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Aza-bridged bis-1,10-phenanthroline acyclic derivatives: synthesis, structure, and regioselective alkylation

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ABSTRACT

A family of acyclic aza-bridged bis-1,10-phenanthroline compounds has been synthesized in a convenient way. The resulting compounds **2** and **2**·HCl were fully characterized and their solid state structures and NMR spectroscopic properties were investigated to assess how the structural units affect the alkylation reactions. The results reveal the *transoid* structure for **2**. The broadening NMR peak in **2** is shown to be due to an unusual intramolecular CH···N hydrogen bond. This unique conformation offers an efficient and regioselective method to prepare the amino-substituted bis-2,2′-1,10-phenanthroline derivatives and 1,10-phenanthrolino-N-alkylated compounds.

Polypyridyl has been known to be an important class of versatile ligands for the chelation of metals. Although so, the 1,10-phenanthroline ligand has the advantage that it can form complexes with metals more rapidly than the 2,2′-bipyridine system. Important properties of transition metal complexes of 1,10-phenanthroline have been extensively investigated because of their photochemical,[1] electrochemical,[2] and biological properties.[3] Also, 1,10-phenanthroline complexes have been found to interact with nucleic acid or protein for the expression of biological activities. The planar and rigid structure of 1,10-phenanthroline can either intercalate or bind to the grooves of DNA or RNA.[4] Much attention has, therefore, been focused on the design and synthesis of new derivatives of 1,10-phenanthroline with extended properties but only few results were reported in the literature.[5] We have previously reported an alternative strategy to synthesize a series of macrocyclic and acyclic derivatives of 1,10-phenanthroline ligand.[6] We now report on the synthesis of an acyclic aza-bridged bis-1,10-phenanthroline, together with its reaction, structure, and spectroscopic properties. We demonstrate here that the acyclic aza-bridged bis-1,10-phenanthroline can be site-selective alkylated.

The strategy and reaction conditions we used to synthesize the desired compounds are shown in Scheme 1 and Table 1. Compound **1** was synthesized using previously described procedure.[6a] It was found that compound **1** sublimed readily to preclude carrying out further reaction at high temperature. This problem was overcome by using the hydrochloric salt, **1**·HCl, for the successive reaction. Treatment of pulverized crystal of **1**·HCl in an NH_3 atmosphere at 240 °C for 6 h was readily shown to give **2**·HCl in excellent yield.[7] The one-pot synthetic route provides a convenient and efficient method for the preparation of the aza-bridged bis-1,10-phenanthroline acyclic compound. The corresponding neutral mono-aza-bridged 1,10-phenanthroline **2** (a brown powder) was readily obtained in quantitative yield[8] by neutralizing the **2**·HCl with NH_4OH, and followed by Soxhlet extraction with acetone.

Compound **2** shows a strong electronic coupling between the NH group and the two 1,10-phenanthroline rings. However, this type of interaction is likely to be weakened in solution, whereby the lone electron pair of the NH group is sensitive to its environment and readily interacts with the surrounding protons.[5c] In solution, the free rotation of the two 1,10-phenanthroline rings around the C–N bonds is expected to induce some impact on the electronic coupling and reactivity, thus resulting in an intramolecular conformational equilibrium between the near planar and twisted conformations in the ground state. In protic solvents, the interaction between the solvent protons and the lone electron pair of the NH group tends to favor the twist-conformation, causing the two 1,10-phenanthroline rings to be out of the plane, disrupting the conjugation.

One of the interesting features of **2** is its existence in the tautomeric form. The consequence of proton-shift imine-enamine tautomerism becomes important in systems of fused aromatic and heterocyclic rings,[9] where the fused three-ring system of 1,10-phenanthroline makes such a process somewhat favorable.[5c,6a]. From

