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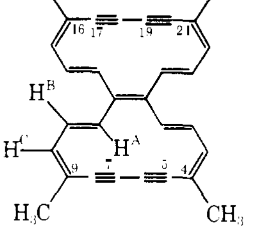
4,9,16,21-Tetramethyl-5,7,17,19-tetrakisdehydro[14]annuleno[14]annulene, a Macrocyclic Analog of Naphthalene[1,2]

Sir:

A little explored aspect of annulene chemistry is the synthesis of fused bicyclic hydrocarbons made up of identical [4*n* + 2]- or of [4*n*]annulene rings. Hitherto, the only well studied example is naphthalene ([6]annuleno[6]annulene), which has been known for a considerable time.[3] It was of interest to make available other representatives of this series, particularly to investigate their "aromaticity" or "antiaromaticity". We now describe the synthesis of 4,9,16,21-tetramethyl-5,7,17,19-tetrakisdehydro[14]annuleno[14]annulene (**1**),[2,4] a simple derivative of the 26π-electron [14]annuleno[14]annulene (e.g., **2**), in which both rings are (4*n* + 2)-membered.

A potential intermediate for the synthesis of **1** was the dialdehyde **14**, a suitable precursor of which appeared to be the previously described dimethylbisdehydro[14]annuleno[*c*]furan, **6**.[5] Since **6** was required in quantity, an improved synthesis was developed, 3,4-Furandicarboxaldehyde[6] was converted to the bisvinylog **3**, mp 158-160° [7a,8,9] in 77% yield by the method of Cresp et al.[10] Reaction of **3** with an excess of the Mg derivative of 3-bromo-1-butyne[11] in ether at −30° for 15 min gave the pale yellow diol **4**[9] as a stereoisomeric mixture, which was coupled to the macrocyclic diol **5** with O_2, CuCl, NH_4Cl, and HCl in aqueous C_2H_5OH and benzene. It was unnecessary to purify or separate the stereoisomers of the noncrystalline **4** and **5**. Treatment of crude **5** with mesyl chloride and $N(C_2H_5)_3$[12] in dimethoxyethane (0°, 1.5 hr, N_2) and subsequent elimination with 1,5-diazabicyclo[4.3.0]non-5-ene at 20° for 3.5 hr then led to **6**[7b] in ~30% yield (based on **3**).[13,14]



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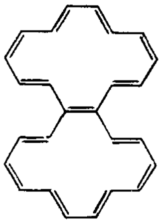

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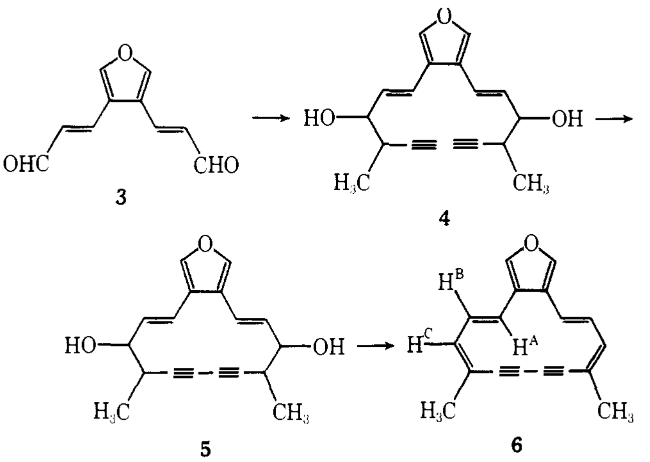

