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Tautomerism of Representative Aromatic α-Hydroxy Carbaldehyde Anils as Studied by Spectroscopic Methods and AM1 Calculations. Synthesis of 10-Hydroxyphenanthrene-9-carbaldehyde.

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Abstract: The synthesis of 10-hydroxyphenanthrene-9-carbaldehyde and its anil are described. The structure of the latter compound has been thoroughly studied by ^{1}H and ^{13}C NMR, UV-visible absorption, fluorescence and IR spectroscopies. All the experimental results support the existence of this anil mainly in the keto-enamine tautomeric form. A comparison is presented with previously studied anils derived from salicylaldehyde and 2-hydroxynaphthalene-1-carbaldehyde. Semiempirical calculations (AM1) concerning the relative stability of tautomers as well as the optimized molecular geometries are in good agreement with the experimental findings

Introduction

Intramolecularly hydrogen bonded systems have been the concern of both chemists and biochemists, for years.[1] Renewed interest on the subject has recently arisen due to the discovery of proton transfer reactions along hydrogen bonds which not only occur in solution but also proceed in the solid state.[2] Furthermore, certain hydrogen bonded organic compounds are also capable of suffering proton transfer in the excited state (ESIPT),[3] a subject relevant to the photoprotection and photostability of polymers.[4] ESIPT phenomena are generally related to ground state proton transfer through the so-called Förster's cycles (Figure 1).[5]

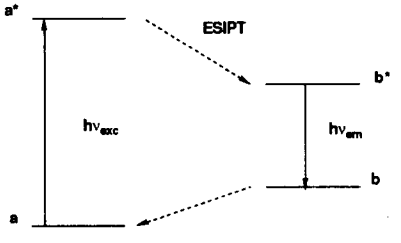


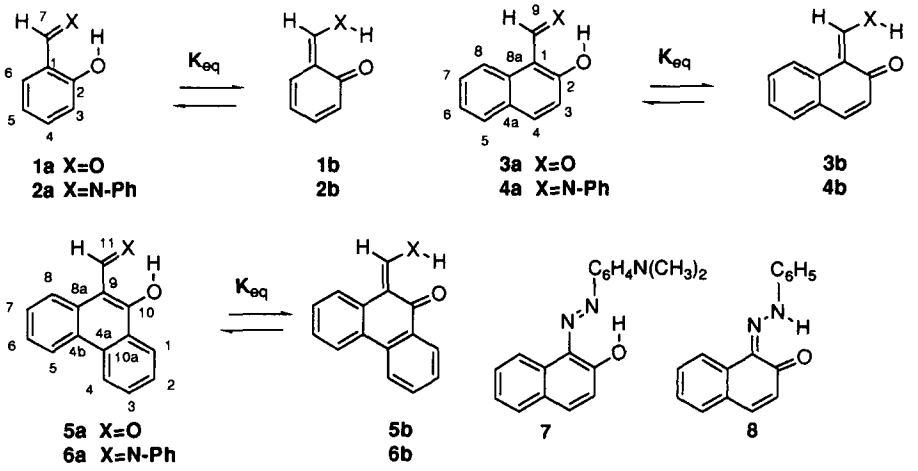
Figure 1: Förster's cycle showing the excited-state intramolecular proton transfer (ESIPT) process from tautomer **a*** to tautomer **b***, both in their respective excited states. The emission of fluorescence have a significant smaller ν_{em} as compared to ν_{exc}.

Anils of salicylaldehyde (i.e., derivatives of **1**, see Scheme 1) are known to undergo ESIPT phenomena both in solution and in crystals.[6] Some of these compounds also suffer combined tautomerization and cis/trans

isomerization upon irradiation in solids, yielding colored photoproducts (hence they are known as photochromic materials and are of interest for developing optical data storage devices).[7]

Salicylidene aniline **2** exists primarily as tautomer **a** in solution, as monitored by ^{1}H and ^{13}C NMR spectroscopy and UV-visible spectrophotometry.[8,9] This is also the expected result on the basis of semiempirical AM1 calculations.[9] Irradiation of **2** at its absorption maximum of 336 nm produces fluorescence at 530 nm, implying a frequency difference of ca. 11,000 cm^{-1} between excitation and emission.[6] This large difference can be explained if it is assumed that the fluorescent emission arises from an excited state of tautomer **b**, which upon deexcitation reverts thermally to the ground state of **a** (see figure 1). We have recently described an NMR study of derivatives of **4** (anils of 2-hydroxynaphthalene-1-carbaldehyde **3**) which were shown to

Scheme 1



exist as an equilibrium mixture of both **a** and **b** tautomers, slightly displaced towards the latter structure.[9] These compounds are also capable of suffering proton transfer in the excited state. Introduction of a second aromatic ring in going from **2** to **4** produces a significant shift of the tautomeric equilibrium towards **b** but still preserving important amounts of **a**. This should have interesting consequences as regards both absorption and emission spectra.

