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SYNTHESIS AND PROPERTIES OF 3,2’-POLYMETHYLENE-2-PHENYLBENZO[*b*]-1,10-PHENANTHROLINES

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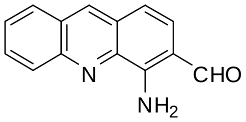
Abstract – Reactions of 4-aminoacridine-3-carbaldehyde with benzo[*b*]cycloalkanones and 3,4-dihydro-1(2*H*)-anthracenone afforded a series of corresponding 3,2’-polymethylene-2-phenylbenzo[*b*]-1,10-phenanthrolines and 3,3’-dimethylene-2-(naphth-2’-yl)benzo[*b*]-1,10-phenanthroline, respectively, as new *N*,*N*,*C*-terdentates. Dehydrogenation of dimethylene-bridged systems afforded the corresponding fully aromatized systems. Flexibility of annulated bridges is highly dependent on the length of the carbon chain, where tetramethylene-bridge is rigid enough to differentiate eight bridge protons in ^{1}H NMR time scale at room temperature.

INTRODUCTION

In earlier reports,[1,2] we described a synthesis of 4-aminoacridine-3-carbaldehyde (**1**) and its utility as a Friedländer synthon for the preparation of 2-phenylbenz[*b*]-1,10-phenanthroline (**2**) and related compounds. As a ligand, the molecule **2aH** is a fused form of the *N*,*N*-bidentate, 1,10-phenanthroline and the *N*,*C*-bidentate, 2-phenylpyridine, and thus can be a good *N*,*N*,*C*-terdentate.[2] Although a plethora of chemistry dealing with metal complexes of *N*,*C*-bidentates have been reported,[3] only very limited *N*,*N*,*C*-terdentates such as 6-phenyl-2,2’-bipyridine (**3H**)[4] and 2-phenyl-1,10-phenanthroline (**4H**)[5] as well as their annulated analogues, and their metal complex chemistry have been studied.



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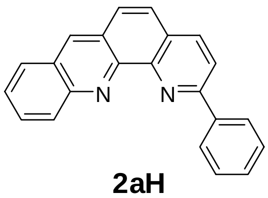
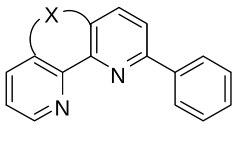


