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AN *ortho*-FUSED TETRAKISDEHYDRO[14]ANNULENO[14]ANNULENE CONSISTING OF TWO DIFFERENT TYPES OF BISDEHYDRO[14]ANNULENES

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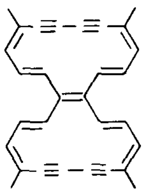
Summary: Tetrakisdehydro[14]annuleno[14]annulene consisting of 'acetylene-cumulene' bisdehydro-[14]annulene and Sondheimer's bisdehydro[14]annulene has been synthesized. It was found that a strong diatropicity was observed in the 'acetylene-cumulene' bisdehydro[14]annulene moiety, whereas diatropicity of another bisdehydro[14]annulene moiety shows marked decrease comparable with that of naphthobisdehydro[14]annulene synthesized by Sondheimer.

Since the independent preparation of two types of annulenoannulenes in 1975 by Cresp and Sondheimer[1] and by our group,[2] the studies on annulenoannulenes have been developed mainly along with these lines, *i.e.*, several kind of *ortho*-fused tetramethyltetrakisdehydroannulenoannulenes (*e.g.*, **1**) and a number of annulenoannulenes having C_{sp}-C_{sp} linkage as the common bond (*e.g.*, **3**) have been prepared and their properties were studied.[3]

Tetramethyltetrakisdehydro[14]annuleno[14]annulene (**1**) synthesized by Cresp and Sondheimer showed marked decrease of diatropicity as compared with monocyclic bisdehydro[14]annulene (**2**). On the other hand, tetra-*t*-butyltrisdehydro[14]annuleno[14]annulene (**3**)[3a] consisting of two 'acetylene-cumulene' bisdehydro[14]annulenes (**4**)[4] was concluded to be a highly delocalized system on the basis of the spectroscopic[5] and X-ray analysis.[6]

In order to clarify the effect of different mode of annelation between **1** and **3**, we have synthesized tetrakisdehydro[14]annuleno[14]annulene (**5**) consisting of our bisdehydro[14]annulene and Sondheimer's. In addition, we might expect to estimate the resonance energy of 'acetylene-cumulene' bisdehydro[14]annulene (**4**), since fusion of a diatropic ring with a [4n+2]annulene exerts characteristic effects on both rings according to their relative stabilities.[3g]

The synthesis of the tetrakisdehydro[14]annuleno[14]annulene (**5**) was carried out by the reaction sequence outlined in Scheme. Treatment of **6**[7] with 2N HCl in THF at room temperature for 4 hrs resulted in a mixture of the dialdehyde (**7**) and the hemiacetal (**8**). The dialdehyde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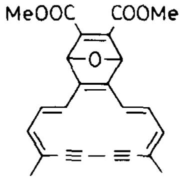

