New class of highly stable nonaromatic tautomers†

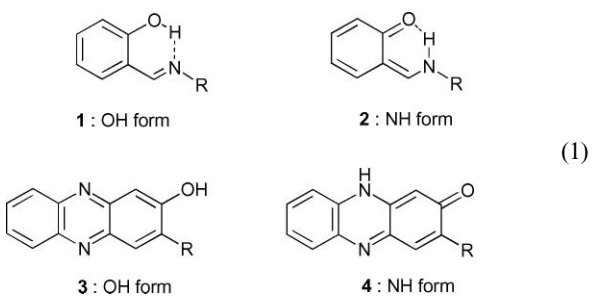
Claire Seillan, Philippe Marsal and Olivier Siri*

Received 23rd February 2010, Accepted 28th May 2010
First published as an Advance Article on the web 2nd July 2010
DOI: 10.1039/c003450a

A new and efficient one-pot synthesis of highly stable bridged-bisphenazine-type molecules with loss of their aromaticity in the ground state in favor of a quinoid-type structure is described (either in solution or in solid-state).

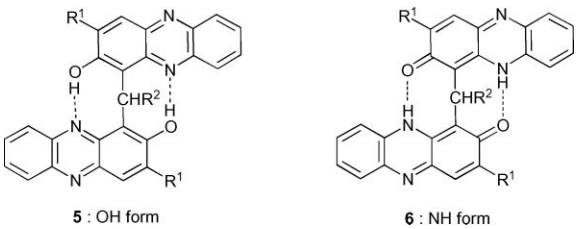
Introduction

Proton transfer is one of the most common and fundamental processes in chemistry and biology.[1] When proton transfer induces redistribution of the π-electrons in the molecule, the colour may change.[2] Such a phenomenon—closely related to the concept of aromaticity and nonaromaticity—[3] is of particular interest because it can be regarded as the origin of photo- and thermochromism.[4] N–H···O/N···H–O competition is among the most studied H-transfer system.[5] Extensive theoretical[5] and experimental[6–8] studies devoted to proton tautomerism from the OH to the NH forms in phenols such as salicylaldimines have revealed that the OH form (**1**) is much more stable than the NH form (**2**) owing to the aromatic character of the former. The nonaromatic tautomers **2** could be isolated pure very seldom in specific cases,[7–9] so that the access to a new class of highly stable NH tautomers is still a challenge of fundamental interest that would open new perspectives in chemistry.[4,5] Heterocyclic phenols of type **3** (R = H) have been much less investigated[10] because of the poor stability of the NH form (**4**) which could be only detected in solution upon irradiation (the proton transfer is facilitated in the excited-state) or in coordinating solvents.[10] Such a difference of stability between **2** and **4** can be explained by the presence of an intramolecular hydrogen bonding interaction in **2** which stabilizes the NH form. Importantly, the formation of **2** is much more favored than **4** due to two different mechanisms of H-transfer which proceed intra- (the more favorable) or intermolecularly for **1** and **3**, respectively.[10a,11]



(1)

In 1961, Cairns-Smith reported the synthesis of the dimeric structure of **3** (molecule **5**, $R^1 = R^2 = H$) and suggested that the presence of the sp^3 carbon bridge in **5** should act as a key structural element for intramolecular H-transfers due to the optimal distances between the H-donor and H-acceptor sites.[12] However, although proton tautomerization was suggested (only based on color changes), no observation of the pure NH form **6** could be reported either in solution or in solid state.[12]



(2)

The very few bridged-bisphenazines of type **5** described in the literature were isolated from natural products[13] because their synthetic access has remained limited.[12] An alternative route that would give new dimeric structures of type **6** would be very attractive in the field of H-transfer but also in other areas of science ranging from biology[13,14] and material science[4,15] to supramolecular[16] and coordination chemistry,[17] by analogy with related dimeric structures, H-donors/acceptors and N,O donors. Our design molecular approach is based on the introduction of secondary amine groups at position 3 (R^1 = R-NH) as H-donor sites due to the presence of two additional intramolecular H-bonding interactions that should lock the NH tautomers **6** at room temperature.

Herein, we describe a versatile and facile synthesis of new functionalized bridged-bisphenazine-type dimeric structures **6** which allows the first successful observations of the NH tautomers of type **4** that could be isolated at room temperature either in solution or in solid-state. Experiments and DFT theoretical calculations clearly demonstrate that the presence of a H-donor substituent is position 3 (R^1 = secondary amines) is crucial to render the molecule in an NH form rather than an OH form.

