



Spectroscopic characterization and crystal structure of the 1,2,3,4,5,6-hexahydrophenanthro[1,10,9,8-*opqra*]perylene

Klaus Wolkenstein,^{a,*} Jürgen H. Gross,^b Thomas Oeser^b and Heinz F. Schöler^a

^a*Institute of Environmental Geochemistry, University of Heidelberg, Im Neuenheimer Feld 236, D-69120, Germany*

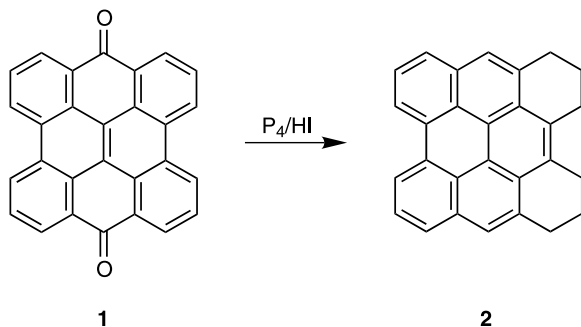
^b*Institute of Organic Chemistry, University of Heidelberg, Im Neuenheimer Feld 270, D-69120, Germany*

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Abstract—The spectroscopic characterization and the crystal structure of the 1,2,3,4,5,6-hexahydrophenanthro[1,10,9,8-*opqra*]perylene, which is known from the fossil record, is described. © 2002 Elsevier Science Ltd. All rights reserved.

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in recent and ancient sediments. The 1,2,3,4,5,6-hexahydrophenanthro[1,10,9,8-*opqra*]perylene (**2**) and few other PAHs could even be isolated from a Jurassic crinoid.^{1–3} During the analysis of similar compounds from geological samples, **2** was synthesized as a standard to enable direct comparison. The perylene **2** could be obtained by reduction of the phenanthro[1,10,9,8-*opqra*]perylene-7,14-dione (**1**)⁴ with red phosphorus and hydriodic acid (Scheme 1).⁵ However, in previous reports on **2** there is only little spectroscopic data and no proof of its constitution.^{1–3,5,6}

In this letter we report the spectroscopic characterization and the crystal structure of **2** and describe an efficient method for the purification of this compound.



Scheme 1.

Keywords: polycyclic aromatic hydrocarbons; fossil crinoids; mass spectrometry; NMR spectroscopy; X-ray crystal structure.

* Corresponding author. Fax: +49-6221-545228; e-mail:

klaus.wolkenstein@urz.uni-heidelberg.de

According to the literature, compound **2** was synthesized by heating 30 mg of **1**, 15 mg red phosphorus and 0.6 mL hydriodic acid for 5 h at 200°C in a sealed (glass) tube.^{3,5} The crude product was washed carefully with distilled water and dried overnight at room temperature under moderate vacuum. The residue was then extracted with toluene for 0.5 h in a sonicator, followed by centrifugation. Analysis of the solution by laser desorption/ionization mass spectrometry revealed the presence of **2** and two related compounds with *m/z* 350 and 362. The latter compounds are probably phenanthroperylene (confirmed by the characteristic absorption bands in the region 500–700 nm)^{6,7} and the dodecahydroderivative. Both of them are very unstable in solution^{3,7} and they were converted to more polar compounds within 2 days, when in contact with air and daylight. The photooxidation of these compounds is accompanied by a distinct color change of the solution from greenish-blue to yellow. Separation of the polar compounds by flash column chromatography on silica gel with toluene as the eluent and subsequent evaporation of the solvent gave pure **2** (~30% yield).⁸

The crystals of **2** have a characteristic sulfur-yellow color with intense green fluorescence in UV light. The solubility of **2** is very low in almost all solvents. Even in toluene the maximum solubility is only ~0.2 mg mL⁻¹. For cyclohexane, a common solvent for PAH extraction, the solubility is much lower.

