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ANNELATED 14π-ELECTRON SYSTEMS. THE SYNTHESIS OF A DIMETHYLBISDEHYDRO[14]ANNULENO[c]THIOPHENE, -[b]THIOPHENE AND -[b]FURAN [1]

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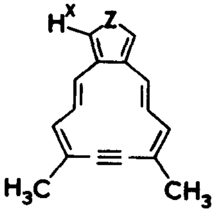
Syntheses of the annelated dimethylmonodehydro[12]annulenes 1, 2, 3, and 4, containing a macrocyclic (4n)-membered ring, were described in the preceding Communication.[1,2] It was desirable to make analogous annelated dehydro[14]annulenes, in which the macrocyclic ring is (4n+2)-membered. Syntheses of the dimethylbisdehydro[14]annuleno[c]furan 6 [3,4] and the dimethyl benzobisdehydro[14]annulene 7 [5] have been reported previously. In order to complete the series and make comparisons with 1-4, we have now prepared the dimethylbisdehydro[14]annuleno[c]-thiophene 5 and -[b]furan 9, as well as the dimethylbisdehydro[14]annuleno[b]thiophene 8.



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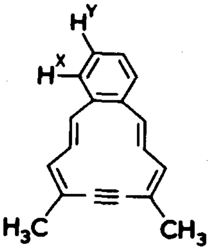

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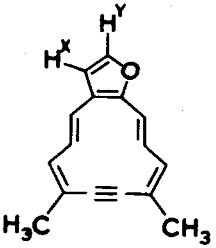

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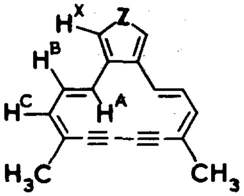

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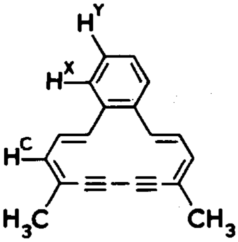

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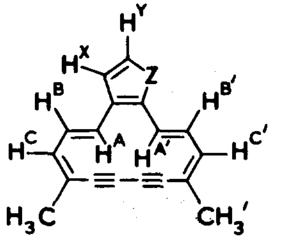
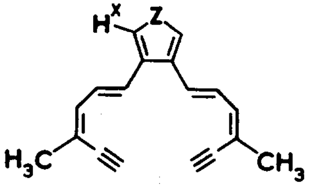


8, Z = S
9, Z = O

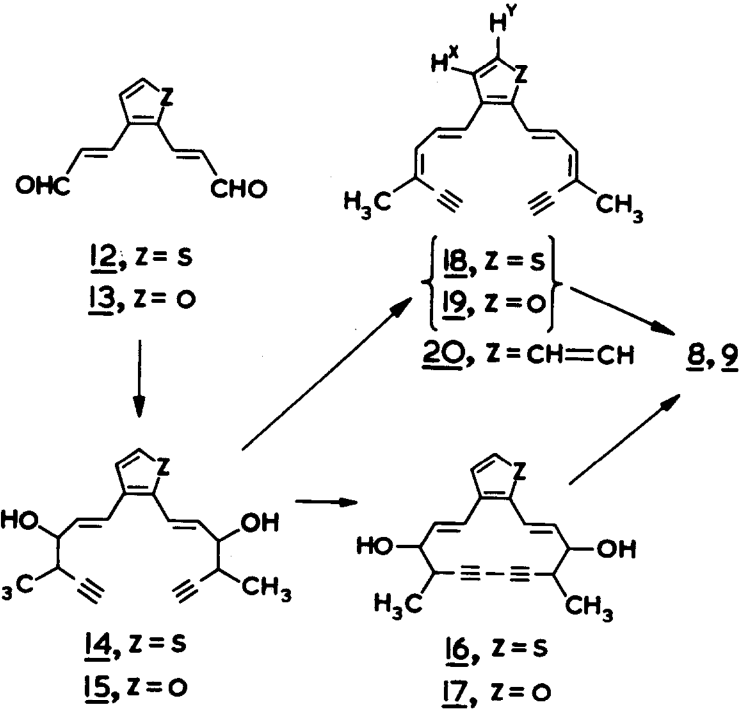
Treatment of 3,4-bis(bromomethyl)thiophene[6] with 2.3 mol equiv of PPh_3 in DMF at 80° for 3 hr yielded 97% of thiophene-3,4-bis(methylenetriphenylphosphonium bromide), mp ca 295° dec.[7] Reaction of this salt with BuLi (2 mol equiv) in THF at -65° to -20° and treatment of the resulting bisylid with "cis"-3-methylpent-2-en-4-yn-1-al[8] (ca 2.3 mol equiv) at -20° to 40° led to 28%[9a] of the di-trans compound 10 as cream coloured crystals, mp 98-99° dec.[7] Oxidative coupling of 10 with cupric acetate in pyridine at 50-55° gave 60%[9a] of the dimethylbisdehydro[14]annuleno[c]thiophene 5 [10a] as golden needles, mp 182° dec; m/e 262; λ_{max} ($CHCl_3$) 296 sh (ε 27,000), 318 (37,000), 401 nm (4500); ^{1}H-nmr ($CDCl_3$, 100 MHz, 27°) τ 2.32 (s, H^X), 3.29 (m, H^B, H^C), 3.63 (d, J = 15.5 Hz, H^A), 7.87 (s, CH_3). The nmr assignments of 5 were confirmed by the spectrum of dideuterio-5 (D instead of H^B), prepared from thiophene-3,4-bis(methylenetriphenylphosphonium bromide) and monodeuterio-"cis"-3-methylpent-2-en-4-yn-1-al (CDO instead of CHO),[11] and subsequent oxidative coupling.[12]

