Solution, solid state structure and fluorescence studies of 2,3-functionalized quinoxalines: evidence for a π-delocalized keto-enamine form with N–H···O intramolecular hydrogen bonds

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Three quinoxaline derivatives **3**, **4** and **5** were prepared by condensation of tetraones RC(=O)–CH_2–C(=O)–(=O)–CH_2–C(=O)R [**1**, R = Ph; **2**, R = *neo*-Pen] with *o*-phenylenediamine or (*R*,*R*)-1,2-diaminocyclohexane. ^{1}H, ^{13}C and ^{15}N NMR studies show that these derivatives are best described as their keto-enamine form with N–H···O intramolecular hydrogen bonds. This preferred tautomeric form is confirmed by X-ray structural studies of **3** and **5**. Compounds **3** and **4**, containing an extended delocalized π-system, exhibit fluorescence properties. In contrast, fluorescence is inhibited in **5**, when the central aromatic part is replaced by a cyclohexyl group.

Metallo-organic complexes containing conjugated nitrogen ligands represent an important class of nonlinear optical chromophores.[1] Efficient systems involving organometallic and coordination compounds with pyridine,[2] diimine,[3] Salen-type[4] or Schiff-base[5] ligands have recently been described. We have also demonstrated the large dipolar and non-dipolar optical non-linearities in metal complexes of functionalized bipyridyl ligands.[6] In connection with our research aimed at developing new metallo-organic NLO-phores, we became interested in the elaboration of highly conjugated bidentate heterocyclic ligands. The 2,3-bis(phenylacyl)quinoxaline, reported many years ago as a keto-imine form[7] (**A**, Scheme 1), was described a few years later as an enol-imine form (**B**);[8] this latter tautomeric form is of particular interest since it presents an extended conjugation pathway with a potentially bis(bidentate) N,O-chelating site. Furthermore, quinoxaline derivatives have also been used as electron-withdrawing groups in π-conjugated polymer chemistry,[9] and are known to be easily functionalized, giving rise to fluorescent materials.[10] Thus, this type of structure should present all the requirements needed for the design of NLO-active molecules. In order to get insight about the exact structure of **A**, which is of crucial importance in terms of electronic delocalization, we have carried out solution and solid-state structural studies, and we have examined the optical properties of the 2,3-bis(phenylacyl)quinoxaline. In addition, the modulation of the conjugation pathway has been studied by the modification of either the phenyl group of the phenylacyl moities or the central aromatic part of the quinoxaline. We now report that (i) the 2,3-bis(phenylacyl)quinoxalines contain two intramolecular N–H···O, not N···H–O, hydrogen bonds both in the solid state and in solution, (ii) they possess a rigid delocalized π-system and display fluorescence properties whatever the nature of the acyl group, (iii) fluorescence is inhibited, however, when the central aromatic part is replaced by a cyclohexyl group.