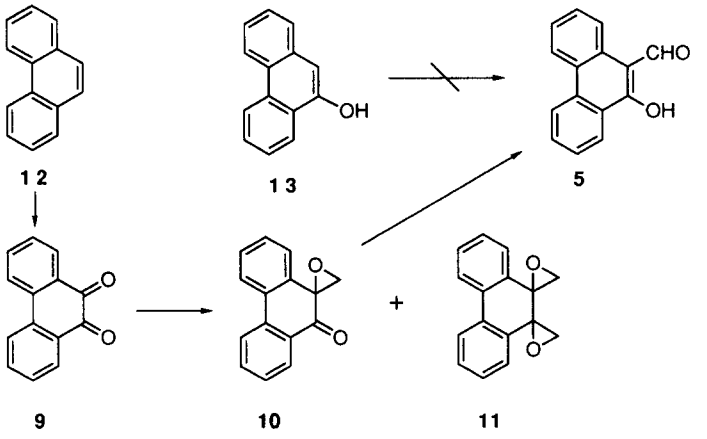
We now report the synthesis of 10-hydroxyphenanthrene-9-carbaldehyde **5** and its anil **6**. We have also studied the spectroscopic properties (both absorptive and emissive) of compounds **4** and **6** in relation to **2**. It is shown that **6** exists primarily as the quinonoid tautomer **b**, NMR and UV-visible spectra being satisfactorily explained on this basis. Furthermore, semiempirical MO calculations (AM1) are shown to be in agreement with the experimental results regarding both the relative stability of tautomers and their molecular geometries.

Results and Discussion

For the synthesis of 10-hydroxyphenanthrene-9-carbaldehyde (**5**), we explored several approaches as shown in Scheme 2. The main problem found through all the attempts was the over oxidation of the starting materials to

produce intractable tars and/or 9,10-phenanthroquinone. The hydroxy aldehyde was finally obtained from phenanthroquinone, using a rather indirect route. The introduction of the extra carbon, with the desired degree of oxidation, was accomplished through the use of a sulfur ylide in an aqueous system,[10] to produce an spiro

Scheme 2



[9-hydro-10-oxophenanthrene-9-oxirane]. The latter was then rearranged to the desired hydroxy aldehyde.[11] The structures of these compounds were firmly established on the basis of their one and two dimensional ^{1}H and ^{13}C NMR spectra.

When aldehydes **1**, **3** and **5** react with one mole of aniline, anils **2**, **4** and **6** are readily obtained. Compounds **2** and **4** have been previously studied by ^{13}C NMR spectroscopy in $CDCl_3$ solution.[9] Carbons which were found to be sensitive to the position of the **a** = **b** equilibrium are C1, C2, C1' (the aromatic carbon bonded to X) and the CH carbon bonded to X (C7 in **2** and C9 in **4**). The recorded values for anils **2** and **4** clearly showed that whereas the former compound mainly exists as tautomer **a**, the latter exhibits significant amounts of both **a** and **b** at equilibrium (Keq = 1.8 for **4** at room temperature).[9] This result was confirmed by variable temperature ^{13}C NMR experiments. The most sensitive carbon to monitor the equilibrium was found to be the C-O carbon C2 (160.9 ppm in **2** and 171.2 ppm in **4**). According to Table 1, the value observed for this carbon in **6** (C10, 181.0 ppm) strongly suggests that this anil exists as tautomer **b**. In fact, an approximate value of 180 ppm was previously used as the extreme C2 chemical shift in tautomers of type **b** in order to derive the values of Keq in several derivatives of **4**.[9] The other sensitive carbons C9, C1' and C11 are also found to be displaced towards tautomer **b**. In all cases, the values registered for **4** appear to lie midway between those corresponding to **2** and **6**, in agreement with the fact that the former compound shows a value of Keq which is not far from unity. Further NMR evidence on the existence of **6** as the quinonoid form **b** stems from its ^{1}H NMR spectrum. The signals ascribed to H11 (δ 8.90) and NH (δ 14.84) are doublets with J = 11.3 Hz. Upon selective irradiation at δ 14.84, the doublet at δ 8.90 collapses into a singlet, supporting the existence of **6** in the form of tautomer **b**.

