Bull. Chem. Soc. Jpn., 61, 1281—1283 (1988)

The Synthesis of a Double-Layered Annulene with 10π-Rings. 1,1 : 2,2-Bis([10]annulene-1,6-diyl)ethylene

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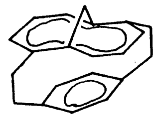
(Received October 17, 1987)

The synthesis of the title compound, a double-layered annulene with 10π-rings, is described. The examination of ^{1}H NMR and electronic spectra suggests that the layered compound exhibits appreciable interaction between two [10]annulene rings.

A progress in the annulene chemistry stimulates our interest in the layered annulenes made up of a various ring size to investigate the transannular interaction between the annulene rings. Although the two annulenophanes, [2]paracyclo[2](2,7)(1,6-methano[10]-annuleno)phane (**1**) and [2](1,5)naphthaleno[2](2,7)-(1,6-methano[10]annuleno)phane (**2**) which consist of the benzenoid ring and 1,6-methano[10]annulene, have been synthesized by Matsumoto et al.[1] and it has been shown that the compound **2** shows appreciable transannular interaction between 1,6-methano[10]-annulene ring and naphthalene ring, none of the layered annulenes has been reported.

On the other hand, 11-methylene-1,6-methano[10]-annulene (**3**) and 1,6-methano[10]annulen-11-one (**4**) were prepared by Vogel et al.[2] and by Itô et al.,[3] respectively, and both the compounds **3** and **4** proved to be like the parent 1,6-methano[10]annulene[4] and to show no interaction between the p_z orbitals of the bridge and peripheral 10π-electron system.[2,3]



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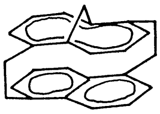

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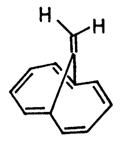

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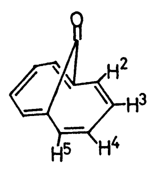

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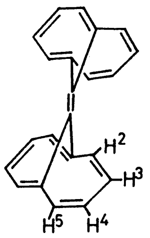

5

In this paper, we describe the first synthesis of the novel double-layered annulene **5**[5] which has two [10]annulene rings held together symmetrically with one ethylenic bridge.

Results and Discussion

The ketone **4** was initially thought to be a key intermediate for the synthesis of the title compound **5**, since **4** has a convenient carbonyl "hand" on the central position of [10]annulene ring for an intermolecular reductive coupling by McMurry method.[6] However, the attempted coupling of **4**, prepared according to the procedure of Itô et al.,[3] employing $TiCl_3$ and $LiAlH_4$ in THF[7] did not give the desired dimeric product **5**, but gave only naphthalene. We reasoned that the failure to obtain **5** from **4** is ascribed to the instability of the ketone **4** under the reaction conditions, as has been observed by us in the couplings of several fully conjugated polyenediynedials.[8] Then we directed our efforts to a two-stage approach which involves an initial coupling of the more stable ketone **6** and a subsequent dehydrogenation of the resulting dimeric hydrocarbon. Thus the reductive coupling of the ketone **6** as before[7] afforded the dimer, 1,1:2,2-bis(cyclodeca-2,4,8-triene-1,6-diyl)ethylene, as a mixture of syn- (**7a**) and anti-isomer (**7b**), which could not be separated by column chromatography on silica gel. When a mixture of **7a**, **b** and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in benzene was heated in a sealed tube under nitrogen atmosphere at 110—120 °C for 24 h, dehydrogenation took place to afford the title compound **5** as stable yellow crystals in 5.9% yield, which was isolated by column chromatography on silica gel.

The ^{1}H NMR and electronic spectral data of **5** are listed in Table 1, together with those of the reference model compounds **3** and **4**. As shown in Table 1, the ring protons of **5** resonate in A_2B_2-type as similar to the cases of **3** and **4**,[2,3] and do in lower field than the olefinic protons of **7a**, **b** (Experimental), revealing that the annulene rings of **5** sustain diamagnetic ring current. Comparison of the central chemical shifts of the annulene protons among **3**, **4**, and **5** indicates that the protons of **5** (δ 6.96) resonate in higher field than those of **3** (δ 7.20) and **4** (δ 7.46). This high-field shift of the annulene protons observed in **5** is reasonably ascribed to diamagnetic anisotropy of thc opposite annulene ring. Thus, this suggests that the two annulene rings in **5** are very suitable to overlap to each other.