2aH



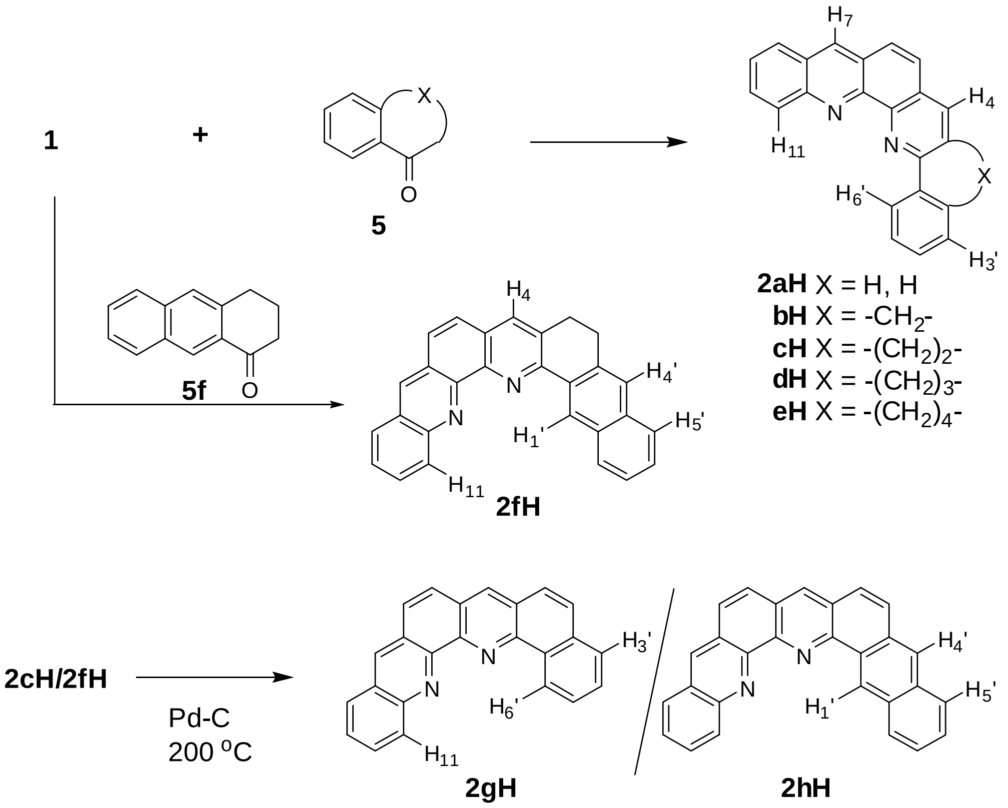
3H X = H, H
4H X = -CH=CH-

As a part of our interest in the design and synthesis of new polydentates, especially *N*,*N*,*C*-terdentates, we herein described the synthesis and properties of 3,2’-polymethylene-2-phenylbenzo[*b*]-1,10-phenanthrolines and related compounds, in which the dihedral angles between the two aromatic rings, benzo[*b*]-1,10-phenanthroline and phenyl, were controlled in a regular fashion depending on the length of the bridge methylene units.[6]

RESULTS AND DISCUSSION

Friedländer condensation of 4-aminoacridine-3-carbaldehyde (**1**) and benzo[*b*]cycloalkanones (**5**) afforded a series of 3,2’-polymethylene-2-phenylbenzo[*b*]-1,10-phenanthrolines (**2b-eH**) in 60-75% yields. Similarly, reaction of **1** with 3,4-dihydro-1(2*H*)-anthracenone (**5f**)[7] afforded **2fH** as a benzo-analogue of **2cH** in 76% yield. Dehydrogenation of **2cH** and **2fH** with 10% Pd-C at 200 °C for 20 h[8] afforded the corresponding fully aromatized **2gH** and **2hH** in 98% and 96% yield, respectively.

Each proton resonance was well resolved enough to be assigned by comparing previously reported data on the related compounds such as 2-phenylbenzo[*b*]-1,10-phenanthroline[1] and 3,2’-polymethylene-2-phenylpyridines,[3b] Modern NMR techniques such as a COSY and DEPT study were employed for confirming each resonance and results are summarized in Table 1.



Two trends are worthy to note for the structural information. ^{13}C NMR of **2eH** showed 26 carbon resonances, of which DEPT (θ = 135°) study showed twelve CH and ten quaternary carbons in the aromatic region and four CH_2 carbons in the aliphatic region that confirmed a single component in 62.5 MHz ^{13}C NMR scale. ^{1}H NMR of **2eH**, however, showed two one-proton doublets of doublets at δ 2.97 (J = 13.4, 8.1 Hz) and δ 2.75 (J = 13.4, 8.1 Hz), and four multiplets for 6 protons in the aliphatic region. This implies that the tetramethylene bridge of **2eH** is rigid enough to differentiate all eight protons in NMR time scale at room temperature. However, the bridges of **2cH** and **2dH** showed two triplets for **2cH**, and two triplets and a quintet for **2dH** implying that the di- and trimethylene-bridges are flexible. In addition, a methylene bridge of **2bH** showed a two-proton singlet at δ 2.29 (δ 29.68 for ^{13}C).

