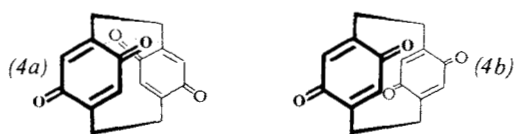
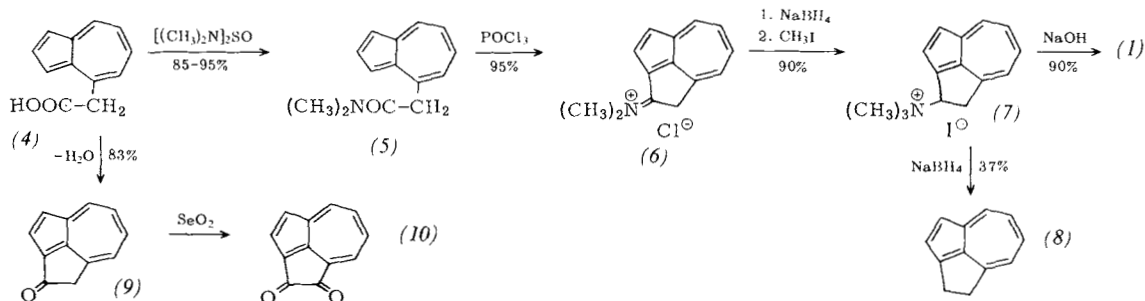


methoxy[2.2]paracyclophanes (*3a*) and (*3b*) was obtained (total yield 35–40%), the now sterically favored (*3b*) with pseudogeminal arrangement of the four methoxy groups prevailing in the ratio of about 2:1. (*3a*)<sup>[4]</sup> (m. p. 137–138 °C) and (*3b*)<sup>[4]</sup> (m. p. 157–159 °C) were separated by chromatography (silica gel; benzene/CCl<sub>4</sub>, 2:1). Halogen-metal exchange of (*3b*) with *n*-butyllithium (ether/*n*-hexane) and hydrolysis yielded (*2b*)<sup>[4]</sup> [56%, m. p. 229–230 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): τ = 4.15 (s, 4 arom. H), 7.6–6.35 (AA'BB', 8 methylene-H)] whereas the corresponding reaction with (*3a*) led to (*2a*)<sup>[1]</sup>. Demethylation of (*2b*) and oxidation of the intermediate tetrahydroxy[2.2]paracyclophane to the bis-quinone (*4b*) were carried out according to the corresponding steps of the synthesis of (*4a*)<sup>[1]</sup> with slight modifications because of the low solubility of the pseudogeminal compounds (60% yield). The pseudogeminal structure of (*4b*)<sup>[4]</sup> (yellow needles, dec. > 200 °C) was confirmed by X-ray analysis<sup>[7]</sup> [<sup>1</sup>H-NMR (CF<sub>3</sub>COOH): τ = 3.44 (s, 4 ring-H), 7.55–6.08 (m, 8 methylene-H); MS: M<sup>+</sup> 268, fragmentation similar to (*4a*)<sup>[1]</sup>].



Catalytic hydrogenation of (*4b*) (Pd/C, 1 equiv. H<sub>2</sub>, dioxane) and subsequent recrystallization from dioxane gave (*1b*) as black crystals [(dec. > 350 °C, 75% yield)<sup>[4]</sup>; MS: M<sup>+</sup> found 270.0898, calc. 270.0891; <sup>1</sup>H-NMR ([D<sub>6</sub>]-dimethyl sulfoxide): τ = 6.5–8.0 (m, 8 methylene-H), 4.14 and 3.98 (singlets for 2 ring-H each), 1.30 (s, 2 hydroxyl-H)]. In contrast to that of (*1a*)<sup>[1]</sup> the IR spectrum (KBr) of (*1b*) shows a very broad ν(OH) absorption around 3200 cm<sup>-1</sup> and a ν(CO) absorption shifted to 1620 cm<sup>-1</sup>, indicating strong hydrogen bonds.

Apart from UV absorptions at 246 (ε 9.350), 277 (5.150), and 320 nm (3.200), (*1b*) exhibits a typical broad charge-transfer absorption between 400 and 600 nm similar to (*1a*) (λ<sub>max</sub> 500 nm). However, its extinction (ε ≈ 1.700, in methanol) is ten times higher than for the corresponding band of (*1a*). In contrast to (*1a*), the <sup>1</sup>H-NMR of which shows no change up to 200 °C (in [D<sub>6</sub>]-dimethyl sulfoxide), a reversible coalescence of the singlets at τ = 4.14 and 3.98 is observed for (*1b*) at 160 °C in the same solvent. Obviously this coalescence is the result of an exchange of oxidation states between the



two rings with simultaneous proton transfer ( $\Delta G_{160}^\ddagger \approx 22.2$  kcal/mol).