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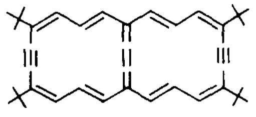
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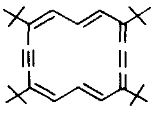
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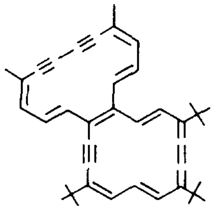
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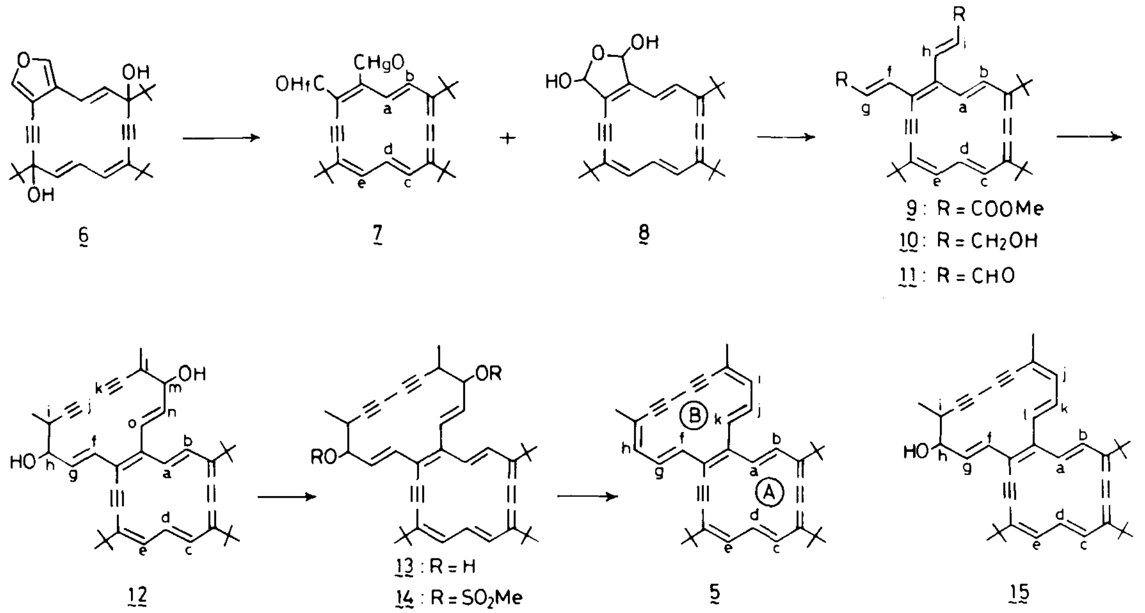
(7)[8] could be isolated by dehydration of the hemiacetal (8) (by column chromatography on silica gel). The Wittig-Horner reaction of the mixture of 7 and 8 with the carbanion derived from trimethyl phosphonoacetate afforded the diester (9)[9] in 43% yield based on 6. Reduction of 9 with diisobutylaluminum hydride gave the diol (10, 83%),[10] which was oxidized with $BaMnO_4$[11] to give the dialdehyde (11, 81%).[12] Grignard reaction of 11 with magnesium derivative of 3-bromo-1-butyne afforded the diol (12),[13] which was converted into the bicyclic glycol (13) by oxidative coupling with copper(II) acetate in DMF. The crude bicyclic glycol (13) was treated successively with methanesulfonyl chloride-triethylamine and with DBU to give the desired tetrakisdehydro[14]-annuleno[14]annulene (5) in 10% yield based on 11. A small amount of a dark purple crystalline solid was obtained as a by-product, to which the structure of monodehydrated compound (15) was assigned on the basis of the spectral data.[14] Reaction of 15 with methanesulfonyl chloride-triethylamine followed by the treatment with DBU yielded 5 in 51% yield.



6

7

8

9: R = COOMe
10: R = CH₂OH
11: R = CHO

12

13: R = H
14: R = SO₂Me

5

15

Scheme

The tetrakisdehydro[14]annuleno[14]annulene (5) was found to be unstable to light and atmospheric oxygen, and decomposed gradually during the evaporation *in vacuo*. Therefore, 5 was isolated by column chromatography at -30°C followed by concentration at low temperature and crystallization at -78°C. The annulenoannulene (5) was obtained as dark reddish brown crystals, Mass (m/e) 524 (M^+); ES: λ_{max}^{THF} (ε) 230 sh (27000), 263 sh (19000), 297 sh (24000), 312 (40000), 358 sh (46000), 389 (54000), 407 (54000), 528 (16000), 559 (16000), 676 (690) nm. The ^{1}H NMR parameters of 5 are summarized in Table.

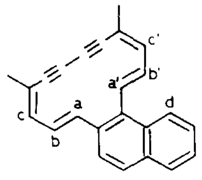
As shown in Table, the strong diatropicity was observed in the A-ring (tri-*t*-butylbisdehydro[14]annulene moiety) being comparable with that of the monocyclic bisdehydro[14]annulene (4, Δτ = 13.81). On the contrary, a marked suppression of the diatropicity of the B-ring (dimethylbisdehydro[14]annulene moiety) was observed being comparable with that of naphtho[1,2-i]-5,14-dimethyl-1,3-bisdehydro[14]annulene (16).[14] It has been demonstrated that the magnitude of

Table. ^1H NMR Parameters of **5** (CS_2, -60°C, τ-values).