Table 1. 250 MHz ^{1}H NMR Data for Selected Protons of **2H**

Compound	H7	H8	H11	H3’	H5’	H6’
2aH	8.76	8.04	8.63	7.55	7.55	8.41
2bH	8.79	8.08	8.63	7.40	7.44	8.37
2cH	8.73	8.26	8.72	7.27	7.51	8.62
2dH	8.75	8.05	8.62	7.25	7.50	8.19
2eH	8.74	7.81[a]	8.56	7.25	7.39	8.03
2fH	8.72	8.14	8.68	-	7.69	9.45[b]
2gH	8.74	8.08	8.72	7.93	7.93	9.95
2hH	8.798	8.45	8.801	-	7.96	10.42[b]

[a]Overlapped with H10. [b]Resonance of H1’.

Chemical shift of H6’ (H1’ of **2fH** and **2hH**) is the most sensitive probe for the conformational information of **2H**. H6’ of the more planar **2cH** and H1’ of **2fH** were resonanced at δ 8.62 and 9.45, thus downfield-shifted by 0.21 and 1.04 ppm, respectively, compared to the value of the unbridged parent system **2aH**. Such shift could be explained by the planarity of the ligands in which H6’ of the more planar **2cH** would position toward the deshielding region of the central and distal pyridine rings. In addition to such deshielding effect, aromatic character of **2gH** and **2hH** would lead the resonance of corresponding H’s being dramatically down-field shifted to δ 9.95 and 10.42, respectively. On the other hand, H6’ of the least planar **2eH** would lie out of such deshielding region as been reported previously for the annulated ligands [3b,4,6] was resonanced at δ 8.03 being upfield-shifted by 0.39 ppm. However, the resonances of H7 are not affected by either the length of bridge or benzo-annulation and appeared constantly in the region of δ 8.72-8.798.

In addition, a monotonic decrease in their melting points, **2bH** [280 °C (decomp)], **2cH** (272-274 °C), **2dH** (120-122 °C), and **2eH** (114-115 °C) may reflect the increasing nonplanarity of these homologues as have been previously observed.[9] Chemical shift of H6'(H2') (δ 8.41) and melting point of **2aH** (218-219 °C) may afford information for the geometry. The values were in between **2cH** and **2dH**, as previously reported in related systems such as 3,2'-polymethylene-2-phenylpyridines[3b] and 3,2'-polymethylene-6-(pyrid-2"-yl)-2-phenylpyridines,[4b] thus implying that the dihedral angle of the most stable conformation of **2aH** in solid as well as in solution is in between 20-55°.

UV absorption spectra of **2H** were taken from 95% EtOH (5 x 10^{-3} mM) and are summarized in Table 2. Three major absorption maxima originated from the π-π^* transition were observed in the region of 243-262, 313-327, and 355-368 nm. The absorption maximum in the region of 313-327 nm increases in energy and decreases in intensity as the length of the bridge 3,2'-polymethylene bridge increases. Such trend reflects a decrease in the electronic interaction between the two aromatic halves of the molecule as the dihedral angle between them increases. Those of the planar and fully conjugated ligands **2gH** and **2hH** were split to two absorption bands at 314 and 326 nm, and 320 and 339 nm, respectively, which reflected the delocalization of the electrons.

Table 2. UV-Visible Absorption Spectral Data for **2H** (95% EtOH)

Compounds	λ_{max} nm (ε, $cm^{-1}M^{-1}$)				
2aH	254 (51,600)	316 (34,300)	357 (8,100)		
2bH	257 (52,600)	273 (31,900, sh)	327 (58,300)	364 (12,900, sh)	
2cH	257 (56,500)	274 (31,300, sh)	327 (61,900)	366 (12,400, sh)	
2dH	255 (57,100)	269 (40,700, sh)	313 (56,000)	368 (6,800, sh)	
2eH	255 (54,600)	268 (41,200, sh)	312 (53,600)	367 (6,900, sh)	
2fH	255 (54,000)	273 (40,000, sh)	293 (26,000)	337 (32,400)	370 (14,000, sh)
2gH	243 (48,000)	262 (27,100)	287 (22,900)	314 (39,100)	326 (53,300)
	354 (24,000)	375 (9,200)	395 (2,600)		
2hH	247 (62,000)	320 (38,300)	339 (38,800)	377 (11,800)	409 (5,800)
	432 (3,900)				

