

Reaction of Phenanthrene-9,10-dione with Phenanthrene-9,10-diol: Synthesis and Characterization of the First *ortho*-Quinhydrone Derivative

by Fausto Calderazzo^a), Claudia Forte^b), Fabio Marchetti^a), Guido Pampaloni^{*a}), and Laura Pieretti^a)

^a) Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa
(e-mail: pampa@dccci.unipi.it)

^b) Istituto per i Processi Chimico-Fisici, CNR, Area della Ricerca, Via G. Moruzzi 1, I-56124 Pisa
(e-mail: claudia@icqem.pi.cnr.it)

Treatment of phenanthrene-9,10-dione (PQ) with phenanthrene-9,10-diol (PQH₂), as prepared by catalytic hydrogenation of PQ, in toluene solution or in the solid state afforded crystalline '9,10-phenanthrenequinhydrone' (PQH), the first example of an *ortho*-quinhydrone. PQH was characterized by analytical and spectroscopic methods, including X-ray and CP/MAS ¹³C-NMR analyses. The crystal structure of PQH showed pairs of planar molecules linked by H-bonds and organized in columns parallel to the crystallographic axis *a*. The solid-state structure of PQH was compared with those of the parent compounds, PQ and PQH₂, the latter being reported for the first time. PQH was found to be stable in the solid state only, the components PQ and PQH₂ being formed upon dissolution in media of even low polarity such as toluene.

1. Introduction. – Quinones are acceptors in donor/acceptor complexes [1], a behavior that depends to some extent on the electron-withdrawing effect of the O-atoms, generating an electron-deficient π -system and two electron-rich O-atoms [2]. The quinone O-atoms are good electron donors and, therefore, likely to be involved in H-bond formation. Quinones have been known for a long time to form 1:1 complexes with hydroquinones, the prototype being quinhydrone, the adduct of 1,4-benzoquinone and 1,4-dihydroxybenzene. This 1:1 adduct consists of alternating 1,4-benzoquinone and 1,4-dihydroxybenzene units linked *via* H-bonds to form a zigzag chain extending through the crystal [3]. The crystal structures of several other compounds of this class investigated by X-ray diffraction methods have also been shown to consist of chains of alternating quinone and hydroquinone moieties, forming infinite H-bonded aggregates stabilized by additional π/π interactions [4].

Concerning the solid-state interactions between quinones and the corresponding phenols, to the best of our knowledge, all known examples involve *p*-quinones and *p*-hydroxyphenols such as 2,5-dimethylbenzene-1,4-dione/2,5-dimethylbenzene-1,4-diol [4h], 2,3,5,6-tetramethylbenzene-1,4-dione/2,3,5,6-tetramethylbenzene-1,4-diol [4j], and naphthalene-1,4-dione/naphthalene-1,4-diol [4d]. Intramolecular interactions have been observed in [3.3]-paracyclophane-type quinhydrone [4g].

Extensive work has appeared on the coordination ability of *o*-quinones toward transition metals [5]; intermolecular interactions are well-established in transition-metal-coordinated *o*-quinones such as phenanthrene-9,10-dione. Catecholato/semi-quinone interactions are observed in complexes of the type Mo(*o*-quinone)₃ [6], which are characterized by stacked structures [7].

The formation of a dark brown to black species by reacting phenanthrene-9,10-dione (PQ) with phenanthrene-9,10-diol (PQH₂) was described first in 1886 [8a] and

later confirmed by others [8b–e], but the actual product of this reaction has not been fully characterized yet. In this paper, we report the first complete description of brown-black ‘9,10-phenanthrenequinhydrone’ (PQH)¹⁾ formed by the 1:1 reaction of PQ (yellow-orange) and PQH₂ (colorless) at room temperature.

2. Results and Discussion. – 2.1. *Synthesis and Structure of PQH₂.* Phenanthrene-9,10-diol (PQH₂) was first prepared in 1910 [9] by reduction of phenanthrene-9,10-dione (PQ) with Zn powder in boiling AcOH, followed by dilution with H₂O, filtration, and drying of the solid product in air. While repeating this procedure, we noticed that the colorless solid, when exposed to air before drying, turns quickly brown, and a strong IR absorption at 1678 cm⁻¹ was observed, which was attributed to PQ. Looking for alternative synthetic procedures for PQH₂, we found that Pd/C-catalyzed hydrogenation of PQ in toluene at atmospheric pressure afforded PQH₂ quantitatively. The IR spectrum of the resulting product showed a broad absorption at 3290 cm⁻¹, assigned to the stretching vibration of the H-bonded OH groups. At variance with the behavior in solution, anhydrous PQH₂ is stable in air over long periods of time.