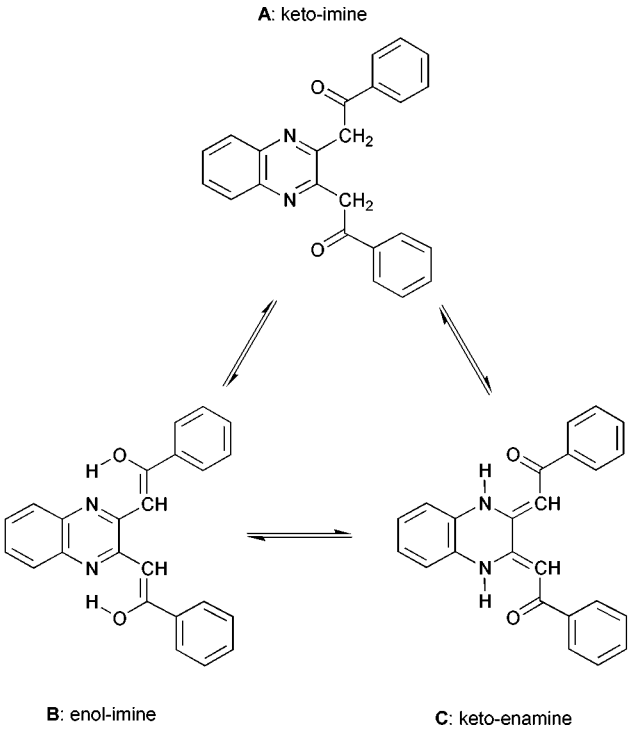
Results and discussion

Synthesis

Quinoxaline derivatives were prepared in a two-step reaction. Tetraketones **1**[11] and **2** (Scheme 2) were first prepared on a large preparative scale in 80 and 60% yields, respectively, by a Claisen condensation of a methyl ketone (acetophenone or *neo*-pentyl methyl ketone) with diethyl oxalate. These tetraketones **1**, **2** are present in solution as their bis-enol tautomeric forms as shown by the strongly deshielded hydroxy (14.5[11] and 15.0 ppm) and vinylic (6.45[11] and 6.30 ppm) protons. Classical condensation of **1** and **2** with cyclic diamines [*o*-phenylenediamine or (*R*,*R*)-1,2-diaminocyclohexane] in refluxing ethanol[12] yielded the corresponding quinoxaline-like derivatives **3**,[7b,8] **4** and **5** (Scheme 2). These compounds were characterized by means of elemental analysis, ^{1}H, ^{13}C and ^{15}N NMR studies and optical measurements and for **3** and **5** by X-ray diffraction analysis.

Solution and solid state structure of 3

The ^{1}H NMR data of **3** reveals the presence of a vinylic proton at 6.5 ppm, clearly excluding the keto-imine form (**A**),[8] and also that of an acidic proton, strongly deshielded at 15.0 ppm (Table 1). It is worth noting that the signals are not significantly affected upon lowering the temperature to 223 K. In order to determine the position of the acidic proton—on the nitrogen or oxygen atom—multiple bond C/H coupling experiments were performed. Selective ^{1}H irradiation in a non-decoupled ^{13}C NMR spectrum reveals that the acidic proton H(1) (Fig. 1) is weakly coupled to C(7) suggesting the predominance of the keto-enamine form (**C**). This result is

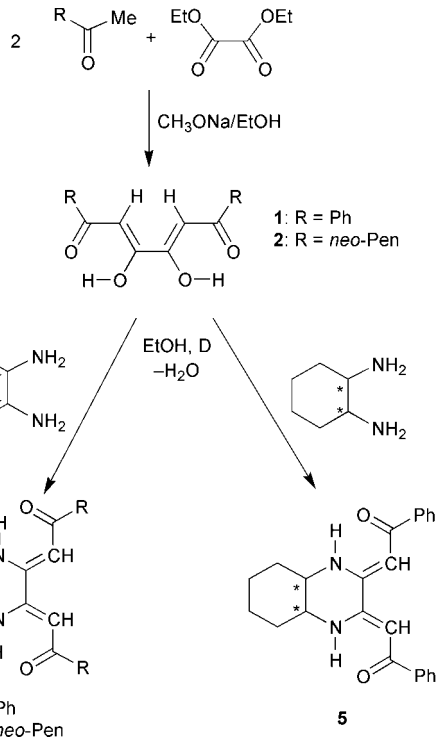


Scheme 1 Different tautomeric forms of quinoxaline derivatives.