In conclusion, a series of 3,2'-polymethylene-2-phenylbenzo[*b*]-1,10-phenanthrolines and 3,3'-dimethylene-2-(naphth-2'-yl)benzo[*b*]-1,10-phenanthroline were prepared by Friedländer reactions of 4-aminoacridine-3-carbaldehyde and benzo[*b*]cycloalkanones and 3,4-dihydro-1(2*H*)-anthracenone. The tetramethylene-bridge of 3,2'-tetramethylene-2-phenylbenzo[*b*]-1,10-phenanthroline is rigid enough to magnetically differentiate all the eight protons at room temperature in NMR time scale. Dehydrogenation of 3,2'-dimethylene-bridged compounds (**2cH** and **2fH**) with 10% Pd-C afforded the corresponding fully aromatized ligand in 98% and 96% yield, respectively. Studies on the metal complexes of the ligands and their properties are ongoing and results will be reported in due course.

EXPERIMENTAL

Melting points were determined using a Fischer-Jones melting points apparatus and are not corrected. IR spectra were obtained using a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained using a Bruker-250 spectrometer 250 MHz for ^{1}H NMR and 62.5 MHz for ^{13}C NMR and are reported as ppm from the internal standard TMS. Chemicals and solvents were commercial reagent grade and used without further purification. The starting 4-aminoacridine-3-carbaldehyde,[1] 2-phenylbenzo[*b*]-1,10-phenanthroline,[1] and 3,4-dihydro-1(2*H*)-anthracenone[7] were prepared by employing previously reported methods. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on a LCQ advantage-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). Elemental analyses were taken on a Hewlett-Packard Model 185B elemental analyzer.

3,2'-Methylene-2-phenylbenzo[*b*]-1,10-phenanthroline (2bH) (General procedure) A mixture of 4-aminoacridine-3-carbaldehyde (180 mg, 0.81 mmol) and 1-indanone (107 mg, 0.81 mmol) in absolute EtOH (20 mL) with saturated ethanolic KOH (1.5 mL) was refluxed for 12 h. The solvent was removed under reduced pressure and resulting brown solid was chromatographed on silica gel, eluting with CH_2Cl_2/EtOAc (1:1) and EtOAc. The latter fractions of EtOAc afforded pale yellow solid which was chromatographed on silica gel eluting with 1% MeOH in CH_2Cl_2 to give 172 mg (67%) of pale yellow needles after recrystallization from $CHCl_3$: mp 280 °C (decomp.). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.79 (s, 1H, H7), 8.63 (d, 1H, *J* = 8.6 Hz, H11), 8.37 (d, 1H, *J* = 7.5 Hz, H6'), 8.24 (s, 1H, H4), 8.08 (d, 1H, *J* = 8.4 Hz, H8), 7.89 (t, 1H, *J* = 7.0 Hz, H10), 7.87 (d, 1H, *J* = 9.0 Hz, H6/H5), 7.71 (d, 1H, *J* = 9.2 Hz, H5/H6), 7.66 (t, 1H, *J* = 8.0 Hz, H9), 7.44 (td, 1H, *J* = 7.1, 1.2 Hz, H5'), 7.40 (d, 1H, *J* = 7.0 Hz, H3'), 7.35 (t, 1H, *J* = 7.5 Hz, H4'), 2.36-2.22 (m, 2H). ^{13}C NMR ($CDCl_3$ 62.5 MHz) δ 149.91, 148.73, 143.91, 136.66, 136.31, 135.61, 131.87, 131.48, 131.03, 130.03, 130.58, 129.14, 127.66, 127.46, 126.74, 124.07, 125.23, 29.68. *Anal* Calcd. for $C_{23}H_{14}N_2{\cdot}H_2O$: C, 82.12; H, 4.79; N, 8.33. Found: C, 82.20; H, 4.82; N, 8.33.

