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Annelated Dehydroannulenes Fused with Azulene Ring. The Synthesis of Bisdehydro[14]- and -[16]annuleno[a]azulene

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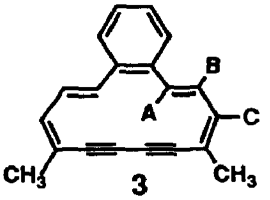
Abstract: 10,12-Bisdehydro-3-isopropyl-9,14-dimethyl[14]- and -11,16-dimethyl[16]annuleno[a]azulene in which the conjugated 14- and 16-membered rings are fused to azulene ring, have been synthesized. It was found that the fusion of azulene ring suppresses the diatropicity of [4n+2], 14π-electron system to a smaller extent than benzene ring.

Annelated macrocyclic annulenes and dehydroannulenes with benzenoid or heterocyclic aromatics have been extensively investigatged.[1] Annelated annulenes fused with another annulene (annulenoannulenes) have also been studied.[2] In contrast, the annelated monocyclic annulenes fused with nonbenzenoid aromatics have been yet unknown. We now describe the synthesis of the title compounds, 10,12-bisdehydro-3-isopropyl-9,14-dimethyl[14]- (1) and -11,16-dimethyl[16]annuleno[a]azulene (2), in which the conjugated 14- and 16-membered rings are fused to azulene ring. The main reason for this investigation was to study the effect of annelation of a 10π azulene ring onto macrocyclic [4n+2]π- and [4n]π-systems by comparison with the closest available models 3 and 4 which were prepared by Sondheimer et al.[3]



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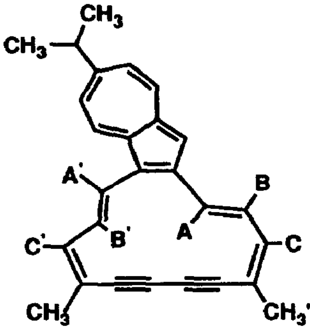

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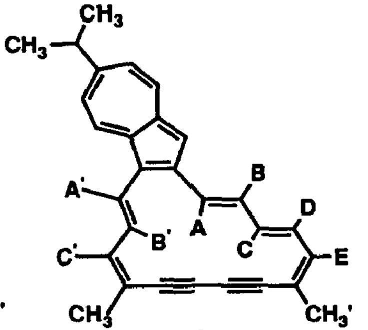

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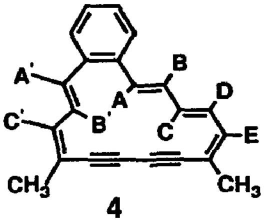

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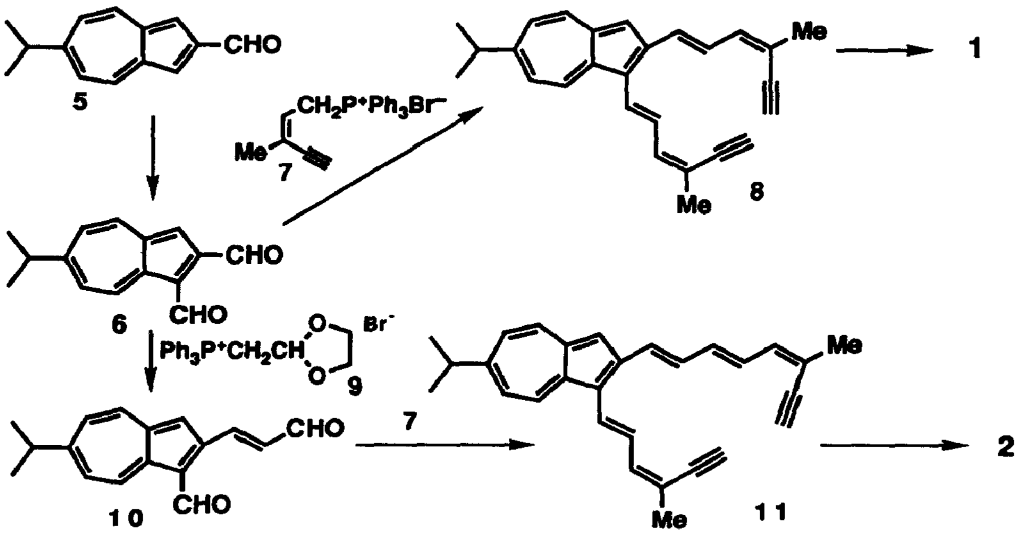
Formylation of 2-formyl-6-isopropylazulene 5[4] by Vilsmeier procedure afforded the dialdehyde 6 (dark violet needles, mp 97-98°C, 63%).[5] The Wittig reaction of 6 with 3-methyl-2-penten-4-ynyltriphenylphosphonium bromide 7[6] in THF with BuLi afforded a stereoisomeric mixture of the acyclic diacetylenes, from which the di-trans isomer 8 (green liquid, 10%) was obtained by chromatography on alumina. Oxidative