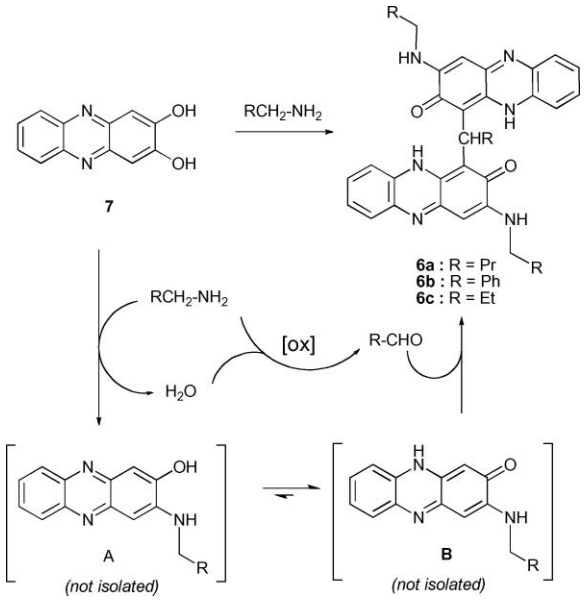
Results and discussion

We showed recently that hydroxyl groups of phenazine-2,3-diol **7** can be replaced by amine functions upon condensation with phenylenediamine derivatives.[18] We now found that the use of primary alkylamines RCH_2-NH_2 (R = Pr, Ph, Et) did not afford the expected 2,3-dialkylaminophenazines but led instead to the

Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), UPR 3118 CNRS Aix-Marseille Université, Campus de Luminy, case 913 F-13288, Marseille cedex 09, France. E-mail: siri@univmed.fr; Fax: +33-491-829-580; Tel: +33-617-248-134

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR of molecule **6a** . CCDC reference numbers 701450 and 701451 for **6a** and **8**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c003450a

formation of unexpected dimeric structures **6a–c** in 52, 44 and 10% yields, respectively (Scheme 1). The poor yield obtained with n-propylamine is due to the low boiling point of this amine.



Scheme 1 One-pot synthesis of **6a–c**.

Single crystals of **6a** could be isolated from a solution of chloroform–n-hexane so that its structural determination was envisaged at room temperature by X-ray diffraction study (Fig. 1). In spite of a poor resolution of the structure due to an important disorder of the alkyl chains, the data of the unsaturated phenazine subunits could be discussed in details (the quality of this part of **6a** remains accessible for discussion).

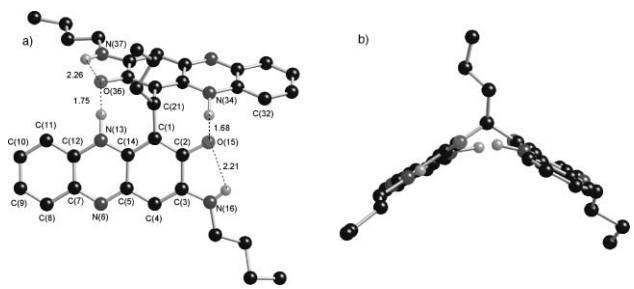


Fig. 1 X-Ray crystallographic structure of **6a**. a) top view and b) side view.‡ C–H hydrogen atoms and the disorder of the alkyl chains are omitted for clarity.

The two phenazine subunits are bridged by the sp^3 carbon and adopt a head-to-tail and concave geometry. Examination of the bond lengths within the N(13)–C(14)–C(1)–C(2)–O(15) and N(6)–C(5)–C(4)–C(3)–N(16) moieties of **6a** clearly shows an alternating succession of single and double bonds, whereas the C(14)–C(5) and C(3)–C(2) bond distances reveal a low degree of conjugation (1.455(7) and 1.491(7) Å, respectively). The N–H hydrogen atoms could be located experimentally and examination of the four intramolecular H-bonds shows that the N(13)–H···O(36) (1.75 Å) and N(34)–H···O(15) (1.68 Å) hydrogen bonding distances are shorter than those inside each phenazine subunit [N(16)–H···O(15) = 2.21 Å and N(37)–H···O(36) = 2.26 Å] (Fig. 1).

Table 1 Selected bond lengths (Å) for **6a** and **8** and calculated for the model of **6a** ($\mathbf{6}_{NHMe}$)

	6a	$\mathbf{6}_{NHMe}$	**8**
N(13)–C(14)	1.351(6)	1.359	1.343(3)
C(14)–C(1)	1.404(6)	1.399	1.407(3)
C(1)–C(2)	1.409(6)	1.425	1.354(3)
C(2)–O(15)	1.273(5)	1.273	1.358(3)
C(7)–N(6)	1.363(6)	1.363	1.354(3)
N(6)–C(5)	1.325(6)	1.352	1.335(3)
C(5)–C(4)	1.410(7)	1.423	1.423(4)
C(4)–C(3)	1.361(6)	1.372	1.350(4)
C(3)–N(16)	1.350(7)	1.354	—
C(12)–C(7)	1.385(7)	1.422	1.424(4)
C(14)–C(5)	1.455(7)	1.475	1.437(3)
C(3)–C(2)	1.491(7)	1.491	1.425(4)

The NH-type structure of **6a** was also confirmed by comparison with the molecular structure of the aromatic phenazine-2-ol **8** (Fig. 2), which could be prepared in different ways.[19] Single crystals suitable for X-ray analysis could be obtained by slow evaporation in acetone. Selected bond lengths for **6a** and **8** are listed in Table 1.

Fig. 2 View of structure of **8**. ‡C–H hydrogen atoms are omitted for clarity.

