A new phenanthrene-based bis-oxime chemosensor for Fe(III) and Cr(III) discrimination

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ABSTRACT

The synthesis of two new 2,7-disubstituted phenanthrene-based bis oximes is described. The ability of these two compound for complexing heavy metal cations have been studied and complexation constants and complex stoichiometry for Cr^{3+} and Fe^{3+} complex have been determined. The fluorescent properties of ligand **2** make this compound able to act as a sensor able to discriminate between Cr^{3+} and Fe^{3+}. Detection limits for these two cations have been evaluated.

1. Introduction

The design and synthesis of new chemosensors for heavy and transition metal cations is an important subject in the field of supramolecular chemistry.[1–3] Optical sensors for cations have consistently demonstrated their potential in a variety of fields, such as biological probes, environmental sensors, food safety, etc.[4,5] and new ligands are developed continuously.[6,7] Trivalent form of iron and chromium are essential elements for life because they play vital roles in structural, catalytic and regulatory aspects of biological systems. On the other hand, chromium is an environmental pollutant and its build-up due to various industrial and agricultural activities is a matter of concern. Particular interest merits the control of water pollution by chromium salts in areas where the tanning industry is relevant[8,9] as it is the case of South American rivers. It is known that the Fe^{3+} and Cr^{3+} sensors are usually coming by interference between them, and then sensitive and selective detection of these metal ions still need to be developed.[10]

One of the best approaches toward the development of chemosensors consists in coupling a binding site with a signaling subunit in such a way that the coordination event in the former induces a change in at least one physical property of the second. Sensors based on ion-induced changes in fluorescence are especially suitable as they are easy to use and give an instantaneous response with high sensitivity.[11,12] Because Fe^{3+} and Cr^{3+} are described as two of the most efficient fluorescence quenchers among the transition metal ions, a fluorescence signal transduction occurrence on chelation was expected.[13]

During the last few years, our research group has been interested in studying chemosensors containing biphenyl units in their structures where the recognition process is coupled to the signaling action.[14,15] In these chemosensors, changes in the colorimetric or fluorescence properties were based on the modification in the dihedral angle between both aromatic rings induced by the complexation event. On the other hand, introduction of different substituents on the biphenyl system gives rise to strong modifications in both, optical and electrochemical properties.[16,17]

Going a forward step we decided to study the influence that the increment of rigidity in the system has on the chemosensor behavior and for this reason now we report the behavior of two (2,7-disubstituted phenanthrene-9,10-dione)-based chemosensors (**1–2**). As binding site two oxime groups were attached at the 9 and 10 positions of the aromatic systems. It is clearly established that oxime groups acts as ligands for cation complexation by formation of five or six-membered chelate rings.[18,19] Thus, phenanthrene-9,10-dioximate and related compounds containing long alkyl

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chains at the 2,7 positions have been used in complexing some transition metal cations.[20,21] In addition, one recent publication describes a method based on the formation of metal complexes by α-benzyl dioxime supported on sodium dodecyl sulfate-coated alumina. In this procedure, metals, such as Cu, Ni, Pb, Co, and Fe can be analyzed in one run by carrying out the simultaneous separation and quantification of them.[22]

