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LETTERS

## A new synthetic route to tribenzo[*a,e,i*][12]annulenes

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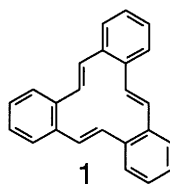
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### Abstract

The tribenzo[*a,e,i*][12]annulene **10** and the corresponding twofold annulene **14** were prepared on synthetic routes which first led from suitably functionalised starting compounds (**2**, **11**) to the 1,2-distyryl- and 1,2,3,4-tetrastyrylbenzene derivatives **9** and **13** with two and four formyl groups, respectively. The cyclisation to **10** and **14** was achieved by applying the McMurry reaction. The extended ring system of compound **14** represents a discotic mesogen. The generation of liquid crystals was obtained with eight hexyloxy chains on the periphery. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* annulenes; cyclisation; liquid crystals.

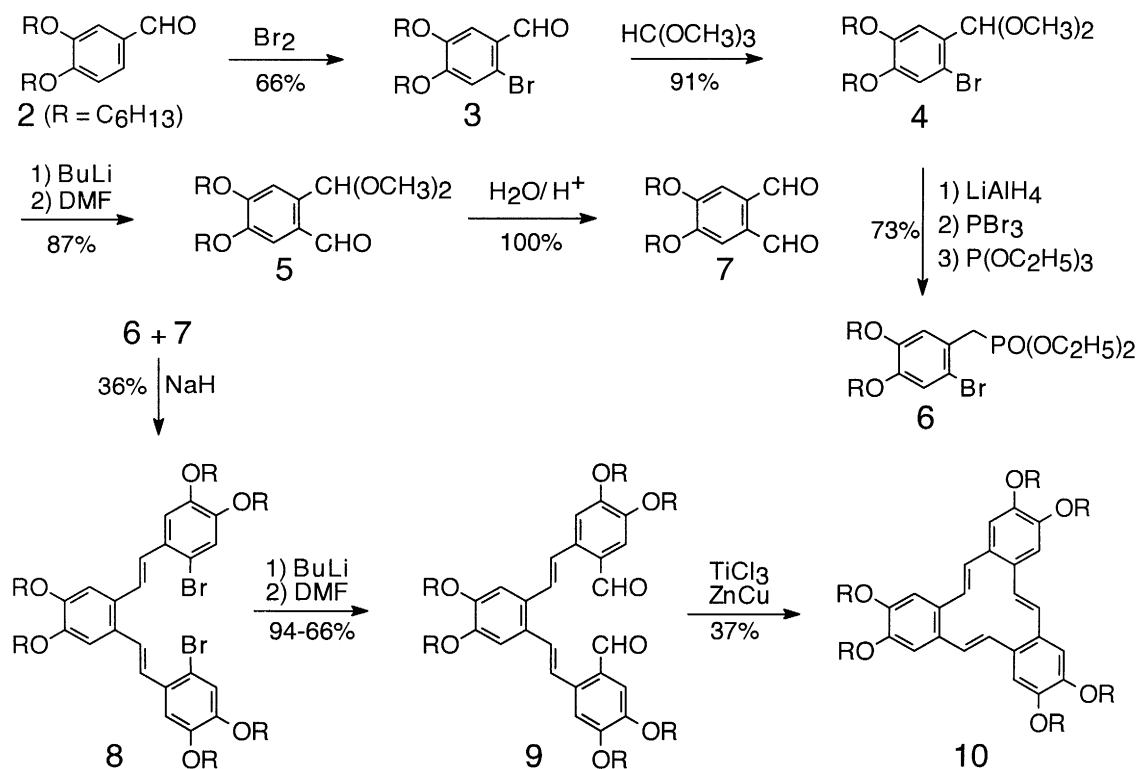
Areno-condensed annulenes represent discotic mesogens which are suitable for the generation of liquid crystals in very broad temperature intervals.<sup>1</sup> Due to their interesting photophysical and photochemical properties they attract considerable attention in materials science.<sup>2</sup> (5*E*,11*E*,17*E*)-Tribenzo[*a,e,i*]cyclododecene (tribenzo[*a,e,i*][12]annulene) **1** was first prepared by H. A. Staab and co-workers.<sup>3</sup> This approach, as well as an alternative route<sup>4</sup> to the parent compound, proved not to be appropriate for the synthesis of derivatives with long flexible alkoxy chains;<sup>5</sup> therefore we had to conceive a novel route for the formation of such ring systems which represent the first substituted tribenzo[*a,e,i*][12]annulenes.