The structure of **8**, which is regarded as the pure OH form, shows indeed an equivalence of the C=N bond lengths, whereas two well differentiated carbon-nitrogen bond distances corresponding to C=N and C–N bonds are observed for **6a** (Table 1). As expected, the C(2)–O(15) bond lengths of 1.358(3) Å for **8** and 1.273(5) Å for **6a** correspond to single and double bond distances, respectively.

The UV-vis spectrum of **6a** in solution ($CHCl_3$) shows two absorption bands at 275 (log ε = 4.95) and 442 nm (log ε = 4.71) in agreement with a red color solution (NH form).[10] Its ^{1}H NMR spectrum in $CDCl_3$ shows two downfield NH signals (I = 1H) (*i.e.* N(13)–H and N(34)–H, see Fig. 1) at δ = 14.84 and 15.78 ppm consistent with the presence of strong hydrogen bonding interactions[20] that can be explained by a head-to-tail arrangement of the two phenazine subunits in solution. The two other NH protons [N(16)–H and N(37)–H] appear as a broad singlet (I = 2H) at δ = 6.34 ppm as expected in quinoid-type structures.[21] These data obtained in solution are consistent with those observed in solid-state which explain the extremely large chemical shift differences between the two upfield and downfield NH protons ($\Delta\delta$ = 8.50 and 9.44 ppm). The peak at δ = 5.38 ppm is the diagnostic signal of the C–H proton of the bridge as already observed for the naturally occurring parent of **5** (R^1 = R^2 = H).[13b] Interestingly, each broad signal observed at 250 MHz for the CH_2 protons (I = 2H) of the bridge in **6a** (*i.e.* –CH-CH_2-CH_2-CH_3) is split into two multiplets integrating for one each when the spectrum is recorded at 500 MHz. This result shows that the methylenic protons of the bridge are diastereotopic,[22] and supports a chiral head-to-tail geometry of **6a** in solution with a "pseudo" C_2 symmetry. The ^{13}C NMR data are in agreement with the absence of symmetry for **6a** as shown by the two signals at 171.0 and 171.2 ppm which prove the presence of two carbonyl groups

(note that $\delta_{C\text{–}OH} = 154.6$ ppm in **7**).[18] The assignment of the peaks and the retained geometry of **6a** in solution were also determined by HMQC and NOESY 2D-NMR experiments, respectively (see ESI†). The downfield N(13)–H and N(34)–H protons are indeed correlated through space to the C(11)–H and C(32)–H protons, respectively (see Fig. 3 and 4).

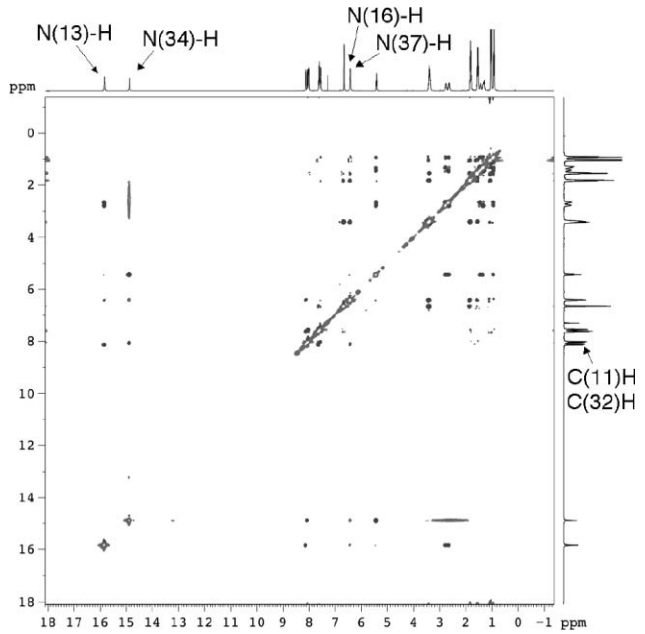


Fig. 3 NOESY NMR of molecule **6a** in $CDCl_3$ at room temperature.

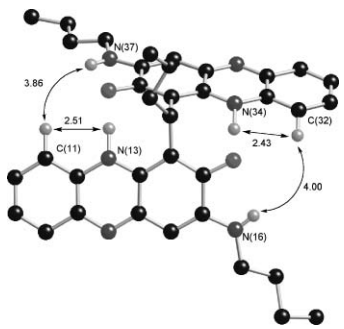
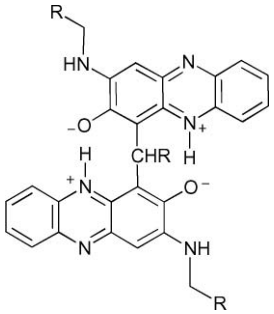


Fig. 4 View molecule **6a** in solution at room temperature.