After several attempts, crystals of PQH₂ suitable for an X-ray-diffraction experiment were grown at room temperature from a saturated toluene solution. The molecular structure is reported in *Fig. 1*. The compound crystallized in the space group *P2₁/n*, with four molecules in the unit cell. Bond distances and angles for the aromatic rings were similar to those found in phenanthrene [10], and are reported in *Table 1*. The bond lengths C(1)–O(1) and C(14)–O(2) amounted to 1.397(2) and 1.383(2) Å, respectively.

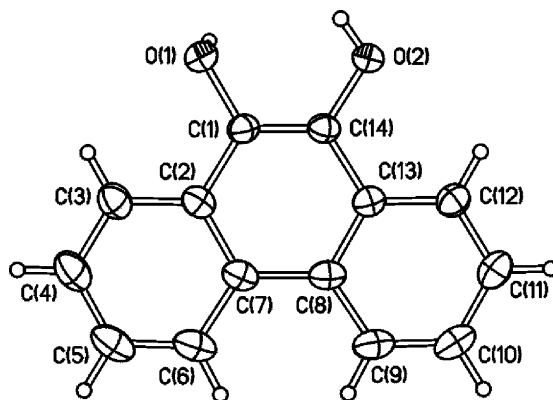


Fig. 1. X-Ray crystal structure of phenanthrene-9,10-diol (PQH₂). Thermal ellipsoids are shown at 30% probability.

The crystal lattice of PQH₂ is shown in *Fig. 2*. The molecules are aligned in double columns related by an inversion center. Columns run parallel to the crystallographic axis *b* and face each other through the OH groups. The molecule is planar within

¹⁾ This compound can be drawn in several mesomeric forms such as **A** or **B** (see the *Scheme*), i.e., as 10-hydroxyphenanthren-9-oxyl or 9-hydroxy-10-oxophenanthren-9-yl radicals, respectively, among others.

Table 1. Bond Lengths (in Å) and Angles (in °) of Phenanthrene-9,10-diol (PQH₂) and '9,10-phenanthrene-quinhydrone' (PQH¹) as Determined by X-Ray Crystal-Structure Analyses^{a)}

	PQH ₂	PQH
O(1)–C(1)	1.397(2)	1.303(2)
C(1)–C(14)	1.345(3)	1.438(3)
C(1)–C(2)	1.435(3)	1.446(3)
C(2)–C(7)	1.411(3)	1.413(2)
C(7)–C(8)	1.461(3)	1.471(2)
C(8)–C(13)	1.417(3)	1.408(2)
C(13)–C(14)	1.432(3)	1.451(3)
C(14)–O(2)	1.383(2)	1.293(2)
O(1)–C(1)–C(2)	118.2(2)	120.9(2)
C(14)–C(1)–O(1)	120.2(2)	119.0(2)
C(14)–C(1)–C(2)	121.6(2)	120.1(2)
C(7)–C(2)–C(1)	118.9(2)	119.9(2)
C(2)–C(7)–C(8)	119.5(2)	120.0(2)
C(13)–C(8)–C(7)	119.4(2)	120.2(2)
C(8)–C(13)–C(14)	118.8(2)	120.0(2)
C(1)–C(14)–C(13)	121.7(2)	119.8(2)
C(1)–C(14)–O(2)	122.3(2)	120.8(2)
O(2)–C(14)–C(13)	116.0(2)	119.4(2)

^{a)} Identical atom numbering for both compounds (see Figs. 1 and 4).