3,4-Dihexyloxybenzaldehyde (**2**) yielded with bromine in acetic acid compound **3** in which the formyl group was protected as acetal **4** by the reaction with trimethoxy orthoformate in the presence of Dowex 50 W-X8<sup>®</sup> (Scheme 1). Bouveault formylation led to the aldehyde **5**; additionally **4** was transformed to the phosphonate **6**. The latter process consisted of three steps, namely reduction of the acetal to the

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corresponding primary alcohol, substitution of the hydroxy group by bromine and an Arbusov reaction with triethyl phosphite. The overall yield amounted to 73%. A twofold Wittig–Horner reaction of **6** and the dialdehyde **7**, obtained by a quantitative deprotection of **5**, gave the diolefin **8** as a mixture of stereoisomers. The equilibration with iodine in boiling *p*-xylene resulted in a 3:1 ratio of (*E,E*)- and (*E,Z*)-configuration. The twofold Bouveault reaction **8**→**9** yielded the starting compound for the McMurry cyclisation to the desired annulene **10**. The recrystallised dialdehyde **9** contained selectively the (*E,E*)-isomer; moreover, **10** was obtained in a pure (*E,E,E*)-configuration. Concerning the parent system **1**, apart from the (*E,E,E*)-isomer the (*Z,Z,Z*)-isomer<sup>6,7</sup> as well as the (*E,Z,Z*)-isomer<sup>7</sup> are stable compounds, whereas the (*E,E,Z*)-isomer<sup>3,4</sup> was only postulated as an intermediate.

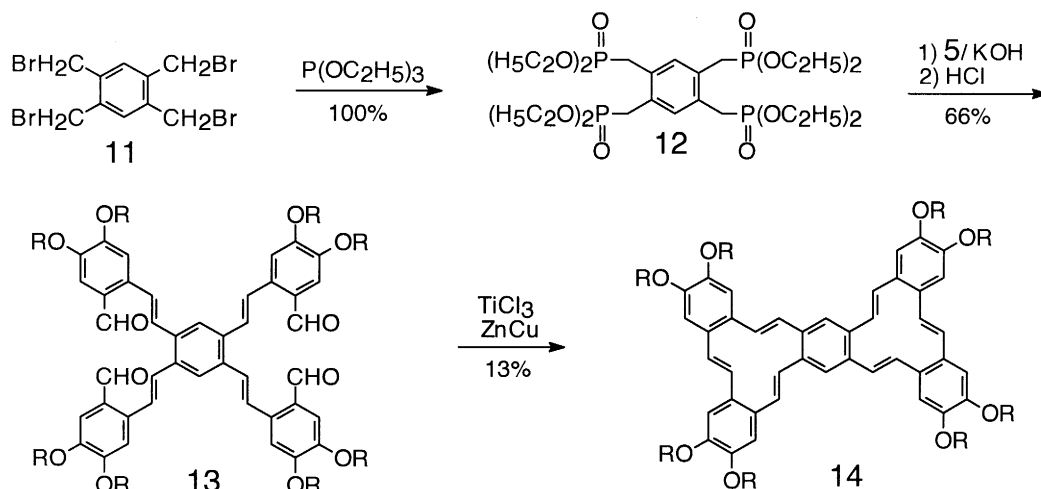


Scheme 1.

The enantiotopic protons of the OCH<sub>2</sub> groups in **10** prove the fast inversion of the central 12-membered ring.<sup>8</sup> Thus, the disk-like shape of **10** resembles strongly the hexahexyloxytricycloquinazoline which forms liquid crystals.<sup>9</sup> Nevertheless, annulene **10** shows a sharp melting point at 108°C. The DSC measurement reveals onset temperatures of 107.5 and 95.5°C for the phase transition solid/liquid in the heating and the cooling curve, respectively. Probably the interaction of neighbouring ring systems is too low to establish a mesophase.

Consequently, we synthesised an enlarged ring system **14** with two [12]annulene units. Starting from tetrakis(bromomethyl)benzene **11**, the tetraphosphonate **12** was prepared by an Arbusov reaction (Scheme 2). The Wittig–Horner olefination with **12** and **5** yielded after deprotection the tetraaldehyde **13** which was subjected to a McMurry reaction. The twofold cyclisation product **14** was obtained as first fraction in the column chromatography (SiO<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>).<sup>10</sup> The DSC (second heating curve) shows at 165°C a transition of the crystalline state to an LC phase. The mosaic textures observed in the polarisation

microscope indicate a columnar phase. The clearing point cannot be determined because decomposition reactions start above 280°C.



Scheme 2.

All compounds were characterised by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectra and gave satisfactory elemental analyses. The characteristic data of the di- and tetrastyrilbenzenes<sup>11</sup> **8**, **9** and **13**, and the [12]annulenes<sup>12</sup> **10** and **14** are listed below.

## Acknowledgements

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- The three inner hydrogen atoms in **1** and **10** prevent a totally planar structure.<sup>3</sup>
- (a) Kumar, S.; Wachtel, E. J.; Keinan, E. *J. Org. Chem.* **1993**, *58*, 3821; (b) Keinan, E.; Kumar, S.; Singh, S. P.; Ghirlando, R.; Wachtel, E. *J. Liq. Cryst.* **1992**, *11*, 157.
- A ketone  $\text{C}_{90}\text{H}_{126}\text{O}_9$  and higher oligomers are the major products in the later fractions.