In addition, the upfield N(16)–H and N(37)–H protons appear coupled to the CH_2 groups of the N(16)-*n*Bu and N(37)-*n*Bu substituents, respectively. In addition, they are also correlated through space to the benzenic proton of the opposite phenazine subunit [C(32)–H and C(11)–H, respectively]. The X-ray data confirms that the distances between the N–H and C–H hydrogens cited above are in the expected range for correlation through space (Fig. 4). The presence of the NH form in solution was further supported by IR measurements in chloroform which revealed a weak band at 3377 cm^{-1} in agreement with the NH stretching vibration (the OH vibration would have appeared as a broad and intense band due to intramolecular interactions).

Thus, although related systems that contain an intramolecular OHN hydrogen bond are characterized by a fast proton transfers (keto-enol tautomerism),[23] on the basis of these structural features, **6a** can be unambiguously interpreted as an NH form with a similar geometry either in solution or solid-state (Fig. 4).

The presence of a zwitterionic form in solution could be excluded owing to the ^{13}C NMR data which are not consistent with an aromatic structure (presence of two carbonyl resonances at 171.0 and 171.2 ppm).



(3)

Interestingly, the temperature-dependent ^1H NMR analysis demonstrated the spectral changes of the signals corresponding to the C(11)–H and C(32)–H protons above 8.0 ppm (Fig. 5). The change of the magnetic environment of these two protons can be interpretated as a result of a breaking of the H-bonding interactions which allows a free rotation of each phenazine subunit. Therefore, the C(11)–H and C(32)–H protons become magnetically equivalent and appear as a broad singlet at 8.10 ppm.

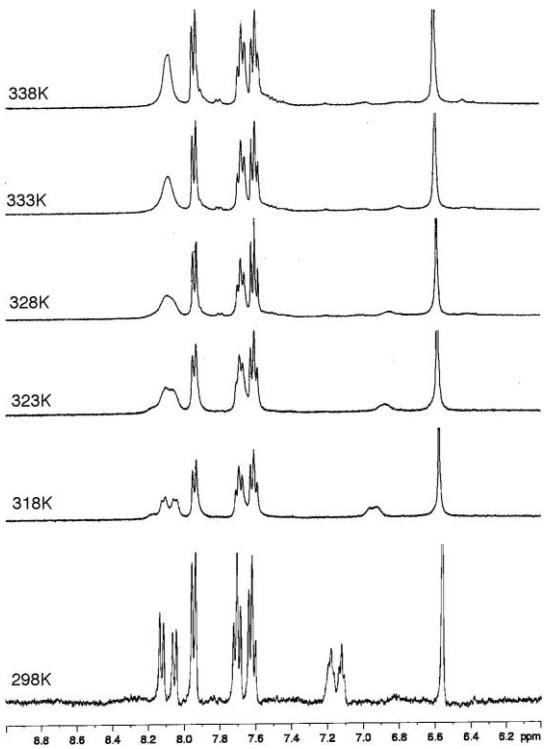


Fig. 5 Temperature dependent ^1H NMR spectra of **6a** at 400 MHz in DMSO in the range 6–9 ppm.

Geometry optimizations have been carried out at the DFT level[24] on models of **6a** (referred to as $\mathbf{6}_{NHMe}$). The N-nBu substituents and the nBu bridge have been replaced by methyl and ethyl groups, respectively, in order to decrease the number of degree of freedom in the molecule. B3LYP[25] reinforced by diffuse and polarization functions 6-31+G(d)[26] was chosen owing

to their satisfactory precision for H-bonded systems either from a geometry[27] or an energetic point of view.[28]

The maximal discrepancy with respect to the distances observed in the real molecule is equal to 0.037 Å (Table 1) which confirms a good agreement between the theory and the experimental results. Geometry optimizations performed on **5** and **6** where R^1 = NHMe and R^2 = Me ($\mathbf{5}_{NHMe}$ and $\mathbf{6}_{NHMe}$) confirmed the higher stabilization of the NH form ($\mathbf{6}_{NHMe}$) compared to the OH tautomer ($\mathbf{5}_{NHMe}$) (ΔE = 17.5 kJ mol^{-1}) (Fig. 6). In order to emphasize the key role of R^1=NHMe, we also performed the same calculations for R^1=H and R^2 = Me ($\mathbf{5}_H$ and $\mathbf{6}_H$), and we show in these cases that the OH form ($\mathbf{5}_H$) is the most stable tautomer (ΔE = 27.0 kJ mol^{-1}) (Fig. 6).

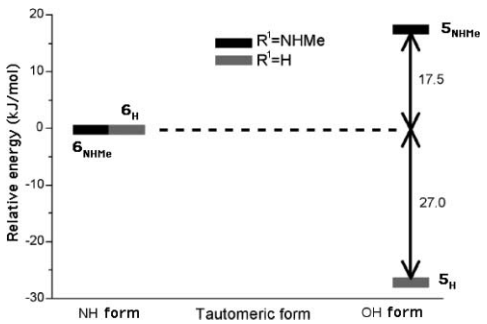
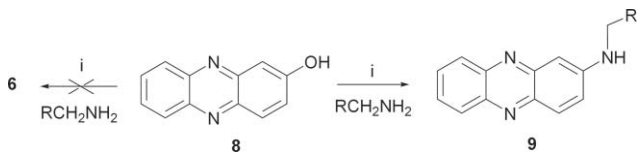


Fig. 6 Relative energy (kJ mol^{-1}) of NH and OH tautomers for **5** and **6** with R^1=NHMe and R^1=H (the NH form is the reference).

