yellow powder. Crystallization of this material from ~50 mL of methanol gave 1.33 g (78%) of **16** in the form of short yellow needles: mp 176–77 °C; R_f 0.67 (2:1 *n*-PrOH/1% NH_3, cellulose); NMR (Me_2SO-d_6, D_2O) δ 8.15 (s, C_6 H, 1 H), 4.56 (d, J = 3.3 Hz, C_1' H, 1 H), 3.79–3.63 (m, C_2' H, 1 H), 3.55–3.17 (ddd, J = 10.8, 5.6, 6.4 Hz, C_3' H, 2 H). Anal. Calcd for $C_8H_{12}N_4O_4$: C, 42.10; H, 5.30; N, 24.55. Found: C, 42.25; H, 5.15; N, 23.79.

Euglenapterin (2). A suspension of 1.22 g (5.35 mmol) of amide **16** in 5 mL of dry DMF was treated with 10.19 g (53.5 mmol, 10 equiv) of tetramethylurea diethyl acetal.[14] After the suspension was stirred for 15 min, solution was complete, and after a total of 4 h the dark yellow-brown solution was concentrated to dryness under high vacuum. The resulting brown oil was concentrated three times from ethanol and three times from water (100 mL each) to remove excess acetal. The residue was then dissolved in 50 mL of water, treated with Darco G-60, filtered, and adjusted to pH 3.5 with 2 N HCl. After the mixture cooled overnight, filtration afforded 0.67 g of **2** as a yellow microcrystalline solid. Concentration to half volume gave an additional 0.48 g of **2** of equal purity (total yield 1.15 g, 77%). The material thus obtained had identical chromatographic and spectroscopic properties with the naturally occurring substance:[15] R_f 0.46 (2:1 *n*-PrOH/NH_3, cellulose); NMR (Me_2SO-d_6, D_2O) δ 8.72 (s, C_7 H, 1 H), 4.74 (d, J = 3.3 Hz, C_1' H, 1 H), 3.78–3.66 (m, C_2' H, 1 H), 3.58–3.32 (ddd, J = 10.8, 6.0, 6.0 Hz, C_3' H, 2 H), 3.07 (s, $N(CH_3)_2$, 6 H); UV λ_{max} (0.1 N NaOH) 381 nm, 272, λ_{max} (0.1 N HCl) 327 nm, 289 (w), 247. Synthetic **2** decomposed over a broad range beginning at ~206 °C.

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Structure and Spectroscopic Properties of So-Called α-Anthrapinacolin

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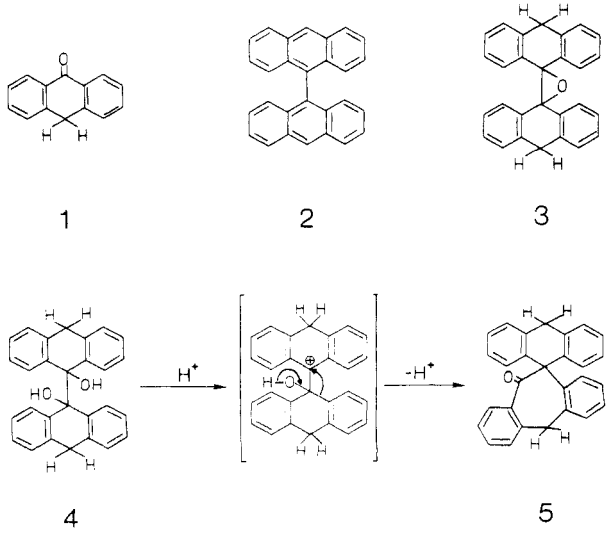
The reductive dimerization of anthrone (**1**) by zinc in the presence of mineral acid has been described to give 9,9′-dianthryl (**2**) and, in about 50% yield, the so-called α-anthrapinacolin (**3**).[1] Concerning the formation of an



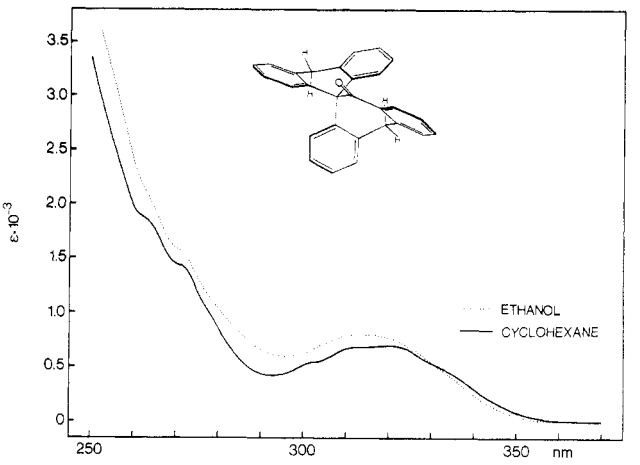


Figure 1. Electronic absorption spectra of anthrapinacolin **5** in cyclohexane (solid line) and in ethanol (dotted line).

