

1,1 : 2,2-Bis([10]annulene-1,6-diyl)ethylene, Double Layered Annulene with 10 π -Rings

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The title compound has been synthesized; the ¹H n.m.r. and electronic spectra suggest that the layered compound experiences appreciable interaction between the two [10]annulene rings.

Progress in annulene chemistry has stimulated our interest in layered compounds consisting of annulenes of various ring-sizes, to investigate how the ring current induced in one annulene ring is affected by that of another annulene ring. Although the benzenoid ring 1,6-methano[10]annulene 'hybrid' annulenophanes have been prepared,¹ no layered annulenes have been reported. 11-Methylene-1,6-methano[10]annulene (**1**) and 1,6-methano[10]annulene-11-one (**2**) have been prepared by Vogel *et al.*² and by Itō *et al.*,³ respectively. Both (**1**) and (**2**) proved to be like the parent 1,6-methano[10]annulene⁴ and show no interaction between the p_z orbital of the bridge and peripheral 10 π -electron system.

In this communication, we describe the first synthesis of a novel double layered annulene (**3**) which has two [10]annulene

units held together symmetrically with one etheno bridge, and has the potential to show an interaction due to the closely spaced face to face arrangement of the annulenes.

The synthesis of (**2**) interested us, since it has a convenient 'carbonyl handle' on the central position of 10 π -ring for intermolecular reductive coupling by the McMurry method,⁵ and so (**2**) appears to be a key intermediate for the synthesis of the title compound (**3**). However, our first attempts at self-coupling of (**2**) using TiCl₃-LiAlH₄ in tetrahydrofuran (THF)⁶ did not give the desired dimeric product (**3**), but gave

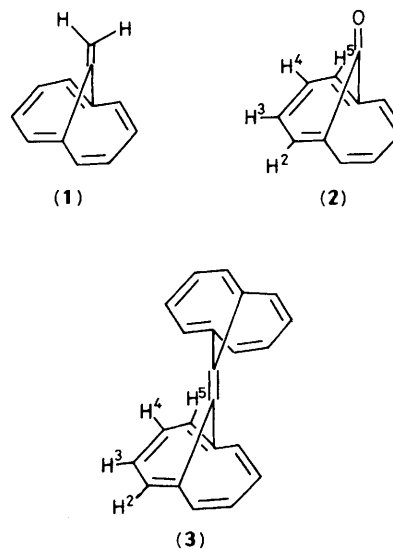
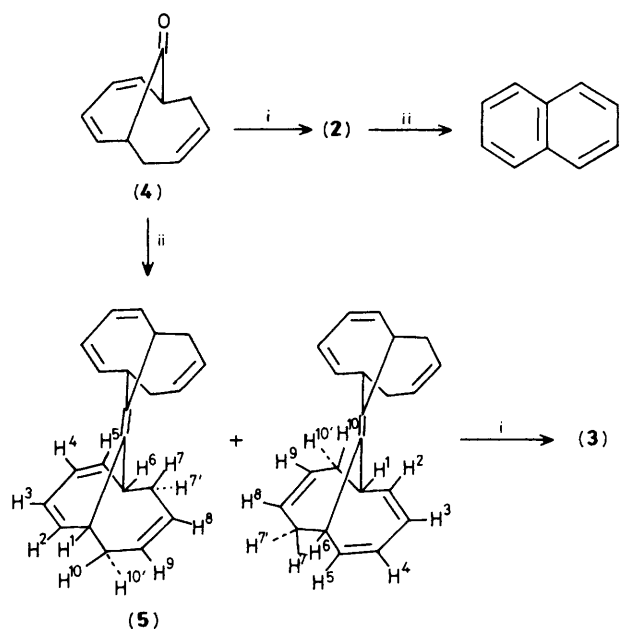


Table 1. Spectral data for (**1**)–(**3**)