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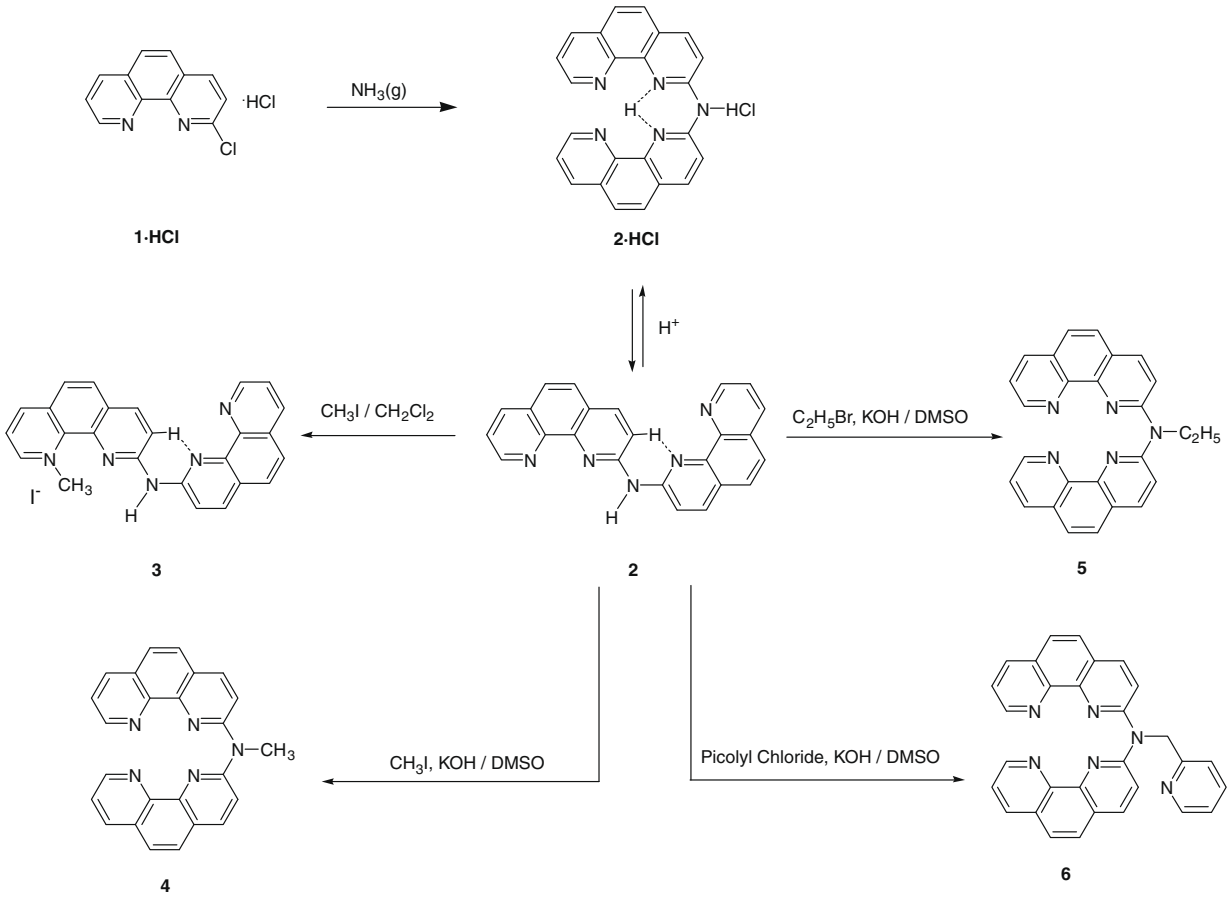

Scheme 1.

Table 1
Reaction conditions of **1**·HCl, **2**·HCl, and **2**

Entry	Substrate	Reagent(s)	Solvent	Temp (°C)	Time (h)	Product	Yield (%)
1	**1**·HCl	NH_3	—	240	6	**2**·HCl	76
2	**2**·HCl	NH_4OH	H_2O	rt	1	**2**	99
3[a]	**2**·HCl	2-BrPy/KOH	DMSO	190	72	—	—
4[a]	**2**·HCl	2-BrPy/KOH/catalyst[b]	ODCB[c]	240	72	—	—
5[a]	**2**·HCl	2-BrPy/KOH/catalyst[d]	DMSO	180	72	—	—
6	**2**	CH_3I	CH_2Cl_2	rt	24	**3**	93
7	**2**	CH_3I/KOH	DMSO	rt	48	**4**	53
8[e]	**2**	C_2H_5Br/KOH	DMSO	rt	120	**5**	50
9	**2**	2-PicCl/KOH	DMSO	110	24	**6**	43

[a] No reaction.
[b] Three treatments with different catalysts (CuI, Cu powder, and Cu powder with $CuSO_4$).
[c] ODCB = *o*-dichlorobenzene.
[d] Two treatments with different catalysts (Cu powder and Cu powder with $CuSO_4$) in solvothermal reactor.
[e] Data were collected in NMR tube reaction without separation.

