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Synthesis and modelling of novel rigid rods derived from a simple pentacyclic *bis*-norbornene [1]

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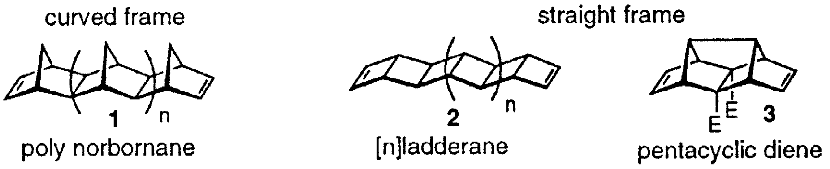
Abstract

New rigid rods with 4σ, 6σ, 10σ, 12σ, and 16σ bond separations have been prepared from the pentacyclic diene **3** using ACE (alkene plus cyclobutene epoxide) and *s*-tetrazine coupling techniques and their shapes evaluated using AM1 calculations. The X-ray structure of the 6σ-rod **5** is reported.

Keywords: *cycloaddition; stereoselection; tetrazines; molecular modelling.*

In recent studies on the synthesis of ribbon molecules based on the coupling of norbornene BLOCKs [2,4], we have exploited the curvature present in the alicyclic framework of such molecules, but become increasingly aware of the need for a rod-like variant. Molecular modelling indicates that fused-norbornane structures have a bent geometry and we have shown that incorporation of cyclobutane rings in the framework reduces the curvature and that a rod-like frame can be obtained using an alicyclic system comprised entirely of cyclobutane rings, eg [n]ladderanes **2** [5] (Scheme 1 and Table 1). From a synthetic chemists viewpoint, however, [n]ladderanes are not a desirable starting material as they require repeated use of cyclobutadiene for their preparation and this is an expensive reagent for large scale use. In this communication, we demonstrate how to prepare rigid rods from the coupling of the pentacyclic *bis*-norbornene **3** [6-11] and report on molecular modelling of their shapes.



Scheme 1

The basic building BLOCKs used in the fabrication of the rigid rods were prepared from pentacyclic diene **3**, which displays typical norbornene reactivity. Conversion of **3** to the *bis*(cyclobutene-1,2-diester) **5** (X-ray structure support, Figure 1) is achieved by ruthenium-catalysed addition of dimethyl acetylene dicarboxylate (DMAD) **4** [12,13], while the

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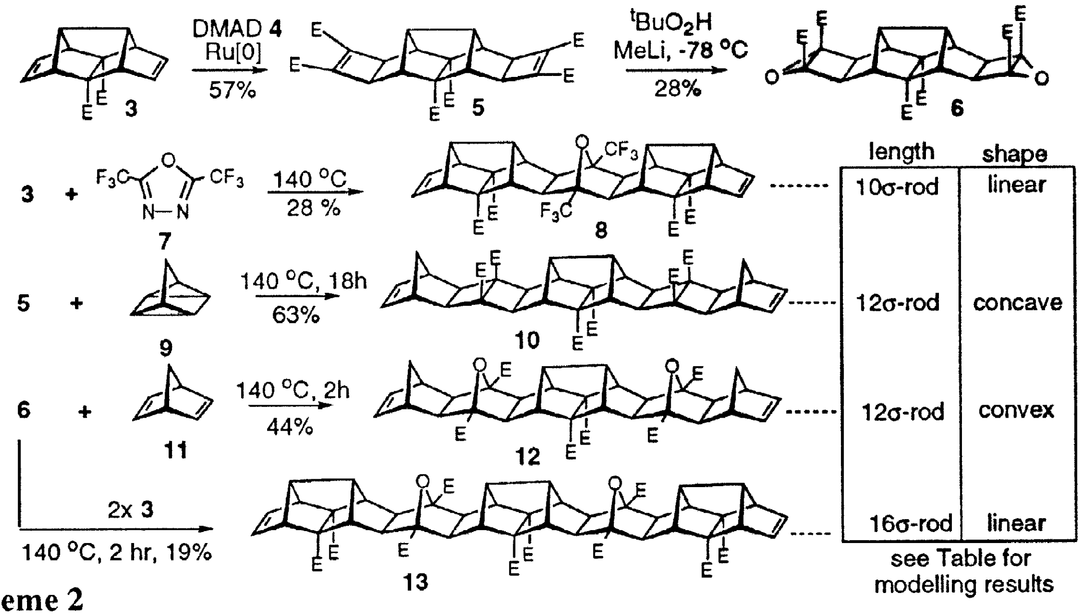
bis(cyclobutene epoxide) BLOCK **6** is prepared from **5** by low-temperature epoxidation ($^tBuO_2H$, MeLi, THF, -78 °C) [2].

