

SYNTHESIS OF [2.2]METACYCLO(1,3)AZULENOPHANE AND ITS CONVERSION TO AZULENO[1,2,3-*cd*]PHENALENE¹⁾

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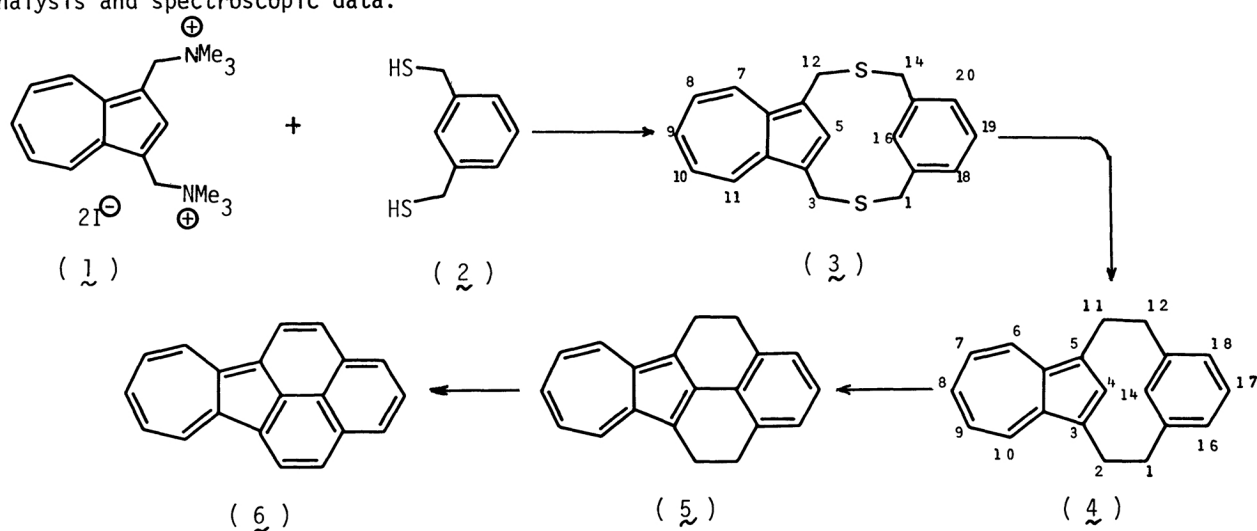
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[2.2]Metacyclo(1,3)azulenophane (**4**) has been synthesized in two steps from azulyl-1,3-bis(trimethylammonium) diiodide (**1**). The cyclophane **4** could be converted to the novel nonalternant hydrocarbon, azuleno[1,2,3-*cd*]phenalene (**6**), through the transannular coupling followed by dehydrogenation sequence. Some properties of **4** are also reported.

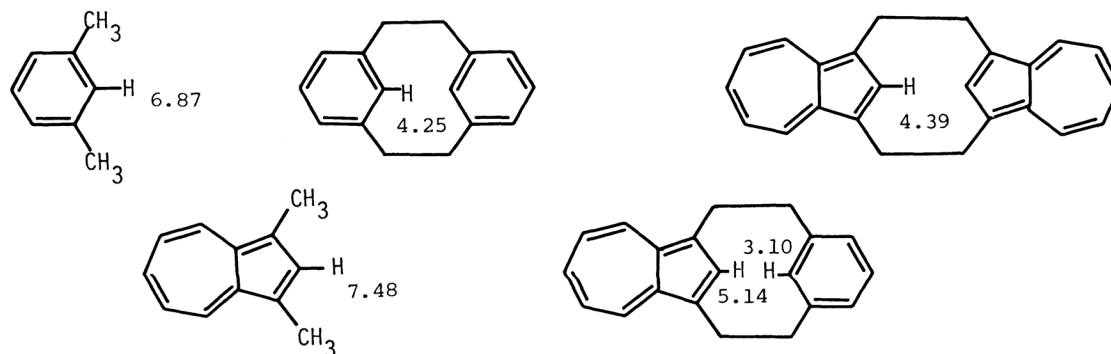
The conspicuous development of benzenoid phane chemistry²⁾ has led to interest in evolving cyclophanes incorporating some nonbenzenoid aromatic rings such as tropyliophanes,³⁾ annuleno-phanes,⁴⁾ and azulenophanes.⁵⁾ In these phane chemistry, attention has been focused mainly on the transannular electronic interaction between two different aromatic π -systems.⁶⁾ In connection with our study on nonalternant polycyclic hydrocarbons, we have recently been attracted to [2.2]-metacycloazulenophanes because this type of compounds will provide a new entry into the synthesis of novel polycyclic hydrocarbons *via* intramolecular transannular coupling reaction. We now wish to describe the synthesis of [2.2]metacyclo(1,3)azulenophane (**4**)⁷⁾ and its conversion to azuleno[1,2,3-*cd*]phenalene (**6**).