Table 1: ^{13}C Chemical shifts in $CDCl_3$ solution for some of the studied compounds.

Cpd/C	12	13[a]	9	10	11	5	6
1	128.3	124.0	135.8	135.8	123.2	125.2	126.5
2	126.3	122.5	129.3	129.2	128.5	126.9	126.8
3	122.4	126.9	130.3	129.3	128.7	131.4	132.1
4	131.9	122.2	123.8	123.2	123.0	122.5	122.5
4a	131.9	132.6	135.7	137.1	133.9	134.8	135.8
4b	126.3	126.5	135.7	133.7	133.9	125.1	124.7
5	122.4	122.4	123.8	123.7	123.0	123.3	123.5
6	126.3	126.2	130.3	126.3	128.7	124.8	124.0
7	126.3	126.6	129.4	127.4	128.5	128.0	127.8
8	128.3	122.0	135.8	123.8	123.2	119.0	118.8
8a	130.1	131.3	130.8	131.9	133.4	129.8	132.1
9	126.6	106.1	180.1	56.9	55.9	108.0	105.4
10	126.6	149.45	180.1	192.8	55.9	164.4	181.0
10a	130.1	125.5	130.8	129.3	133.4	124.6	130.3
11				62.4	56.35	193.1	146.8
1'							139.0
2'; 6'							117.9
3'; 5'							129.7
4'							125.3

[a] The numbering of this compound was altered for comparison reasons.

IR spectra of **2**, **4** and **6** show bands in the region expected for C=O or C=N moieties for all three compounds. In agreement with the above discussion, compound **2** displays an intense band at 1615 cm^{-1} which can be ascribed to the C=N stretching vibration, whereas compound **6** shows a similarly intense band at 1625 cm^{-1}, corresponding to the C=O stretching. On the other hand, the anil **4** shows a broad absorption with maxima at 1622 and 1595 cm^{-1}, which can be attributed to the fact that on the IR time scale the proton transfer tautomerism is slow, and overlapped bands for tautomers **4a** and **4b** are detected.

Optical spectra provide further agreement with the latter findings. As previously reported, compound **2** absorbs strongly at 336 nm and shows a weak absorption band at 430 nm (Table 2 and Figure 2). These two bands have been ascribed to tautomers **2a** and **2b** respectively. Upon excitation, both of these bands produce fluorescence at 530 nm, although with different relative intensities (Table 2). The large Stokes shift observed upon irradiation of **a** can be ascribed to the ESIPT phenomenon suffered by the excited state of this species through a Förster cycle (Figure 1). In comparison, the corresponding results for anil **4** reflect the increased stability of tautomer **4b**. Both absorption bands display similar intensities, as well as the fluorescence emission bands (Table 2). One could therefore expect that **6** will exhibit spectra consistent with a structure which is frozen as tautomer **b**. Indeed, the quinonoid band recorded for **6** at 435 nm is significantly more intense than its enolic band at 344 nm (Table 2). Furthermore, the fluorescence emission is dominated by the normal Stokes shifted band arising from excitation of tautomer **6b**, although a weaker ESIPT fluorescence is still obtained if the band at 344 nm (corresponding to **6a**) is excited (Table 2).

AM1 calculations were performed on all compounds in order to shed light on the changes observed in the relative stability of tautomers. As seen in Table 3a, heats of formation for **1**, **3** and **5** agree with the NMR information in showing that tautomer **a** is preferred in all cases. On the other hand, as regards the Schiff bases **2**, **4** and **6**, AM1 results are also in agreement with the spectroscopic data (Table 3b). In the case of anil **2**, tautomer **a** is preferred over **b**, whereas the reverse is true for **6**. As previously discussed, compound **4** shows heats of formation of its two tautomers which can be readily interpreted in terms of an equilibrium containing

Figure 2: Absortion spectra of the studied anils in ethanol solutions. a) Compound **2** $1.2x10^{-4}$M. b) Compound **4**, $4.0x10^{-5}$M. c) Compound **6**, $1.6x10^{-5}$M.