3,2'-Dimethylene-2-phenylbenzo[*b*]-1,10-phenanthroline (2cH) Yield (60%): mp 272-274 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.98 (d, 1H, *J* = 7.3 Hz, H11), 8.73 (s, 1H, H7), 8.62 (d, 1H, *J* = 8.5 Hz, H6'), 8.05 (d, 1H, *J* = 8.3 Hz, H8), 7.99 (s, 1H, H4), 7.86 (ddd, 1H, *J* = 8.3, 7.0, 1.2 Hz, H10), 7.82 (d, 1H, *J* = 9.0 Hz, H6), 7.64 (d, 1H, *J* = 9.2 Hz, H5), 7.63 (t, 1H, *J* = 8.0 Hz, H9), 7.51 (td, 1H, *J* = 7.1, 1.2 Hz, H5'), 7.38 (td, 1H, *J* = 8.0, 1.5 Hz, H4'), 7.27 (d, 1H, *J* = 8.5 Hz, H3'), 3.21 (t, 2H, J = 7.3 Hz), 3.05 (t, H, J =

7.3 Hz). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 152.98, 148.38, 147.26, 145.51, 138.69, 135.73, 134.72, 134.62, 132.96, 131.03, 129.89, 129.63, 128.70, 127.66, 127.59, 127.34, 127.22, 127.05, 126.82, 126.55 (two C's), 125.82, 28.64, 28.14. *Anal* Calcd. for $C_{24}H_{16}N_2$•$0.5H_2O$: C, 84.43; H, 5.02; N, 8.21. Found: C, 84.42; H, 5.04; N, 8.23.

3,2'-Trimethylene-2-phenylbenzo[*b*]-1,10-phenanthroline (2dH) Yield (69%): mp 124-125 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.75 (s, 1H, H7), 8.62 (d, 1H, *J* = 8.8 Hz, H11), 8.19 (dd, 1H, *J* = 8.1, 1.3 Hz, H6'), 8.05 (d, 1H, *J* = 7.5Hz, H8), 8.03 (s, 1H, H4), 7.85 (d, 1H, *J* = 9.0 Hz, H6), 7.83 (ddd, 1H, *J* = 8.3, 7.0, 1.2 Hz, H10), 7.70 (d, 1H, *J* = 9.0 Hz, H5), 7.62 (ddd, 1H, *J* = 8.0, 7.5 , 1.2 Hz, H9), 7.50 (td, 1H, *J* = 7.5, 1.2 Hz, H5'), 7.40 (td, 1H, *J* = 8.0, 1.5 Hz, H4'), 7.25 (d, 1H, *J* = 7.5 Hz, H3'), 2.77 (t, 2H, *J* = 7.0 Hz), 2.60 (t, 2H, *J* = 7.0 Hz), 2.31 (quintet, 2H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 159.45, 148.38, 147.31, 145.43, 140.48, 139.38, 135.95, 135.74, 135.42, 131.05, 130.02, 129.83, 129.10, 128.51, 128.24, 127.56, 127.23, 126.91, 126.81, 126.75, 126.54, 125.79, 32.55, 31,01, 30.65. *Anal* Calcd. for $C_{25}H_{18}N_2$•$0.5H_2O$: C, 84.48; H, 5.39; N, 7.88. Found: C, 84.50; H, 5.40; N, 7.83.