The synthesis of **4** was accomplished from azulyl-1,3-bis(trimethylammonium) diiodide (**1**)⁸⁾ following the well-known dithiacyclophane method.⁹⁾ Condensation of **1** with 1,3-bis(mercapto-methyl)benzene (**2**) in the presence of sodium ethoxide in a mixture of methanol and ethanol utilizing the high dilution technique gave, after usual workup and chromatographic separation (alumina deactivated with 3% water, benzene-hexane(2:1)), 2,13-dithia[3](1,3)azuleno[3]metacyclophane (**3**), blue plates, mp 173-175°C (decomp.) (from benzene); UV λ_{\max} (cyclohexane) 243 nm (log ϵ 4.27), 307 (4.34), 366 (3.60), 384 (3.55), 624 (2.38), 750 (sh, 1.77); ¹H-NMR (CDCl₃) 3.70 (s, 4H, -S-CH₂-bz.),¹⁰⁾ 4.30 (s, 4H, -S-CH₂-azul.),¹⁰⁾ 6.37-7.48 (m, 7H), 7.61 (s, 1H, H-5), 8.10 (d, 2H, J=9.0 Hz, H-7,11), in 25% yield.

Irradiation of **3** in a mixture of trimethylphosphite and benzene (1:1) using a 450-w high pressure Hg lamp for 4-5 h under nitrogen afforded [2.2]metacyclo(1,3)azulenophane (**4**), dark blue leaflets, mp 148°C (decomp.), in 20% yield. The structure of **4** follows from its elemental analysis and spectroscopic data.



$^1\text{H-NMR}$ spectrum of **4**, δ (CDCl_3 , 100 MHz) 2.14, 2.66, 3.01, 3.71 (8H, AGMX-system, $-\text{CH}_2-\text{CH}_2-$), 3.10 (bs, 1H, H-14), 5.14 (s, 1H, H-4), 7.01 (t, 2H, $J=9.5$ Hz, H-7, 9), 7.04-7.37 (m, 3H, H-16, 17, 18), 7.50 (t, 1H, $J=9.5$ Hz, H-8), 8.29 (d, 2H, $J=9.5$ Hz, H-6, 10), is consistent with the fixed structure with stepped conformation. Thus, the intra-annular protons, H-4 and H-14, resonate upfield region at δ 5.14 and 3.10 due to the diamagnetic ring current of the opposite benzene and azulene rings, respectively. The azulenic proton H-4 was shifted upfield from δ 7.48 in 1,3-dimethylazulene to 5.14 in **4**. The chemical shift difference ($\Delta\delta=2.34$ ppm) is comparable to that between *m*-xylene¹¹⁾ and [2.2]metacyclophane¹²⁾ ($\Delta\delta=2.62$ ppm). However, intra-annular benzenoid proton H-14 is featured to upfield shift from δ 6.87 in *m*-xylene to δ 3.10 in **4**. Since the intra-annular protons of [2.2](1,3)azulenophane⁷⁾ resonate at δ 4.39, the shielding effect due to the faced azulene ring in [2.2](1,3)azulenophane is assumed to be $\alpha\alpha$. 3ppm. The observed chemical shift difference of 3.77 ppm is substantially greater than the predicted value. This discrepancy is partly due to the subtle conformational change going from [2.2](1,3)azulenophane to **4**.