A-ring	$\Delta\tau$ (τ_a-τ_b) = 12.79	H_a	12.99 d, J=14.0	H_b	0.20 d, J=14.0
	$\Delta\tau$ (τ_d-τ_e) = 12.19	H_d	13.25 dd, J=12.0, 13.5	H_c	1.08 d, J=13.5
		t-Bu	8.11 s, 8.17 s, 8.20 s	H_e	1.06 d, J=12.0
B-ring	$\Delta\tau$ (τ_f-τ_g) = 2.66	H_f	4.85 d, J=16.0	H_g	2.19 dd, J=7.5, 16.0
	$\Delta\tau$ (τ_k-τ_j) = 3.22	H_k	4.72 d, J=15.5	H_h	2.74 d, J=7.5
		Me	7.49 s, 7.53 s	H_i	2.65 d, J=8.5
				H_j	1.50 dd, J=8.5, 15.5

suppression of diatropicity of annulene moiety annelated with benzenoids or annulenes is proportional to the resonance energy of the benzenoid or annulene system. It has also been shown that less diatropic annulene ring suffers more suppression on fusion with benzenoid or other annulene as compared with more strongly diatropic annulene moiety.[3f,3g] The $\Delta\tau$-values of **5** shows that the B-ring has considerably localized structure as compared with the rather delocalized A-ring. The coupling constants of vicinal hydrogens give concordant results, *i.e.*, the small difference in the coupling constants (J_{ab}, J_{cd} and J_{de}) indicates that the A-ring should be highly delocalized, whereas the coupling constants (J_{fg}, J_{gh}, J_{ij} and J_{jk}) reflect the marked bond alternation of the B-ring. Furthermore, the steric repulsion between H_b and H_j in **5** seems to be an important factor, which may twist the B-ring reducing its diatropicity. Therefore, the marked decrease of diatropicity of **1** relative to **2** may be attributable to the small resonance energy and probably to the steric repulsion between outer protons in **1**.

^1H NMR parameters and $\Delta\tau$-values of naphtho[1,2-i]-5,14-dimethyl-1,3-bisdehydro[14]annulene (**16**) shows a marked decrease of diatropicity in the annulene ring. Additionally, steric repulsion between $H_{b'}$ and H_d may play an important role in the reduction of diatropicity, since the naphthalene ring is rigid and planar. The geometry of $H_{b'}$ and H_d in **16** is similar to that of H_b and H_j in **5**. Although it is difficult to estimate the extent of the steric factor, loss of planarity of **16** seems to be nearly the same as that of **5**. The diatropicity of the B-ring of **5** is slightly larger than that of **16**. Therefore, the bisdehydro[14]annulene (**4**) and naphthalene (fused at 1,2-positions) exerts nearly the same effect on the dimethylbisdehydro[14]annulene ring. The relationship between the resonance energies and ring current in [4n+2]annulenes has been reported by Haddon[15] and by Aihara.[16] The small $\Delta\tau$-values of the dimethylbisdehydro[14]-annulene moiety in both **5** and **16** seem to indicate fairly large resonance energy of the bisdehydro-[14]annulene (**4**) being comparable with that of a naphthalene ring (annelation of naphthalene seems to have an effect consistent with the energy required to convert naphthalene into dihydronaphthalene).[17]



16

$\Delta\tau$ (τ_c-τ_a) = 1.97

$\Delta\tau$ ($\tau_{c'}$-$\tau_{a'}$) = 1.80

It is premature to deduce conclusion from the above-mentioned results, but the difference in the mode of fusion seems not to be the main cause of marked difference of diatropicity between **1** and **3**.

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8) **7**: deep red solid, Mass (m/e) 402 (M^+); ^1H NMR (pyridine-d_5) τ -1.78 d (J=2.0) H_g, -1.25 s H_f, -0.36 d (J=13.5) H_b, 0.43 d (J=14.0) H_e, 0.48 d (J=12.5) H_c, 8.06 s, 8.09 s, 8.10 s *t*-Bu, 13.55 t (J=13.5) H_d, 13.68 d (J=14.0) H_a; IR (KBr-disk) 2090, 1685, 1668 cm^{-1}.