2. Results and discussion

2.1. Synthesis and X-ray structure

Ligands **1** and **2** were easily prepared as described in Scheme 1, starting from phenanthrene-9,10-dione, which under nitration conditions, gives 4,4′-dinitro derivative **3** in 61% yield as yellow crystals from MeOH. Reduction of dinitro groups to amino groups course under standard conditions with a 69% yield. For the synthesis of dioxime compounds **1** and **2**, it was necessary to optimize the reaction conditions, especially the solvent and base, because it is usual a dehydration process in the reaction progress and mono-dioxime can be isolated as secondary product. Finally, successful transformation into bis-oxime **1** was performed using an excess of hydroxylamine hydrochloride in a mixture of pyridine and ethanol (1:8) as co-solvents under reflux (2 days), with 64 and 66% yield, respectively.[23,24] The bis-dioxime, under these conditions, is obtained as a mixture of isomers being the thermodynamically more stable *E,E*-isomer highly predominant.
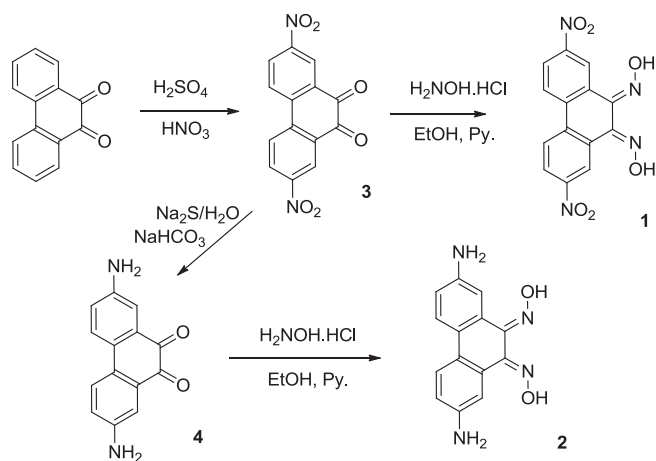
Scheme 1. Synthesis of ligands **1** and **2**.

As the vicinal dioxime showed to be a quite sensitive group, direct reduction of **1** to **2** was not tested. Thus, the synthesis of **2** was carried out from compound **4** under the same conditions proved useful in the preparation of ligand **1**. As previously, compound **2** was obtained as a mixture, being major the *E,E*-isomer. The parent compound **4** was obtained by reduction of **3** with sodium sulfide. Compound **4** was isolated as blue crystals that were suitable for X-ray diffraction. The crystal structure determination process revealed that the single molecule is essentially flat with standard bond distance and angle values. However, a water molecule appears as a crystallization molecule, that induces a crystal packing with hydrogen bonds between the 2,7-diamino-9,10-phenan-threnequinone molecules (**4**) among them and with the water molecules. As a result of these interactions, molecules with two different orientations (A and B) are alternately present in a zigzag network. Molecules A and B are interconnected through water molecules. The connection is due to the presence of hydrogen bonds (Fig. 1a) formed between the NH₂ group of a molecule in orientation A with the O=C group of a molecule in orientation B
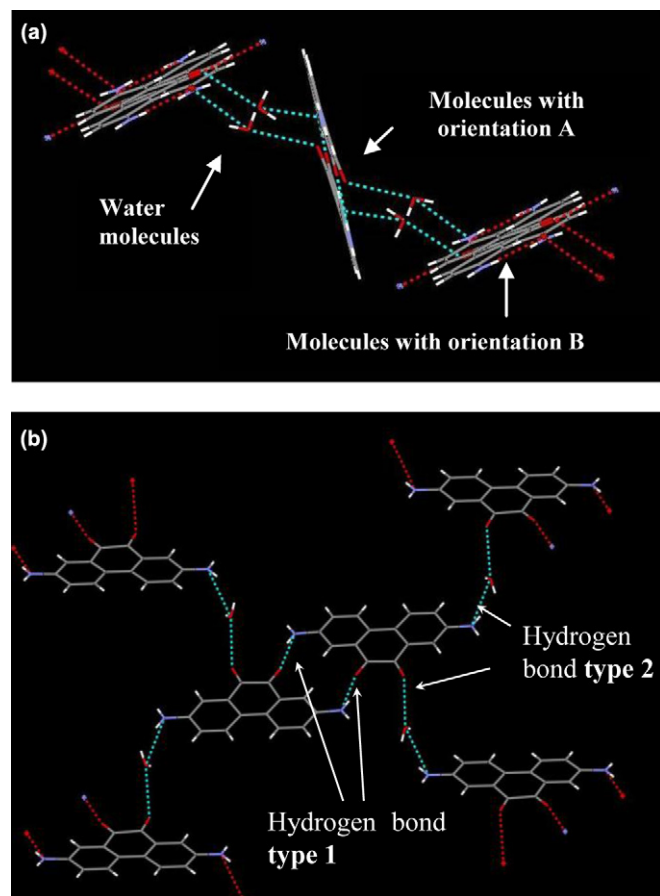
Fig. 1. (a, top) Zigzag conformation of **4** molecules with water molecules as a bridge. (b, bottom) Two types of H-bonds.