Although the formation of the bisphenazine-type molecules **6** is not hitherto fully understood, the following mechanism can be reasonably envisaged: (i) the first step would result from an OH replacement by the amino group, affording water elimination and the formation of a intermediate **A** which could rearrange by proton tautomerization into its nonaromatic form **B** (Scheme 1), (ii) in the presence of **A** (or **B**) and H_2O, the remaining primary amine precursor R-CH_2-NH_2 would be oxidized into RC(O)H, (iii) the nucleophile olefinic carbon of two molecules of **B** might then react with RC(O)H affording the bridged-bisphenazines **6**. This hypothesis was supported by the use of phenazine-2-ol **8**, instead of phenazine-2,3-diol **7**, which afforded only the corresponding 2-aminophenazine **9**[29] (no dimeric structure **6** could be detected) (Scheme 2). Attempts to isolate intermediates of type **B** are currently under investigations for a comprehensive study of this new class of dimeric structures.



Scheme 2 Synthesis of phenazine **9**. i) *n*-BuNH_2 (4 equiv.), 100 °C, 24 h, 50% yield.

Conclusions

In summary, we have disclosed a versatile and convenient one-pot synthesis of new dimeric structures (**6**) that would allow to enlarge the scope of this class of heterocyclic molecules. We have demonstrated from experiments and DFT theoretical calculations that the NH form in the ground state, fully characterized in the solid-state by X-ray analysis at room temperature, is also attainable in solution for **6** which adopt a rigid and chiral head-to-tail geometry. Consequently, although aromaticity is often associated in the ground state to a higher stability, we described here a rare example of molecules which sacrifice by prototropic rearrangement their aromatic character (OH form) in favor of a new class of highly stable nonaromatic NH tautomers. The successful observation of the NH forms of heterocyclic phenols of type **4** in solution at the molecular level (*i.e.* in apolar aprotic solvents at room temperature) is—to the best of our knowledge—unprecedented. The presence of a H-donor substituent at position 3 (R^1 = secondary amines) appeared crucial to render the molecule an NH form rather than an OH form because it leads to two additional H-bonding interactions which lock the nonaromatic tautomer **6**. Importantly, these findings in **6** would be applicable to other systems and open new perspectives in photo- and thermochromism[4–9] but also in other areas of science by analogy with related dimeric structures, H-donors/acceptors and N,O-donors.[4,14–17]

Experimental Section

General remarks

Analytical-grade reagents were obtained from commercial suppliers and were used directly without further purification. ^{1}H (250, 400 or 500 MHz) and ^{13}C (62 MHz) NMR spectra were recorded in $CDCl_3$ or DMSO on a Bruker AC250, AC400 or AC500 spectrometer. Splitting patterns are described as s, singlet; br, broad; d, doublet; dd, doublet of doublet; ddd, doublet of doublet of doublet; t, triplet; td, doublet of triplet; qt, quintuplet; sext, sextuplet; m, multiplet. Diastereotopic protons are noted CH. The assignments of the signals were determined by ^{1}H/^{13}C HMQC, ^{13}C NMR and ^{1}H-^{1}H COSY experiments. The geometry of **6a** in solution was established by NOESY NMR experiment at room temperature. Elemental and MS analyses were performed by Marseille Spectropole. ESI mass spectral analyses were recorded on a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed on a QStar Elite (Applied Biosystems SCIEX) mass spectrometer.

General procedure for the synthesis of bisphenazine-type dimeric structures 6

In a test tube, phenazine-2,3-diol 7[30] (1 equiv.) and primary amine (4 equiv.) were heated at 100 °C for 24 h. The crude product was taken up in dichloromethane and purified by chromatography over silica gel (eluent: cyclohexane/ethyl acetate 8/2) to afford the dimeric structure.

Compound 6a. Phenazine-2,3-diol (201 mg, 0.95 mmol), n-butylamine (375 µL, 3.78 mmol), 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, 3 H, ^3J(HH) = 7.5 Hz, CH_3), 1.00 (t, 6 H, ^3J(HH) = 7.5 Hz, CH_3), 1.27 (m, 1 H, CH), 1.38 (m, 1 H, CH), 1.51 (sext, 4 H, ^3J(HH) = 7.5 Hz, CH_2), 1.79 (qt, 4 H, ^3J(HH) = 7.5 Hz, CH_2), 2.59 (m, 1 H, CH), 2.71 (m, 1 H, CH), 3.35 (m, 4 H, CH_2), 5.38 (t, 1 H, ^3J(HH) = 7.5 Hz, CH), 6.34 (br. s, 2 H, NH), 6.61 (br. s, 2 H, olefinic H), 7.53 (dd, 2 H, J_{ortho} = 7.5 Hz,