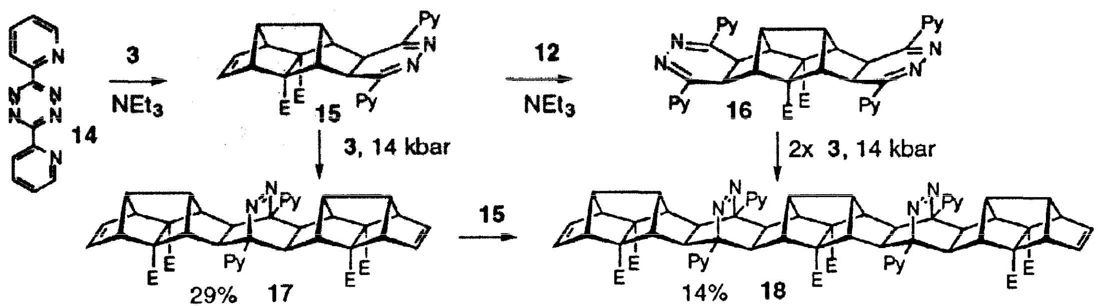
Coupling of the pentacyclic diene **3** by heating (140 °C, 16h) with 2,5-*bis*(trifluoro methyl)-1,3,4-oxadiazole **7** yields the linear 10σ-rod **8** [14]. The structure of **8** is supported by its ^1H NMR spectrum, where the single ester resonance (δ 3.65) and the single set of vinylic protons at δ 5.89 confirms the C_{2v}-symmetry of the product. Addition of quadricyclane **9** to cyclobutene-1,2-diesters is another recognised method for framework extension [15], and when applied to *bis*(cyclobutene-1,2-diester) **5** (Scheme 2) (140 °C, CH_2Cl_2, sealed tube, 18h), affords the 12σ-system **10**. Molecular modelling indicates that **10** has an unusual saucer shape (Table 1).

The *bis*(cyclobutene epoxide) **6** was used as starting material for the production of the 12σ-rod **12** by ACE (alkene plus cyclobutene epoxide) coupling [2] with norbornadiene **11**. The expected high symmetry of **12** is evident in the ^1H NMR spectrum with two sets of ester resonances (ratio 2:1) and a single set of vinylic resonances at δ 6.11. The higher order 16σ-rod **13** is also prepared from the *bis*(cyclobutene epoxide) **6** by double ACE coupling, this time by reaction with two equivalents of pentacyclic diene **3**. There are three separate ester resonances (ratio 2:2:1) in the 16σ-rod **13** which are clearly evident in the ^1H NMR and reflect the high symmetry (C_{2v}) of this rod.



Scheme 2

The related *s*-tetrazine BLOCK coupling procedure [16] is used to convert the pentacyclic diene **3** to an alternative set of rigid rods, this time containing a diazabicyclo[2.2.2]octene as the linking bicyclic system. Reaction of pentacyclic diene **3** with 3,6-di(2-pyridyl)-*s*-tetrazine **14** yields a mixture of 10σ-rod **17** and 16σ-rod **18** (CH_2Cl_2, NEt_3, 14 kbar, overnight). It is assumed that intermediate dihydropyridazine **15** is formed first and reaction with **3** yields **17**; formation of **18** is more speculative, however, as it can be formed by reaction of **17** with **15** or it can involve formation of the *bis*(dihydropyridazine) **16** (Scheme 3). These alternative pathways have not been further evaluated. The triethylamine is added in this first step to stabilise the dihydropyridazines in the conjugated 1,3-diene form (Diels-Alder active); in the absence of base, rapid prototropic isomerisation occurs to form the non-conjugated 1,4-isomer (Diels-Alder inactive).



Scheme 3

Molecular Modelling [17]

The basic ring systems have been optimised using AM1 calculations and the following points established. The calculated shapes of representative molecular frameworks are shown in Table 1.