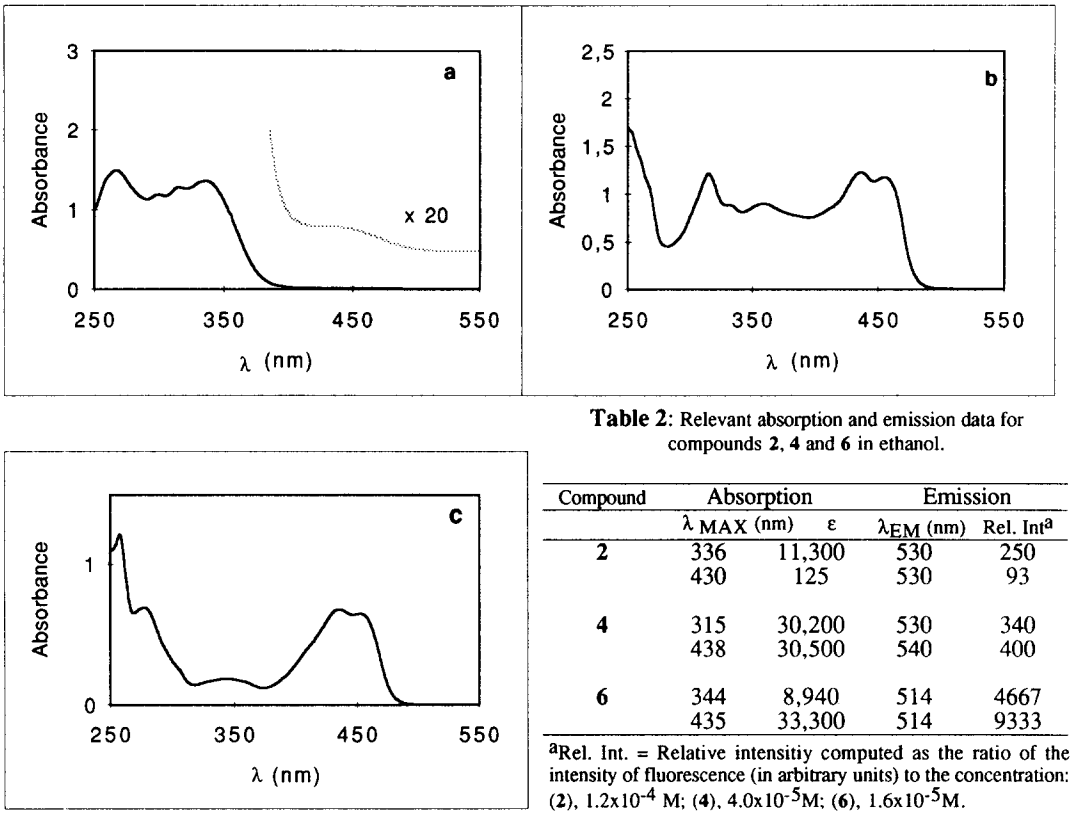


Table 2: Relevant absorption and emission data for compounds **2**, **4** and **6** in ethanol.

Compound	Absorption		Emission	
	λ_{MAX} (nm)	ε	λ_{EM} (nm)	Rel. Int[a]
2	336	11,300	530	250
	430	125	530	93
4	315	30,200	530	340
	438	30,500	540	400
6	344	8,940	514	4667
	435	33,300	514	9333

[a]Rel. Int. = Relative intensitiy computed as the ratio of the intensity of fluorescence (in arbitrary units) to the concentration: (**2**), $1.2x10^{-4}$ M; (**4**), $4.0x10^{-5}$M; (**6**), $1.6x10^{-5}$M.

appreciable amounts of both **a** and **b**. Furthermore, the calculated bond distances with the aromatic rings of the aldehyde portion shows several interesting trends (Table 3b).

Table 3a: Relevant AM1 parameters for the studied compounds; calculated $\Delta H°_f$ (kJ x mol^{-1}).