the point of view of ligand design, **2** is difficulty to modify because the lone pair electrons on the nitrogen are integrated into as a part of the delocalized π-system. Many efforts on the preparation of nitrogen-substituted bis-1,10-phenanthrolines have been evaluated.[5,6]

Initially, we were uncertain as to whether selective alkylation can be carried out between the bridging and the pyridine N-atom. Thus, we first attempted the methylation of **2**·HCl with iodomethane in dimethyl sulfoxide (or in methanol) in the presence of KOH (or K_2CO_3), and those experiments were unsuccessful. Furthermore, we also attempted to couple aryl halide with **2**·HCl by Ullmann-type reaction under various conditions (CuI, Cu powder, Cu powder with $CuSO_4$, high temperature, or high pressure) and again these experiments were unsuccessful.

However, after treatment of **2** with iodomethane in dichloromethane and then stirring at room temperature overnight, the ring nitrogen mono-methylated product **3** in high yields was resulted (Scheme 1).[10] We then turned our attention to the preparation of methylation of the bridging amino-substituted bis-1,10-phenanthrolines. Upon refluxing **2** in dimethyl sulfoxide in the presence of potassium hydroxide and iodomethane, the corresponding bridge-amino-substituted bis-1,10-phenanthrolines **4**[11] (Scheme 1) was readily obtained in good yields. The regioselectivity of methylation is thus strongly dependent on the reaction conditions, such as the solvent and base. In aprotic solvent (such as dichloromethane) and without base, the reaction gives phenanthroline–N-added product **3**, whereas that in aprotic solvent with base gives amino-substituted product **4**. We then chose to use other bromoalkane

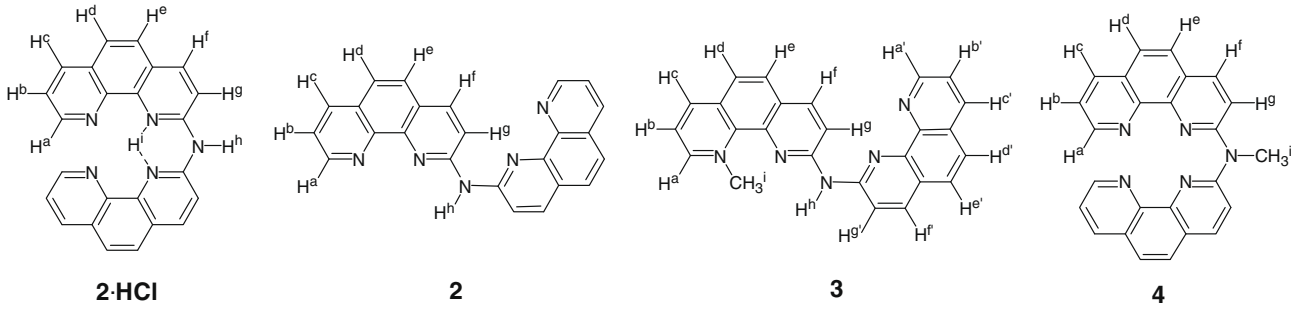

Figure 1. Structure of **2**·HCl, **2**, **3**, and **4**.

