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SYNTHESES OF NAPHTHO[2,3-i]-5,14-DIMETHYL-1,3-BISDEHYDRO[14]ANNULENE AND NAPHTHO[1,2-i]-5,14-DIMETHYL-1,3-BISDEHYDRO[14]ANNULENE, RING-EXPANDED ANALOGUES OF ANTHRACENE AND PHENANTHRENE [1]

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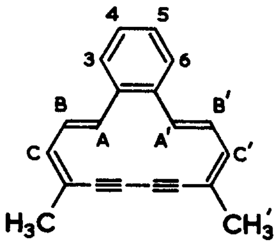
A method has recently been developed in these laboratories, whereby benzannelated bisdehydroannulenes [e.g., benzo[i]-5,14-dimethyl-1,3-bisdehydro[14]annulene (1)] can be obtained readily.[2] We now describe the use of this method for the synthesis of the title compounds (2) and (3), dimethylbisdehydro[14]annulenes containing a naphthalene ring fused in the 2,3- and 1,2-position,[3] respectively. These are analogues of anthracene (5) and phenanthrene (6) [in the same way as (1) is an analogue of naphthalene (4)], in which a terminal 6π- ring has been formally expanded to a 14π-ring. The main reason for this investigation was to study the difference in aromaticity of the terminal rings between such anthracene and phenanthrene analogues by ^{1}H-nmr spectrometry. This can be established much more readily when one of the terminal rings is a $(4n + 2)$ macrocycle [as in (2) and (3)] than in the basic systems [(5) and (6)], since local anisotropy effects play a much greater role in the latter compounds.



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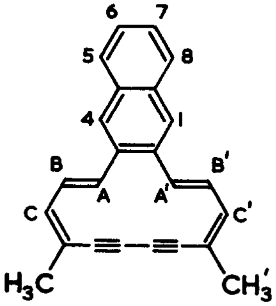

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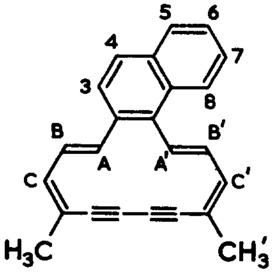

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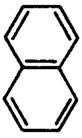

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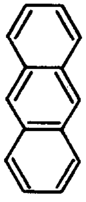

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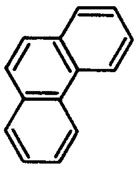

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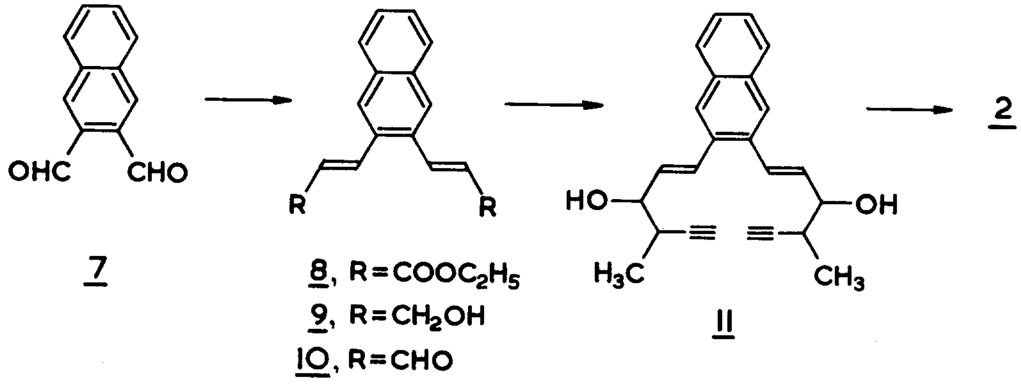
Wittig reaction of naphthalene-2,3-dicarboxaldehyde (7)[4] with 2 molar equivalents of carbethoxymethylenetriphenylphosphorane[5] in boiling benzene led to 86 % of the (E,E)-diester (8),[6a] mp. 84-85 °C.[7] Reduction with excess diisobutylaluminium hydride in benzene at 5 °C yielded 92 % of the diol (9), mp. 140-142 °C,[7] which was oxidized in 88 % yield to the dialdehyde (10), mp. 202-203 °C[7] by means of active manganese dioxide[8] in methylene chloride.

