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9,10-Bis(4,5-diphenylimidazol-2-yliden)-9,10-dihydroanthracene - A Folded *p*-Quinodimethane

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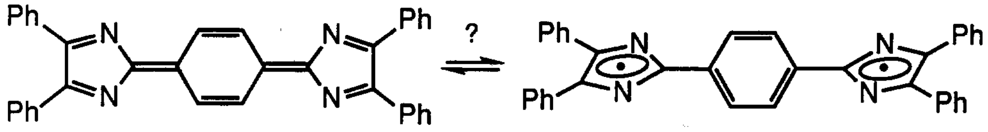
Key Words: Pyramidalization, *p*-quinodimethanes, imidazoles

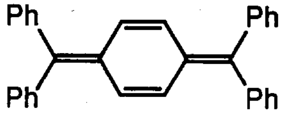
Abstract: Dehydrogenation of 9,10-bis(4,5-diphenyl)-imidazol-2-yl)-anthracene furnishes the title compound. 1,4-Bis-[4,5-bis(*p*-methoxyphenyl-imidazol-2-ylidene)]-1,4-cyclohexadiene doesn't show any thermochromism.

An equilibrium[1-3] between a quinoid 1 and a diradical form 2 of dehydrogenated *p*-phenylene-diimidazoles[1-6] has been discussed occasionally. Sakaino[2,3] reports that 1 exists predominantly in the quinoid structure at room temperature and reversibly isomerizes to 2 (0.1% at 200 °C based on ESR) on heating. Shienok[5,6] states that the thermochromism of 1 results mainly from a change in intermolecular interaction, not from biradical formation. If formed during heating or irradiation of 1, 2 is expected to exist in a twisted conformation in order to minimize the coupling of the unpaired electrons. The situation is related to that with Thiele's (3) and Chichibabin's hydrocarbons.[7,8] In order to find out whether the formation of 2 can be favoured by increased steric crowding we set out to synthesize dibenzo derivatives of 1/2.



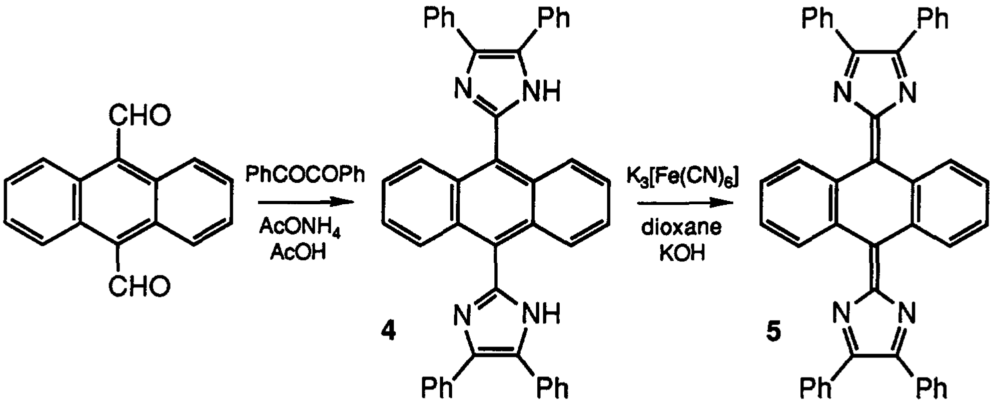
1 **2**

3



Using the standard procedure[2,9] for the preparation of *p*-phenylene-diimidazoles, we obtained 9,10-bis(4,5-diphenyl)-imidazol-2-yl)-anthracene **4**[10] (λ_{max} = 402 nm) starting from anthracene-9,10-dicarbaldehyde[11] in high yield. Dehydrogenation of **4** with potassium ferricyanide produced