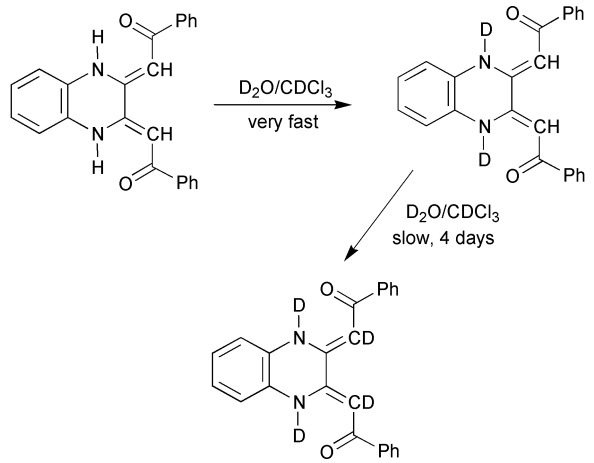
confirmed by the non-decoupled ^{15}N NMR spectrum (Table 1), which shows a doublet ($^{1}J_{H-N} = 87$ Hz) at -250.3 ppm. The position of the signal is characteristic of an sp^2 hybridized nitrogen and the large coupling constant is explained by an intramolecular N–H···O hydrogen bond,[13] rather than the reported N···H–O one.[8]

In order to get more information about the dynamic equilibria between the different tautomeric forms, an H/D exchange experiment with D_2O in purified $CDCl_3$ was performed (Scheme 3). Not surprisingly, the acidic H(1) hydrogen atoms were immediately replaced by deuterium atoms, whereas the H/D exchange of the vinylic protons H(9) was very slow. This experiment clearly indicates that the equilibrium between the tautomeric forms **C** and **A** is very slow (Scheme 1), confirming the predominance and the high stability of the keto-enamine form (**C**) in solution.[14]

The solid state structure (Fig. 1) is fully in agreement with the structure proposed in solution for **3**. Crystal data and selected bond lengths and angles are reported in Tables 2 and 3, respectively. The molecule is quasi-planar with a C_2 symmetry axis: the external phenyl rings are twisted by 25°. The nitrogen atom N(1) is trivalent with an N(1)–H(1) bond length of about 0.88 Å, confirming the position of the acidic proton. In addition, N(1), C(2), C(8a) and H(1) are perfectly coplanar, resulting from the sp^2 hybridization of the nitrogen atom due to the conjugation with the delocalized π-system. The C(10)–O(1) distance [1.250(2) Å] is in the range for those of carbonyl



Scheme 2 Synthesis of the quinoxaline-like derivatives **3**–**5**



Scheme 3 H/D exchange reaction.

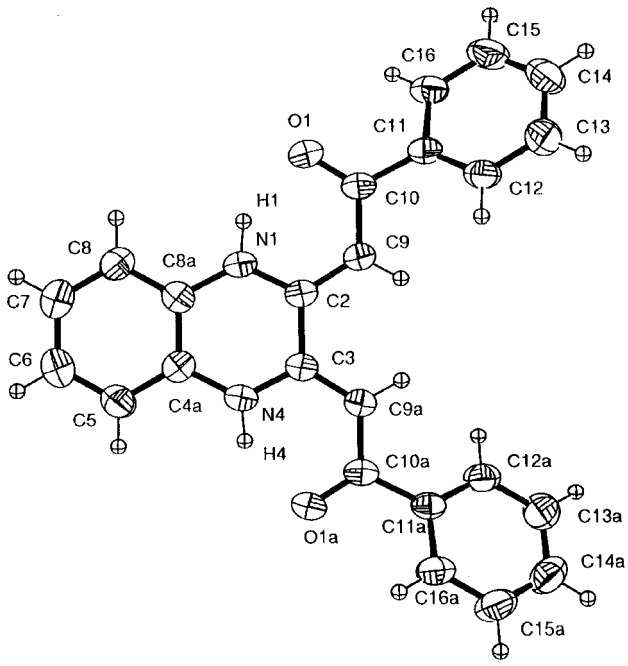


Fig. 1 ORTEP drawing of compound **3**.