The "intramolecular quinhydrones" (*1a*) and (*1b*) as well as the bis-quinones (*4a*) and (*4b*) form paramagnetic anions

in which according to ESR measurements a fast electron exchange between both rings takes place<sup>[8]</sup>.

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[1] Transannular Interactions in [2.2]Phanes, Part 5.—Part 4: W. Rebařka and H. A. Staab, Angew. Chem. 85, 831 (1973); Angew. Chem. internat. Edit. 12, 776 (1973).

[2] First attempts to prepare these "exotic quinhydrones" were discussed by D. J. Cram and A. C. Day, J. Org. Chem. 31, 1227 (1966).

[3] Cf. H. A. Staab and M. Haenel, Chem. Ber. 106, 2190 (1973); M. Haenel and H. A. Staab, *ibid.* 106, 2203 (1973).

[4] Correct elemental analyses were obtained for these compounds; <sup>1</sup>H-NMR and mass spectra as well as other spectroscopic results are in accordance with the structures proposed.

[5] 1,4-Dimethoxy-2,5-dimethylbenzene was obtained from 1,4-dimethoxybenzene by chloromethylation and subsequent hydrogenolysis (LiAlH<sub>4</sub>/tetrahydrofuran) in 47% overall yield.

[6] In this reaction only one of the two possible stereoisomeric dithia[3.3]paracyclophanes—most probably the compound with pseudogeminal arrangement of the methoxy groups—was obtained.

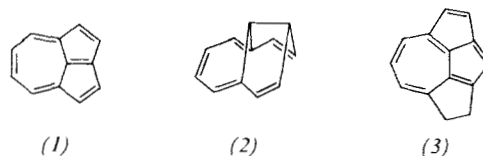
[7] (*4b*) crystallizes in space group P2<sub>1</sub>/n with two molecules in the unit cell (a = 7.930, b = 9.280, c = 8.024 Å, β = 93.30); the molecules are placed on centers of symmetry and therefore must be centrosymmetric themselves (H. Irngartinger, unpublished).

[8] J. Valenzuela, F. A. Neugebauer, W. Rebařka, and H. A. Staab, unpublished.

### Cyclopent[cd]azulene and 1,2-Dihydrodicyclopent[cd,ij]azulene

By Klaus Hafner, Klaus-Peter Meinhardt, and Winfried Richarz\*

Alkyl and aryl derivatives<sup>[1]</sup> of cyclopent[cd]azulene (*1*) exhibit a notable reactivity in cycloaddition reactions with alkenes, alkynes, and carbenes<sup>[2]</sup>. An examination of the hitherto unknown parent hydrocarbon (*1*) therefore appeared desir-



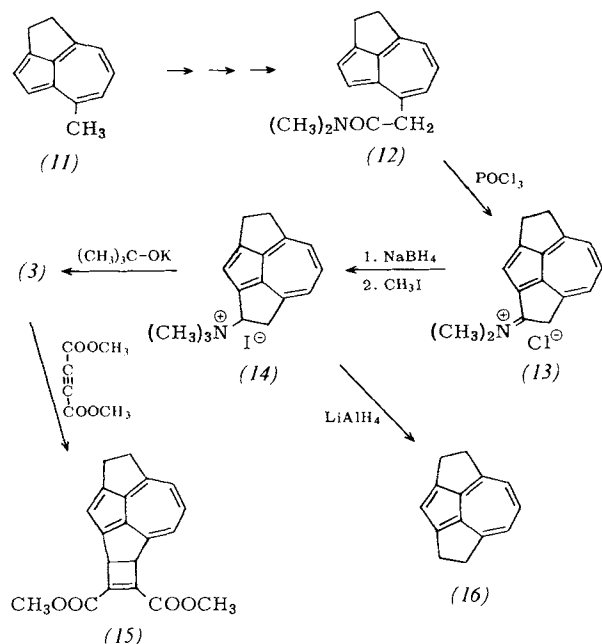
able. The 2a,8b-dihydro derivative (*2*) has recently been prepared by Paquette *et al.*<sup>[3]</sup> and by Vogel *et al.*<sup>[4]</sup>. We wish to report a simple synthesis of (*1*) and of 1,2-dihydrodicyclopent[cd,ij]azulene (*3*) which is likewise characterized by a pronounced reactivity of the double bonds in its five-membered rings.

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4-Azulenylacetic acid (4) (m. p. 122°C, decomp.)<sup>[5]</sup>, prepared in 75% yield by reaction of 4-methylazulene<sup>[6]</sup> with sodium *N*-methylanilide and subsequent carboxylation of the resulting sodium 4-methyleneazulene<sup>[7]</sup>, proved to be useful as starting material for the synthesis of (1). By treatment with sulfinylbis(dimethylamine)<sup>[8]</sup> in benzene for 2 h at 60°C (4) can be converted almost quantitatively into the carboxamide (5). Cyclization in POCl<sub>3</sub> (60°C, 2 h) yields 95% of the ketimonium chloride (6) (perchlorate: red-brown crystals, m. p. 243 to 244°C, decomp.). Reduction of (6) by NaBH<sub>4</sub> in methanol at 20°C followed by quaternization with methyl iodide affords the iodide (7) (yield 90%; blue-violet crystals, decomp. >110°C), and Hofmann degradation with 2 N NaOH at 20°C finally gives rise to a 90% yield of the hydrocarbon (1) (brown leaflets having metallic luster, m. p. 69–70°C, decomp.). Compound (1) is yellowish brown in solution and prone to autoxidation but thermally stable.