The electronic absorption spectra, taken in cyclohexane, are illustrated in Fig. 1. As is seen from Fig. 1, all the spectra exhibit three bands which arise from [10]annulene chromophore[9] and which is characteris-

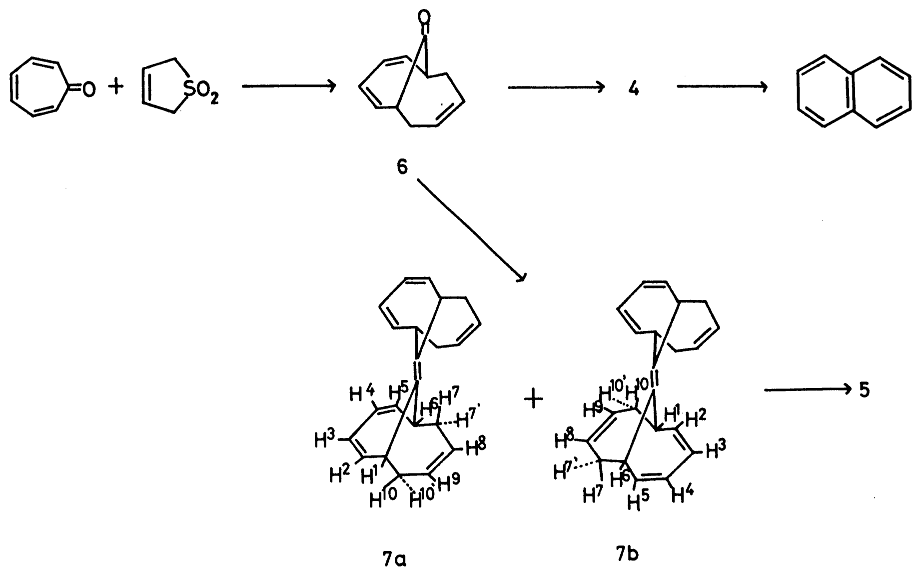

Table 1. Spectral Data of **3**—**5**

Compd		Spectral data
3[a]	^{1}H NMR (CCl$_4$):	δ 7.2 (center, A$_2$B$_2$-system, 8H), 3.2 (=CH$_2$, 2H);
	UV (cyclohexane):	λ_{max} 258 (67500), 300 (6700), 368 (135), 377 (170), 385 (190), 394 (184), 408 nm (180)
4[b]	^{1}H NMR (CDCl$_3$):	δ 7.55 (H^2, H^5, H^7, H^{10}, 4H), 7.36 (H^3, H^4, H^8, H^9, 4H) (A$_2$B$_2$-system, center 7.46);
	UV (cyclohexane):	λ_{max} 250.5 (77500), 296 (7000), 352 (92), 362 (124), 371 (169), 379 (228), 391 (275), 402 nm (326)
5	^{1}H NMR (CDCl$_3$):	δ 7.21—7.15 (H^2, H^5, H^7, H^{10}, 8H), 6.76—6.72 (H^3, H^4, H^8, H^9, 8H) (A$_2$B$_2$-system, center 6.96) (J_{23}=8.27 Hz, J_{34}=10.48 Hz, J_{24}=0.58 Hz, J_{25}=1.16 Hz)
	UV (cyclohexane):	λ_{max} 253 (141000), 306 sh (10900), 374 sh (481), 405 (577), 418 (513), and 432 nm (353)

a) See Ref. 2. b) See Ref. 3.

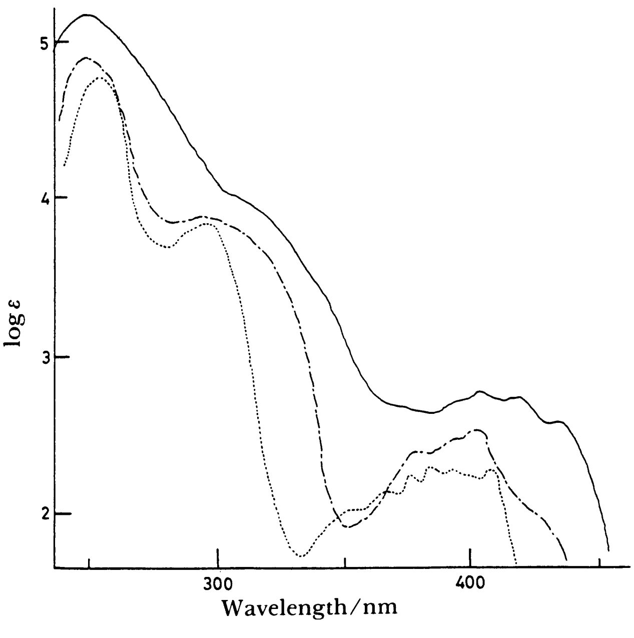

Fig. 1. Electronic spectra of **3** (----), **4**, (-·-·-), and **5** (——) in cyclohexane.

tic of [4n+2]π-electrons.[10] However, the longest wavelength band of **5** shows a remarkable bathochromic shift (20—30 nm) (Table 1), when compared with those of **3** and **4**, demonstrating that the transition associated with the longest wavelength band of [10] annulene chromophore is affected by the transannular interaction between the two annulene rings.