The UV–vis spectrum in toluene with maxima at 419, 392, 372, 354, 334, 313 and 304 nm is in good agreement with the reported spectral data of **2** (in benzene).⁶

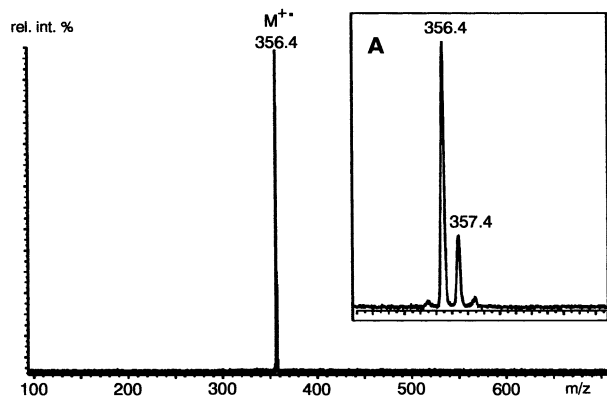


Figure 1. Positive-ion LDI time-of-flight mass spectrum of purified **2**. The inset A shows the expanded molecular ion signal.

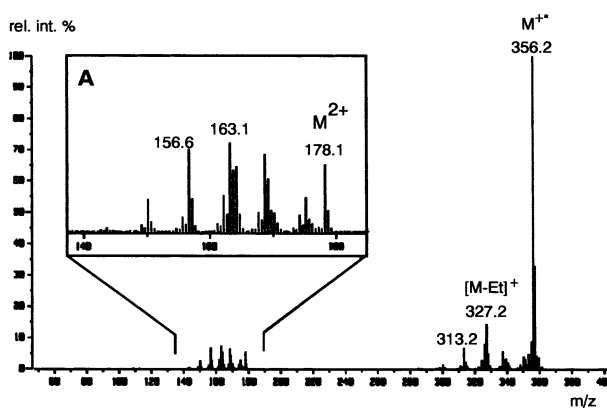


Figure 2. 70 eV EI mass spectrum of **2**. The inset A shows an expansion of the m/z range where doubly charged ions occurred.

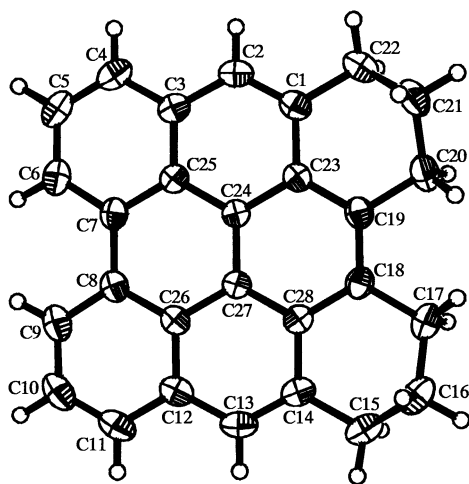


Figure 3. ORTEP drawing¹⁰ of **2** at the 50% probability level.

Compound **2** was further characterized by laser desorption/ionization (LDI) and electron ionization (EI) mass spectrometry. In the LDI spectrum only the molecular ion, $M^{+\bullet}$, m/z 356, and its isotopic peaks were observed, confirming the absence of perylene by-products in the sample (Fig. 1). In addition to the molecular ion, the EI

spectrum showed some fragment ions, the doubly charged molecular ion, M^{2+} , m/z 178, and several doubly charged fragment ions of low abundance (Fig. 2); the total appearance corresponds well with that of other PAH spectra. By high resolution EI MS, the elemental compositions of some significant ions were confirmed.

The appearance of seven signals in the ^1H NMR spectrum (500 MHz, CDCl_3) is indicative for the symmetrical structure of the PAH. The characteristic proton signals observed in the aromatic area at δ 8.93, 8.07, 7.94, 7.81 and the signals of the methylene protons at δ 3.37, 3.31 and 2.29 confirm the expected structure of **2**. The ^{13}C NMR spectrum of **2** was not recorded due to its very low solubility.

A suitable single crystal of **2** was obtained from a toluene solution by slow evaporation at room temperature. Because of a low photooxidation sensitivity also of **2**, the solution was stored under an argon atmosphere with exclusion of light.