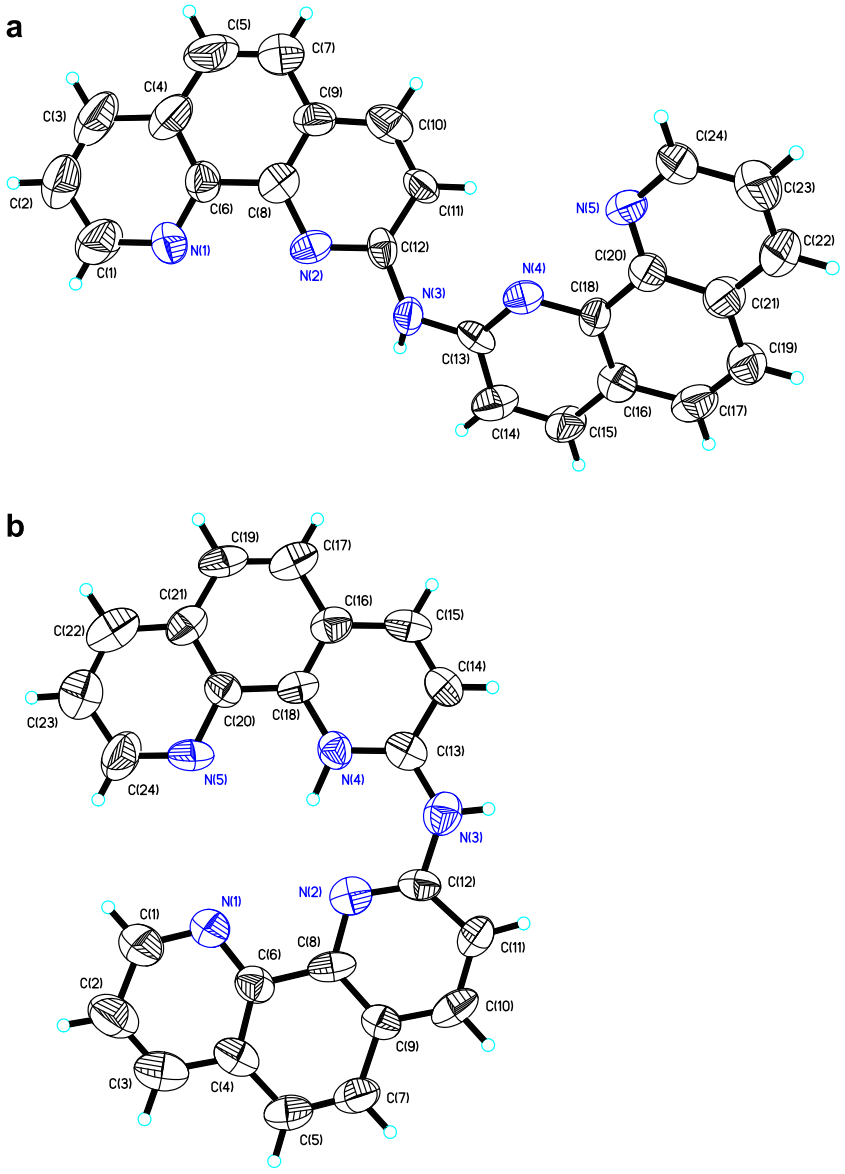

Figure 2. (a) ORTEP representations of the X-ray crystal structures of compound **2** showing 50% probability thermal ellipsoids. Solvent and anion atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.368(12), N(1)–C(6) 1.352(11), N(2)–C(8) 1.378(10), N(2)–C(12) 1.366(10), N(3)–C(12) 1.386(10), N(3)–C(13) 1.362(10), N(4)–C(13) 1.325(9), N(4)–C(18) 1.371(9), N(5)–C(20) 1.344(10) and N(5)–C(24) 1.334(11) Å; C(13)–N(3)–C(12) 127.4(6). (b) ORTEP representations of the X-ray crystal structures of the **2**·HCl cation showing 50% probability thermal ellipsoids. Solvent and anion atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.311(15), N(1)–C(6) 1.330(15), N(2)–C(8) 1.361(14), N(2)–C(12) 1.305(16), N(3)–C(12) 1.423(16), N(3)–C(13) 1.374(14), N(4)–C(13) 1.338(14), N(4)–C(18) 1.378(13), N(5)–C(20) 1.385(14), N(5)–C(24) 1.316(18); C(13)–N(3)–C(12) 131.4 (10).

and chloroalkane to investigate the mono-alkylation of the bridging-N. Using bromoethane and picolyl chloride furnished **5** and **6** (Scheme 1) in moderate to good yields, respectively (see Table 1).

In the ^{1}H NMR spectrum of the symmetric compound **2**·HCl (Fig. 1), seven absorption signals were observed, confirming that the acyclic **2**·HCl has a C_2 symmetry structure. The lowest field res-

onance is the H^a hydrogen (at 9.25 ppm) which is adjacent to the nitrogen of the side pyridine ring. In the acyclic **2**·HCl structure, the NH proton can be exchanged with solvent so that it was not observed.

The ^{1}H NMR spectrum (in DMSO-d_6) of compound **2** (Fig. 1) has a quite different pattern from the protonated **2**·HCl. The lowest field resonance gives a very sharp peak for the NH (at 10.98 ppm) that bridges the two 1,10-phenanthroline rings. Surprisingly, a broad peak for H^g proton (at 8.88 ppm) was observed in compound **2**, instead of the sharp NH peak observed for compound **2**·HCl. Based on the comparison of NMR spectra with **2**·HCl, a large downfield shift of the H^g proton was observed ($\Delta\delta$ = 0.90 ppm). The large downfield shift for H^g proton implies that it is further deshielded by the nearby 1,10-phenanthroline ring in the presumed *transoid* planar arrangement. It may be expected that the *transoid* structure can provide an environment to generate the interaction of the CH^g group with nitrogen atom of the nearby 1,10-phenanthroline ring, leading to the formation of CH···N hydrogen bond.