Grignard reaction of (10) with an excess of the magnesium derivative of 3-bromo-1-butyne[9] led to a stereoisomeric mixture of the diols (11), which was oxidatively coupled to the corresponding macrocyclic "monomer" in aqueous ethyl alcohol, benzene and hydrochloric acid with oxygen in the presence of cuprous chloride and ammonium chloride at 60 °C. Treatment of the crude diol with an excess of methanesulphonyl chloride and triethylamine[10] at 0 °C yielded the dimesylate, which was then subjected to elimination with 1,5-diazabicyclo[4.3.0]-non-5-ene. This procedure, which did not necessitate purification of the intermediates, yielded 19 % (based on (10)) of the 2,3-naphthodimethylbisdehydro[14]annulene (2)[6b] as orange needles, dec > 200 °C[7]; λ_{max} (CH_2Cl_2) 248 nm (ε 17,500), 261 (16,500), 337 (45,500), ∿ 400 sh (4,500).



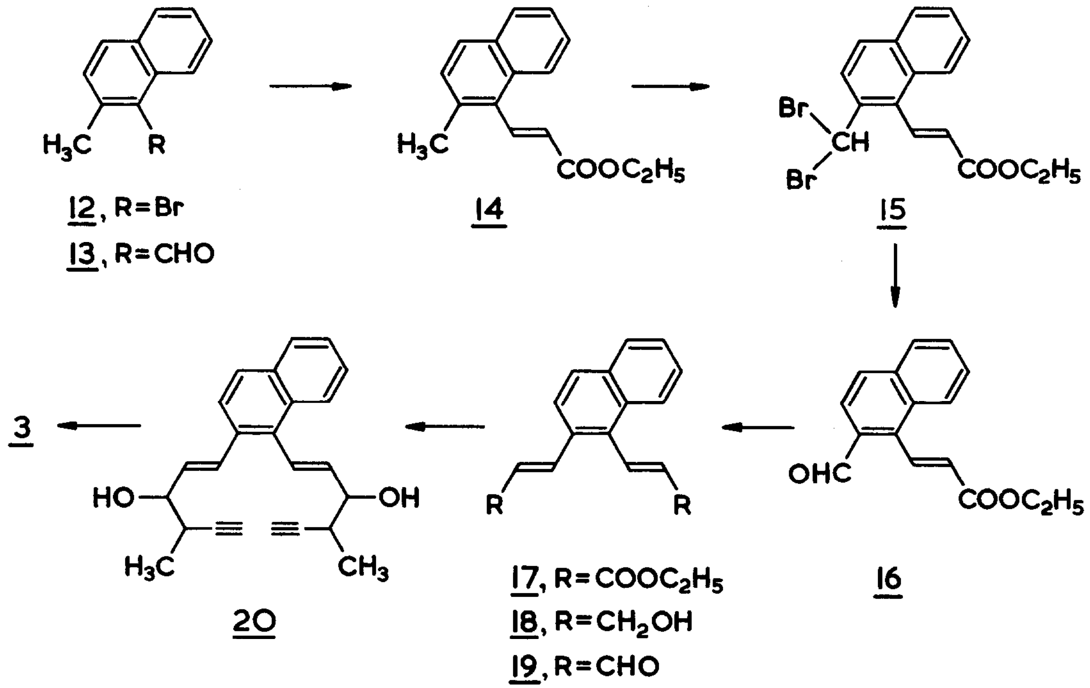
7

8, R=$COOC_2H_5$
9, R=CH_2OH
10, R=CHO

11

The synthesis of the 1,2-isomer (3) presented some difficulty, since naphthalene-1,2-dicarboxaldehyde is unknown, and some attempts to prepare it were unsuccessful. After some experimentation, the following route to (3) proved to be successful. Grignard reaction of the readily available 1-bromo-2-methylnaphthalene (12) with magnesium and dimethylformamide yielded 88 % of 2-methylnaphthalene-1-carboxaldehyde (13), mp. 49-50 °C (lit.[11] mp. 51.5-52 °C). Wittig reaction of (13) with carbethoxymethylenetriphenylphosphorane[5] in boiling benzene led to 97 % of the ester (14)[6a] as a viscous liquid.[7] Bromination of (14) with 3 molar equivalents of N-bromosuccinimide in boiling carbon tetrachloride containing azobisisobutyronitrile yielded the oily crude dibromide (15)[6a] which on hydrolysis with sodium acetate in boiling acetic acid gave 67 % [based on (14)] of the aldehyde (16) as an oil. Wittig reaction of (16) with carbethoxymethylenetriphenylphosphorane[5] in boiling benzene then led to the(E,E)-diester (17),[6a] mp. 67-68 °C[7] in 67 % yield.

The conversion (17) → [(18), 100 %, oil]→[(19), 57 %, mp. 160-161 °C] → (20)→ macrocyclic



"monomer" → dimesylate → [(3), 32 % over-all yield based on (19)] was carried out essentially as described for the synthesis of (2) from the diester (8). The resulting 1,2-naphthodimethylbisdehydro[14]annulene (3)[6b] was obtained as orange needles, mp. 143-144 °C[7]; λ_{max} (CH_2Cl_2) ∿ 250 nm (ε 12,500), 333 (45,000), ∿ 396 nm (8,500), ∿ 420 sh (4,000).

