

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

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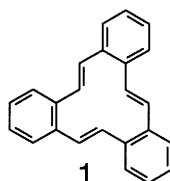
Received 11 November 1999; accepted 14 December 1999

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-tetrastyrilbenzene 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.

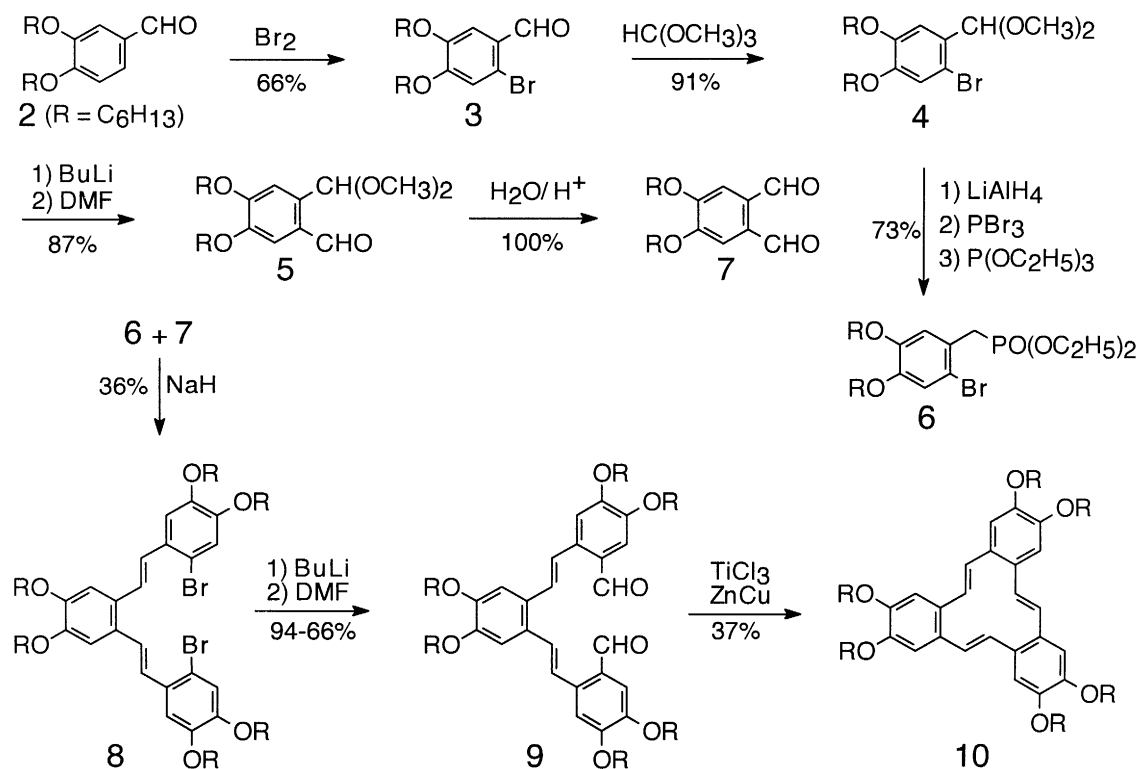
Areno-condensed annulenes represent discotic mesogens which are suitable for the generation of liquid crystals in very broad temperature intervals.¹ Due to their interesting photophysical and photochemical properties they attract considerable attention in materials science.² (5*E*,11*E*,17*E*)-Tribenzo[*a,e,i*]cyclododecene (tribenzo[*a,e,i*][12]annulene) **1** was first prepared by H. A. Staab and co-workers.³ This approach, as well as an alternative route⁴ to the parent compound, proved not to be appropriate for the synthesis of derivatives with long flexible alkoxy chains;⁵ 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® (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^{6,7} as well as the (*E,Z,Z*)-isomer⁷ are stable compounds, whereas the (*E,E,Z*)-isomer^{3,4} was only postulated as an intermediate.

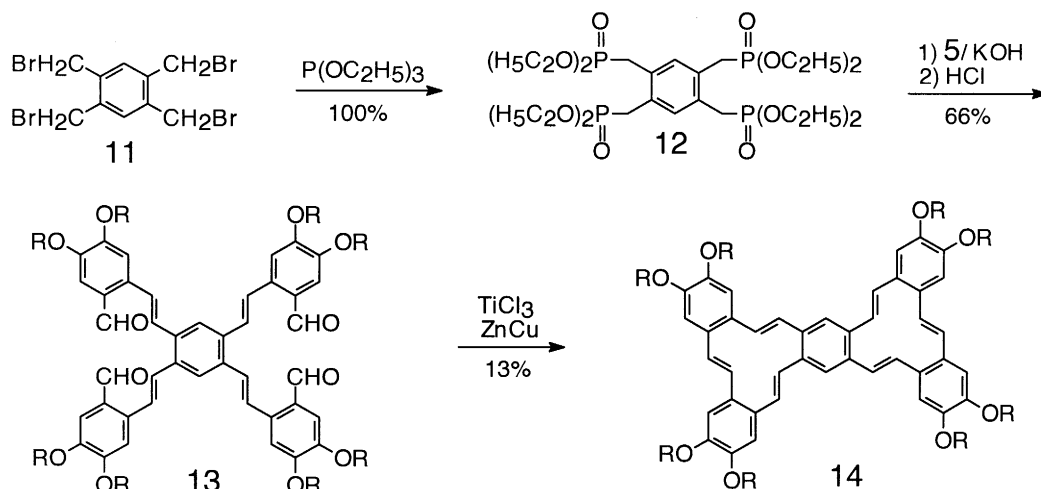


Scheme 1.