J_{ortho} = 8.0 Hz, aromatic H), 7.62 (dd, 2 H, J_{ortho} = 7.5 Hz, J_{ortho} = 8.0 Hz, aromatic H), 7.98 (d, 2 H, J_{ortho} = 8.0 Hz, aromatic H), 8.03 (d, 1 H, J_{ortho} = 8.0 Hz, aromatic H), 8.09 (d, 1 H, J_{ortho} = 8.0 Hz, aromatic H), 14.84 (s, 1 H, NH), 15.78 (s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): δ = 14.0 (CH_3), 14.2 (CH_3), 20.5 (CH_2), 22.5 (CH_2), 30.8 (CH_2), 31.9 (CH_2), 33.5 (CH), 42.8 (CH_2), 95.7, 95.8 (central olefinic C), 109.8, 111.1 (C), 118.9, 125.8, 125.9, 127.96, 128.02, 128.2, 128.6, 128.7 (aromatic CH), 133.8, 135.9, 137.7, 137.8, 146.8, 146.9, 147.3, 148.1 (C), 171.0, 171.2 (C=O) ppm. Only 30 peaks instead of 36 could be observed due to signal overlap. MS (ESI): m/z = 589.5 $[M+H]^+$. $C_{36}H_{40}N_6O_2$: calcd. C 73.44, H 6.85, N 14.27; found: C 73.08, H 7.04, N 14.15.

Compound 6b. Phenazine-2,3-diol (200 mg, 0.94 mmol), benzylamine (410 µL, 3.76 mmol), 44% yield. ^1H NMR (250 MHz, $CDCl_3$): δ = 4.51 (dd, 2 H, $^3J(HH)$ = 7.0 Hz, $^4J(HH)$ = 1.0 Hz, CH_2), 4.60 (dd, 2 H, $^3J(HH)$ = 7.0 Hz, $^4J(HH)$ = 2.0 Hz, CH_2), 6.61 (t, 1 H; $^3J(HH)$ = 7.0 Hz, NH), 6.69 (s, 1 H, olefinic H), 6.73 (t and s, 2 H, $^3J(HH)$ = 7.0 Hz, NH and olefinic H), 7.01 (s, 1 H, CH), 7.11 (m, 2 H, aromatic H), 7.19 (m, 2 H, aromatic H), 7.28–7.50 (m, 15 H, aromatic H), 7.99 (m, 4 H, aromatic H), 14.95 (br s, 1 H, NH), 15.40 (br s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): δ = 36.6 (CH_2), 47.3 (CH), 42.8 (CH_2), 97.0, 97.2 (central olefinic C), 108.2, 109.1 (C), 118.8, 125.9, 126.06, 126.14, 127.2 (aromatic CH), 127.7, 128.0, 128.3, 128.4 (aromatic CH), 128.6, 128.8, 128.87, 128.9, 133.9, 136.6, 137.3, 137.5, 137.7, 137.8, 138.1 (C), 170.8, 171.8 (C=O) ppm. Only 29 peaks instead of 45 could be observed due to signal overlap. HRMS (ESI): calcd. for $C_{45}H_{34}N_6O_2$ $[M+H]^+$ 691.2816; found, 691.2819.

Compound 6c. Phenazine-2,3-diol (200 mg, 0.94 mmol), n-propylamine (310 µL, 3.77 mmol), 10% yield. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.94 (t, 3 H, $^3J(HH)$ = 7.2 Hz, CH_3), 1.07 (t, 6 H, $^3J(HH)$ = 7.25 Hz, CH_3), 1.82 (sext, 4 H, $^3J(HH)$ = 7.2 Hz, CH_2), 2.60 (m, 1 H, CH), 2.81 (m, 1 H, CH), 3.32 (m, 4 H, CH_2), 5.25 (t, 1 H, $^3J(HH)$ = 7.2 Hz, CH), 6.38 (brs, 2 H, NH), 6.62 (s, 2 H, olefinic H), 7.50–7.64 (m, 4 H, aromatic H), 7.97–8.09 (m, 4 H, aromatic H), 14.85 (br s, 1 H, NH), 15.77 (br s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): δ = 11.9 (CH_3), 13.8 (CH_3), 22.1 (CH_2), 22.8 (CH_2), 35.8 (CH), 44.8 (CH_2), 95.6, 95.7 (olefinic C), 109.6, 111.1 (C), 118.97, 118.98, 126.0, 126.2, 127.81, 127.83, 128.4, 128.76, 128.77 (aromatic CH), 133.9, 136.3, 137.5, 137.5, 146.62, 146.64, 147.4, 148.2 (C), 170.8 (C=O) ppm. Only 28 peaks instead of 33 could be observed due to signal overlap. HRMS (ESI): calcd. for $C_{33}H_{34}N_6O_2$ $[M+H]^+$ 547.2816; found, 547.2820.