through a water molecule (N2–O3=3.018 Å and O2–O3=2.940 Å), where O3 is the oxygen atom of the water molecule (Fig. 1b). The different zigzag networks are also connected through hydrogen bond interactions. In this case, the interactions are established between the NH₂ group of one molecule and the O=C group of the other, being both molecules in the same plane (bond length of N1–O1=3.003 Å).

2.2. Complexation and sensing experiments

The UV–vis spectrum of the oxime **1** (1.0×10^{-5} mol dm^{-3}) in DMSO/MeOH (9:1) showed three bands at 264, 292 and 345 nm with ε=11,100, 11,040 and 10,920 M^{-1}cm^{-1}, respectively. On the other hand, compound **2** (1.0×10^{-5} mol dm^{-3}) in CH₃CN/MeOH (9:1) showed a band at 330 nm (ε=15,570 M^{-1}cm^{-1}) with a shoulder at 417 (ε=1460 M^{-1}cm^{-1}) nm. In addition, **2** exhibits fluorescence emission at λ_{em}=515 nm (λ_{exc}=417 nm).

In order to know the influence that the amino groups had in the fluorescent properties of **2**, a simple theoretical energy minimization of ligand **2** was carried out by using the HF-3-21G basis set. The obtained results shows that the lone pair on the amino nitrogen are placed in a deeper MO (HOMO-2, −9.66 eV) than oxyme's both lone pairs and π bonds (−7.70 and −9.66 eV). As a consequence the amino groups seem not to be involved in a PET process. This hypothesis was experimentally corroborate. Thus, a clear quenching of the fluorescence was observed when the fluorescence spectrum of compound **2** was registered under acid conditions (see Supplementary data).

The ability of ligands **1** and **2** in cation complexation was studied with Cr^{3+} and Fe^{3+}, as their nitrate salts. As can be seen in Fig. 2,
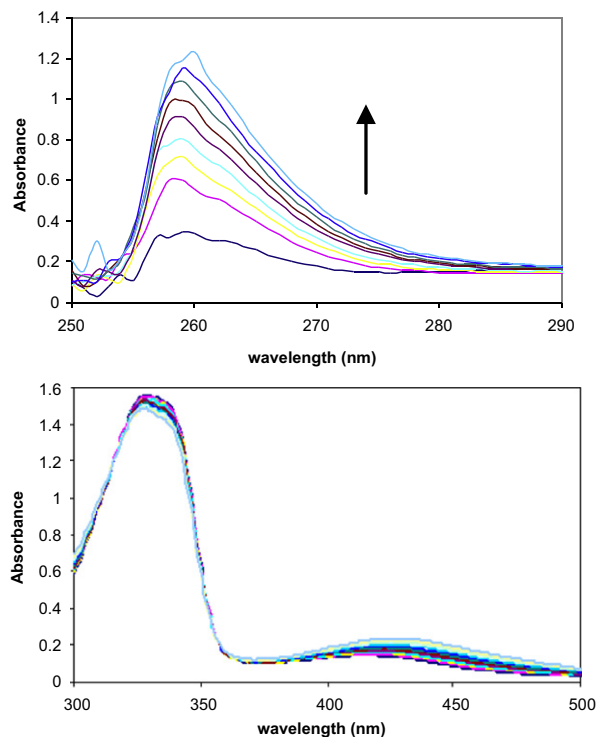
Fig. 2. (up) UV–vis titration spectra of **1** with Cr^{3+} in (1.0×10^{-5} mol dm^{-3}) DMSO/MeOH (9:1); (bottom) UV–vis titration spectra of **2** with Cr^{3+} in (1.0×10^{-5} mol dm^{-3}) DMSO/MeOH (9:1).