Thiophene-2,3-dicarboxaldehyde [13] was converted to the bisvinylogue 12, mp 189-190° [7,9b] in 30% yield by the method of Cresp, Sargent, and Vogel.[14] The dialdehyde 12 was then transformed to the dimethylbisdehydro[14]annuleno[b]thiophene 8 [10b] in 18% yield via the crude diols 14 and 16, essentially as described by Cresp and Sondheimer [4] for the [c]furan 6. Compound 8 formed scarlet needles, mp 169-170°;[9a] m/e 262.081 (calcd. 262.082); λ_{max} (Et_2O) 260 (ε 10,100), 273 (11,400), ca 317sh (46,500), 332 (71,900), 343 (82,900), 392 (11,800), 418 (5100), 463 (520), 504 (345), 545 nm (115); ^{1}H-nmr ($CDCl_3$, 100 MHz, 27°) τ 2.08 (d, J = 5.5 Hz, H^X), 2.41 (dd, J = 16, 8 Hz, H^B or $H^{B'}$), 2.50 (d, J = 5.5 Hz, H^Y), 2.54 (dd, J = 16, 8 Hz, $H^{B'}$ or H^B), 2.55 (m, H^C, $H^{C'}$),[15] 7.23 (broad d, J = 16, H^A, $H^{A'}$), 7.41 (s, CH_3, CH_3').

Furan-2,3-dicarboxaldehyde [16] was similarly converted to the bisvinylogue 13 (29% yield, mp 192-193°),[7,9b] which was transformed to the dimethylbisdehydro[14]annuleno[b]furan 9 [10c] in 15% yield via the diols 15 and 17. Compound 9 formed orange needles, mp 134-135°;[9a] m/e 246.104 (calcd 246.105); λ_{max} (Et_2O) 327 (ε 62,300), 384 (8600), 404 (6500), 411sh (6200), 456sh (730), 501 (520), 545 nm (240); ^{1}H-nmr ($CDCl_3$, 100 MHz, 64°) τ 2.22 (d, J = 2.2 Hz, H^Y), 2.25 (broad d, J = 9 Hz, H^C, $H^{C'}$), 2.76 (d, J = 2.2 Hz, H^X), 4.26 (dd, J = 16, 9 Hz, H^B or $H^{B'}$), 4.90 (dd, J = 16, 9 Hz, $H^{B'}$ or H^B), 6.11 (d, J = 16 Hz, H^A or $H^{A'}$), 6.47 (d, J = 16 Hz, $H^{A'}$ or H^A), 7.38 (s, CH_3, CH_3').



10, Z = S
11, Z = O



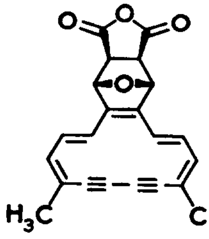
12, Z = S
13, Z = O

18, Z = S
19, Z = O
20, Z = CH=CH

8, 9

14, Z = S
15, Z = O

16, Z = S
17, Z = O



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The 2,3-disubstituted thiophene 18 and furan 19, required as models, were obtained from 14 and 15 by conversion to the dimesylates and treatment with 1,5-diazabicyclo[4.3.0]non-5-ene.[4] The stereochemistry of 18 (yellow needles, which decomposed on attempted mp determination)[7,9b] and 19 (yellow needles, mp 83-84°)[7,9a] was established by nuclear Overhauser experiments, and oxidative coupling with cupric acetate in pyridine at 55-60° to 8 and 9, respectively, in ca 15% yield.

The trans double bonds of 5 appear to be conformationally mobile on the ^{1}H-nmr time scale, as those of 6,[3] although the spectrum was essentially unchanged on cooling to -80°. On the other hand, the trans double bonds of 8 seem to be fixed in the indicated conformation, even at a temperature as high as 85°, in view of the chemical shifts of H^A, $H^{A'}$ (τ 7.18) and H^B, $H^{B'}$ (τ 2.54) at this temperature, and the spectrum was essentially unchanged on cooling to -65°. The trans double bonds of 9 apparently are fixed in the indicated conformation at low temperature, in view of the relative chemical shifts of H^A, $H^{A'}$ and H^B, $H^{B'}$. The ^{1}H-nmr spectrum of 9 showed a classical temperature dependence: the H^A, $H^{A'}$ and H^B, $H^{B'}$ resonances appeared respectively at τ 7.35 and ca 2.5 at -72°, coalesced at ca -25°, appeared as broad multiplets at τ 6.20, 6.64 and 4.32, 4.97 at 27°, and sharpened to the above mentioned patterns at 64°.