Table 1 Selected NMR data

Compound	Acidic proton H(1) δ	Vinylic proton δ	^{15}N $\delta(^{1}J_{H-N}/Hz)$
3	15.0	6.5	−250.3 (87)
4	14.6	5.6	−252.3 (87)
5	11.3	6.3	−270.7 (94)

Table 2 Crystallographic data and refinement details for compounds **3** and **5**

	3	**5**
Formula	$C_{24}H_{18}N_2O_2$	$C_{24}H_{24}N_2O_2$
M	366.40	372.45
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	P_{21}
a/Å	23.255(3)	11.008(3)
b/Å	11.484(2)	18.305(3)
c/Å	6.936(9)	10.524(6)
α/°	90	90
β/°	90	109.91(3)
γ/°	90	90
U/Å^3	1852(2)	1994(1)
Z	4	4
λ(Mo-Kα)/Å	0.710 73	0.710 73
μ/cm^{-1}	0.85	0.79
T/K	293	293
Meas. reflections (R_{int})	1777(0.000)	4483(0.414)
Indep. reflections $[I > 2\sigma(I)]$	1005	1794
R_1 $[I > 2\sigma(I)]$, all data	0.0408, 0.1056	0.0511, 0.2081
wR_2 $[I > 2\sigma(I)]$, all data	0.0957, 0.1156	0.1040, 0.1464

compounds and the C(2)–C(9) bond [1.371(2) Å] is slightly elongated as compared to classical carbon–carbon double bonds (Table 3). The C(9)–C(10) and C(2)–C(3) distances [1.431(2) and 1.482(3) Å, respectively] lie in between single and double bond lengths, confirming the high electronic delocalization. The H(1)···O(1) distance of about 1.8 Å and the N(1), H(1), O(1) angle of *ca.* 154°, suggests an intra-molecular N(1)–H(1)···O(1) hydrogen bond in accordance with the strong NMR deshielding of H(1) [15.0 ppm].[15] Thus, in contrast to previously reported studies,[7b,8] it appears that compound **3** is best described both in the solid state and in solution by the keto-enamine form (**C**).

NMR studies of 4 and optical data of 3 and 4

Replacing the external phenyl ring by neopentyl moieties, as in compound **4**, does not significantly affect the structure of the molecule. ^{1}H and ^{15}N NMR data (Table 1) are similar to those of **3** and are in agreement with the keto-enamine structure (**C**). Representative absorption and emission spectra for **3** are reported in Fig. 2. All the optical data, measured in dichloromethane, are summarized in Table 4. The two compounds exhibit the same absorption profile: intense and structured bands between 400 and 500 nm.[16] The molecular absorption coefficients are quite large (*ca.* 25 000 dm^3 mol^{-1} cm^{-1}) and the bathochromic shift (**3** > **4**) is consistent with a better delocalization in the π-conjugated system of **3** as compared to **4**. Luminescence is observed for both compounds; modification of the substituents (neopentyl *vs.* phenyl) only induces a modulation of the quantum yield efficiency. Thus, the two quinoxaline derivatives **3** and **4**, better described by their keto-enamine tautomeric form (**C**), bear similar extended π-conjugated systems as they present very similar absorption and fluorescence properties.

Table 3 Selected bond lengths (Å) and angles (°) for compounds **3** and **5**

	3		**5**
N(1)–C(2)	1.349(2)	N(1)–C(2)	1.345(7)
		N(4)–C(3)	1.335(7)
N(1)–C(8a)	1.388(2)	N(1)–C(8a)	1.459(7)
		N(4)–C(4a)	1.477(7)
N(1)–H(1)	0.878(19)	N(1)–H(1)	0.80(6)
		N(4)–H(4)	0.90(7)
C(2)–C(3)	1.482(3)	C(2)–C(3)	1.482(8)
C(4a)–C(8a)	1.393(4)	C(4a)–C(8a)	1.471(7)
C(2)–C(9)	1.371(2)	C(2)–C(9)	1.381(7)
		C(3)–C(9a)	1.391(8)
C(9)–C(10)	1.431(2)	C(9)–C(10)	1.432(8)
		C(9a)–C(10a)	1.425(8)
C(10)–O(1)	1.250(2)	C(10)–O(1)	1.245(6)
		C(10a)–O(1a)	1.239(6)
C(8a)–N(1)–C(2)	125.20(15)	C(8a)–N(1)–C(2)	123.1(5)
		C(4a)–N(4)–C(3)	121.8(5)
C(8a)–N(1)–H(1)	122.50(12)	C(8a)–N(1)–H(1)	121(4)
		C(4a)–N(4)–H(4)	118(4)
C(2)–N(1)–H(1)	112.20(12)	C(2)–N(1)–H(1)	116(4)
		C(3)–N(4)–H(4)	120(4)
N(1)–C(2)–C(3)	166.77(10)	N(1)–C(2)–C(3)	115.9(5)
		N(4)–C(3)–C(2)	116.8(5)
N(1)–C(8a)–C(4a)	118.01(10)	N(1)–C(8a)–C(4a)	107.9(5)
		N(4)–C(4a)–C(8a)	107.4(5)