	Aldehydes			Anils		
Compound	**1**	**3**	**5**	**2**	**4**	**6**
Tautomer **a**	-232.2	-147.3	-71.5	122.6	208.4	284.1
Tautomer **b**	-174.9	-117.2	-59.8	140.6	201.7	258.6

In compound **2**, the aldehyde ring looses its aromaticity in going from **a** to **b**, as monitored by the bond length alternation which is apparent in Table 3b. However, both in **4** and **6** alternate bond distances are already present in **4a** and **6a**, as expected from the contributing Kekule structures to naphthalene and phenanthrene respectively. In the case of tautomers **b**, the unsubstituted rings display a significant constancy in bond lengths. This suggests that the increased stability of **b** in anils **4** and **6** is due to the "transfer" of aromaticity to the unsubstituted rings upon tautomerization. The latter transfer is not possible in compound **2**. Experimental evidence concerning this

transfer of aromaticity can be found in the reported X-ray structures of arylazonaphthols such as **7** and **8**.[12] The former compound exists mainly (ca. 80%) of a tautomer which is analogous to **a**, whereas the reverse is true for **8**.[12] In the case of **7**, the bond lengths of both rings of the naphthyl portion are clearly alternating between relatively longer and shorter bonds.[12] Furthermore, it is apparent that the differences in bond lengths for the unsubstituted ring are significantly smaller than those observed for both rings of compound **7**.[12] Indeed, in view of the reported standard deviation for bond lengths in **8**, C4a-C5, C6-C7, C7-C8 and C8-C8a are not significantly different.[12]

Table 3b: Relevant AM1 parameters for the studied compounds; Geometries of anils

Bond	**compd.2** Length/Å Taut. **a**	Taut. **b**	Bond	**compd.4** Length/Å Taut. **a**	Taut. **b**	Bond	**compd.6** Length/Å Taut. **a**	Taut. **b**
C1-C2	1.408	1.465	C8a-C1	1.434	1.454	C8a-C9	1.444	1.455
C2-C3	1.415	1.466	C1-C2	1.390	1.466	C9-C10	1.378	1.467
C3-C4	1.383	1.350	C2-C3	1.432	1.468	C10-C10a	1.450	1.475
C4-C5	1.401	1.437	C3-C4	1.365	1.344	C4a-C4b	1.446	1.457
C5-C6	1.385	1.355	C4-C4a	1.425	1.446			
C6-C1	1.410	1.442				C10a-C1	1.412	1.403
			C4a-C5	1.418	1.398	C1-C2	1.381	1.390
			C5-C6	1.374	1.389	C2-C3	1.404	1.395
			C6-C7	1.412	1.397	C3-C4	1.382	1.390
			C7-C8	1.375	1.388	C4-C4a	1.414	1.405
			C8-C8a	1.422	1.404			
						C5a-C5	1.413	1.405
			C8a-C4a	1.419	1.415	C5-C6	1.381	1.389
						C6-C7	1.403	1.395
						C7-C8	1.381	1.388
						C8-C8a	1.415	1.407
						C10a-C4a	1.416	1.415
						C8a-C4b	1.412	1.410

In conclusion, we have succeded in obtaining a series of three anils (compounds **2**, **4** and **6**) displaying properties of an almost pure imine-enol tautomer (**2**), an almost pure keto-enamine tautomer (**6**), and an equilibrium mixture in which both of these tautomeric structures are present in appreciable amounts (**4**). This is reflected in the spectroscopic data for these compounds in the following manner:

1) Solution ($CDCl_3$) ^1H NMR spectra of anils **2** and **4** show a broad singlet for the OH (or OH in equilibrium with NH) proton, whereas **6** exhibits a J=11 Hz doublet between the NH and C11-H.

2) Solution ($CDCl_3$) ^{13}C NMR chemical shifts recorded for the C-O carbon C2 shows a progressive downfield trend in going from **2** to **4** to **6**, reflecting the presence of increasing amounts of the keto tautomer.

3) UV-visible electronic absorption bands change their intensities according to the different amounts of enolic and keto tautomers. Whereas the band having a maximum at ca. 340 nm (and attributed to tautomer **a**) decreases in going from **2** to **4** to **6**, the one at ca. 430 nm (ascribed to tautomer **b**) increases.

4) Fluorescence measurements reveal both ESIPT and normal Stokes shifted bands in all three compounds which arise from excitation of tautomers **a** and **b** respectively. However, the relative intensities reflect the different populations of both tautomers.