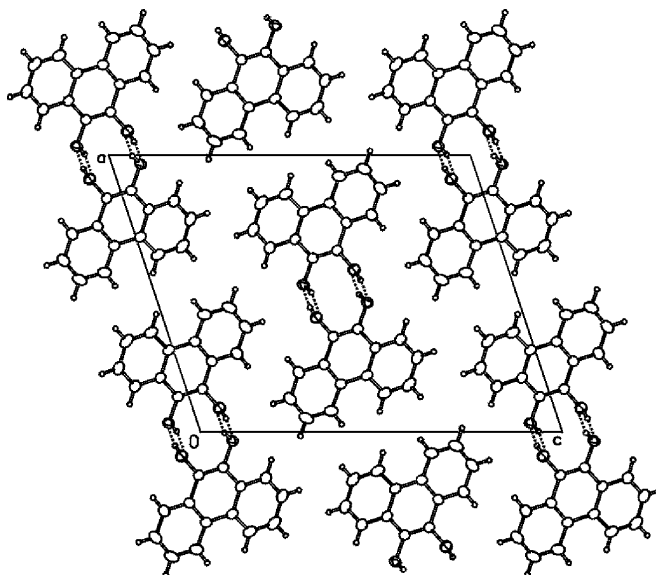


Fig. 2. Crystal lattice of phenanthrene-9,10-diol (PQH₂) viewed along the b-axis

0.05 Å, the molecular planes being separated by 3.62 Å and tilted by 60.3° with respect to the column axis. Within pairs of columns, each OH group interacts with two OH groups of the nearest column, at distances O(1) ⋯ O(2') of 2.707 and O(1) ⋯ O(2'') of

2.710 Å ($' = 1 - x, 1 - y, 1 - z; '' = 1 - x, -y, 1 - z$), respectively. These OH groups give rise to a net of H-bonds, as depicted in Fig. 3.

2.2. *Synthesis and Structure of PQH*. When a toluene solution of PQ was treated with PQH_2 , a dark-colored solid was formed, which was shown to be pure PQH (Scheme). The reaction was fast in toluene or THF, and proceeded even in the solid state by warming the solid mixture at ca. 80°.

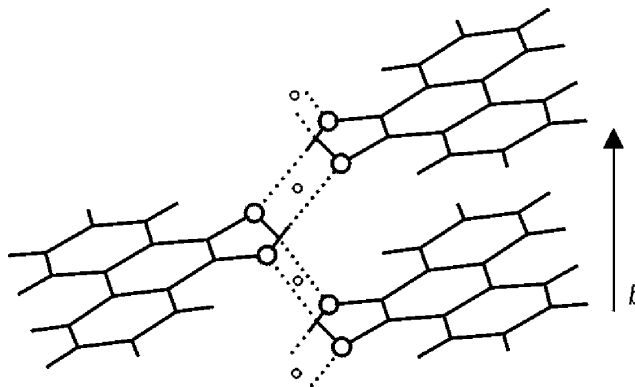
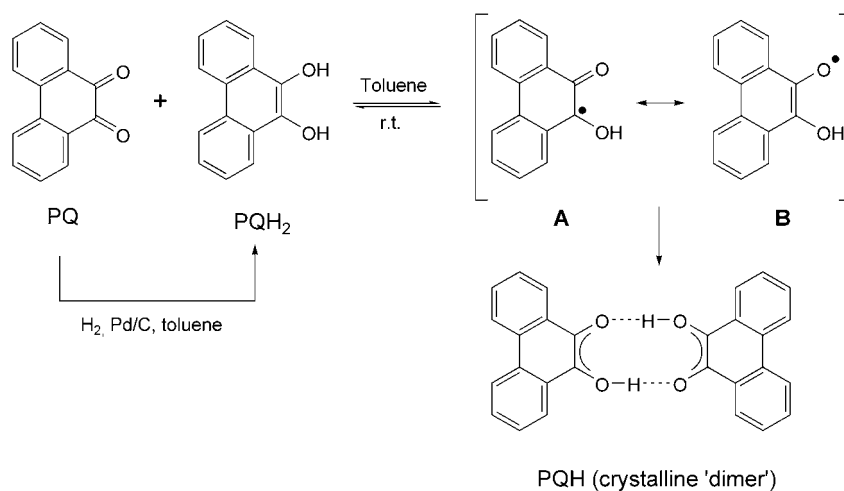


Fig. 3. H-Bonded chain of phenanthrene-9,10-diol (PQH_2) molecules

Scheme. *Synthesis of '9,10-Phenanthrenequinhydrone' (PQH)*. The mesomeric radicals **A** and **B**, as well as other mesomeric forms of PQH, are unstable in solution. However, upon crystallization, PQH is obtained in the form of fairly stable, brown-black crystals, which are stabilized by formation of H-bonded 'dimers'.



Anhydrous PQH is stable in air for long periods of time. The compound is diamagnetic (magnetic susceptibility < 0 at room temperature) and melts at 180–182°, which is intermediate between the melting points of PQ (215°) and PQH_2 (145–149°). It sublimes at 120° at a pressure of 10^{-3} – 10^{-5} Torr, to give brown-black crystals. The solid state IR spectrum, which remained unchanged after exposure to dry air, showed a

band of medium intensity at 1655 cm^{-1} , corresponding to a shift towards lower wavenumbers of *ca.* 20 cm^{-1} with respect to PQ, thus suggesting a reduction of the C=O bond.