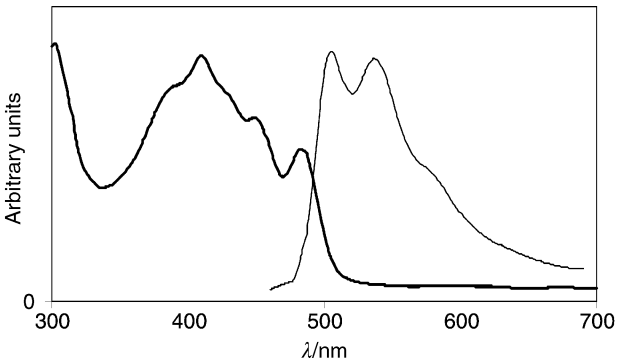


Fig. 2 UV-vis (bold line) and fluorescence spectra of compound **3**.

NMR studies, X-ray structure and optical data for 5

In order to get more insight into the structure–properties relationship, we envisaged replacing the central aromatic part of the quinoxaline group by a cyclohexyl fragment. It is worth noting that the resulting compound **5** (Scheme 2) is no longer a quinoxaline but a 4a,5,6,7,8,8a-hexahydroquinoxaline. In spite of this modification of the molecular structure, the keto-enamine form of type **C** is always predominant, as suggested by the ^{15}N NMR data (Table 1), but the ^{15}N chemical shift is displaced to lower field ($\Delta\delta$ = 20 *vs.* **3**) suggesting a lesser sp^2 character of the nitrogen atoms. This tendency is also confirmed by the shielding of the acidic proton ($\Delta\delta$ = 3.7 *vs.* **3**). The X-ray study shows that the solid state structure of **5** is composed of two independent molecules that are very similar. For clarity only one, presented in the ORTEP drawing (Fig. 3), will be discussed. The cyclohexyl ring adopts a "chair" configuration, inducing an important torsion in the vicinal heterocycle with a dihedral angle [N(1), C(8a), C(4a), N(4)] of *ca.* 53°. The nitrogen atoms N(1) and N(4) are trivalent with N(1)–H(1) and N(4)–H(4) bonds of 0.80(6) and 0.90(7) Å, respectively; they remain planar, indicating an sp^2 hybridization. Confirmation of the keto-enamine structure **C** is also given by the strong carbonyl character of the C(10)–O(1) and C(10a)–O(1a) bonds [1.245(6) and 1.239(6) Å, respectively] and by the double bonds C(2)–C(9) and C(3)–C(9a) [1.381(7) and 1.391(8) Å, respectively]. Good electronic delocalization is

Table 4 UV-vis and fluorescence data for compounds **3**–**5**

Compound	Absorption λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Emission λ_{em}/nm [ϕ(%)]
3	486 (26 000)	499, 523 [0.14]
	453 (31 000)	
4	465 (18 000)	488, 512 [0.06]
	435 (21 000)	
5	425 (28 000)	None