The 60 MHz <sup>1</sup>H-NMR spectrum of (1) (in CCl<sub>4</sub>), which provides structural proof for the compound, contains a multiplet centered at τ = 1.93 for the four protons of the seven-membered ring in addition to the signals of the two AB systems for the protons of the five-membered rings at τ = 3.18 and 2.54 (*J*<sub>AB</sub> = 4.5 Hz). The electronic spectrum of (1) (in *n*-hexane) shows a pronounced vibrational structure in the UV and visible regions.

Reduction of the quaternary salt (7) by NaBH<sub>4</sub> in methanol at 0°C yields 1,2-dihydrocyclopent[*cd*]azulene (8) (yield 37%; dark blue needles, m. p. 71°C) which is isomeric to (2) and whose 2-oxo derivative (9) is accessible by direct cyclization of (4) in acetic anhydride/pyridine (yield 83%; red-brown crystals, m. p. 131–132°C). Oxidation of (9) with selenium



dioxide in dioxane (60°C, 3 h) affords cyclopent[*cd*]azulene-1,2-dione (10) (10% yield, dark green needles, decomp. >240°C), an isomer of acenaphthenequinone.

Compound (3) was prepared similarly to (1) starting from 4,8-dimethylazulene<sup>[6]</sup>. 5-Methyl-1,2-dihydrocyclopent[*cd*]azulene (11) (blue needles, m. p. 132°C) obtained analogously to (8) is converted into the carboxamide (12) (yield 95%; blue rhomboids, m. p. 115°C) which is cyclized to the tetracyclic ketimonium salt (13) (yield 45%; perchlorate: red-brown

needles, decomp. >270°C). Reduction (NaBH<sub>4</sub>) and quaternization with methyl iodide finally yield the iodide (14) (air-sensitive blue powder). Treatment of (14) with potassium *tert*-butoxide in tetrahydrofuran at –20°C furnishes the highly strained, thermally unstable tetracyclic hydrocarbon (3) which is yellowish green in solution and could hitherto only be trapped as the cycloadduct (15) (dark green crystals, m. p. 108°C) by reaction with dimethyl acetylenedicarboxylate at 0°C. Reduction of (14) by lithium tetrahydridoaluminate in ether at 20°C affords 1,2,4,5-tetrahydrodicyclo[*cd,ij*]azulene (16) as pale blue needles (m. p. 180°C, decomp.; yield 85%).

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[5] The structures of the products described were confirmed by elemental analysis, and UV, NMR, and MS spectra.

[6] K. Hafner and H. Weldes, Liebigs Ann. Chem. 606, 90 (1957).

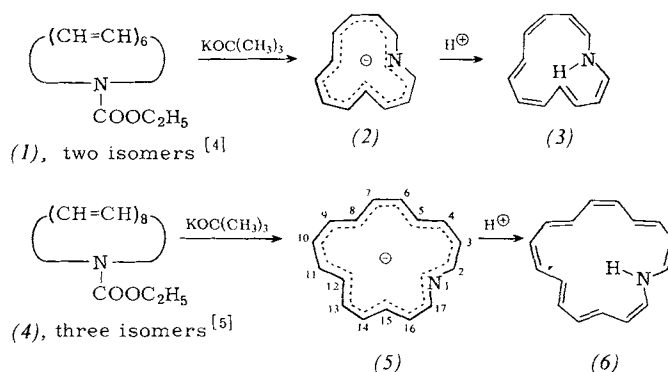
[7] Cf. K. Hafner, H. Pelster, and H. Patzelt, Liebigs Ann. Chem. 650, 80 (1961).

[8] G. Rosini, G. Baccolini, and S. Cacchi, Farmaco, Ed. Sci. 26, 153 (1971).

## An Aza[13]- and an Aza[17]annuleny Anion<sup>[1][\*\*]</sup>

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The pyrrolyl or aza[5]annuleny anion has long been known and possesses considerable interest from both a theoretical and a preparative standpoint<sup>[2]</sup>. The synthesis and properties of the azoninyl or all-*cis*-aza[9]annuleny anion have recently been described<sup>[3]</sup>. We now wish to report an aza[13]- (2) and an aza[17]annuleny anion (5).



Photolysis of the adduct of ethoxycarbonylnitrene to the double bond of the four-membered ring in tricyclo[6.4.0.0<sup>9,12</sup>]dodeca-2,4,6,10-tetraene at –70°C affords two isomeric *N*-

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