Experimental Section

General procedures: Melting points were obtained on a Electrotermal 9100 apparatus and are uncorrected. Infrared spectra were recorded on a Bruker FT I-25 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 200.1 and 50.3 MHz on a Bruker Ac 200E NMR spectrometer, 2D experiments were run using standard Bruker software. UV-Visible spectra were recorded on a Beckman DV-640 spectrophotometer and fluorescence spectra were recorded on a JASCO FP 770 spectrofluorometer equipped with a 150w Xe lamp. AM1 Calculations were performed on a 80486 PC micro computer, using the AMPAC MO package version 2.10 with gradient optimization, in all cases using the PRECISE option. Mass spectroscopic analyses were obtained at UMYMFOR, Universidad de Buenos Aires, on homogeneous samples verified by t.l.c. on three solvent systems. All reactions were carried out under a dry, oxigen-free nitrogen atmosphere. Tlc analyses were performed on aluminum foil plates coated with 0.1 mm Merck silicagel 60 F_{254}. Column Chromatograpy was run on Merck silicagel 60H, under a low pressure of nitrogen, using increasing EtOAc- Hexane gradients as solvent. All solvents were dried and glass destilled before use.

9,10-Phenanthrenequinone (**9**): In a two-necked flask fitted with a magnetic stirrer and a thermometer, was placed a solution of chromium trioxide (673 mg, 0.84 mmole) in 80% AcOH (0.84 mL). The mixture was cooled to 0°C and a solution of phenanthrene (500 mg, 2.81 mmole) in glacial AcOH (8 mL) was gradually added, with constant stirring, over a period of 2-3 hs, in such a way as to keep the internal temperature about 10-15°C. The stirring was continued while the mixture was allowed to reach room temperature and then was set aside for two days. Later, the mixture was poured into 40 mL of water, the yellow precipitate was taken up in EtOAc (40 mL), washed with 10% $NaHCO_3$ solution and water, dried over anh. sodium sulphate and evaporated in vacuo. The product separates as yellow needles (530 mg, 90%), mp: 206-207°C, (Lit[13] 208.5-210°C).

Spiro [9-Hydro-10-oxo-phenanthrene-9-oxirane] (10): 9,10-Phenanthroquinone (**9**) (100 mg, 0.48 mmole) and tetrabuthyl ammonium iodide (TBAI: 1.25 mg, 3.37 mmole) are dissolved in Cl_2CH_2 (1,5 mL) and a layer of 50% aqueous sodium hydroxide (1 mL) was introduced underneath this solution. Trimethylsulfonium iodide (98.5 mg, 0.48 mmole) was the added and the mixture was warmed at 50°C for 30 min., while stirring vigorously, whereupon the undissolved sulfonium salt disappears. The reaction was followed by tlc, and stopped as soon as the diepoxide (dispiro [9,10-Dihydrophenanthrene-9,10-dioxirane] **11**), began to appear. The reaction mixture was next poured on brine, and extracted with ether and ethyl acetate. The organic phase was separated washed with brine, dried and evaporated affording after column chromatography, unreacted quinone (50%), mono epoxide (**10**)(42%) and di epoxide (**11**) (7%).

Compound (**10**): mp 164-167 °C from (EtOAc-Hexane; 2:1); IR (KBr), ν 3050, 1676, 1484, 1280, 752, 726 and 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.09 (d, J=7.6, H11), 3.43 (d, J=7.6, H12), 7.34 (dd, J=7.8, 1.6 Hz, H8), 7.38 (dd, J=7.8, 1.6 Hz, H7), 7.43 (ddd, J=7.8, 7.6, 1.6 Hz, H6), 7.46 (ddd, J=7.8, 7.4, 1.6 Hz, H2), 7.75 (ddd, J=7.4, 7.8, 1.4 Hz, H3), 8.05 (dd, J=7.3, 1.6 Hz, H5), 8.18 (dd, J=7.8, 1.6 Hz, H4), 8.16 (dd, J=7.8, 1.6 Hz, H1);^{13}C NMR see Table 1; MS, m/z 223(M+1, 12.7), 222(M^+, 100), 180(17.4), 165(41), 164(30.7), 163(43.3), 82(14.4), 81(14.3) and 69(13.7).EIHRMS (Found for M^+, 222.068437; $C_{15}H_{10}O_2$ requires M^+, 222.068080)

