrile, respectively (Fig. 3d&e). For the resulting network polymer, there was poor N_2 uptake at 77 K. However, CO_2 uptake of 4 mmol g^{-1} at 1 bar (273 K) suggests significant microporosity with the pore size distribution being predominantly ultramicroporous (<0.7 nm), which combined with high rigidity, may restrict access of N_2. The non-network polymer proved soluble in polar aprotic solvents, and once the polymerisation was optimised, a high average molecular mass (M_n = 140,000 g mol^{-1}) was obtained. Gas adsorption of the powdered form of PIM-NP confirmed intrinsic microporosity with significant N_2 uptake at 77 K allowing an apparent SA_{BET} of 635 m^2 g^{-1} and total pore volume of 0.40 ml g^{-1} to be estimated. Thermal Gravimetric Analysis (TGA) of PIM-NP showed no loss of mass below 400 °C with a mass loss of only 27% at 850 °C, which is consistent with the predominately aromatic nature of the components of the polymer. Although self-standing films of PIM-NP could be cast from DMF solution, these proved too brittle for gas permeability measurements despite the high average molecular mass of the polymer. It should be noted that the ability to fabricate robust self-standing films from many PIMs, despite their fused ring structures, has been attributed to the relative flexibility of the dibenzodioxane linking group.[39] However, a comparison of the flexibility of the dibenzodioxane linking group with that of tribenzo-1,4-dioxonine using molecular mechanical modelling (Fig. Si 2), suggests that the latter is much more rigid, which is likely to be detrimental to film formation for PIM-NP. Nevertheless, a cavitand-containing PIM that can be processed from solution to form coatings may be useful for making adsorbents or sensors and the use of NP **1** for making microporous polymers is the focus of current work.[40]

Conclusions

With the increasing complexity of modern synthetic chemistry, it is gratifying to obtain a novel compound that possesses both an interesting structure and useful reactivity from a very simple reaction between two readily available precursors. The ease in which NP **1** is prepared suggests that it will have further applications beyond cavitand and microporous polymer synthesis. For example, NP **1** could replace various hydroxylated triptycene precursors, each of which require a complex multi-step synthesis,[41] in the preparation of pincer catalysts[12e] and materials for which the structure and properties are controlled by triptycene self-assembly. Potential target materials include liquid crystals,[42] highly ordered thin-films[43] and polymers with unusual mechanical properties.[3b,d,44] As noted by Swager, triptycene self-assembly is driven by the requirement to eliminate intermolecular free volume (IMFV), thus favouring the interlocking of triptycene units.[3g,h] As the naphthalene units of NP generate larger IMFV than the benzene rings of triptycene (Fig. 1) the NP component may enhance self-assembly in these materials, in addition to allowing their scale-up for commercial development.

Acknowledgements

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