- *The presence of the pentacyclic moiety in the alicyclic framework provides rod-like geometries, eg* ***20*** *and* ***22****..*
- *Introduction of 7-oxanorbornanes cause some downward curvature of the framework, but less than that associated with the 2,3-diazabicyclo[2.2.2]octene subunit (compare* ***21*** *with* ***23****).*
- *[n]Ladderanes (all cyclobutane rings), eg* ***25*** *are straight, while combinations oj cyclobutanes and pentacyclic dienes curve the framework in an upward direction, eg, the unique saucer shaped configuration of* ***24*** *(present in compound* ***10****).*
- *Dramatic increases in curvature occur when the pentacyclic diene is replaced with a pair of fused norbornanes, compare* ***20*** *with* ***21*** *or* ***22*** *with* ***23****.*

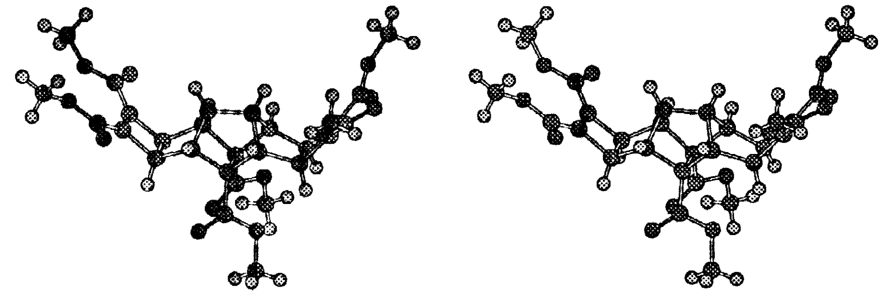


Figure 1: *Stereoview of X-Ray structure of 6σ-rod 5 [18]*

In conclusion, we have shown that rod-shaped structures can be prepared from the pentacyclic diene **3**. Future papers will demonstrate how such systems can be used in the preparation of structures containing porphyrin and other effector groups.

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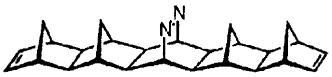
[18] Crystallographic data has been deposited in the Cambridge Crystallographic Data Centre-CSD No P-015/03/98.

Table 1.

AM1 optimised geometries of representative molecular frameworks (rods and curves) formed by fusion of alicyclic ring elements. Calculations were conducted on substituent-free systems.



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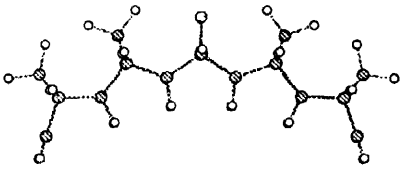
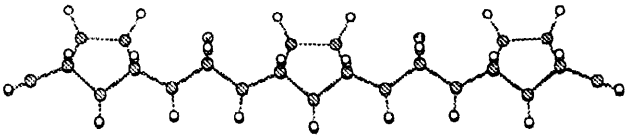


20 (see compound **13**)



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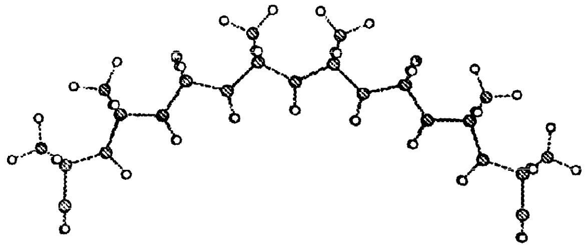
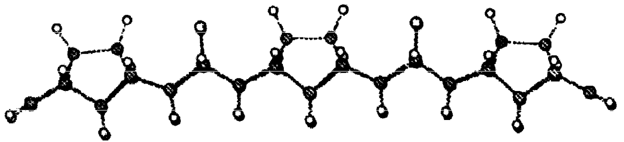


22 (see compound **18**)



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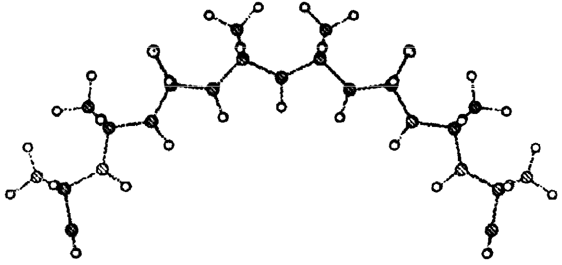
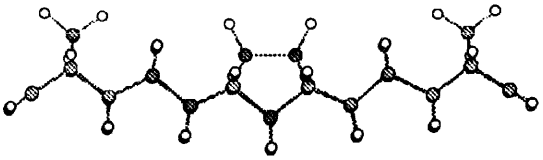


24 (see compound **10**)



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