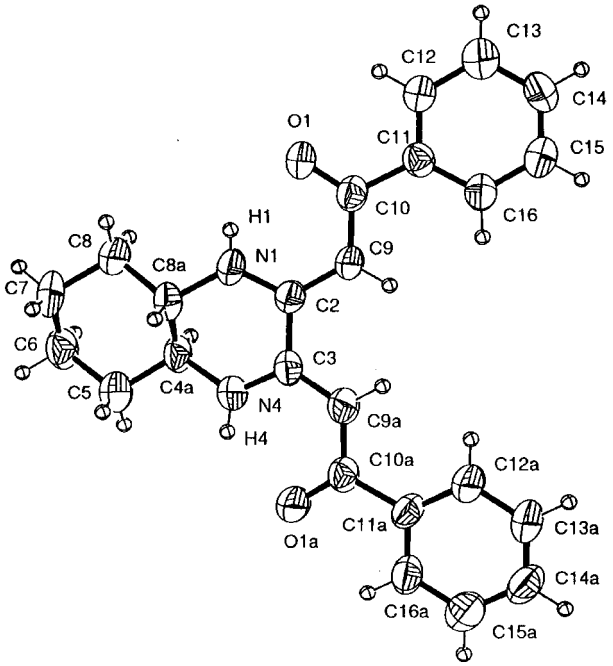


Fig. 3 ORTEP drawing of compound **5**.

also suggested by the short C(2)–C(3), C(9)–C(10) and C(9a)–C(10a) single bonds [1.482(8), 1.432(8) and 1.425(8) Å, respectively]. It is worth noting that the phenyl rings lie perfectly in the plane of the conjugated π-system, in contrast to those of **3**. The distances H(1)···O(1) and H(4)···O(1a) (1.8 Å) compare well with that of compound **3**, and confirm the intramolecular hydrogen bond. Replacing the central aromatic part of the 2,3-bis(phenylacyl)quinoxaline, **3**, by a cyclohexyl fragment does not significantly affect the structure of the molecule. Of course the heterocyclic ring is distorted, but the compound is already present as the keto-enamine tautomer (**C**) with a highly conjugated π-system. The absorption spectrum of **5** (Table 4) presents an hypsochromic shift compared to **3** ($\Delta\lambda = 60$ nm), consistent with the breaking of the quinoxaline conjugation pathway. The most striking difference between **3** and **5** lies in the fact that **5** shows no fluorescence. This result points out the role of the molecular structure: replacement of the fused aromatic ring by a cyclohexyl fragment inhibits the fluorescence properties.

Conclusion

We have shown that 2,3-substituted quinoxaline or hexahydroquinoxaline, bearing alkyl- or phenylacetyl moieties, exist as the keto-enamine form (**C**) in both solution and the solid state. The structure of these molecules has a dramatic impact on their fluorescence properties: the latter being restricted to the quinoxaline derivatives. The excellent rigid delocalization system observed in compound **3** is of major interest for the design of new metallo-organic NLO-phores. Further studies are currently in progress in order to increase the intra-molecular charge transfer by functionalization with electron-donating and -withdrawing groups, and to examine the coordination of these bis-bidentate N,O-ligands to transition metals.

Experimental

General procedures

NMR spectra (^{1}H, ^{13}C) were recorded on a Bruker DPX 200 (operating at 200.12 MHz for ^{1}H, 50.32 MHz for ^{13}C) or on a Bruker AM 300 (operating at 300.13 MHz for ^{1}H, at 75.47 MHz for ^{13}C and at 30.42 MHz for ^{15}N) spectrometer. NMR data are listed in ppm and are reported relative to tetramethylsilane (^{1}H, ^{13}C), residual solvent peaks being used as internal standard or relative to nitromethane (^{15}N) with external calibration. Complete assignments of the ^{13}C spectra required non-decoupled ^{13}C NMR spectra with selective ^{1}H decoupling. Non-decoupled ^{15}N NMR spectra were measured in 15 mm diameter NMR tubes. UV-vis spectra were recorded on a Kontron Uvikon 941 spectrophotometer in dichloromethane solution. Infra-red spectra were recorded in KBr pellets using a Brucker IFS28 FTIR spectrometer. Elemental analysis were performed by the Service Central d'Analyse du CNRS (Solaize, France).