anthrapinacolin from anthrone, a reviewer[2] had deemed it conceivable that the intermediate anthrapinacol (**4**) had undergone cationic rearrangement to give the seven-membered ketone **5**, but "this speculation" was rejected[3] as being devoid of any experimental basis. Indeed, a later investigation of anthrapinacolin also failed to provide chemical evidence for the presence of a carbonyl group.[4] Subsequently, anthrapinacolin **3** was described to be directly accessible from anthrapinacol (**4**) by treatment with thionyl chloride,[5] and as recently as 1973 the IR, UV, and ^1H NMR spectral data of anthrapinacolin obtained by this latter method were reported and believed to be in agreement with structure **3**.[6]

An interest in the electron spectral properties of the 9,10-dihydroanthracene chromophore[7] prompted us to investigate the structure of anthrapinacolin. We have confirmed that anthrapinacolin obtained by treatment of anthrone with zinc in the presence of acid indeed is identical with the product of dehydration of anthrapinacol by thionyl chloride. We also found anthrapinacolin to be nonfluorescent, as had been noted most recently.[6] All other spectroscopic data for anthrapinacolin, though in perfect agreement with the literature,[6] are from our point of view obviously at variance with the accepted epoxide structure **3**. Thus, the IR spectrum of anthrapinacolin (in KBr) exhibits a strong band at 1680 cm^{-1} which is indicative of an α,β-unsaturated carbonyl group. The UV spectrum of anthrapinacolin in cyclohexane solution exhibits a weakly structured absorption maximum around 315 nm (ε 690) which we attribute to an enhanced n–π* transition typical of a β,γ-unsaturated carbonyl chromophore.[8] In agreement with this assignment is the solvent dependence of the absorption spectrum (see Figure 1). In ethanol solution, the absorption maximum characteristic of the carbonyl n–π* transition is shifted hypsochromically as the onset of the π–π* transition is shifted toward lower energy. The presence of a carbonyl group in anthrapinacolin is also supported by its ^{13}C NMR spectrum (see Experimental Section).

Convincing evidence for structure **5**, rather than **3**, was obtained by ^1H NMR spectroscopy. The integration of the

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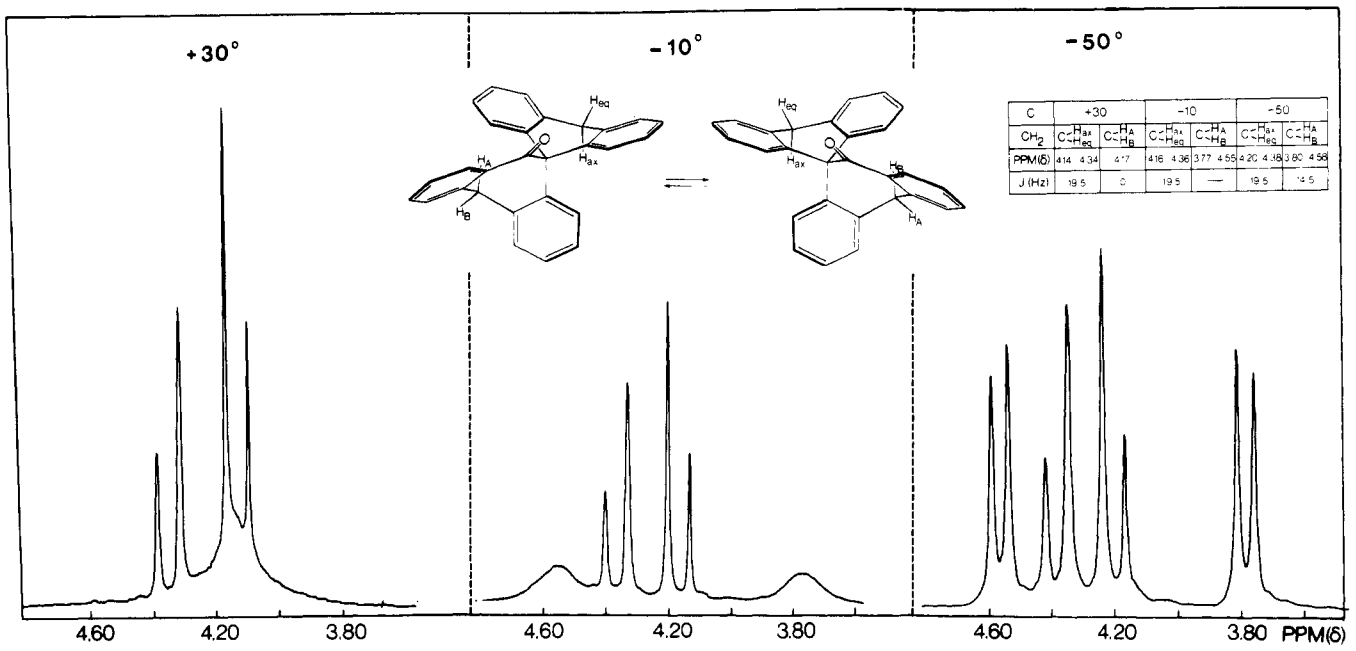