The crystal structure of **2** is almost planar (Fig. 3).⁹ In both rings with aliphatic units only the central atoms C16 and C21 of the trimethylene groups deviate out of the aromatic ring plane by 48° into the same direction. The atoms C21 and C22 in one of these trimethylene groups are disordered with a multiplicity of 85:15%. The minor part of C21 deviates into the opposite direction out of the aromatic ring plane by 46° .

Acknowledgements

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- UV–vis, FT-IR and ^1H NMR spectra were recorded using the Lange CADAS 100, Bruker VECTOR 22 and Bruker DRX 500 instruments. The LDI mass spectrum was acquired on a Bruker Biflex time-of-flight instrument in positive-ion reflector mode with pulsed-ion extraction turned on. The solid sample was spread on a chromium

coated sample target. Low and high resolution 70 eV EI spectra were obtained from a JEOL JMS-700 magnetic sector instrument.

Compound **2**: prismatic sulphur-yellow crystals; sublim. 200–205°C; UV-vis (toluene): λ_{max} 419 (3.20), 392 (4.22), 372 (4.16), 354 (3.88), 334 (sh, 3.69), 313 (4.62), 304 (4.56) nm (log ϵ); FT-IR (KBr): ν 3034, 2936, 2863, 1619, 1590, 768 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.93 (d, $J=8.0$ Hz, 2H), 8.07 (d, $J=7.4$ Hz, 2H), 7.94 (dd, $J=7.4$, 8.0 Hz, 2H), 7.81 (s, 2H), 3.37 (t, $J=6.0$ Hz, 4H), 3.31 (t, $J=6.0$ Hz, 4H), 2.29 (q, $J=6.0$ Hz, 4H) ppm; EI MS: m/z (%) 356 (100) $\text{M}^{+\bullet}$, 355 (9), 327 (14), 313 (7), 178 (5); HR-EI MS: m/z 356.1541, $\text{M}^{+\bullet}$, calcd for $\text{C}_{28}\text{H}_{20}$: 356.1565; m/z 355.1469, $[\text{M}-\text{H}]^+$, calcd for $\text{C}_{28}\text{H}_{19}$: 355.1487; m/z 327.1155, $[\text{M}-\text{C}_2\text{H}_5]^+$, calcd for $\text{C}_{26}\text{H}_{15}$: 327.1174; m/z 313.1017, $[\text{M}-\text{C}_3\text{H}_7]^+$, calcd for $\text{C}_{25}\text{H}_{13}$: 313.1017; m/z 178.0768, M^{2+} , calcd for $0.5^*\text{C}_{28}\text{H}_{20}$: 178.0782.

9. The X-ray diffraction data were collected with a Bruker SMART APEX diffractometer (Mo $\text{K}\alpha$ -radiation, graphite monochromator). Data collection and reduction were performed with the Bruker SMART and SAINT software (Bruker AXS, Inc., 5465 East Cheryl Parkway,

Madison, WI 53711-5373, USA, 2001). The structure was solved by direct methods (SHELXTL). The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). All hydrogen atoms were calculated and included in refinement process. Refinement was carried out with SHELXTL (Sheldrick, G. M., Bruker AXS, Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373, USA, 2000).

Crystallographic data for **2**: $\text{C}_{28}\text{H}_{20}$, $M=356.44$, yellow fragment, crystal dimensions $0.5\times 0.3\times 0.3$ mm, monoclinic, space group $P2_1/c$, $a=10.263$ (1), $b=14.128$ (1), $c=12.012$ (1) Å, $\beta=101.045$ (2)°, $Z=4$, $D_{\text{calcd}}=1.39$, $F(000)=752$, 10119 measured reflections, 3871 unique ($R_{\text{int}}=0.018$), 3078 observed, $R=0.053$, $R_w=0.148$, 261 parameters, $(\Delta\rho)_{\text{max}}=0.23$ e Å $^{-3}$, $(\Delta\rho)_{\text{min}}=-0.31$ e Å $^{-3}$. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 171945.

10. ORTEP-3 for Windows: Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.