X-Ray data

A suitable single crystal of **6a** and **8** for X-ray analysis was mounted on a Nonius Kappa-CCD area detector diffractometer (Mo-Kα, λ = 0.71069 Å). The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The structure was solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software.[31]

6a. Hexagonal space group $R\bar{3}$ with a = 26.389(2), b = 26.389(2), c = 23.753(1), α = 90.00, β = 90.00, γ = 120 at 293(2) K with Z = 18. Refinement of 6613 reflections, and 469 parameters, yielded wR_2 = 0.2621 for all data (2791 reflections with $I > 2\sigma(I)$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 701450).†

8. Monoclinic space group $C2/c$ with a = 18.931(1), b = 4.4136(3), c = 22.572(2), β = 96.459(2) at 293(2) K with Z = 8. Refinement of 1177 reflections, and 140 parameters, yielded wR_2 = 0.1084 for all data (803 reflections with $I > 2\sigma(I)$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 701451).†

Acknowledgements

This work was supported by the Centre National de la Recherche Scientifique, the Ministère de la Recherche et des Nouvelles Technologies. We also thank the Provence Alpes Côte d'Azur Region (grant C. S.), Prof. F. Fages for fruitful discussions, M. Giorgi for the crystal structure determinations, and R. Rosas and G. Herbette for the NMR studies.

Notes and references

1 (*a*) J. T. Hynes, J. P. Klinman, H.-H. Limbach, R. L. Schowen, in *Hydrogen tranfer reactions*, Wiley, John & Sons, 2007; (*b*) V. Bertalosi, P. Gilli and G. Gilli, *Curr. Org. Chem.*, 2009, **13**, 250; (*c*) F. Fillaux, A. Cousson and M. J. Gutmann, *Pure Appl. Chem.*, 2007, **79**, 1023.
2 (*a*) A. M. Winter, K. Eichele, H.-G. Mack, W. C. Kaska and H. A. Mayer, *Dalton Trans.*, 2008, 527; (*b*) X. Zhang, Q. Liu, A. Son, Q. Zhang, F. Zhang and F. Zhao, *Photochem. Photobiol. Sci.*, 2008, **7**, 299; (*c*) X. Zhang, Q. Liu, H. Wang, F. Zhang and F. Zhao, *Photochem. Photobiol. Sci.*, 2008, **7**, 1079.
3 M. Randic, *Chem. Rev.*, 2003, **103**, 3449.
4 (*a*) E. Hadjoudis, in *Studies in organic chemistry*, Vol. 40. *Photochromism: Molecules and Systems*, Eds H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990; (*b*) E. Hadjoudis, *Mol. Eng.*, 1995, **5**, 301.
5 (*a*) P. Gilli, V. Bertolasi, L. Pretto, A. Lycka and G. Gilli, *J. Am. Chem. Soc.*, 2002, **124**, 13554; (*b*) A. Koll, A. Karpfen and P. Wolschann, *J. Mol. Struct.*, 2006, **790**, 55; (*c*) T. Irshaidat, *Tetrahedron Lett.*, 2009, **50**, 825.
6 (*a*) A. Grabowska, K. Kownacki, J. Karpiuk, S. Dobrin and L. Kaczmarek, *Chem. Phys. Lett.*, 1997, **267**, 132; (*b*) M. Ziólek, G. Burdzinski, K. Filipczak, J. Karolczak and A. Maciejewski, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1304; (*c*) S.-J. Lim, J. Seo and S. Y. Park, *J. Am. Chem. Soc.*, 2006, **128**, 14542; (*d*) J. W. Ledbetter, *J. Phys. Chem.*, 1966, **70**, 2245.
7 (*a*) J. Harada, H. Uekusa and Y. Ohashi, *J. Am. Chem. Soc.*, 1999, **121**, 5809; (*b*) Z. Rozwadowski, E. Majewski, T. Dziembowska and P. E. Hansen, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2809.
8 (*a*) K. Ogawa, Y. Kasahara, Y. Ohtani and J. Harada, *J. Am. Chem. Soc.*, 1998, **120**, 7107; (*b*) K. Ogawa, J. Harada, T. Fujiwara and S. Yoshida, *J. Phys. Chem. A*, 2001, **105**, 3425; (*c*) K. Ogawa and J. Harada, *J. Mol. Struct.*, 2003, **647**, 211; (*d*) K. Ogawa, J. Harada, I. Tamura and Y. Noda, *Chem. Lett.*, 2000, 528.
9 (*a*) S. V. Linderman, M. Y. Antipin and Y. T. Struchkov, *Kristallogr.*, 1988, **33**, 365; (*b*) A. K. Mukherjee, R. Lalde, I. Banerjee, C. Samanta and N. P. Nayak, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, **55**, 407; (*c*) S. R. Salman, S. K. Kanber and L. K. Arsalan, *Spectrosc. Lett.*, 1991, **24**, 1153.
10 (*a*) K. Ogawa, M. Miura, T. Nakayama and J. Harada, *Chem. Lett.*, 2003, **32**, 840; (*b*) G. M. Badger, R. S. Pearce and R. Pettit, *J. Chem. Soc.*, 1951, 3204; (*c*) T. Nakagawa, S. Khotani and M. Itoh, *J. Am. Chem. Soc.*, 1995, **117**, 7952; (*d*) M. Itoh, T. Adachi and K. Tokumura, *J. Am. Chem. Soc.*, 1984, **106**, 850; (*e*) M. Itoh, T. Adachi and K. Tokumura, *J. Am. Chem. Soc.*, 1983, **105**, 4828; (*f*) J. F. Corbett, *Spectrochim. Acta*, 1964, **20**, 1665.
11 W. M. F. Fabian, L. Antonov, D. Nedeltcheva, F. S. Kamounah and P. J. Taylor, *J. Phys. Chem.*, 2004, **108**, 7603.
12 A. G. Cairns-Smith, *J. Chem. Soc.*, 1961, 182.