The ^{1}H NMR spectrum of compound **3** (Fig. 1) in DMSO-d_6 at room temperature shows sixteen absorption signals in the spectrum resulting from an asymmetric conformation of **3**. The detailed assignment of these absorption peaks with the assistance of homo-COSY technique indicated that the methylation takes place on the outer nitrogen atom of 1,10-phenanthroline.

The ^{1}H NMR spectrum of compound **4** (Fig. 1) in DMSO-d_6 at room temperature displays seven absorption signals that imply an acyclic C_2 symmetry structure, similar in pattern to **2**·HCl. The results of NMR spectral analysis indicate that **4** has an amino-substituted bis-1,10-phenanthrolines structure.

The ORTEP[12] representations of **2** and **2**·HCl with atomic numbering are given in Figure 2.[13] The X-ray crystal structure of **2** (Fig. 2a) shows that two 1,10-phenanthroline rings are connected by bridging NH group, confirming the proposed *transoid* structures. It has a near planar geometry, and the dihedral angle between the two 1,10-phenanthroline ring planes is only 28.9°. This crystal packing is quite typical for the aromatic molecules in a pseudo-herringbone pattern. The molecular packing diagram does not show any short intermolecular distance (less than 4.0 Å) between the centers of gravity of different rings, indicating no π–π interactions in the lattice. In addition, a geometry optimization calculation for the torsional angles was performed with CAChe[14] using the PM3-Hamiltonian. The calculated minimum (35.8°) is close to the experimental value observed in the X-ray crystal structure (28.9°). However, the torsion angle can vary from 90° to 5° with only 0.5 kcal mol^{-1} changes in the heat of formation. These results give support for a twisted structure also in solution. This twisted structure is further supported by the presence of a broad peak of CH^g proton (at 8.88 ppm) and a sharp singlet peak at 10.98 ppm, as resulted from the NH proton in its ^{1}H NMR spectrum recorded in DMSO-d_6.

The interannular bond lengths of N(3)–C(12) and N(3)–C(13) are 1.386(10) and 1.362(10) Å, respectively, and have a partially double bond character. This indicates the presence of electronic coupling between the NH group and the two 1,10-phenanthroline ring systems. The C(11)H–N(4) distance is only 2.95 Å, shorter than the summation of their van der Waal's radius, suggesting a formation of hydrogen bond. Indeed, an investigation of their NMR spectra revealed that a broad peak of CH^g proton appeared in solution state. These results indicate the presence of a weak CH–N interaction between the two 1,10-phenanthroline rings in both solid and solution states.

Compound **2**·HCl (Figure 2.b) was shown to have a planar *syn*-structure, contrary to the results of *transoid* structure of **2**. The dihedral angle between the two 1,10-phenanthroline planes is only 3.4°. Meanwhile, a proton bonded to N(4) atom was found in the crystal structure analysis that resulted in the formation of intramolecular hydrogen bond with nitrogen atom on the opposite 1,10-phenanthroline ring with a pseudo six-member ring structure. The hydrogen bonding is one of the driving forces for such an acyclic molecule to retain the planar structure in *syn*-structure. The interannular bond lengths of N(3)–C(12) and N(3)–C(13) are 1.423(16) and 1.374(14) Å, respectively. The latter one displays a partial double bond character. The observed bond lengths indicate that the bridging nitrogen atom prefers to connect the protonated 1,10-phenanthroline ring through a partial C=N imine bond. The results suggest an electronic coupling between the bridging NH group and the protonated 1,10-phenanthroline ring system is presented, where the NH group to the nonprotonated 1,10-phenanthroline has more amine character.