The $^1\text{H-NMR}$ spectrum of PQH in CDCl_3 showed signals at 8.58, 8.00, 7.55, and 5.40 ppm (typical of PQH_2 in CDCl_3), and at 8.15, 7.95, 7.70, 7.45 ppm (typical of PQ in CDCl_3), confirming that the PQH dimer is not stable in solution. Similar observations have been made with *p*-quinones, where solid-state reactions have been adopted to prepare compounds not accessible in solution [11].

PQH was further characterized by X-ray diffraction and $^{13}\text{C-NMR}$ spectroscopy. Well-shaped, single crystals of PQH have been obtained by sublimation of the solid at 120° (10^{-3} – 10^{-5} Torr) or at 150° (5×10^{-2} Torr). The molecular structure of PQH is shown in Fig. 4, and bond distances and angles are reported in Table 1. The OH H-atom was statistically distributed on both O(1) and O(2), with a small prevalence of O(1) (*vide infra*). The molecule, by overlooking the OH H-atom, is substantially planar, the major deviation from planarity being due to the O(2) atom, which is 0.036 \AA out of plane. The C–C bond distances are similar to those observed in phenanthrene [10], while the C–O and the C(1)–C(14) bond distances ($1.293(2)$, $1.303(2)\text{ \AA}$ and $1.438(3)\text{ \AA}$, respectively) are intermediate between the corresponding distances in the α - (1.23 and 1.51 \AA , mean values) or β -form of PQ (1.20 and 1.53 \AA , mean values) [12] and in PQH_2 ($1.383(2)$, $1.397(2)$ and $1.345(3)\text{ \AA}$), thus suggesting a progressive reduction of the C=O bond order on going from PQ to PQH to PQH_2 .

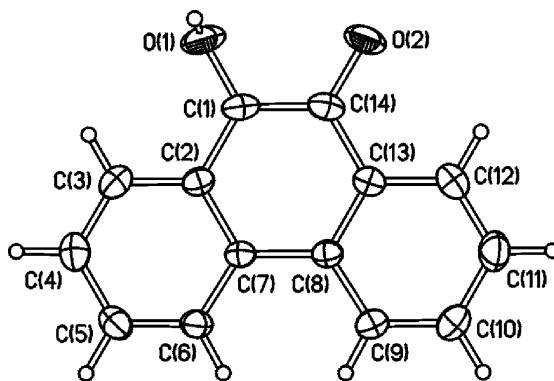


Fig. 4. X-Ray crystal structure of '9,10-phenanthrenequinhydrone' (PQH^1). Only the most-populated position of the disordered OH H-atom is depicted. Thermal ellipsoids are shown at 30% probability.

The crystal structure of PQH is characterized by pairs of molecules related by inversion symmetry, the O-atoms facing each other at a distance of 2.955 \AA . Within the couples, the two molecules are linked by H-bonds. Due to the 'disordered' OH H-atom, each O-atom alternatively acts as a H-bond donor or acceptor, with a small predominance (53%) of donor character at O(1). Couples of molecules are organized in columns parallel to the *a* direction, as shown in Fig. 5. The molecular planes run parallel and form an angle of 84.3° with the axis of the column, the stacking step being 3.451 \AA .

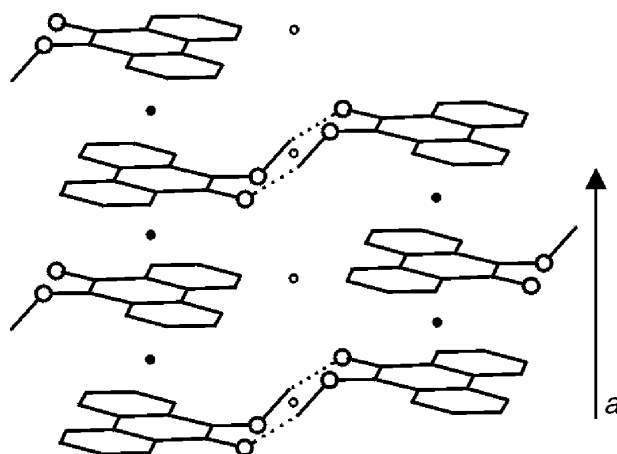


Fig. 5. Stacking and H-bonding interactions in columns and pairs of '9,10-phenanthrenequinhydrone' (PQH)¹ molecules, resp. Filled circles represent the inversion centers at 0, $\frac{1}{2}$, $\frac{1}{2}$, and at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; open circles refer to those at 0, 0, $\frac{1}{2}$, and at $\frac{1}{2}$, 0, $\frac{1}{2}$.

