

## Phanes Derived from 1,5- and 1,7-Dihydro-*s*-indacene\*\*

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Frontier orbital analysis of two conjugated, cyclic polyenes held face-to-face in close proximity suggests that when both polyenes have  $4n\pi$ -electron systems the interaction will be stabilizing, whereas when both have  $(4n+2)\pi$ -electron systems the interaction will be destabilizing<sup>[1]</sup>. To test this prediction experimentally it would be of especial interest to examine phanes having nonbenzenoid aromatic and also antiaromatic decks as model compounds.

In the course of experiments directed toward a synthesis of [2.2](2,6)-*s*-indacenophane, we have now prepared, *inter alia*, the tetrahydro-*s*-indacenophane **4** by means of a cyclization method not previously employed in phane chemistry.

The 2,6-disubstituted dihydro-*s*-indacene, needed as a precursor for this synthesis, was prepared in a straight-forward fashion from dimethyl 2,5-bis(bromomethyl)terephthalate<sup>[2]</sup>. On reaction with diethyl malonate in the presence of excess sodium ethoxide it was converted in 85% yield into diethyl 1,5-dioxo-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarboxylate (m. p. = 158–161 °C (dec.)), which after reduction with NaBH<sub>3</sub>CN/acetic acid followed by elimination of water using TsOH/CHCl<sub>3</sub> gave diethyl 1,5-dihydro-*s*-indacene-2,6-dicarboxylate<sup>[3a]</sup> as stable colorless needles (m. p. = 186–187 °C), intensely fluorescent under long wavelength UV light. Reduction of this with diisobutylaluminum hydride gave 1,5-dihydro-*s*-indacene-2,6-dimethanol<sup>[3b]</sup> as air-sensitive, colorless crystals (m. p. = 197–199 °C (dec.)) which was converted by treatment with SOCl<sub>2</sub> into a mixture of 2,6-bis(chloromethyl)-1,5-dihydro-*s*-indacene **1** and its 1,7-dihydro isomer (m. p. = 137–140 °C (dec.)). The overall yield from the bis(β-keto ester) was 50%.

Treatment of **1** with 4,4'-biphenyldimethanethiol under high dilution conditions gave the corresponding dithia[3](4,4')biphenyl[3](2,6)dihydro-*s*-indacenophane **2** (colorless crystals, dec. > 250 °C)<sup>[3c]</sup>, and desulfurization by irradiation in a solution of trimethyl phosphite/benzene gave the [2.2]phane **3** (colorless crystals, dec. > 250 °C) in 33% yield<sup>[3d]</sup>.

Attempts to prepare tetrahydro-*s*-indacenophane **4** from **1** by standard methods of cyclophane synthesis failed. However, when **1** was treated with tetracarbonylnickel in *N,N*-dimethylformamide, following the procedure of Corey *et al.*<sup>[4]</sup> for converting allyl halides into macrocycles, the desired phane **4** was formed in 10% yield as a mixture of double bond isomers (air-sensitive, colorless crystals, dec. > 100 °C)<sup>[3e]</sup>. Catalytic hydrogenation of **4** readily gave the novel, bridged "cyclophane" **5** (colorless crystals, m. p. = 204–206 °C (dec.))<sup>[3f]</sup>.

The intermediate diethyl 1,5-dioxohexahydro-*s*-indacene-2,6-dicarboxylate has also been shown to be a useful precursor for a logically-designed synthesis of 1,5- and 1,7-dihydro-*s*-indacene, interesting molecules for which there are other known literature procedures<sup>[5]</sup>. Hydrolysis and decarboxylation of the bis(β-keto ester) with TsOH/acetic acid gave tetrahydro-*s*-indacene-1,5-dione (m. p. = 230–231 °C)<sup>[3g]</sup>, which on reduction with NaBH<sub>4</sub> to the corresponding 1,2,3,5,6,7-hexahydro-*s*-indacene-1,5-diol followed by dehydration using TsOH in CHCl<sub>3</sub>/tetrahydrofuran gave 1,5(1,7)-dihydro-*s*-indacene in 56% overall yield.

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[3] a) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.72 (s, 2H); 7.62 (s, 2H), 4.31 (q, 4H), 3.70 (s, 4H), 1.36 (t, 6H); UV (dioxane): λ<sub>max</sub> = 331 nm (lg ε = 4.58), 347 (4.55); IR (KBr): ν(C=O) = 1680 cm<sup>-1</sup>; b) <sup>1</sup>H-NMR ([D<sub>2</sub>]DMSO): δ = 7.36 (s, 2H), 6.68 (s, 2H), 5.95 (t, 2H), 4.37 (d, 4H), 3.30 (s, 4H); c) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.68–6.97 (m, 10H), 6.62 (s, 1H), 6.05 (s, 1H), 4.08–2.68 (m, 12H); d) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.64–6.55 (m, 10H), 5.95 (s, 2H), 3.76–2.29 (m, 2H); e) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.38–6.86 (m, 4H), 6.48 (br. s, 4H), 5.30–4.86 (m, 4H), 4.18–2.54 (m, 12H); MS: *m/z* 360.1868; f) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.01 (s, 4H), 3.23–1.44 (m, 28H); MS: *m/z* 368.2484; g) <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.82 (s, 2H), 3.31–3.11 (m, 4H), 2.90–2.67 (m, 4H); IR (KBr): ν(C=O) = 1710 cm<sup>-1</sup>.  
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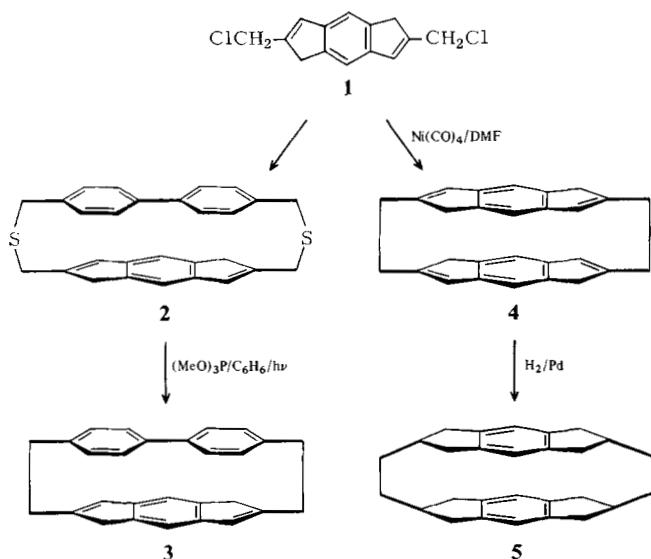
## Active Transport of Amino Acid Anions by a Synthetic Metal-Complex Carrier

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Although membrane transport of amino acid anions, ATP, and other compounds has been recognized to play important roles in biology, and to have wide applications in separation science, very few artificial carriers have been reported for the selective transport of these anionic species<sup>[3,4]</sup>.

Here we report that a new series of transition-metal complexes of the macrocyclic polyamine 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane (tbcyclen) display novel

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