a strong hyperchromic effect was observed in the UV spectrum of **1** upon the gradual addition (0–30 equiv) of a solution of Cr^{3+} in DMSO/MeOH (9:1). A 1:1 stoichiometry was evaluated for the complex following the method of continuous variations (see Supplementary data) with a complexation constant of log $\beta = 3.7 \pm 0.1$ as determined by the Specfit programe.[25] By contrast ligand **2** gave rise to different results probably due to the presence of the amino groups. In this case a 1:2 stoichiometry is observed for the complex with a complexation constant of log $\beta = 6.2 \pm 0.2$.

Even though, the modifications in the UV spectrum observed with ligand **2** are smaller than those observed with ligand **1** it presents the additional advantage of its fluorescent properties that allow to use it as a fluorescent sensor. Thus, Fig. 3 shows the fluorescence emission ($\lambda_{exc} = 417$ nm) changes of **2** in DMSO/MeOH (9:1) solution (1.0×10^{-5} mol dm^{-3}) upon the addition of Cr^{3+}. The addition of the salt gives rise up to a 62% enhancement of the fluorescence. It is well established that some metal complexes with oximes can involve deprotonation of the C=N–OH group[26] and in ligand **2**, this proton could protonate the aniline moiety. However the enhancement of the fluorescence cannot be related to this possible effect because it has been established that protonation of ligand **2** induces the quenching of the fluorescence. On the other hand, the complex stoichiometry seems to play an important role in the emission properties of the complex. This fact was demonstrated by carrying out complementary complexation studies with Fe^{3+}. UV experiments with this cation showed a 1:1 stoichiometry with a complexation constant of log $\beta = 4.4 \pm 0.1$. In this case, no enhancement of the fluorescence was observed and only quenching due to the heavy atom effect was produced.

To have information about the different complexes, IR spectra of ligand **2** and its Cr^{3+} complex were registered. The free ligand shows bands at ca. 3470 and 3338 cm^{-1} that correspond to the aniline moiety and at 1602 (C=N) and 1017 cm^{-1} (N–O) that are due to the oxime group. In addition the characteristic absorption
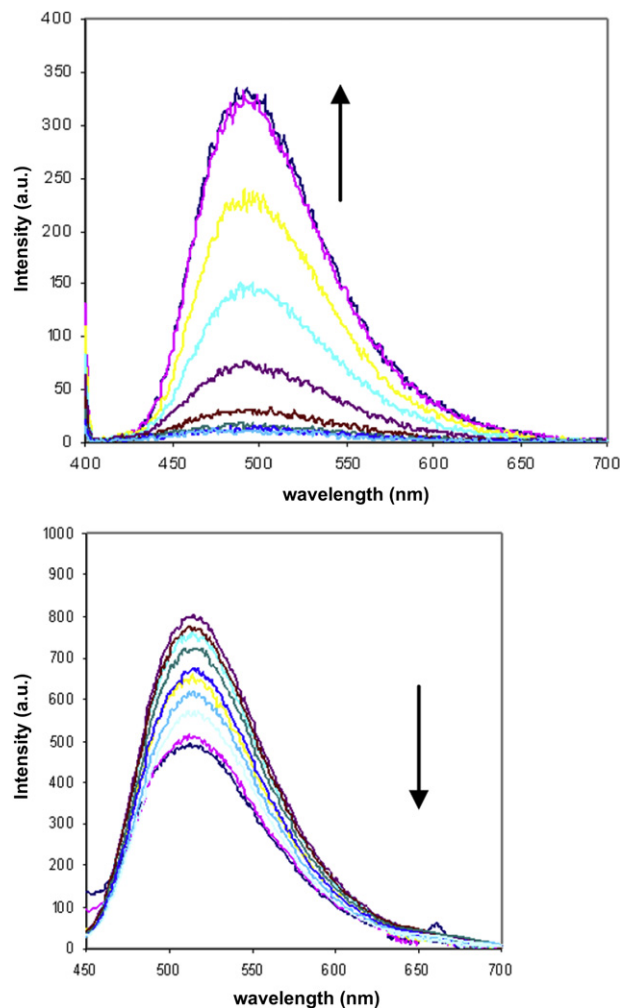
Fig. 3. Fluorescence titration spectra of ligand **2** (1.0×10^{-5} mol dm^{-3}) in DMSO/MeOH (9:1) ($\lambda_{exc} = 417$ nm) with (up) Cr^{3+} and (bottom) Fe^{3+}.