Fluorescence

Fluorescence experiments were performed in dilute dichloromethane solution (*ca.* 10^{-5} mol l^{-1}) using a PTI spectrometer. Fluorescence quantum yields were measured on non-degassed samples at room temperature. A solution of quinine sulfate in H_2SO_4 was used as the standard for the quantum yield measurement ($\phi = 0.546$ for $\lambda_{ex} = 365$ nm). Refraction index correction has been performed.[17]

Crystallography

The samples were studied on an automatic CAD4 Nonius diffractometer with graphite monochromated Mo-Kα radiation.[18] The cell parameters were obtained by fitting a set of 25 high-theta reflections. After Lorentz and polarization corrections,[19] the structure was solved with SIR-97,[20] which reveals the non-hydrogen atoms of the structure. After anisotropic refinement, all the hydrogen atoms are found with a Fourier difference map. The entire structure was refined with SHELXL97[21] by the full-matrix least-square techniques (using *F* magnitude; *x*, *y*, *z*, U_{ij} for C, N and O atoms, *x*, *y*, *z* in riding mode for H atoms). ORTEP views were realized with PLATON98.[22] All the calculations were performed on a Silicon Graphics Indy computer. Crystal data and refinement details for compounds **3** and **5** are presented in Table 2.

CCDC reference number 440/247. See http://www.rsc.org/suppdata/nj/b0/b009667i/ for crystallographic files in .cif format.

Syntheses

1,6-Bis(neopentyl)hexan-1,3,4,6-tetraone (2). A suspension of methylate NaOMe (27 g, 0.5 mol) was stirred in dry diethyl ether (300 ml) at 0 °C. A mixture of 4,4-dimethyl-2-pentanone (57 g, 0.5 mol) and diethyl oxalate (36.5 g, 0.25 mol) was added, drop by drop, over 25 min. The mixture was stirred for 12 h until TLC indicated that all the 4,4-dimethyl-2-pentanone had been consumed. Compound **2** was precipitated and collected by simple filtration, dissolved in aqueous solution and neutralized with glacial acetic acid to yield 42.3 g (60%) as a white–yellow precipitate. Mp = 96–98 °C. ^{1}H NMR ($CDCl_3$): δ 15.0 (br s, $w_{1/2} = 70$ Hz, 2H, OH), 6.30 (s, 2H, =CH), 2.30 (s, 4H, CH_2), 1.0 (s, 18H, CH_3). ^{13}C NMR ($CDCl_3$): δ 201.5 (C=O), 172.9 (=C–OH), 100.6 (C–H), 53.9 (CH_2–^{t}Bu), 32.2 (CMe_3), 29.9 (CH_3). IR (KBr/cm^{-1}) 1604 ($\nu_{C=O}$). LRMS (EI): *m*/*z* 282 ($C_{16}H_{26}O_4$, M^+, 100%).

3. *o*-Phenylenediamine (108 mg, 1 mmol) and tetraketone (**1**; 290 mg, 1 mmol) were stirred in refluxing ethanol (50 ml) for 30 min. After cooling the mixture to room temperature, the desired compound crystallized as analytically pure orange crystals from dichloromethane (293 mg, 80%). Mp = 218–220 °C. ^{1}H NMR ($CDCl_3$): δ 15.0 (br s, $w_{1/2} = 8.2$ Hz, 2H, H_1), 8.0–7.8 (m, 4H, *m*-H), 7.6–7.4 (m, 6H, *o*-H, *p*-H), 7.10 (m, 4H, H_{5-7}), 6.5 (s, 2H, CH-CO). ^{13}C NMR ($CDCl_3$): δ 188.9 (C=O), 146.4 (C_2, C_3), 139.3 (*i*-C), 131.7 (*p*-C), 128.6 (*m*-C), 127.2 (*o*-C), 126.3 (C_{4a}, C_{8a}), 125.1 (C_6, C_7), 116.9 (C_5, C_8), 87.5 (CH–CO). ^{15}N NMR ($CDCl_3$): δ −250.3 (d, $^1J_{N-H} = 87$ Hz). IR (KBr cm^{-1}): 1591 (s, $\nu_{C=O}$). UV [CH_2Cl_2, λ/nm