11. Di- and tetrastyrilbenzenes: compound **8**: colourless crystals, mp 110°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.89 (m, 18H,  $\text{CH}_3$ ), 1.31 (m, 24H,  $\text{CH}_2$ ), 1.46 (m, 12H,  $\text{CH}_2$ ), 1.81 (m, 12H,  $\text{CH}_2$ ), 3.97 (m, 8H,  $\text{OCH}_2$ ), 4.07 (t, 4H,  $\text{OCH}_2$ ), 7.02, s, 2H/7.06, s, 2H/7.12, s, 2H (aromat. CH), 7.10/7.17 (AB,  $^3J=15.9$  Hz, 4H, olefin. H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.0 ( $\text{CH}_3$ ), 22.6/25.6/29.2/31.6 ( $\text{CH}_2$ ), 69.5/69.8 ( $\text{OCH}_2$ ), 112.0/112.4/117.6 (aromat. CH), 114.9 ( $\text{C}_q\text{Br}$ ), 127.5/128.7 (olefin. CH), 129.3/129.8 ( $\text{C}_q$ ), 148.8/149.3/149.6 ( $\text{C}_q\text{O}$ ); compound **9**: yellow crystals, mp 113°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.88 (m, 18H,  $\text{CH}_3$ ), 1.32 (m, 24H,  $\text{CH}_2$ ), 1.46 (m, 12H,  $\text{CH}_2$ ), 1.81 (m, 12H,  $\text{CH}_2$ ), 4.04 (m, 12H,  $\text{OCH}_2$ ), 7.00, s, 2H/7.08, s, 2H/7.33, s, 2H (aromat. CH), 7.17/7.61 (AB,  $^3J=15.9$  Hz, 4H, olefin. H), 10.24 (s, 2H, CHO);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.0 ( $\text{CH}_3$ ), 22.6/22.6/25.6/25.7/29.0/29.2/31.5/31.6 ( $\text{CH}_2$ ), 69.2/69.3 ( $\text{OCH}_2$ ), 110.6/111.6/113.1 (aromat. CH), 125.3/130.7 (olefin. CH), 126.3/129.0/135.7 ( $\text{C}_q$ ), 148.7/149.6/154.0 ( $\text{C}_q\text{O}$ ), 190.2 (CHO); compound **13**: yellow crystals, which decompose above 200°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.89 (m, 24H,  $\text{CH}_3$ ), 1.33 (m, 32H,  $\text{CH}_2$ ), 1.47 (m, 16H,  $\text{CH}_2$ ), 1.83 (m, 16H,  $\text{CH}_2$ ), 4.05 (t, 8H,  $\text{OCH}_2$ ), 4.09 (t, 4H,  $\text{OCH}_2$ ), 7.07 (s, 4H, aromat. CH), 7.23/7.85 (AB,  $^3J=15.8$  Hz, 8H, olefin. H), 7.34 (s, 4H, aromat. H), 7.81 (s, 2H, aromat. H), 10.25 (s, 4H, CHO);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.0 ( $\text{CH}_3$ ), 22.6/25.6/29.0/31.5 ( $\text{CH}_2$ ), 69.2 ( $\text{OCH}_2$ ) 110.7/113.6/126.0 (aromat. CH), 126.5/135.1/135.7 ( $\text{C}_q$ ), 127.8/130.3 (olefin. CH), 149.0/154.0 ( $\text{C}_q\text{O}$ ), 190.3 (CHO).
12. [12]Annulenes: compound **10**: light beige crystals, mp 107.5°C (DSC);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.90 (t, 18H,  $\text{CH}_3$ ), 1.35 (m, 24H,  $\text{CH}_2$ ), 1.48 (m, 12H,  $\text{CH}_2$ ), 1.83 (m, 12H,  $\text{CH}_2$ ) 4.04 (t, 12H,  $\text{OCH}_2$ ), 6.88 (s, 6H, aromat. H), 7.02 (s, 6H, olefin. H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.0 ( $\text{CH}_3$ ), 22.6/25.8/29.4/31.6 ( $\text{CH}_2$ ), 69.6 ( $\text{OCH}_2$ ), 113.9 (aromat. CH), 130.9 ( $\text{C}_q$ ), 132.6 (olefin. CH), 148.4 ( $\text{C}_q\text{O}$ ); compound **14**: light yellow solid which is transformed at 165°C (DSC) to the LC phase;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.91 (m, 24H,  $\text{CH}_3$ ), 1.36 (m, 32H,  $\text{CH}_2$ ), 1.49 (m, 16H,  $\text{CH}_2$ ), 1.84 (m, 16H,  $\text{CH}_2$ ), 4.04 (t, 16H,  $\text{OCH}_2$ ), 6.90 (s, 4H, aromat. H), 6.91 (s, 4H, aromat. H), 7.03 (s, 4H, olefin. H), 7.07/7.13 (AB,  $^3J=16.5$  Hz, 8H, olefin. H), 7.37 (s, 2H, aromat. H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.1 ( $\text{CH}_3$ ), 22.7/25.8/29.3/31.6 ( $\text{CH}_2$ ), 69.4 ( $\text{OCH}_2$ ), 113.3/113.3/128.2 (aromat. CH), 130.5/130.8/136.7 ( $\text{C}_q$ ), 132.3/132.7/133.7 (olefin. CH), 148.3/148.4 ( $\text{C}_q\text{O}$ ).