Compd.	¹ H n.m.r., δ^a	λ_{max}/nm (ϵ) ^b
(1) ^c	7.2 (centre A ₂ B ₂ , 8H), 3.2 (=CH ₂ , 2H)	258 (67 500), 300 (6700), 360–410 (130–190)
(2) ^d	7.55 (2-, 5-H, 4H), 7.36 (3-, 4-H, 4H) (A ₂ B ₂ , centre δ 7.46)	250.5 (77 500), 296 (7000), 352 (92), 362 (124), 371 (168), 379 (228), 391 (275), 402 (326)
(3)	7.21–7.15 (2-, 5-H, 8H), 6.76–6.72 (3-, 4-H, 8H) (A ₂ B ₂ , centre δ 6.96)	253 (141 000), 306 sh (10 900), 374 sh (481), 4 (577), 418 (513), 432 (353)

^a CCl₄ for (**1**), CDCl₃ for (**2**) and (**3**). ^b Cyclohexane. ^c Ref. 2.
^d Ref. 3.



Scheme 1. i, DDQ in benzene; ii, $\text{TiCl}_3\text{-LiAlH}_4$ in THF.

only naphthalene in a low yield. We reasoned that this failure can be ascribed to the inherent lower stability of the ketone (2). We then directed our efforts to a two-stage synthetic approach involving reductive coupling of the more stable ketone (4) and dehydrogenation of the dimer (5). The reductive coupling of the ketone (4) as before⁶ afforded the desired dimer (5)^{†‡} (colourless needles, m.p. 138 °C, 3.1%) as a mixture of *syn*- and *anti*-isomers. When a mixture of (5) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (1.2 mol) in benzene was heated in a sealed tube under nitrogen atmosphere for 24 h at 110–120 °C, dehydrogenation of (5)

[†] The elemental analyses, i.r., and mass spectra were consistent with the assigned structures.

[‡] ¹H n.m.r. (CDCl_3): δ 5.93–5.88 (m, 4H, 3-, 4-H), 5.77–5.73 (m, 4H, 2-, 5-H), 5.57–5.55 (m, 4H, 8-, 9-H), 3.79–3.76 (m, 4H, 1-, 6-H), 2.56–2.50 (m, 4H, 7-, 10-, or 7'-, 10'-H), 2.19–2.13 (m, 4H, 7'-, 10'-, or 7-, 10-H); λ_{max} (cyclohexane) 250 (ϵ 9500), 261 (9800), 273 sh nm (8600).

took place to afford the title compound (3)[†] (pale yellow needles, m.p. 245 °C, 5.9%), which was isolated by chromatography on silica-gel.

The ¹H n.m.r. and electronic spectral data of (3) are listed in Table 1, together with those of the reference model compounds (1) and (2). The ring protons of (3) resonate as an A_2B_2 type system, similar to (1) and (2),^{2,3} and do so at a lower field than those of (5), suggesting that the annulene rings of (3) sustain a diamagnetic ring current. Comparison of the central chemical shifts of the annulene protons in (1), (2), and (3) indicates that the protons of (3) (δ 6.96) resonate in higher field than those of (1) (δ 7.20) and (2) (δ 7.46). This high-field shift observed in (3) is reasonably ascribed to diamagnetic anisotropy of the opposite annulene ring.

The electronic spectrum of (3) shows three bands arising from the [10]annulene chromophore⁷ and is characteristic of a $[4n + 2]\pi$ -electron system,⁸ as observed in the spectra of (1) and (2). However, the longest wavelength band of (3) shows a marked bathochromic shift (20–30 nm), when compared with those of (1) and (2), demonstrating that the transition associated with the longest wavelength band of the [10]annulene chromophore is affected by the transannular interaction caused by the two annulene rings held together with the etheno bridge. Thus, as revealed in the examination of the ¹H n.m.r. spectrum, this suggests that the two chromophores of the same ring size in (3) are suitable to overlap extensively with each other.

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