bands corresponding to the O–H of quinonodioximes appear at 2917 and 2848 cm^{-1}. In the complex, a broad band centered at 3219 cm^{-1} appears. This band could be assigned to an ammonium group generated by a proton transfer from the oxime group in the presence of the metal. This idea is supported by the absence of the O–H bands. On the other hand, the C=N band in the complex appears at higher values 1653 cm^{-1} whereas the N–O band is shifted to lower values (958 cm^{-1}). These data suggest that the cations are bound to the oxygen of the oximate moieties.[27]

In relation with de 1:1 complex formed between ligand **1** and Cr^{3+} it was observed in the IR spectrum that the strongest modification appears in the C=N band that is shifted toward lower values (from 1579 cm^{-1} in the free ligand to 1506 cm^{-1} in the complex). This fact suggest that the C=N groups are involved in the metal coordination.[28] On the other hand, the observed stoichiometry in the complex formed between **2** and Fe^{3+} suggests a complex with a similar geometry that those showed by **1** Cr^{3+}.

These data suggests that the observed increment in the fluorescence in the 1:2 complex could be related to the different type of complex formed in these case when it is compared with the 1:1 complex.

To gain information about the selectivity exhibit by ligand **2**, other cations of interest were studied but they gave no appreciable response (Fig. 4).
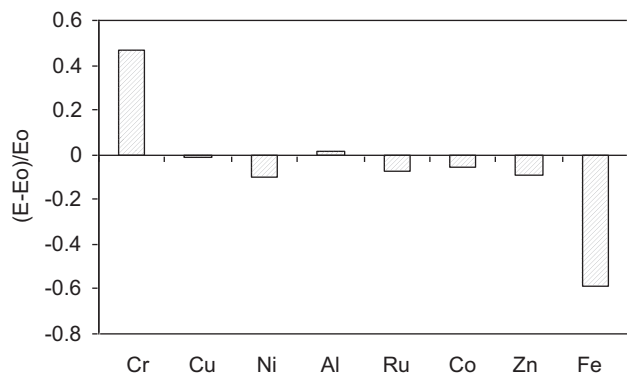
Fig. 4. Metal-ion selectivity of ligand **2**.

Thus, ligand **2** is a sensor able to distinguish between Cr^{3+} and Fe^{3+} due to the different stoichiometry of the complexes, giving rise to a different fluorescence response. From fluorescence titrations, detection limits of 140 μM for the sensing of Fe^{3+} and of 400 μM for Cr^{3+} can be attained.

3. Conclusions

Two new 2,7-disubstituted phenanthrene-based bis oximes have been prepared and their heavy metal cation complexation ability has been explored. Ligand **2** give rise to different complex stoichiometries depending on the cation. Thus, a 1:2 **2**·Cr^{3+} complex is formed, whereas a 1:1 stoichiometry is observed for **2**·Fe^{3+}. Complex stoichiometry has strong influence on the fluorescent properties of **2** and, for this reason; this ligand can be used in the discrimination of these two cations: Cr^{3+} induced an enhancement of the fluorescence whereas Fe^{3+} gives rise to a quenching.