13 (*a*) W.-G. Kim, I.-J. Ryoo, B.-S. Yun, K. Shin-Ya, H. Seto and I.-C. Yoo, *J. Antibiotics*, 1999, **52**, 758; (*b*) W. Neuenhaus, A. Römer, H. Budzikiewicz, H. Korth and G. Pulverer, *Z. Naturforsch.*, 1980, **35b**, 385; (*c*) J. B. Laursen and J. Nielsen, *Chem. Rev.*, 2004, **104**, 1663.
14 (*a*) S. B. Mekapati, W. A. Denny, A. Kurup and C. Handsch, *Bioorg. Med. Chem.*, 2001, **9**, 2757; (*b*) A. J. Stewart, P. Mistry, W. Dangerfield, D. Bootle, M. Baker, B. Kofler, S. Okiji, B. C. Baguley, W. A. Denny and P. A. Charlton, *Anti-Cancer Drugs*, 2001, **12**, 359; (*c*) J. Dai, C. Punchihewa, P. Mistry, A. T. Ooi and D. Yang, *J. Biol. Chem.*, 2004, **279**, 46096.
15 A. S. Jana, *J. Photochem. Photobiol., A*, 2000, **132**, 1.
16 V. R. Thalladi, T. Smolka, A. Gehrke, R. Boese and R. Sustmann, *New J. Chem.*, 2000, **24**, 143.
17 (*a*) M. A. Zuideveld, P. Wehrmann, R. Roehr and S. Mecking, *Angew. Chem., Int. Ed.*, 2004, **43**, 869; (*b*) S. Richeter, C. Jeandon, J.-P. Gisselbrecht, R. Ruppert and H. J. Callot, *J. Am. Chem. Soc.*, 2002, **124**, 6168; (*c*) D. Zhang and G.-X. Jin, *Organometallics*, 2003, **22**, 2851; (*d*) J.-p. Taquet, O. Siri, P. Braunstein and R. Welter, *Inorg. Chem.*, 2004, **43**, 6944.
18 C. Seillan, H. Brisset and O. Siri, *Org. Lett.*, 2008, **10**, 4013.
19 (*a*) U. Beifuss and M. Tietze, *Top. Curr. Chem.*, 2005, **244**, 77; (*b*) R. Ott, *Monatsh. Chem.*, 1959, **90**, 827.
20 H. Rumpel and H.-H. Limbach, *J. Am. Chem. Soc.*, 1989, **111**, 5429.
21 O. Siri, P. Braunstein, M.-M. Rohmer, M. Bénard and R. Welter, *J. Am. Chem. Soc.*, 2003, **125**, 13793.
22 C. F. Tormena, M. P. Freitas, R. Rittner and R. J. Abraham, *Magn. Reson. Chem.*, 2002, **40**, 279.
23 (*a*) S. Sharif, D. Schagen, M. D. Toney and H.-H. Limbach, *J. Am. Chem. Soc.*, 2007, **129**, 4440; (*b*) H.-H. Limbach, M. Pietrzak, S. Sharif, P. M. Tolstoy, I. G. Shenderovich, S. N. Smirnov, N. S. Golubev and G. S. Denisov, *Chem.–Eur. J.*, 2004, **10**, 5195; (*c*) I. Alkorta, P. Goya, J. Elguero and S. P. Singh, *Natl. Acad. Sci. Lett*, 2007, **30**, 139.
24 M. J. Frisch, *et al.*, *Gaussian 03*, ReVision C.02. Gaussian, Inc., Wallingford, CT, 2004.
25 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785; (*c*) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200; (*d*) A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098.
26 (*a*) V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern and L. A. Curtiss, *J. Comput. Chem.*, 2001, **22**, 976; (*b*) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.
27 (*a*) M. Lozynski, D. Rusinska-Raszak and H.-G. Mack, *J. Phys. Chem. A*, 1998, **102**, 2899; (*b*) J. J. Novoa and C. Sosa, *J. Phys. Chem.*, 1995, **99**, 15837.
28 Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.*, 2005, **1**, 415.
29 S. Pietra and M. Argentini, *Annali Chim.*, 1971, **61**, 290.
30 (*a*) J. L. Pozzo, G. M. Clavier and J. P. Desvergne, *J. Mater. Chem.*, 1998, **8**, 2575; (*b*) F. Placin, G. Clavier, F. Najera, J. P. Desvergne and J. L. Pozzo, *Polycyclic Aromat. Compd.*, 2000, **19**, 107.
31 *Gaussian 03, Revision C.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.