The CP/MAS ^{13}C -NMR spectrum of PQH showed signals at δ_{C} 177.6 and 138.5 ppm attributed to the C=O and to the C–OH C-atoms, respectively, in addition to the aromatic resonances between 123 and 135 ppm. This spectrum was compared with those of PQ (178.6 (C=O), 135.5, 129.5, 127.0, 125.0 ppm) and of PQH₂ (135 (C–OH), 130, 124–126, 120 ppm) obtained under the same conditions. The spectrum of PQH is clearly intermediate between those of PQ and of PQH₂, with the resonance of the C=O group being slightly shifted toward higher fields. Moreover, the intensity of this resonance was nearly half the intensity of the corresponding resonance of PQ, in agreement with the hypothesis that only one C=O functionality had been reduced.

2.3. The PQ/PQH₂ System. As reported in the *Introduction*, examples exist of the interaction between quinones and their corresponding (or related) diols present in nonequimolar ratios. These studies concern *p*-quinones exclusively, and the formation of 1:2 or 2:1 compounds has been related to the steric hindrance of the reagents. For example, 2,3,5,6-tetramethylbenzene-1,4-dione and benzene-1,4-diol, or 2,3,5,6-tetramethylbenzene-1,4-diol and benzene-1,4-dione, afford 1:2 complexes, while combination of two tetramethyl-substituted substances affords the 1:1 complex only [4j][4k]. Although PQ is not alkyl-substituted, it can be considered sterically hindered due to the fact that the functional groups are *ortho* to a condensed-ring system. It was, therefore of interest to study the reaction between PQ and PQH₂ in different stoichiometric ratios. Tests have been performed in the presence of toluene, with PQ/PQH₂ molar ratios ranging from 2:1 to 1:2. In all cases, the quickly formed brown solid was identified as PQH on the basis of IR, ^{13}C -NMR, and X-ray powder-diffraction experiments. Also, by evaporation of the solvent from the filtrate, mixtures of PQH and the reagent in excess were isolated and characterized, showing that the *solid-state* 1:1 adduct of PQ with PQH₂ is the most favorable combination. Similar results have been obtained by heating the solid components in different molar ratios.

3. Conclusions. – The reaction of phenanthrene-9,10-dione (PQ) with phenanthrene-9,10-diol (PQH₂) both in solution or in the solid state affords ‘9,10-phenanthrenequinhydrone’ (PQH)¹). The solid-state structure of PQH consists of parallel chains of molecules held together by H-bonds. The spatial disposition of the molecules within the couples is similar to that observed in PQH₂. This is the first report of the interaction between an *o*-quinone and the corresponding mono-reduced species, showing that, at variance with the species obtained in the case of *p*-quinones, only the product made from a 1:1 molar ratio of the components is stable.

Experimental Part

General. Unless stated otherwise, all operations were carried out under an atmosphere of purified N₂ or Ar gas, solvents being dried by conventional methods prior to use. ‘9,10-Phenanthrenequinone’ (= phenanthrene-9,10-dione (PQ); Aldrich, 99%, m.p. 217–219°) was used as received. PQ Samples of lower quality (95%) were purified by sublimation at ca. 180°/0.05 Torr. Melting points (m.p.) were measured on a Kofler apparatus in glass capillaries. UV/VIS Spectra: Perkin-Elmer Lambda-9 instrument, at 25°; λ in nm. Due to the O₂ sensitivity of dissolved PQH₂ or PQH, all UV solns. were introduced via cannulae into 10-mm cuvettes equipped with a ROTAFLO two-way inlet. IR Spectra: FT-1725X IR spectrophotometer, either in solution or in nujol or nujol/polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air; in cm⁻¹. ¹H- and ¹³C-NMR Spectra: Varian Gemini-200 instrument, at 200 and 50 MHz, resp.; chemical shifts δ rel. to SiMe₄ (= 0 ppm). CP/MAS ¹³C-NMR spectra were recorded on a Bruker AMX-300WB spectrometer at 75.43 MHz, using 4-mm ZrO₂ rotors. Acquisition conditions: contact pulse, 1.5 ms; acquisition delay, 60 s; cross-polarization radiofrequency, 81 kHz; 90° pulse, 3.1 ms. Nonquaternary suppression experiments were performed with a 50 ms delay after cross-polarization. Powder X-ray diffraction patterns were recorded on a Philips PW1050/25 instrument, using CuK_α radiation and a graphite monochromator.