4. Experimental section

4.1. General procedures and materials

All reagents commercially available were used without purification. ^{1}H and ^{13}C NMR spectra were recorded with the deuterated solvent as the lock and residual solvent as the internal reference. High-resolution mass spectra were recorded in the positive ion mode on a VG-AutoSpec. UV–vis spectra were recorded using a 1 cm path length quartz cuvette. All measurements were carried out at 293 K (thermostated). Fluorescence spectra were carried out in a Varian Cary Eclipse Fluorimeter.

4.2. Synthesis of 2,7-dinitro-9,10 phenanthrenequinone (3)[29,30]

In a two necked flask, 9,10-phenanthrenequinone (3.00 g, 15.625 mmol) was placed in a mixture of fuming nitric acid (40 mL) and 95–98% sulfuric acid (4 mL). After 45 min refluxing a yellow solid was obtained. This solid was recrystallized from acetic acid for obtained 2.825 g of yellow crystals identified as (**3**) (yield 61%).[29,30] ^{1}H NMR (300 MHz, solvent DMSO-d_6): δ=8.79 (2H, d, J=7.8 Hz, H-4 and H-5), 8.78 (2H, d, J=2.0 Hz, H-1 and H-8), 8.64 (2H, dd, J=7.8 and 2.0 Hz, H-3 and H-6).

4.3. Synthesis of 2,7-diamino-9,10 phenanthrenequinone (4)

To a stirred solution of sodium sulfide (0.70 g, 9.0 mmol) in the minimum amount of hot water, sodium carbonate (0.72 g) was slowly added. The resulting solution was added to 2,7-dinitro-9,10 phenanthrenequinone (**3**) (1.0 g, 3.36 mmol) in methanol (20 mL)

under reflux. The resulting mixture was stirred under reflux for 30 min. The dark blue crystals formed were filtered and recrystallized from hot methanol for obtained 0.544 g of (**4**) (yield 68%). IR (KBr) ν (cm^{-1})=3580, 3300, 1580, 1505, 1345, 1090, 738, 711. ^{1}H NMR (300 MHz, solvent DMSO-d_6): δ=8.05 (2H, br s, H-1 and H-8), 7.75 (2H, d, J=7.8 Hz, H-H-4 and H-5), 7.06 (2H, J=7.8 Hz, H-3 and H-6), 6.25 (4H, 2-NH$_2$).

4.4. Synthesis of 2,7-dinitro-9,10 phenanthrenequinone dioximes (1)

Hydroxylamine hydrochloride (8 g), pyridine (16 mL) and **3** (0.50 g, 1.68 mmol) in ethanol (95%, 100 mL) was stirred under reflux for 48 h; a colour change from yellow-orange to dark occurs. After two additionally hours at room temperature, pyridine hydrochloride as colorless needles was filtrated. Water (100 mL) addition at room temperature to the filtrate led to a green precipitated, which was purified from aqueous methanol to give dioxime **1** (0.352 g, 64% yield). ^{1}H NMR (500 MHz, solvent DMSO-d_6): δ=10.07 (2H, br s, −OH), 8.54 (2H, d, J=2.0 Hz, H-1 and H-8), 8.51 (2H, d, J=7.5 Hz, H-4 and H-5), 8.36 (2H, dd, J=7.5 and 2.0 Hz, H-3 and H-6). ^{13}C NMR (125 MHz, solvent DMSO-d_6): 148.4, 141.5, 135.7, 133.6, 128.1, 125.6, 119.8. HRMS (M$^+$−H): found 327.0367, calcd for $C_{14}H_7N_4O_6$ 327.0366.