The crystal structure analysis revealed that its central hydrogen atom is localized on one of the opposite central nitrogen atoms similar to those of free base porphyrin and H_2HAPP.[6a] Although there is no significant difference for the C–N bond distances of the two different inner nitrogen atoms,[15] the C–N–C angle of the protonated N atom (121.5°) is larger than that of nonprotonated one (116.9°). This angle difference is in agreement with similar structures reported.[16]

In conclusion, a family of acyclic bis-1,10-phenanthroline derivatives has been synthesized and characterized by using X-ray crystal structure analysis. These compounds are quite distinctive from other related macrocycles, where the acyclic compounds show a *transoid* structure upon alkylation. We have developed a convenient and efficient method to prepare methylated 1,10-bis-phenanthroline with high regioselectivity. Efforts to prepare other derivatives are currently being pursued in our laboratory. The unusual intramolecular CH···N hydrogen bond in acyclic derivatives has shown to cause a broadening in NMR peaks. The free rotation of the two phenanthroline rings around C–N bond gives the sharp NH peak. These two unique phenomena confirmed the *transoid* structure of compound **2** in solution and solid state, respectively. We believe that this class of ligands has a great potential for future research involving analogs of 1,10-phenanthroline with biological activities.

Acknowledgments

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Supplementary data

Supplementary data (chemical structures, selected ^{1}H, and ^{13}C NMR data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.05.039.