9) **9**: reddish brown fine needles, dp > 200°C, Mass (m/e) 514 (M^+); ^1H NMR ($CDCl_3$) τ 0.63 d (J=14.0) H_b, 0.78 d (J=13.5) H_c, H_e, 1.04 d (J=16.0) H_f, 1.36 d (J=15.0) H_h, 2.58 d (J=15.0) H_i, 3.53 d (J=16.0) H_g, 6.01 s, 6.09 s O-CH_3, 8.09 s, 8.14 s, 8.15 s *t*-Bu, 13.55 t (J=13.5) H_d, 13.68 d (J=14.0) H_a; IR (KBr-disk) 2090, 2020, 1718, 1712, 1612 cm^{-1}.

10) **10**: deep yellow-green needles, dp > 170°C, Mass (m/e) 458 (M^+); ^1H NMR (acetone-d_6) τ 0.47 d (J=14.0) H_b, 0.64 d (J=13.5) H_c, H_e, 2.24 d (J=15.5) H_a, 2.26 d (J=16.0) H_f, 2.51 dt (J=15.5, 5.0) H_i, 3.60 dt (J=16.0, 5.0) H_g, 5.31 $\sim$ 5.50 m CH_2, 5.74 t (J=5.5) OH, 5.94 t (J=5.5) OH, 8.11s, 8.13 s, 8.15 s *t*-Bu, 13.14 t (J=13.5) H_d, 13.62 t (J=14.0) H_a.

11) **11**: reddish brown fine crystals, dp > 220°C, Mass (m/e) 454 (M^+); ^1H NMR ($CDCl_3$) τ -0.18 d, (J=7.5), 0.20 d (J=7.5) CHO, 0.61 d (J=14.0) H_b, 0.72 d (J=13.5) H_c, H_e, 1.13 d (J=16.0) H_f, 1.53 d (J=15.0) H_h, 2.31 dd (J=15.0, 7.5) H_i, 3.18 dd (J=16.0, 7.5) H_g, 8.10 s, 8.12 s, 8.14 s *t*-Bu, 13.45 t (J=13.5) H_d, 13.61 d (J=14.0) H_a; IR(KBr-disk) 2080, 2025, 1685 cm^{-1}.

12) **12**: red solid, Mass (m/e) 562 (M^+); ^1H NMR ($CDCl_3$) τ 0.62 d (J=14.0) H_b, 0.81 d (J=13.5) H_c, H_e, 2.20 d (J=15.5) H_o, 2.23 d (J=16.0) H_f, 2.59 dd (J=15.5, 6.0) H_n, 3.73 dd (J=16.0, 6.0) H_g, 5.43 m H_k, H_m, 6.92 $\sim$ 7.19 m H_i, H_l, 7.44 br. s OH, 7.71 d (J=2.0) H_j or H_k, 7.75 d (J=2.0) H_j or H_k, 8.13 s, 8.14 s, 8.16 s *t*-Bu, 8.52 d (J=7.0) CH_3, 8.61 d (J=7.0) CH_3, 13.65 t (J=13.5) H_d, 13.73 d (J=14.0) H_a; IR (CCl_4) 3350, 3310, 2120, 2025 cm^{-1}.

13) **15**: dp > 135°C, Mass (m/e) 542 (M^+); ^1H NMR ($CDCl_3$) τ 0.60 d (J=13.5) H_b, 0.86 d (J=15.0) H_l, 0.91 d (J=13.5) H_c, H_e, 2.23 d (J=16.0) H_f, 2.26 dd (J=15.0, 7.0) H_k, 3.34 d (J=7.0) H_j, 3.74 dd (J=16.0, 5.0) H_g, 5.08 $\sim$ 5.16 m H_k, 6.91 m H_i, 7.73 br. s OH, 7.99 s CH_3, 8.17 s, 8.19 s *t*-Bu, 8.63 d (J=7.0) CH_3, 13.20 t (J=13.5) H_d, 13.27 d (J=13.5) H_a; IR (KBr-disk) 3450, 2220, 2135, 2030 cm^{-1}.

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