The enantiotopic protons of the OCH₂ groups in **10** prove the fast inversion of the central 12-membered ring.⁸ Thus, the disk-like shape of **10** resembles strongly the hexahexyloxytricycloquinazoline which forms liquid crystals.⁹ 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 (SiO₂/CH₂Cl₂).¹⁰ 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 ^1H NMR, ^{13}C NMR and mass spectra and gave satisfactory elemental analyses. The characteristic data of the di- and tetrastyrilbenzenes¹¹ **8**, **9** and **13**, and the [12]annulenes¹² **10** and **14** are listed below.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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- The three inner hydrogen atoms in **1** and **10** prevent a totally planar structure.³
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- 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; ^1H NMR (CDCl_3): δ 0.89 (m, 18H, CH_3), 1.31 (m, 24H, CH_2), 1.46 (m, 12H, CH_2), 1.81 (m, 12H, CH_2), 3.97 (m, 8H, OCH_2), 4.07 (t, 4H, 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}C NMR (CDCl_3): δ 14.0 (CH_3), 22.6/25.6/29.2/31.6 (CH_2), 69.5/69.8 (OCH_2), 112.0/112.4/117.6 (aromat. CH), 114.9 (C_qBr), 127.5/128.7 (olefin. CH), 129.3/129.8 (C_q), 148.8/149.3/149.6 (C_qO); compound **9**: yellow crystals, mp 113°C; ^1H NMR (CDCl_3): δ 0.88 (m, 18H, CH_3), 1.32 (m, 24H, CH_2), 1.46 (m, 12H, CH_2), 1.81 (m, 12H, CH_2), 4.04 (m, 12H, 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}C NMR (CDCl_3): δ 14.0 (CH_3), 22.6/22.6/25.6/25.7/29.0/29.2/31.5/31.6 (CH_2), 69.2/69.3 (OCH_2), 110.6/111.6/113.1 (aromat. CH), 125.3/130.7 (olefin. CH), 126.3/129.0/135.7 (C_q), 148.7/149.6/154.0 (C_qO), 190.2 (CHO); compound **13**: yellow crystals, which decompose above 200°C; ^1H NMR (CDCl_3): δ 0.89 (m, 24H, CH_3), 1.33 (m, 32H, CH_2), 1.47 (m, 16H, CH_2), 1.83 (m, 16H, CH_2), 4.05 (t, 8H, OCH_2), 4.09 (t, 4H, 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}C NMR (CDCl_3): δ 14.0 (CH_3), 22.6/25.6/29.0/31.5 (CH_2), 69.2 (OCH_2) 110.7/113.6/126.0 (aromat. CH), 126.5/135.1/135.7 (C_q), 127.8/130.3 (olefin. CH), 149.0/154.0 (C_qO), 190.3 (CHO).
12. [12]Annulenes: compound **10**: light beige crystals, mp 107.5°C (DSC); ^1H NMR (CDCl_3): δ 0.90 (t, 18H, CH_3), 1.35 (m, 24H, CH_2), 1.48 (m, 12H, CH_2), 1.83 (m, 12H, CH_2) 4.04 (t, 12H, OCH_2), 6.88 (s, 6H, aromat. H), 7.02 (s, 6H, olefin. H); ^{13}C NMR (CDCl_3): δ 14.0 (CH_3), 22.6/25.8/29.4/31.6 (CH_2), 69.6 (OCH_2), 113.9 (aromat. CH), 130.9 (C_q), 132.6 (olefin. CH), 148.4 (C_qO); compound **14**: light yellow solid which is transformed at 165°C (DSC) to the LC phase; ^1H NMR (CDCl_3): δ 0.91 (m, 24H, CH_3), 1.36 (m, 32H, CH_2), 1.49 (m, 16H, CH_2), 1.84 (m, 16H, CH_2), 4.04 (t, 16H, 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}C NMR (CDCl_3): δ 14.1 (CH_3), 22.7/25.8/29.3/31.6 (CH_2), 69.4 (OCH_2), 113.3/113.3/128.2 (aromat. CH), 130.5/130.8/136.7 (C_q), 132.3/132.7/133.7 (olefin. CH), 148.3/148.4 (C_qO).