9,10-bis(4,5-diphenylimidazol-2-ylidene)-9,10-dihydroanthracene **5**.[12] In contrast to blue **1** (λ_{max} = 602 nm [$CHCl_3$])[1], **5** is red (λ_{max} (lg ε)= 408 nm (4.44), 513 (4.71)). The X-ray crystallographic analysis[13] reveals (Figure 1) that **5** is not as expected a twisted molecule but instead a folded one. The dihydroanthracene ring adopts a butterfly-like conformation (cf. bianthronylidene[14]) leading to a syn arrangement of the dihydroimidazole rings.The planes of the 5-membered rings make an angle of 121.2°. The C1-C15 bond (137.8 pm) is longer than the central C=C bond in bianthronylidene. The bond length alternation in the middle ring of **5** (C1-C14 = 146.4 pm and C9-C14 = 141.8 pm; cf. C16-C17 = 146.8 pm) corresponds to a *p*-quinoid structure. As a result of the bending of the quinoid system, the conjugation between the imidazole systems of **5** via the 9,10-dihydroanthacene moiety is diminished which accounts for the hypsochromic shift as compared with **1**.



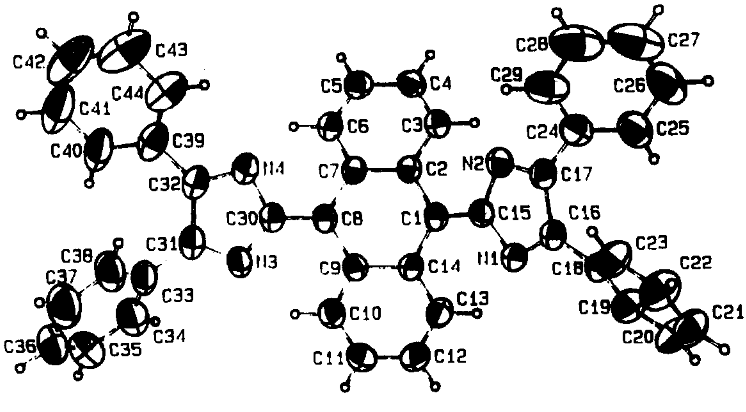


Fig. 1a. ORTEP view of the molecular structure of **5**, showing the atom labeling scheme, selected bond lengths (Å): C1-1-C15 137.8(3), C1-C14 146.4(3), C9-C14 141.8(2), C16-C17 146.8(3), N2-C15 140.0(3), N2-C17 130.6(3).

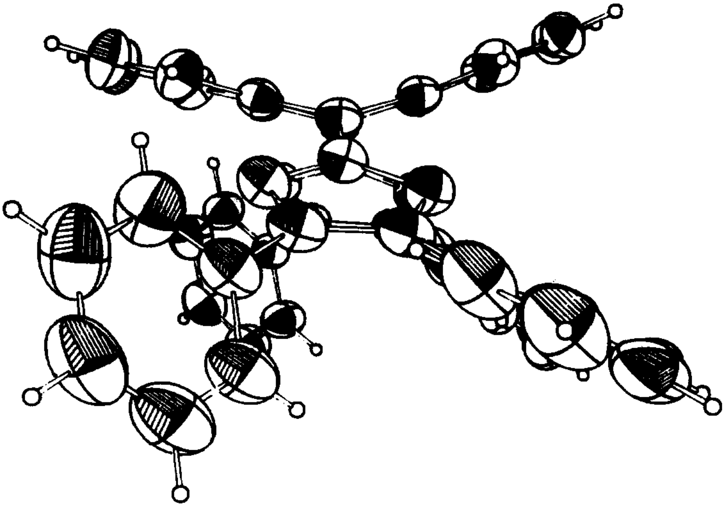
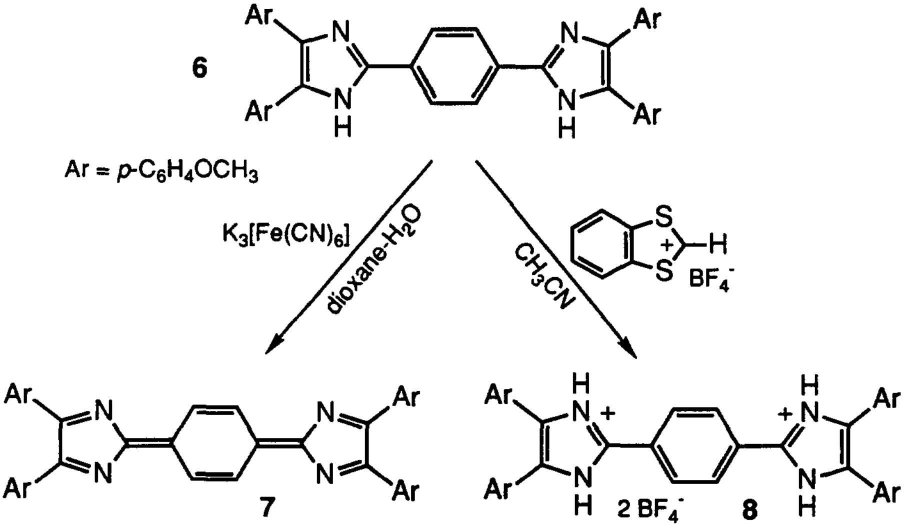