3 4 5 6

After considerable experimentation it was found that suitable modification of the furan ring of **6** could be effected by treatment with $Pb(OAc)_4$ in CH_3COOH[15] (20°, 30 min, N_2), which led to the diacetate **7** (red gum;[9] λ_{max} (ether) 307 sh (ϵ 62,500), 319 (91,500), 371 (9800), 393 (9300), 458 sh (330), 504 sh (280), 552 sh nm (190)). Hydrolysis of **7** with oxalic acid in aqueous THF (20°, 12 hr, N_2), gave the corresponding diol **8** (orange solid; *m/e* 262 ($M^+ - H_2O$)) instead of the dialdehyde **14**, as evidenced by the ^1H NMR and ir spectra. The ^1H NMR spectra of **7** and **8** indicated them to be ca. 1:1 mixtures of the cis and trans isomers,[15] which were not separated. Substance **8** proved to be base-sensitive, but could be condensed with carbethoxymethylenetriphenylphosphorane[16] in benzene (80°, 16 hr, N_2). The reaction led to ~50% (based on **6**) of the trans, trans diester **9**[7a,17] as red needles: mp 141-142°:[9] λ_{max} (ether) 343 (ϵ 62,500), 405 sh (14,800), 418 nm (15,600). Reduction of **9** with *i*-Bu_2AlH in benzene (6°, 15 min, N_2) gave the diol **10** as red needles:[9,18] λ_{max} (ether) 336 (ϵ 56,400), 384 sh (9900), 396 sh (10,700), 413 (13,400), 476 (4900), 520 (540), 569 nm (400). Oxidation of **10** with MnO_2 in CH_2Cl_2 (20°, 1 hr, N_2) yielded 74% (based on **9**) of the dialdehyde **11** as orange needles;[9,18] λ_{max} (ether) 265 (ϵ 10,000), 347 (51,900), 420 nm (15,900), with absorption to 600 nm (Scheme I).

Treatment of **11** with an excess of the Mg derivative of 3-bromo-1-butyne,[11] as previously, gave the diol **12** which was coupled to **13** with $Cu(OAc)_2 \cdot H_2O$ in DMF at 65° for ~4 hr. The red noncrystalline diols **12** and **13** are mixtures of stereoisomers, which were not separated. Dehydration of crude **13** via the dimesylate, essentially as before, then yielded 5% (based on **11**) of the tetrakisdehydro[14]annuleno[14]annulene **1** as dark red-brown prisms: *m/e* 384.1871 (calcd 384.1878);[7a,18] λ_{max} (ether) 258 (ϵ 14,400), 278 sh

Scheme I

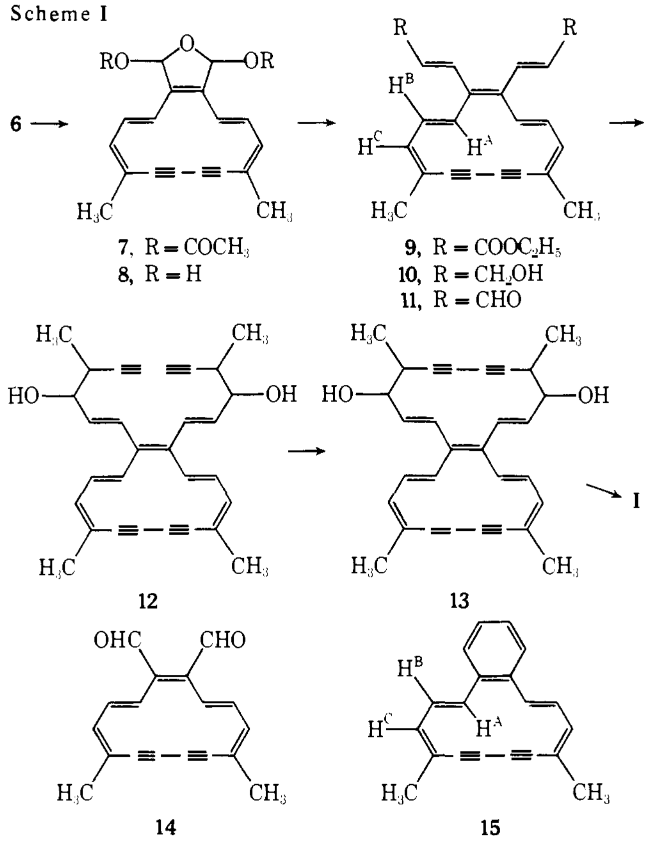

Table I. Some ^{1}H NMR Parameters of 9, 10, 11, 1, 15, and 6 at 100 MHz in $CDCl_3$ (τ Values; Internal Standard TMS)[a]

Compd	H^A	H^B	H^C	CH_3
9	8.83	2.07	2.31	7.29
10	9.24	1.88	2.22	7.28
11	8.56	← 2.06–2.34 →		7.26
1	6.18	2.13	2.69	7.52
15	5.01	2.56	2.92	7.64
6	3.48	3.69	3.28	7.94

[a] H^A (d, J = 15–16 Hz), H^B (dd, J = 7.5–10, 15–16 Hz), H^C (d, J = 7.5–10 Hz), CH_3 (s), for all compounds.