(ε/dm^3 mol^{-1} cm^{-1})]: 292 (21 000), 313 (21 000), 427 (31 000), 453 (31 000), 486 (26 000). Anal calc. (found) for $C_{24}H_{18}N_2O_2$: C 78.67 (77.71), H 4.95 (4.80), N 7.65 (7.51%).

4. *o*-Phenylenediamine (100 mg, 1 mmol) and (280 mg, 1 mmol) of tetraketone **2** were stirred in refluxing ethanol (50 ml) for 30 min. After cooling, the yellow precipitate was filtered off and recrystallized from dichloromethane (210 mg, 60%). Mp = 220–222 °C. ^{1}H NMR ($CDCl_3$): δ 14.6 (br s, 2H, H_1), 7.0 (s, 4H, H_{5-7}), 5.6 (s, 2H, CH–CO), 2.3 (s, 4H, CH_2–^{t}Bu), 1.0 (s, 18H, Me). ^{13}C NMR ($CDCl_3$): δ 198.8 (C=O), 144.5 (C_2, C_3), 126.1 (C_{4a}, C_{8a}), 124.5 (C_6, C_7), 116.5 (C_5, C_8), 92.0 (CH–CO), 56.1 (CH_2–^{t}Bu), 31.9 [CH_2–C(CH_3)], 30.1 [CH_2–C(CH_3)]. ^{15}N NMR ($CDCl_3$): δ −254.3 (d, $^1J_{N-H}$ = 87 Hz). IR (KBr cm^{-1}): 1595 (s, $\nu_{C=O}$). UV [CH_2Cl_2, λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 389 (19 000), 409 (22 000), 435 (21 000), 465 (18 000). Anal. calc. (found) for $C_{22}H_{30}N_2O_2 \cdot H_2O$: C 71.13 (71.87), H 8.41 (8.37), N 7.54 (7.63%).

5. (*R*,*R*)-1,2-diaminocyclohexane (114 mg, 1 mmol) and the tetraketone **1** (280 mg, 1 mmol) were stirred in refluxing ethanol (50 ml) for 30 min. After cooling to room temperature, the yellow precipitate was filtered and recrystallized in dichloromethane (260 mg, 70%). Mp = 254–256 °C. ^{1}H NMR ($CDCl_3$): δ 11.30 (br s, 2H, H_1), 8.0–7.8 (m, 4H, *m*-H), 7.6–7.4 (m, 6H, *o*-H, *p*-H), 6.3 (s, 2H, CH–CO), 3.20 (m, 2H, $H_{4a, 8a}$), 1.8 (m, 4H, $H_{5, 8}$), 1.2 (m, 4H, $H_{6, 7}$). ^{13}C NMR ($CDCl_3$): δ 190.2 (C=O), 153.2 (C_2, C_3), 140.0 (*i*-C), 131.4 (*p*-C), 128.5 (*m*-C), 127.1 (*o*-C), 89.0 (CH–CO), 54.7 (C_{4a}, C_{8a}), 29.7 (C_5, C_8), 24.0 (C_6, C_7). ^{15}N NMR ($CDCl_3$): δ −270.7 (d, $^1J_{N-H}$ = 94 Hz). IR (KBr/cm^{-1}): 1600 (s, $\nu_{C=O}$). UV [CH_2Cl_2, λ/nm, (ε/dm^3 mol^{-1} cm^{-1})]: 425 (28 000), 370 (20 000). Anal. calc. (found) for $C_{24}H_{24}N_2O_2 \cdot H_2O$: C 73.82 (73.07), H 6.65 (6.08), N 7.17 (6.54%).

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References and notes

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