Phenanthrene-9,10-diol (PQH₂). To a suspension of PQ (5.12 g, 24.6 mmol) in toluene (125 ml) was added Pd/C (3%; 0.41 g), and the resulting orange suspension was stirred at r.t. for 48 h under atmospheric pressure of H₂. The resulting nearly colorless mixture was filtered, and the solid was dissolved by refluxing in toluene for 3 h. After cooling to r.t., the colorless PQH₂ crystals were filtered off and dried *in vacuo* at r.t.: 3.86 g (75%). The anh. compound was stable in air for long periods of time, but was immediately oxidized to PQ in soln. M.p. 145–149° (toluene). IR (nujol/PCTFE): 3269s, 3075w, 1634m, 1608m, 1500m, 1452m, 1438m, 1350m, 1331s, 1286m, 1262m 1234m, 1176w, 1154w, 1109m, 1050w, 1016s, 897w, 854w, 801w, 783w, 748s, 719s, 681w, 638w, 618w, 583w, 445w, 419m. ¹H-NMR (200 MHz, CDCl₃, 25°): 5.28 (s, 2 OH); 7.55 (t, 4 CH); 8.00 (d, 2 CH); 8.58 (d, 2 CH). Anal. calc. for C₁₄H₁₀O₂ (210.07): C 80.0, H 4.8; found: C 79.8, H 4.9. X-Ray: see Figs. 1–3, Tables 1 and 2, as well as the crystallographic section below.

Preparation of ‘9,10-phenanthrenequinhydrone’ (PQH)¹ in Solution. A soln. of PQ (0.611 g, 2.94 mmol) in toluene (100 ml) was treated with PQH₂ (0.615 g, 2.93 mmol). Immediate formation of a black-brown microcrystalline solid was observed. After 3 h of stirring at r.t., the mixture was filtered, and the solid was dried *in vacuo*: 0.768 g (63%). Evaporation of the mother liquid afforded another 0.244 g of PQH (total yield: 83%). The anh. compound was stable in air for at least one week, but should preferably be stored under N₂ atmosphere. M.p. 180–182° (toluene; dec.). IR (nujol/PCTFE): 3494s, 3405s, 3066w, 3032w, 1658s, 1646m, 1626m, 1594s, 1501w, 1478w, 1451s, 1339w, 1291s, 1277m, 1234s, 1178w, 1166w, 1123w, 1109m, 1042w, 1018m, 928m, 754s, 721m, 711s, 536m, 432m. ¹³C-NMR (CP/MAS; CDCl₃): 177.6 (C=O); 138.5 (C–OH); 135; 130; 128; 125; 123. Anal. calc. for C₁₄H₉O₂ (209.22): C 80.4, H 4.3; found: C 80.7, H 4.3.

Preparation of ‘9,10-Phenanthrenequinhydrone’ (PQH)¹ in the Solid State. A mixture of PQ (0.506 g, 2.43 mmol) and PQH₂ (0.507 g, 2.41 mmol) was heated at ca. 80° for 2 h with periodic shaking. The initially orange solid mass quickly turned dark brown. The product was identified as PQH on the basis of both its IR spectrum and its X-ray powder diagram.

Reaction between PQ and PQH₂ at Different Molar Ratios. a) PQ/PQH₂ 2:1. A suspension of PQ (1.544 g, 7.42 mmol) in toluene (100 ml) was treated with PQH₂ (0.780 g, 3.71 mmol). Immediate formation of a dark-brown microcrystalline solid was observed. After 3 h of stirring at r.t., the mixture was filtered, and the solid was dried *in vacuo* and identified as PQH based on its IR and X-ray powder diagram: 1.373 g (88%). The filtrate, after evaporation of the solvent, afforded 0.674 g of unreacted PQ.

b) *PQ/PQH₂ 1:2*. A suspension of PQ (0.389 g, 1.87 mmol) in toluene (50 ml) was treated with PQH₂ (0.780 g, 3.71 mmol). Immediate formation of a dark brown microcrystalline solid was observed. After 3 h of stirring at r.t., the mixture was filtered, and the solid was dried *in vacuo* and identified as PQH: 0.704 g (90%). The filtrate, after evaporation of the solvent, afforded 0.229 g of unreacted PQH₂.