coupling of the mixture with copper(II) acetate in pyridine, diethyl ether, and methanol afforded the bisdehydro[14]annuleno[a]azulene **1**(black purple needles, mp 189-190°C (dec), 20%) in which the conformation of 14-membered ring was different from that of the model **3** as shown in the formula. Wittig reaction of **6** with 1 mol equivalent of 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide **9**[7] and LiOMe in DMF, followed by hydrolysis with hydrochloric acid afforded the monovinylog of **6**, the dialdehyde **10** (green needles, mp 108-109°C(dec), 67%), Wittig reaction of **10** with the salt **7** as before afforded a stereoisomeric mixture, from which

Table 1. ^{1}H NMR Parameters of Annulene Part of Compounds 1- 4 in CDCl$_3$[a]

Compound	1[b]	3[c]	2[b]	4[c]
H^A	3.81 d (16.2)	4.99	9.89 d (15.9)	8.90
$H^{A'}$	6.83 d (16.2)		6.55 d (15.5)	6.11
H^B	8.10 dd (16.2, 8.1)	7.44	6.35 dd (15.5, 10.0)	6.20
$H^{B'}$	4.70 dd (16.2, 9.4)		10.00 dd (15.5, 10.5)	9.45
H^C	7.36 d (8.1)	7.08	8.75 dd (15.0, 10.0)	9.42
$H^{C'}$	7.74 d (9.4)		6.11 d (10.5)	6.07
H^D			7.11 dd (15.0, 7.5)	5.73
H^E			5.90 d (7.5)	5.94
CH_3	2.55 s	2.36	1.66 s	1.70
CH_3'	2.48 s		1.65 s	

a) Chemical shifts are given in δ ppm. In parentheses are coupling constants in Hz. s: singlet; d: doublet; dd: double doublet. b) At 600 MHz. c) Ref. 3.

the isomer **11** (yellow green liquid, 7%) was obtained. Oxidative coupling of the mixture as before afforded the bisdehydro[16]annuleno[a]azulene **2** (dark brown microcrystals, mp 202-203°C(dec), 16%).

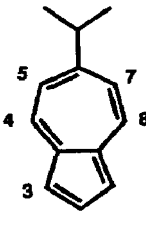
The ^1H NMR parameters of annulene part of compounds **1** and **2** are summarized in Table 1 together with those of the models **3** and **4**. The assignments of the protons were assisted by decoupling and NOE experiments. As can be seen from Table 1, the compound **1** is diatropic as expected for both the 14-membered ring in annulene part and the peripheral 22-π system in a whole molecule since the olefinic inner H^A and $H^{B'}$ protons resonate at very high field and the outer $H^{A'}$, H^B, H^C, $H^{C'}$, and methyl protons at low field as well as the low-field resonances of the azulene ring protons as compared with those of 6-isopropylazulene **12** (see below). In contrast, the compound **2** is paratropic as expected for both the 16-membered and the 24π system, since the outer protons including azulene ring protons (see below) resonate at high field and the inner protons at low field.