Experimental

Melting points are uncorrected. IR spcctra were measured on Hitachi 260-10 spectrophotometer as KBr disc; only significant maxima are reported. Electronic spectra were recorded on Hitachi 220-A spectrophotometer in nm, in cyclohexane solution. Mass spectra were measured with JEOL JMX-303 spectrometer at 70 eV using a direct inlet system. ^{1}H NMR spectra were taken on JEOL GX-500 (500 MHz) spectrometer, and refer to solutions in CDCl$_3$, in δ-values with TMS as an internal standard. The coupling constants (J) are given in Hz. Silica gel (Merck) was used for column chromatography.

The Reductive Coupling of the Ketone 4. LiAlH$_4$ (95 mg, 2.5 mmol) was added in one portion to titanium trichloride ($TiCl_3$) (0.77 g, 5 mmol) in dry THF (300 ml) under argon. The resultant black mixture was heated under reflux for 30 min. To the mixture, a soln of the ketone **4** (350 mg, 2.24 mmol) in dry THF (25 ml) was added dropwise during 30 min and then the mixture was stirred under reflux for further 4 h. Then after addition of ethanol (10 ml), the mixture was filtered through Hyflo Super-Cel under suction to remove inorganic materials and was washed with THF. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel (30 g). The fractions eluted with hexane afforded naphthalene (55 mg).

1,1 : 2,2-Bis(cyclodeca-2,4,8-triene-1,6-diyl)ethylene (7a,b). To the refluxing mixture of $LiAlH_4$ (0.92 g, 24.2 mmol) and $TiCl_3$ (7.50 g, 48.4 mmol) in dry THF (200 ml), prepared as described above, was added dropwise a soln of the ketone **6** (3.50 g, 21.8 mmol) in dry THF (200 ml) under argon and the mixture was stirred under reflux for further 4 h. After work-up as described above, the residue was chromatographed on silica gel (120 g). The initial fractions eluted with hexane gave a colorless liquid (310 mg) which proved to be a complex mixture of hydrocarbons by analysis of gas chromatography. The structures of the hydrocarbons are not established. The later fractions eluted with the same solvent afforded the desired dimer **7a,b** (100 mg, 3.1%) as a solid. Recrystallization from hexane afforded colorless needles: mp 138—139 °C; MS m/z 288 (M^+, 70%) and 234 (100); mol wt 288.4; IR 1595 (C=C), 710 and 705 cm^{-1} (cis C=C); UV λ_{max} (cyclohexane) 250 (9500), 261 (9800), and 273 nm sh (8600); ^1H NMR δ=5.93—5.88 (m, H^3, H^4, 4H), 5.77—5.73 (m, H^2, H^5, 4H), 5.57—5.55 (m, H^8, H^9, 4H), 3.79—3.76 (m, H^1, H^6, 4H), 2.56—2.50 (m, H^7, H^{10} or $H^{7'}$, $H^{10'}$, 4H), 2.19—2.13 (m, H^7, H^{10} or $H^{7'}$, $H^{10'}$, 4H).

Found: C, 91.29; H, 8.45%. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39%.

1,1:2,2-Bis([10]annulene-1,6-diyl)ethylene (5). A mixture of the hydrocarbons **7a,b** (70 mg, 0.243 mmol) and DDQ (270 mg, 1.2 mmol) in dry benzene (4 ml) was heated in a sealed tube under nitrogen atmosphere at 110—120 °C for 24 h. After removing insoluble materials by filtration under suction and washing with benzene, the filtrate was concentrated. The residue was chromatographed on silica gel (10 g). The fractions eluted with hexane afforded the layered annulene **5** (4.0 mg, 5.9%) as a solid. Recrystallization from hexane-benzene afforded pale yellow needles: mp 245—247 °C; MS m/z 280 (M^+, 100%); mol wt 280.3; IR 750 cm^{-1} (cis C=C); UV: see Table 1 and Fig. 1; ^1H NMR: see Table 1.

Found: C, 93.69; H, 5.87%. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75%.

The authors thank Professor Shô Itô, Tohoku University, for providing us the details for preparing the ketone **4** and helpful suggestions, Professor Yoshiteru Sakata, Osaka University, for helpful discussion, and Professor E. Vogel, Köln University, for providing us the electronic spectrum of **3**.

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