Single-Crystal X-Ray Structure Analysis of PQH₂ and PQH. X-Ray diffraction measurements were carried out on a four-circle diffractometer, operating under graphite-monochromated MoK_α radiation. Intensity-data collection was carried out in the $\omega/2\theta$ scan mode, collecting a redundant set of data. Data reduction of measured intensities was carried out with the XSCANS [13] and the SHELXTL [14] packages. The structure solution, obtained by means of the automatic direct methods, and the refinements, based on full-matrix least-squares on F^2 , were done by means of the SHELXL97 program [15]. Some other utilities contained in the WINGX suite [16] were also used.

Crystals of PQH₂ were obtained as colorless sticks from a sat. toluene soln. A crystal of $0.52 \times 0.20 \times 0.12$ mm was analyzed. The unit-cell parameters for PQH₂ are listed in Table 2. A total of 2298 data points were collected between $2.2 \leq \theta \leq 24.0^\circ$. By merging the equivalent ones, a set of 1563 independent intensities ($R_{\text{int}} = [\sum |F_o - F_o(\text{mean})| / \sum (F_o)] = 0.0209$) was obtained. The systematic absences indicated the space group $P2_1/n$. All H-atoms were found in the difference *Fourier* map and were refined by allowing them to ride on the connected C-atoms. The final refinement cycle, performed by using anisotropic thermal parameters for the C-atoms, gave the reliability factors listed in Table 2.

Table 2. *Crystal Data and Structure Refinement for Phenanthrene-9,10-diol (PQH₂) and '9,10-Phenanthrenequinhydrone' (PQH)¹*

	PQH ₂	PQH
Empirical formula	C ₁₄ H ₁₀ O ₂	C ₁₄ H ₈ O ₂
Formula weight	210.22	209.21
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
<i>a</i> [Å]	14.278(3)	6.936(1)
<i>b</i> [Å]	4.172(1)	7.935(1)
<i>c</i> [Å]	17.706(3)	9.740(1)
α [deg]		69.02(1)
β [deg]	108.38(1)	81.20(1)
γ [deg]		73.93(1)
<i>V</i> [Å ³]	1,000.9(4)	480.0(1)
<i>Z</i>	4	2
<i>D</i> _{calc} [Mg · m ⁻³]	1.395	1.447
μ [mm ⁻¹]	0.093	0.097
Reflections measured	2298	2112
Unique reflections { <i>R</i> _{int} }	1563 {0.0209}	1663 {0.0136}
No. of parameters	147	158
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.044, 0.138	0.043, 0.127
Goodness-of-fit on F^2	0.877	0.968

Crystals of PQH were grown by sublimation at $150^\circ/4 \times 10^{-4}$ Torr as reddish-black tablets flattened on (001). One of them, with the dimensions $0.57 \times 0.32 \times 0.08$ mm, was used for the X-ray study. The corresponding unit-cell parameters are listed in Table 2. A total of 2112 data points were collected between $2.2 \leq \theta \leq 25^\circ$. By merging the equivalent ones, a set of 1663 independent intensities ($R_{\text{int}} = 0.0136$) was obtained. The structure solution was done in the space group $P\bar{1}$. The H-atoms were found in the difference *Fourier* map. The disorder of the OH H-atoms was established by finding some peaks of residual electron density near the O(1)- and O(2)-atoms. A fraction of H-atoms was then placed near these O-atoms, each alternatively acting as a H-bond donor or acceptor, with a small predominance (53%) of donor character on O(1), the total occupancy factor being fixed at 100%. In the final refinement cycle, performed by means of anisotropic thermal parameters for the C-atoms, the positions of the H-atoms were refined with constrained angles. The reliability factors are listed in Table 2.

Crystallographic data (excluding structure factors) for PQH₂ and PQH have been deposited with the Cambridge Crystallographic Data Centre as deposition numbers CCDC-212404 and -212405, resp. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

The authors wish to thank the *Ministero dell'Istruzione dell'Università e della Ricerca (MIUR, Roma)* and the *Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale (2002-3)* for financial support. We are also grateful to the COST Action D17/003 of the European Community for promoting scientific activity.