4.5. Synthesis of 2,7-diamino-9,10 phenanthrenequinone dioximes (2)

Hydroxylamine hydrochloride (8 g), pyridine (16 mL) and **4** (0.50 g, 2.10 mmol) in ethanol (95%, 100 mL), was stirred under reflux for 48 h; a colour change from yellow-orange to dark occurs. After 2 h at room temperature, pyridine hydrochloride, as long colorless needles, was filtered off. Upon addition of water (100 mL) at room temperature to the filtrate, and one week left in refrigerator a few amount of a green precipitate was filtered off. Then, the solution was extracted with ethyl acetate, the combined organic phases washed with water and brine, dried with sodium sulfate and the solvent evaporated to give a solid residue that was purified from aqueous methanol to give dioxime **2** (0.371 g, 66% yield). IR (KBr) ν (cm^{-1})=3580, 3569, 1685, 1578, 1509, 1090, 739, 711. ^{1}H NMR (300 MHz, solvent CD$_3$CN): δ=8.60 (1H, Br s, −OH), 8.36 (1H, Br s, −OH), 7.37 (2H, d, J=7.0 Hz, H-4 and H-5), 7.22 (4H, m, H-1, H-3, H-6, H-8). ^{13}C NMR (125 MHz, solvent DMSO): 148.4, 141.5, 135.7, 133.6, 128.1, 125.6, 119.8.

4.6. Titration experiments

Binding constants of ligand **1** and **2** toward cations were evaluated by UV–vis and fluorescence titrations in acetonitrile. Typically, 10^{-5} M solutions of the receptors in DMSO/MeOH (9:1) (3 mL) were titrated by adding 0.5 equiv aliquots of the envisaged cations in CH$_3$CN and registering the UV–vis or fluorescence spectrum after each addition. The value of log K_c was calculated by fitting all spectrophotometric titration curves with the SPECFIT program.[25]

4.7. X-ray structure analysis of compound 4

Intensity measurements were made on an Oxford Xcalibur Nova diffractometer using a blue prismatic single crystal of dimensions 0.80×0.30×0.10 mm. Graphite-monochromated Cu-Kα radiation (λ=1.54184 Å) and ω-scan technique was used. Data collection was carried out at room temperature (293 K). Three reference reflections were measured every 2 h as an intensity and orientation check and no significant fluctuation was noticed during the collection of the data. Lorentz-polarization correction was made.

The crystal structure was solved by direct methods using the SHELX system[31] and refined by full-matrix least-squares techniques[31] on F^2. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were geometrically constructed with fixed displacements parameters. Molecular graphic of the structure (Fig. 5) was made with ORTEP[32] and graphic showing the H-bond packing (Fig. 1) were made with MERCURY.[33] Solution, refinement, geometrical calculations and graphics was performed with the WinGX package.[34]
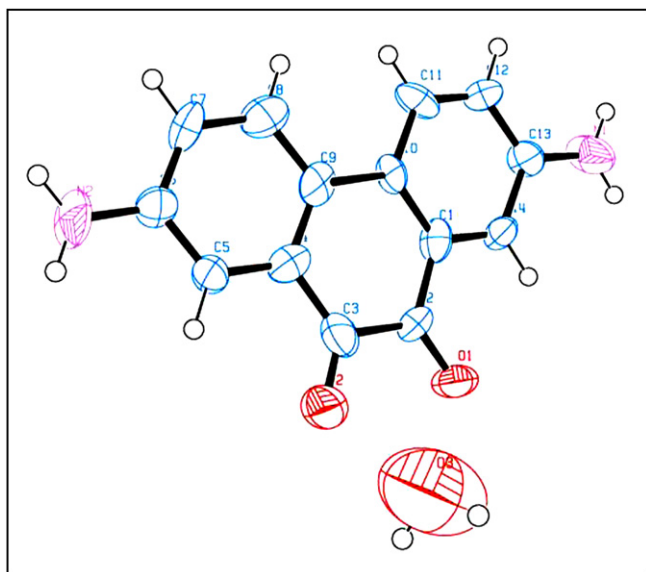

Fig. 5. Molecular structure with crystallographic numbering scheme for compound **4**. Atoms have been drawn with thermal ellipsoids set at a 50% probability level.