The electronic spectrum of **4** is shown in Fig. 1. Although vibrational fine structure is not perceived in Lb band of **4**, the spectrum is almost superimposable with that of 1,3-dimethylazulene¹³⁾ suggesting no appreciable interaction between azulene and benzene π -systems.

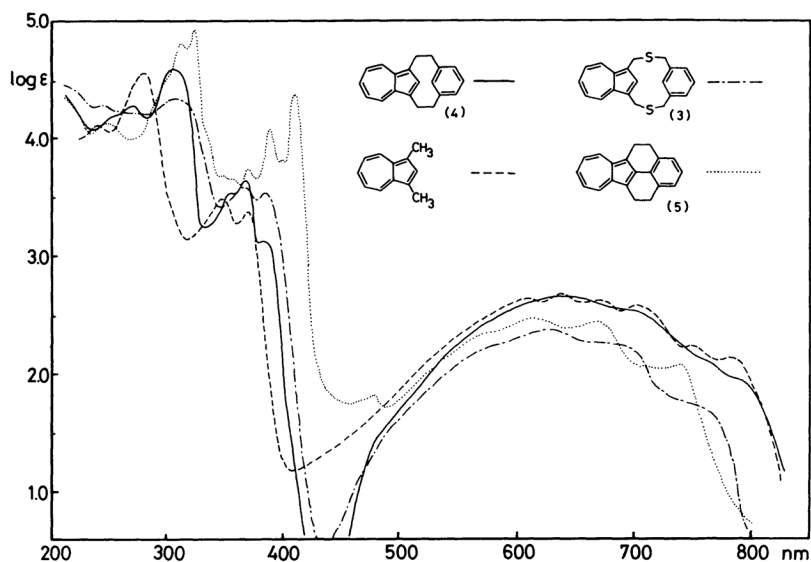


Fig. 1

Electronic Spectra of **3**, **4**, **5**,
and 1,3-Dimethylazulene
(in cyclohexane)

Irradiation of a solution of **4** in methylene chloride with 6-w low pressure Hg lamp for 6 h followed by column chromatographic workup (alumina deactivated with 5% water, hexane) gave the 4,5,11,12-tetrahydroazuleno[1,2,3-*cd*]phenalene (**5**), greenish blue leaflets, mp 168-170°C (decomp) from ethanol. The structure of **5** was identified by its elemental analysis and spectroscopic data, $^1\text{H-NMR}$ δ (CDCl_3 , 100 MHz) 3.23 (m, 8H, $-\text{CH}_2-\text{CH}_2-$), 6.94 (t, 2H, $J=9.0$ Hz, H-7, 9), 7.16 (bs, 3H, H-1, 2, 3), 7.26 (t, 1H, $J=9.0$ Hz, H-8), 8.04 (d, 2H, $J=9.0$ Hz, H-6, 10); UV λ_{max} (cyclohexane) 249 nm ($\log \epsilon$ 4.12), 262 (sh, 4.02), 294 (sh, 4.49), 310 (4.80), 323 (4.94), 479 (2.13), 576 (sh, 2.45), 610 (2.56), 666 (2.45), 725 (2.05), 739 (2.09), 809 (sh, 0.75), (see Fig. 1).

The tetrahydro compound **5** was finally converted into the corresponding azuleno[1,2,3-*cd*]-phenalene **6**¹⁴⁾ in 79% yield by stirring with dichlorodicyano-*p*-benzoquinone in benzene at room temperature for over night. The compound **6** prepared in this way was identical in every respect with the authentic sample synthesized recently by us.¹⁴⁾

In order to examine the nonalternant character of **6** through the electronic spectra of its methyl derivatives, we are now attempting to prepare some of these compounds by a related route.

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