REFERENCES

- [1] R. Foster, M. I. Foreman, in 'The Chemistry of Functional Groups', Ed. S. Patai, John Wiley & Sons., New York, 1974.
- [2] B. Rees, *Acta Crystallogr., Sect. B* **1970**, 26, 1311.
- [3] H. Matsuda, K. Osaki, I. Nitta, *Bull. Chem. Soc. Jpn.* **1958**, 31, 611.
- [4] a) T. Sakai, *Acta Crystallogr.* **1965**, 19, 320; b) J. Gaultiern, C. Hauw, *Acta Crystallogr.* **1967**, 23, 1016; c) T. Sakurai, *Acta Crystallogr., Sect. B* **1968**, 24, 403; d) A. Thozet, J. Gaultier, *Acta Crystallogr., Sect. B* **1977**, 33, 1052; e) A. Artiga, J. Gaultier, C. Hauw, N. B. Chanh, *Acta Crystallogr., Sect. B* **1978**, 34, 1212; f) G. R. Desiraju, D. Y. Curtin, I. C. Paul, *Mol. Cryst. Liq. Cryst.* **1979**, 52, 259; g) H. A. Staab, C. P. Herz, C. Krieger, M. Rentea, *Chem. Ber.* **1983**, 116, 3813; h) A. O. Patil, S. R. Wilson, D. Y. Curtin, I. C. Paul, *J. Chem. Soc., Perkin Trans. 2* **1984**, 1107; i) A. O. Patil, D. Y. Curtin, I. C. Paul, *J. Am. Chem. Soc.* **1984**, 106, 4010; j) W. T. Pennington, A. O. Patil, D. Y. Curtin, I. C. Paul, *J. Chem. Soc., Perkin Trans. 2* **1986**, 1693; k) A. O. Patil, D. Y. Curtin, I. C. Paul, *J. Chem. Soc., Perkin Trans. 2* **1986**, 1687; l) W. T. Pennington, A. O. Patil, I. C. Paul, D. Y. Curtin, *J. Chem. Soc., Perkin Trans. 2* **1986**, 557; m) K. Nakasuji, K. Sugiura, T. Kitigawa, J. Toyoda, H. Okamoto, K. Okaniwa, T. Mitani, H. Yamamoto, I. Murata, A. Kawamoto, T. Tanaka, *J. Am. Chem. Soc.* **1991**, 113, 1862.
- [5] C. G. Pierpont, R. M. Buchanan, *Coord. Chem. Rev.* **1981**, 38, 45; C. G. Pierpont, C. W. Lange, *Prog. Inorg. Chem.* **1994**, 41, 331.
- [6] C. G. Pierpont, R. M. Buchanan, *J. Am. Chem. Soc.* **1975**, 97, 4912.
- [7] R. M. Buchanan, S. L. Kessel, H. H. Downs, C. G. Pierpont, D. N. Hendrickson, *J. Am. Chem. Soc.* **1978**, 100, 7894; C. G. Pierpont, R. M. Buchanan, *J. Am. Chem. Soc.* **1975**, 97, 6450; G. Tripepi, Ph. D. Thesis, Scuola Normale Superiore at Pisa, 1998.
- [8] a) H. Klinger, *Ber. Dtsch. Chem. Ges.* **1886**, 19, 1862; b) 'Beilsteins Handbuch der Organischen Chemie', 4th edn., Vol. VII, p. 796, E I 416, E II 724, E III 4084; c) R. F. Moore, W. A. Waters, *J. Chem. Soc.* **1953**, 3405; d) E. J. Moriconi, F. T. Wallenberger, W. F. O'Connor, *J. Org. Chem.* **1959**, 24, 86; e) S. Coffey, J. Van Alphen, in 'Chemistry of Carbon Compounds', Ed. E. H. Rodd; Elsevier, Amsterdam, 1956, Vol. III, Part b, p. 1355.
- [9] J. Schmidt, H. Lumpp, *Ber. Dtsch. Chem. Ges.* **1910**, 43, 787.
- [10] V. Patříček, I. Čisářová, L. Kummel, J. Kroupa, B. Březina, *Acta Crystallogr., Sect. B* **1990**, 46, 830.
- [11] A. O. Patil, D. Y. Curtin, I. C. Paul, *J. Am. Chem. Soc.* **1984**, 106, 348.
- [12] S. Y. Matsuzaki, M. Gotoh, A. Kuboyama, *Mol. Cryst. Liq. Cryst.* **1987**, 142, 127; A. D. Rae, A. C. Willis, *Z. Kristallogr.* **2003**, 218, 221.
- [13] XSCANS, X-ray Single Crystal Analysis System, Rel. 2.1, Bruker AXS, Madison, Wisconsin, USA, 1994.
- [14] G. M. Sheldrick, SHELXTL-Plus, Rel. 5.1, Siemens Bruker AXS, Madison, Wisconsin, USA, 1997.
- [15] G. M. Sheldrick, SHELX97, Program for Crystal Structure Analysis (Rel. 97-2), University of Göttingen, Germany, 1998.
- [16] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, 32, 837.

Received October 23, 2003