Fig. 1b. Side view of **5**.

In order to find out about the influence of substituents in the phenyl rings on the potential thermochromic behavior of **1** we synthesized the tetramethoxy derivative **7** (λ_{max} = 677 nm) by dehydrogenation of 1,4-bis[4,5-bis(*p*-methoxyphenylimidazol-2-yl)]benzene **6** with potassium ferricyanide (cf.[4]). Obviously, donor groups in the phenyl rings have a strong bathochromic effect on the UV-vis absorption. Heating of **7** up to its melting point didn't show any thermochromism. When **6** is reacted with benzo-1,3-dithiolium tetrafluoroborate in acetonitrile surprisingly the bishydrotetrafluoroborate **8** is formed in 77% yield (yellow needles, m. p. > 350 °C (dec.)).



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10. **4**: Anthracene-9,10-dicarbaldehyde[11] (0.23 g, 1 mmol), benzil (0.42 g, 2 mmol) and ammonium acetate (1.01 g, 0.014 mol) were refluxed in acetic acid (25 ml) for 7 h. After cooling, water (20 ml) was added, the yellow precipitate collected by filtration, washed with EtOH and Et_2O and after drying recrystallized from AcOH-H_2O (2:1). Yield 75%; yelllow crystals. m. p. > 350 °C. Correct elemental analysis for $C_{44}H_{30}N_4 \times 2\ H_2O$.
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12. **5**: A suspension of **4** (0.61 g, 1 mmol) in dioxane (30 ml) was mixed with 15 ml of 6% aqueous KOH and to the mixture added dropwise over 2 h 120 ml of 20% aqueous $K_3[Fe(CN)_6]$ at 5-10 °C. The red solid was collected by filtration, washed with water, dissolved in benzene and the solution mixed with *n*-hexane until it turned turbid. Yield 61%; red crystals, m. p. 299-301 °C. Correct elemental analysis.
13. X-ray Crystallographic Analysis of **5**: Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation, $T = 296$ K. Crystallographic data: $C_{44}H_{28}N_4$, $M = 612.74$, triclinic, 0.20 × 0.53 × 0.10 mm, space group $P\bar{1}$, $a = 1047.8(3)$ pm, $b = 1305.6(4)$ pm, $c = 1358.8(5)$ pm, $\alpha = 114.61(2)°$, $\beta = 93.16(2)°$, $\gamma = 100.49(2)°$, $V = 1.6436$ nm^3, $Z = 2$, $\delta_{calcd} = 1.238$ g cm^{-3}, $F(000) = 640$, $\mu = 0.682$ cm-1. ω-scan $4° < 2\theta < 44°$, scan time 60 s. Data collected ± h, ± k, ± l; 4216 reflections collected, 4009 independent reflections, and 3092 "observed" with $I > 3\sigma(I)$. The structure was solved by direct methods (MULTAN). Refinement with MolEn of 433 parameters gave residuals R and R_w of 0.0352 and 0.0480, respectively; largest residual densities = 0.188/-0.53 e pm^{-3} 10^6. Supplementary material on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-57607, the names of the authors and the journal citation.
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