The ^{1}H-nmr resonances of the external H^C and CH_3 protons in 5, 6, 7, 8, and 9 are given in Table 1, together with those of the tetraalkylated bisdehydro[14]annulene 21[17] and the "open" models of type 10, 11,[3] 18, 19, and 20.[5] All the bisdehydro[14]annulenes are clearly diatropic, the ring current of the macrocycle being reduced in the order tetraalkylannulene 21 > annuleno[b]furan 9 > annuleno[b]thiophene 8 > benzannulene 7 > annuleno[c]thiophene 5 ≏ annuleno[c]furan 6. This is the same order as found for the reduction of paratropicity in the alkylated and annelated monodehydro[12]annulenes of type 1-4[1] and is presumably a reflection of a decrease in the importance of different participating Kekulé structures of the macrocyclic rings in these substances.

Table 1. H^C and CH_3 ^{1}H-Nmr Resonances of Annelated and Alkylated Bisdehydro[14]annulenes, and of their "Open" Models, in $CDCl_3$ at 100 MHz, 27° (τ Values; Internal Standard, TMS).

Compound	H^C	CH_3
21, alkyl	1.76	7.09
9, [b]furan	2.23	7.37
8, [b]thiophene	2.55	7.41
7, benzo	2.92	7.64
5, [c]thiophene	3.29	7.87
6, [c]furan	3.28	7.94
10, 11, 18-20, models	3.51-3.62	7.98-8.04

It is also of interest to note the effect on the ^{1}H-nmr resonances of the 6π-systems caused by annelation of the macrocyclic rings.[18] It can be seen from Table 2 that, compared with the "open" models, fusion of a paratropic 12π-ring shifts the thiophene, furan, and benzene proton resonances to higher field, whereas fusion of a diatropic 14π-ring shifts them to lower field.

Table 2. Thiophene, Furan, and Benzene ^{1}H-Nmr Resonances of Annelated Monodehydro[12]-annulenes, Bisdehydro[14]annulenes, and of their "Open" Models, in $CDCl_3$ at 100 MHz, 27° (τ Values; Internal Standard, TMS).

Series	[c]Thiophene H^X	[c]Furan H^X	Benzo H^X	Benzo H^Y	[b]Thiophene H^X	[b]Thiophene H^Y	[b]Furan H^X	[b]Furan H^Y
[12]	1, 3.01	2. 2.79	3, 2.92	2.92	-		4, 3.94	2.91
Model	10, 2.68	11, 2.47	20, 2.47	2.78	18, 2.92	2.79	19, 3.37	2.63
[14]	5, 2.32	6, 2.18	7, 1.75	2.49	8, 2.08	2.50	9, 2.76	2.22

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1. Unsaturated Macrocyclic Compounds. CXVI. For part CXV, see R.H. Wightman and F. Sondheimer, preceding Communication.
2. No particular conformation is implied in these and the other annelated dehydroannulene formulae in this Communication, unless otherwise indicated.
3. P.J. Beeby, R.T. Weavers, and F. Sondheimer, Angew. Chem. 86, 163 (1974).
4. T.M. Cresp and F. Sondheimer, J. Amer. Chem. Soc. 97, 4412 (1975).
5. R.T. Weavers and F. Sondheimer, Angew. Chem. 86, 167 (1974).
6. R. Helmers, J. Prakt. Chem. 314, 334 (1972). We prepared this compound in 30% yield by bromination of 3,4-dimethylthiophene with N-bromosuccinimide (W. Koller and P.J. Garratt, private communication).
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9. Isolated by chromatography on (a) Al_2O_3 (Woelm, act. III); (b) SiO_2 (Woelm, act. III).
10. IUPAC name: (a) 7,12-dimethyl-8,9,10,11-tetradehydrocyclotetradeca[c]thiophene; (b) 7,12-dimethyl-8,9,10,11-tetradehydrocyclotetradeca[b]thiophene; (c) 7,12-dimethyl-8,9,10,11-tetradehydroxyçyclotetradeca[b]furan.
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14. T.M. Cresp, M.V. Sargent, and P. Vogel, J. Chem. Soc. Perkin Trans I 37 (1974).
15. The H^C, $H^{C'}$ resonance showed Nuclear Overhauser enhancement on irradiation of CH_3, CH_3'.
16. Prepared from 2,3-dibromofuran by a modification of the method of M. Zaluski, M. Robba, and M. Bonhomme, Bull. Soc. Chim. France 1838 (1970).
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18. See D. Cremer and H. Günther, Justus Liebigs Ann. Chem. 763, 87 (1972).