Figure 2. 270-MHz ^1H NMR spectra of anthrapinacolin **5** in $CDCl_3$ at 30 °C, −10 °C, and −50 °C.

room-temperature NMR spectrum of the nonaromatic protons in anthrapinacolin (see Figure 2) reveals that an absorption by two protons coincides with the upfield half of an AB spectrum (J = 19.5 Hz). When the temperature is lowered, the overlapping two-proton absorption first separates into two broad bands which finally give rise to an additional AB spectrum (J = 14.5 Hz). This finding leaves no doubt that anthrapinacolin actually has the previously rejected dibenzocycloheptadienone structure **5** in which the methylene protons of the seven-membered ring become magnetically nonequivalent as the intramolecular mobility of the ring system decreases. From the observed coalescence temperature of about 5 °C, the free energy of activation for the folding motion of the cycloheptadienone ring was calculated[9] to be 13 kcal/mol.

Experimental Section

Melting points were determined on a hot-stage microscope and are not corrected. NMR spectra were recorded on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Absorption spectra were obtained on a Beckman Acta III spectrophotometer.

Preparation of Anthrapinacolin (5) from Anthrone. A solution of anthrone (2 g) in acetic acid (10 mL) containing concentrated hydrochloric acid (1.2 mL) and granulated zinc (1.2 g) was refluxed for 2.5 h. After cooling the reaction mixture to room temperature, the crystalline precipitate was removed by filtration, washed successively with acetic acid, dilute hydrochloric acid, and water, and then dried (yield 1.69 g). Column chromatography (SiO_2/CH_2Cl_2) gave 0.60 g of 9,9′-bianthryl (33%), and 0.84 g (43%) of anthrapinacolin (**5**): mp 218–219 °C (lit.[1] mp 219 °C; ^{13}C NMR at 60 °C in $CDCl_3$) 35.8 (CH_2), 40.9 (CH_2), 69.7 (C), 125.9, 126.3, 126.4, 127.1, 127.31, 127.32, 127.6, 128.3, 128.6, 130.3, 130.6, 134.6, 136.8, 138.4, 139.1, 139.7, 139.9, 144.3 (aromatic C), 202.5 ppm (CO). The aromatic carbons of the 9,10-dihydroanthracene moiety are pairwise equivalent.

Preparation of Anthrapinacolin (5) from Anthrapinacol. A solution of anthrapinacol[10] (**4**, 1 g) in thionyl chloride (15 mL) was refluxed for 2 h. Vacuum evaporation of solvent left a solid residue which was dissolved in methylene chloride. Acidic material was removed from the organic solution by extraction with water. Column chromatography (SiO_2/CH_2Cl_2) of the organic portion gave 760 mg (80%) of anthrapinacolin, mp 218–219 °C.

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Registry No. **1**, 90-44-8; **2**, 1055-23-8; **3**, 161-84-2; **4**, 4393-30-0; **5**, 79483-37-7.

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cis-1,2-Bis(9-anthryl)ethylene: Preparation and Photochemical Properties

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1,2-Bis(9-anthryl)ethylene (**1**) was first found to be formed by pyrolysis of poly-9-thioanthraldehyde,[1] and it was subsequently reported to be accessible by reacting 9-anthraldehyde with sodium diphenylphosphine oxide at 200 °C.[2] The yellow compound obtained by these two methods is characterized by its low solubility and by its high melting point (~335 °C), and it has tacitly been assumed to be the trans isomer. Concerning the seemingly more straightforward formation of **1** from 1,2-bis(9-anthryl)ethanol reported in 1966,[3] the structures of all compounds involved in that sequence of reactions were recently revised and shown to be derivatives of 9,10-dihydroanthracene.[4] We have found during the course of the present investigation that *trans*-1,2-bis(9-anthryl)-ethylene is most conveniently prepared by the Wittig re-

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