(16,800), 292 (21,100), 386 (45,400), 552 sh (1050), 607 sh nm (580); ν_{max} (KBr) 2130 m (C≡C), 970 s (trans C═C) cm^{-1}. Substance **1** was relatively stable, both in the solid state and in ether solution.

It has been shown previously that the ^{1}H NMR spectra of certain 1,3-bisdehydro[14]annulenes are temperature dependent, due to rotation about the trans double bonds,[19] and this proved to be the case with the diacetate **7**. On the other hand, the ^{1}H NMR spectra of the dehydroannulenes **9, 10, 11,** and **1** were essentially temperature independent in the range −60 to 100°, and showed the macrocyclic rings to exist in the indicated conformations.

Some ^{1}H NMR parameters of various 1,3-bisdehydro-[14]annulenes are given in Table I. As expected, the substituted compounds **9, 10,** and **11** are diatropic ("aromatic"), the inner H^A protons resonating at unusually high field, and the outer H^B, H^C, and CH_3 protons at unusually low field. It has already been found that the diatropicity of a 1,3-bisdehydro[14]annulene is considerably reduced by fusion of a benzene ring (see **15** in Table I),[20] and almost completely eliminated by fusion of a [*c*]furan ring (see **6** in Table I).[5] It is evident from the NMR spectrum of **1** that fusion of a second bisdehydro[14]annulene also reduces the diamagnetic ring current of the bisdehydro[14]annulene, although to a lesser extent than benzene. The decreasing order of diatropicity of the macrocyclic ring of the various compounds in Table I (**9, 10, 11** > **1** > **15** > **6**) is presumably a reflection of a decrease in the importance of different participating Kekulé structures of that ring.

Acknowledgment. We thank the Royal Society and the Science Research Council for financial support.

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(1) Unsaturated Macrocyclic Compounds. CXIV. For part CXIII, see R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Lett.*, 1043 (1975).

(2) We suggest that the trivial nomenclature of dehydroannulenes containing one, two, three, four, etc. acetylenes should contain the prefix monodehydro-, bisdehydro-, trisdehydro-, tetrakisdehydro-, etc., respectively, in order to avoid confusion in the literature (see P. J. Garratt and K. Grohmann in "Houben-Weyl, Methoden der Organischen Chemie", Vol V, Part 1d, Georg Thieme Verlag, Stuttgart, 1972, pp 543–544). Unless otherwise indicated, the rings in annulenoannulenes are considered to be ortho fused.

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(7) Isolated by chromatography on (a) SiO_2 (Woelm, act II); (b) Al_2O_3 (Woelm, act III).

(8) The ^{1}H NMR, electronic, and ir spectra of all new pure compounds were in accord with the assigned structures.

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(13) The conversion of **3** to **6** is based on the synthesis of related benzobisdehydroannulenes, carried out by Dr. N. Darby in these laboratories.

(14) Reaction of **3** with propargylaluminum bromide,[11] followed by coupling and then dehydration, led to the unstable bisdemethyl-**6**. We prefer to retain the methyl groups, as they confer increased stability and are useful probes for the study of ring currents by ^{1}H NMR spectrometry.

(15) See N. Elming and N. Clauson-Kaas, *Acta Chem. Scand.*, **6**, 535 (1952); N. Elming, *ibid.*, **6**, 578 (1952).

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(17) A small amount of *cis,trans*-**9** was also formed, but was readily removed by crystallization from petroleum ether–CH_2Cl_2.

(18) The substance decomposed on attempted melting point determination.

(19) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 165 (1974).

(20) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 167 (1974).

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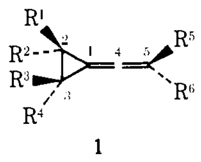
Cycloadditions of Alkenylidenecyclopropanes with Acetylenic Dienophiles. An Exclusive Formation of the (2 + 2) Cycloadduct

Sir:

Alkenylidenecyclopropane (**1**) has been shown recently by Pasto and his coworkers to react with 4-phenyl-1,2,4-triazoline-3,5-dione via a concerted $[(_{\pi}2 + _{\pi}2 + _{\sigma}2) + _{\pi}2]$ pathway,[1] while with chlorosulfonylisocyanate (CSI) **1** reacts via a dipolar intermediate followed by cyclopropane ring opening and recyclization[2] and with methylenemalondinitriles[3] and dichlorodifluoroethylene[4] in a (2 + 2) fashion via a radical mechanism. In view of the above variety of



1