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7. A dichloromethane solution (5 mL) of **1** (0.9 g, 4.2 mmol) was added with $HCl_{(aq)}$ solution until no white precipitate was generated. The precipitate was collected and dried under vacuum by heating under N_2 at 120 °C (10 min). During this period of time, the material changed its color from white to yellow, which was then heated under NH_3 atmosphere at 240 °C (6 h) until the material color turned to deep brown. After washing with dichloromethane and cold methanol, the brown powder was recrystallized by slow diffusion from diethyl ether into concentrated methanol solution to afford **2**·HCl (1.3 g, 76%). ^{1}H NMR (DMSO-d_6) δ 9.25 (d, J = 1.8, 4.4 Hz, 1H), 8.85 (d, J = 8.3 Hz, 1H), 8.71 (dd, J = 8.3, 1.8 Hz, 1H), 8.18 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.98 (dd, J = 8.3, 1.8 Hz, 1H), 7.97 (d, J = 7.97 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ158.6; 150.9; 150.6; 142.2; 142.1; 138.3; 138.0; 131.0; 127.7; 127.3; 124.9; 124.1; 122.8; 115.0. ESI-MS (M+H) = 374.
8. The crude product of **2**·HCl was dissolved in water (280 mL) and then adjusted to pH 8 by addition of NH_4OH solution. The deep brown precipitates were generated while the pH value changes. The product was collected by filtration and was thoroughly extracted by Soxhlet with acetone to afford **2** in quantitative yield. ^{1}H NMR (DMSO-d_6) δ 10.98 (s, 1H), 9.12 (d, J = 1.8, 4.2 Hz, 2H), 8.88 (br d, 2H), 8.46 (d, J = 9.0 Hz, 2H), 8.45 (dd, J = 1.8, 8.4 Hz, 2H), 7.93 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 9.0, 2H), 7.74 (dd, J = 4.2, 8.4 Hz, 2H). ^{13}C-NMR (DMSO-d_6) δ 153.8; 149.7; 144.5; 144.1; 138.2; 136.1; 128.6; 126.3; 124.1; 123.7; 122.9; 115.1. Anal. Calcd for $C_{24}H_{15}N_5$: C, 77.20; H, 4.05; N, 18.76. Found: C, 77.25; H, 4.20; N, 18.78.
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10. A dichloromethane solution (10 mL) of **2** (100 mg, 0.27 mmol) was added with iodomethane dropwise (62 μL, 0.35 mmol), and the resulting yellow solution was stirred at room temperature overnight. The yellow precipitate thus formed was collected by filtration, washed thoroughly with dichloromethane and *n*-hexane, and dried to yield **3** as a light yellow solid (97 mg, 93%). ^{1}H NMR (DMSO-d_6) δ 10.85 (s, 1H), 9.58 (d, J = 9.5 Hz, 1H), 9.36 (d, J = 5.7 Hz, 1H), 9.24 (d, J = 8.6 Hz, 1H), 9.13(dd, J = 3.8, 1.9 Hz, 1H), 8.76 (d, J = 9.5 Hz, 1H), 8.47 (dd, J = 7.6, 1.9 Hz, 1H), 8.44 (d, J = 8.6 Hz, 1H), 8.31 (d, J = 8.6 Hz, 1H), 8.24 (dd, J = 8.6, 5.7 Hz, 1H), 8.12 (d, J = 8.6, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.70 (dd, J = 7.6, 3.8 Hz, 1H), 5.30 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 152.8; 150.6; 149.9; 146.5; 144.7; 144.4; 139.5; 139.4; 138.3; 136.3; 136.1; 132.4; 130.2; 129.0; 127.8; 126.4; 124.3; 124.0; 123.6; 123.3; 123.2; 117.0; 114.9; 52.2. Anal. Calcd for $C_{25}H_{18}N_5I$: C, 58.26; H, 3.52; N, 13.59. Found: C, 58.09; H, 3.66; N, 13.55.
11. Into dimethyl sulfoxide (20 mL) were successively added potassium hydroxide (85 mg, 1.5 mmol) and **2** (100 mg, 0.27 mmol). The resulting deep-orange-colored solution was stirred at room temperature for 30 min. Iodomethane (62 μL, 0.35 mmol) was then added and the orange solution was stirred at room temperature for 48 h. It was then diluted with water (100 mL), which lead to the immediate deposition of a fine yellow precipitate and was collected by filtration, washed with water (3 × 20 mL), and the yellow solid was recrystallized from methanol and dried to yield **4** (55 mg, 53%). ^{1}H NMR (DMSO-d_6) δ 9.13(dd, J = 4.2, 3.0 Hz, 2H), 8.54 (dd, J = 9.0, 3.0 Hz, 2H), 8.53(d, J = 8.8 Hz, 2H), 8.27 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 9.0 Hz, 2H), 7.90 (d, J = 9.0 Hz, 2H), 7.80 (dd, J = 9.0, 4.2 Hz, 2H), 5.25 (s, 3H). ESI-MS (M+H) = 388. Anal. Calcd for $C_{25}H_{17}N_5$: C, 77.50; H, 4.42; N, 18.08. Found: C, 77.02; H, 4.58; N, 17.83.
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13. *Crystallographic data and data collection parameters*:
(a) *Crystallographic data for* **2**·HCl: $C_{25}H_{16}N_5O_1Cl_1$, Orthorhombic, space group *Pca*21, yellow, a = 23.8555(26) Å, b = 7.1932(8) Å, c = 24.3363(24) Å, V = 4176.0(8) Å^3, T = 298 K, Z = 8. Final R (I >2r(I)), R_1 = 0.088, wR_2 = 0.171, Final R (all data), R_1 = 0.148, wR_2 = 0.2030, GOF = 1.117. 10,913 reflections were measured (5685 unique, R_{int}_0.088) on a Siemens P4 diffractometer in the range 1.90 < u < 25.10°, −25 < h < 25, −8 < k < 1, −27 < l < 25, operating in v scan mode and using graphite-monochromated Mo-Kα radiation (l_0.71073 Å). Semi-empirical absorption correction via eight scans was applied. *Structure solution and refinement*: The structure was solved by the direct method and refined anisotropically based on *F*2 by full-matrix least-squares techniques using the SHELXTL (Ver 5.10) program. All hydrogen atoms were located by Fourier synthesis and refined isotropically without any constraints or restraints. The final refinement gave R_1_0.088, wR_2_0.171.
(b) *Crystallographic data for* **2**: $C_{24}H_{15}N_5$, Monoclinic, space group *P*21/*c*, red, a = 13.8168(61) Å, b = 16.7479(73) Å, c = 9.9491(87) Å, β = 108.375(54)°, V = 2184.86(414) Å^3, T = 298 K, Z = 1. Final R (I >2r(I)), R_1 = 0.277, wR_2 = 0.286, GOF = 0.848. 4080 reflections were measured (3839 unique, R_{int}_0.277) on a Siemens P4 diffractometer in the range 2.0 < u < 25.0°, −16 < h < 15, −19 < k < 1, −1 < l < 11, operating in v scan mode and using graphite-monochromated Mo-Kα radiation (l_0.71073 Å). Semi-empirical absorption correction via eight scans was applied. *Structure solution and refinement*: The structure was solved by the direct method and refined anisotropically based on *F*2 by full-matrix least-squares techniques using the SHELXTL (Ver 5.10) program. All hydrogen atoms were located by Fourier synthesis and refined isotropically without any constraints or restraints. The final refinement gave R_1_0.099, wR_2_0.229.
The crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC reference number 750240 and 750265. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or email: deposit@ccdc.cam.ac.uk].
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