Dispiro [9,10-Dihydrophenanthrene-9,10-dioxirane] (**11**): mp 85.6-86.8°C from (EtOAc-Hexane 1:8); IR (KBr), ν 3066, 3034, 1484, 1446, 1282, 1204, 892, 756, and 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.72(d, J=6.6 Hz, 1H), 3.36 (d, J= 6.6 Hz, 1H), 7.32 (d, J= 7.6 Hz, H2 and H8), 7.30-7.44 (overlap. mult., H2, H3, H6 and H7), 7.84 (d, J= 7.6 Hz, H4 and H5); ^{13}C NMR see Table 1. MS m/z 236(M^+, 17.8) 235(M-1, 2.0), 218(21.0), 206(80.3), 189(18.4), 178(100), 176(33.9) 152(18.2) and 76(14.1).

10-hydroxyphenanthrene-9-carbaldehyde (**5**)**:** Boron trifluoride etherate (0.1 mL) was added to a solution of **10** (70 mg, 0.36 mmole) in anh. toluene (12 mL), and the mixture was stirred for 5 min at room temperature. The resulting dark solution was then poured into cold 10% aqueous sodium bicarbonate, extracted with ethyl ether (3x15 mL), dried (anh. sodium sulphate) and evaporated. The resulting brown crude residue was purified by column chromatography (petroleum ether) to give pure **5** (24 mg, 41%), as yellow crystals.

Compound (**5**): mp 127-128°C from EtOH; IR (KBr), ν 2950, 1630, 1610, 1464, 1342, 936, 764 and 718 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.54 (ddd, J= 7.9, 7.1, 1.7 Hz, H6), 7.58 (ddd, J= 7.9, 7.1, 1.7 Hz, H7), 7.66 (ddd, J= 7.1, 7.1, 1.7 Hz, H2), 7.83 (ddd, J= 7.9, 7.1, 1.7 Hz, H3), 8.34 (dd, J= 7.9, 1.7 Hz, H8), 8.57 (d, J= 7.9 Hz, H5), 8.58 (d, J= 7.9 Hz, H1 and H4), 10.67 (s, C<u>H</u>O), 10.67 (s, -O<u>H</u>); ^{13}C NMR see Table 1; MS

m/z 222(M^+, 100) 221(M-1, 21.7), 194(13.8), 166(18.3), 165(81.0), 163(21.3), 139(6.8) 111(7.3) and 81(10.0). (Found for $M^{+\cdot}$ 222.068184; $C_{15}H_{10}O_2$ requires M^+, 222.068080)

Anil of the 10-hydroxyphenanthrene-9-carbaldehyde (6): Hydroxy aldehyde **5** (24.0 mg, 0.11 mmole) in methanol (2 mL) and aniline (10 mL, 0.11 mmole), was heated for 15 min and the clear solution was allowed to cool, the anil separated from the solution as yellow needles (100%).

Anil (**6**): mp. 133-134°C from MeOH; IR (KBr), ν 3020, 2902, 1624, 1606, 1594, 1364, 1316, 854, 750 and 724 cm^{-1}; ^1H ($CDCl_3$) δ 7.19-7.25 (overlp. d, H2' and H6'), 7.32-7.50 (overl. mult, H7, H6, H3', H4' and H5'), 7.56 (ddd, J= 7.8, 8.0, 1.2 Hz, H2), 7.71 (ddd, J= 8.0, 7.1, 1.4 Hz, H3), 7.89 (dd, J= 7.8, 1.2 Hz, H8), 8.35 (dd, J= 8.0, 1.3 Hz, H5), 8.38 (dd, J= 7.2, 1.1 Hz, H4), 8.56 (ddd, 7.8, 8.0, 1.0 Hz, H2), 8.57 (dd, J= 7.8, 1.4 Hz, H1), 8.88 (d, J= 11.2 Hz, =CH(NH)), 14.84 (d, J=11.2 Hz, NH); ^{13}C NMR see Table 1. MS, m/z 298(M+1, 8.9) 297(M^+, 41.3) 296(M-1, 39.7), 165(10.9), 97(18.3), 165(15.1), 95(22.2), 81(52.9) 69(100) 55(30.6) and 41(23.7). (Found for $M^{+\cdot}$ 297.115494; $C_{21}H_{15}O_1N_1$ requires M^+, 297.115364).

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