Information concerning crystallographic data collection is summarized in Table 1. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are shown in Table 2. Hydrogen bonds between the 2,7-diamino-9,10 phenanthrenequinone molecules, among them and with the water molecules are summarized in Table 3. Additional crystallographic data (bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and torsion angles, excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 853490. These data can be obtained via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk free of charge, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **4**. U(equiv) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(equiv)
O(3)	3342(8)	7046(6)	−630(20)	233(6)
C(10)	1446(5)	3759(4)	1551(13)	40(2)
C(4)	3253(6)	4235(4)	1611(12)	44(2)
C(1)	1123(5)	4201(4)	−656(12)	41(2)
C(9)	2502(6)	3756(4)	2631(13)	40(2)
C(14)	146(5)	4205(4)	−1715(13)	45(2)
C(5)	4272(5)	4231(4)	2660(14)	53(2)
C(11)	699(5)	3309(4)	2594(13)	49(2)
C(12)	−280(5)	3310(4)	1516(13)	47(2)
C(8)	2878(5)	3303(4)	4802(13)	49(2)
C(2)	1846(5)	4735(4)	−1814(13)	44(2)
C(3)	2947(6)	4760(5)	−547(14)	50(2)
N(2)	5639(5)	3722(4)	5680(13)	75(2)
N(1)	−1608(4)	3788(4)	−1717(12)	64(2)
O(1)	1599(4)	5144(3)	−3717(10)	60(2)
C(6)	4635(6)	3752(5)	4688(14)	54(2)
C(13)	−597(5)	3768(5)	−637(14)	47(2)
C(7)	3909(6)	3288(4)	5772(14)	57(2)
O(2)	3532(4)	5247(3)	−1447(11)	74(2)

Table 3
Summary of intermolecular H-bond distances (Å)

	Atom 1	Atom 2	'Symm. op. 1'	'Symm. op. 2'	Length	Length-VdW
1	O3	O2	x, y, z	x, y, z	2.940	−0.100
2	O3	N2	x, y, z	1−x, 1/2+y, 1/2−z	3.018	−0.052
3	N2	O3	x, y, z	1−x, −1/2+y, 1/2−z	3.018	−0.052
4	N1	O1	x, y, z	−x, 1−y, −1−z	3.003	−0.067
5	O1	N1	x, y, z	−x, 1−y, −1−z	3.003	−0.067
6	O2	O3	−x, 1−y, −1−z	−x, 1−y, −1−z	2.940	−0.100

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.03.089.

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Table 1
Crystal data and structure refinement for **4**

Empirical formula	$C_{14}H_{10}N_2O_2 + H_2O$
Formula weight	256.26
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a=13.324(3)$ Å, $\alpha=90°$
	$b=16.067(2)$ Å, $\beta=97.778(13)°$
	$c=5.3951(7)$ Å, $\gamma=90°$
Volume	1144.3(3) Å^3
Z	4
Density (calculated)	1.487 Mg/m^3
Absorption coefficient	0.882 mm^{-1}
F (000)	536
Crystal size	0.80×0.30×0.10 mm^3
θ range for data collection	3.35−64.13°
Index ranges	−15≤h≤15, −14≤k≤18, −5≤l≤5
Reflections collected	3854
Independent reflections	1720 [R(int)=0.0696]
Completeness to θ=64.13°	89.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9169 and 0.5387
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1720/0/172
Goodness-of-fit on F^2	0.692
Final R indices [I>2σ(I)]	R1=0.0678, wR2=0.1880
R indices (all data)	R1=0.1834, wR2=0.2326
Largest diff. peak and hole	0.286 and −0.352 e Å^{-3}

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