The ^1H-nmr parameters of the two naphthodimethylbisdehydro[14]annulenes (2) and (3) described in this communication are given in Table 1, as well as those of the previously reported benzodimethylbisdehydro[14]annulene (1).[2,12] It is clear that the fourteen-membered ring of the

TABLE 1. ^1H-nmr parameters of (2), (3), and (1) in $CDCl_3$ at 100 MHz (τ values; internal standard TMS; J values in footnotes).

PROTON	(2)	(3)	(1)[2,12]
A,A'	3.65d [a]	4.82d,[a] 4.99d [a]	5.01d [a]
B,B'	2.78dd [b]	1.84-2.93 region [c]	2.56dd [d]
C,C'	3.18d [e]	3.02d [e]	2.92d [f]
CH_3, CH_3'	7.81s	7.72s	7.64s
naphthalene	1.53s (1,4)	1.09-1.20m (8)	-
	2.01-2.58m (5-8)	1.84-2.93m (3-7)	
benzene	-	-	1.75m (3,6)
			2.49m (4,5)

[a] J = 16 Hz. [b] J = 7,16 Hz. [c] Covered by the 3-7 naphthalene proton resonances.
[d] J = 7.5, 16 Hz. [e] J = 7 Hz. [f] J = 7.5 Hz.

phenanthrene analogue(3)is more diatropic ("aromatic") than that of the anthracene analogue(2). This follows unequivocally from an inspection of the spectra, in which the inner A,A' protons of (3) resonate at considerably higher field than those of (2), while the outer C,C' and CH_3,CH_3' protons resonate at lower field.[13] A simple explanation for this observation is based on a consideration of Kekulé structures. In the 1,2-naphtho[14]annulene (3), as in phenanthrene (6), Kekulé structures can be written for a terminal ring which does not destroy the delocalization of the other terminal ring. This is not the case with the 2,3-naphtho[14]-annulene (2), or with anthracene (5).

Interestingly, the 14-membered ring of the benzobisdehydro[14]annulene (1) is more diatropic than either (2) or (3). However, it is not justified to make a direct diatropicity comparison of the bicyclic substance (1) with the tricyclic compounds (2) and (3).

ACKNOWLEDGEMENT. T.C.W. wishes to thank the Science Research Council for a Research studentship.

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13. Direct comparison of the B,B' proton resonances of 2 and 3 cannot be made, since this band in 3 overlaps with the 3-7 naphthalene proton resonances.