It was pointed out by Sondheimer et al.[3] that the best ring current probe for the compounds **3** and **4** of the bisdehydrodimethylannulene type is provided by the outer H^C, $H^{C'}$, H^E, and methyl proton chemical shifts, since these protons are furthest from the point of fusion and must be conformationally fixed. In order to examine the difference of the effect on the bisdehydro[14]- and -[16]annulene system produced by fusion between benzene and azulene, the chemical shifts of these protons are compared in Table 1. The diatropicity of the [4n+2]-, 14-membered ring greatly decreases on going from azulene to benzene, while the paratropicity of the [4n]-, -[16]membered ring varies little. This observation is in accord with the reputed result that annelation of benzenoid or annulene ring causes larger suppression of the diatropicity of the [4n+2]annulene than the paratropicity of [4n] one.[2,3,8]

Table 2. ^1H NMR Parameters of Azulene Part of Compounds **1**, **2**, and **12** in $CDCl_3$[a]

Compund	1[b]	Δδ(12-1)	12[c,d]	2[b]	Δδ(12-2)
H^3	8.19 s	-0.87	7.32 d	6.94 s	0.38
H^4	8.39 d (10.5)	-0.11	8.28 d	7.68 d (10.5)	0.60
H^5	7.26 d (10.5)	-0.16	7.10 d	6.76 d (10.5)	0.34
H^7	7.38 d (9.8)	-0.28	7.10 d	6.76 d (10.5)	0.34
H^8	9.00 d (9.8)	-0.72	8.28 d	7.72 d (10.5)	0.52
CH	3,15 sept (6.9)	-0.10	3.05 sept	2.84 d (7.0)	0.21
CH_3	1.41 d (6.9)	-0.07	1.34 d	1.26 d (7.0)	0.08

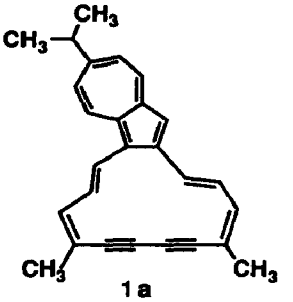
a, b) See Table 1. c) At 200 MHz. d) Ref. 4.



12

It is also of interest to examine the effect on the azulene ring caused by annelation of the macrocyclic π-systems. The ^1H NMR parameters of azulene part of compounds **1** and **2** are listed in Table 2 together with those of the model compound, 6-isopropylazulene **12**.[4] The chemical shift differences of the corresponding protons among compounds **1**, **2**, and **12** are also given. The protons of compound **1** fused by the 14-membered ring resonate at lower field than those of **12**, revealing that these protons receive the deshielding effect of (4n+2)π-system, while the protons of compound **2** fused by the 16-membered ring resonate at higher field than those of **12**, indicating that these protons receive the shielding effect of fused (4n)π-ring. In addition these effects are greater for H^3, H^4, and H^8 protons than for H^5 and H^7 ones in both compounds **1** and **2**, reflecting the distance from the point of fusion. This result suggests that the ring current effects of the diatropic bisdehydro[14]annulene and of the paratropic bisdehydro[16]annulene are larger than that of azulene (deshielding) and that both of compounds **1** and **2** can not be regarded as the peripheral conjugated systems, but those are rather composed of azulene-annulene type π-systems.

Thus, from this study it was found that the fusion of azulene ring having smaller resonance energy suppresses the diatropicity of [4n+2], 14π-electron system to a smaller extent than benzene ring having larger resonance energy. However, the fact that, unlike **3**, the bisdehydro[14]annuleno[a]azulene **1** possesses the two Kekulé structures **1a** and **1b**, may be partly responsible for the reduced diatropicity of **1**.



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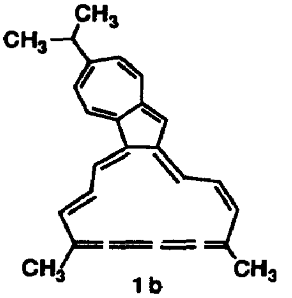

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