3,2'-Tetramethylene-2-phenylbenzo[*b*]-1,10-phenanthroline (2eH) Yield (75%): mp 114-115 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.74 (s, 1H, H7), 8.56 (d, 1H, *J* = 8.5 Hz, H11), 8.07 (s, 1H, H4), 8.03 (d, 1H, *J* = 8.5 Hz, H6'), 7.85 (d, 1H, *J* = 9.0 Hz, H6), 7.81-7.77 (m, 2H, H8 and H10), 7.70 (d, 1H, *J* = 9.2 Hz, H5), 7.60 (td, 1H, *J* = 8.0, 1.2 Hz, H9), 7.39 (overlapped td, 2H, *J* = 7.5, 1.2 Hz, H5' and H4'), 7.25 (dd, 1H, *J* = 8.0, 1.5 Hz, H3'), 2.97 (dd, 1H, *J* = 13.4, 8.1 Hz), 2.75 (dd, 1H, *J* = 13.5, 8.0 Hz), 2.50-2.40 (m, 1H), 2.36-2.20 (m, 2H), 2.15-2.07 (m, 1H), 1.74-1.61 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 159.15, 148.31, 147.30, 144.78, 142.54, 139.60, 139.14, 136.36, 135.81, 131.07, 129.97, 129.76, 129.28, 129.00, 128.95, 127.52, 127.23, 126.83, 126.79, 126.54, 125.81, 125.77, 32.61, 32.13, 30.35, 29.10. *Anal* Calcd. for $C_{26}H_{20}N_2$•H_2O: C, 82.51; H, 5.86; N, 7.40. Found: C, 82.52; H, 5.87; N, 7.43.

3,3'-Dimethylene-2-(naphth-2'-yl)benzo[*b*]-1,10-phenanthroline (2fH) Yield (42%): mp 276 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 9.45 (s, H1'). 8.72 (s, 1H, H7), 8.68 (d, 1H, *J* = 8.5 Hz, H11), 8.14 (dd, 1H, *J* = 8.5, 1.0 Hz, H8), 8.01 (t, 1H, *J* = 8.5 Hz, H10), 8.01 (s, 1H, H4), 7.87 (ddd, 1H, *J* = 8.5, 7.8, .08 Hz, H9), 7.80 (d, 1H, *J* = 9.0 Hz, H5/H6), 7.79 (s, 1H, H4'), 7.69-7.60 (m, 3H), 7.50-7.46 (m, 2H), 3.22 (br s, 4H). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 153.04, 148.40, 147.21, 145.69, 136.08, 135.83, 134.91, 134.09, 133.98, 132.99, 132.73, 130.99, 129.96, 129.33, 128.79, 127.60, 127.23, 126.99, 126.87, 126.72 (two C's), 126.63 (two C's), 125.82, 125.63, 125.52, 29.00, 28.82. Mass (ESI) calcd. for $C_{28}H_{19}N_2$ $[M+H]^+$ 383, found 383. *Anal* Calcd. for $C_{28}H_{18}N_2$•$0.75H_2O$: C, 84.93; H, 4.96; N, 7.07. Found: C, 84.92; H, 5.02; N, 7.05.

Benzo[*b*]naphtho[2,1-*j*]-1,10-phenanthroline (2gH) A mixture of **2cH** (33.2 mg, 0.1 mmol) and 10% Pd-C (33.2 mg, 100 wt. %) in 5 mL of nitrobenzene was heated at 200 °C for 20 h. Resulting reaction mixture was cooled to rt and filtered through Celite. Resulting crude product was chromatographed on silica gel eluting with CH_2Cl_2. The latter fractions [R_f = 0.1 (CH_2Cl_2)] afforded 32 mg (98%) of pale yellow solid: mp 260 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.95 (d, 1H, *J* = 7.8 Hz, H6'), 8.74(s, 1H, H7), 8.72 (d, 1H, *J* = 8.4 Hz, H11), 8.66 (s, 1H, H4), 8.08 (d, 1H, *J* = 8.4 Hz, H8), 7.95 (t, 1H, *J* = 8.4 Hz, H10), 7.93-7.87 (m, 4H, H5, H6, H3', H5'), 7.86-7.82 (AB quartet, 2H, H7' and H8'), 7.78 (td, 1H, *J* = 7.8, 1.2 Hz, H4'), 7.68 (t, 1H, *J* = 7.5 Hz, H9). ^{13}H NMR ($CDCl_3$, 62.5 MHz) δ 148.27, 147.62, 146.69, 145.96, 135.65, 135.03, 133.81, 131.86, 131.22, 129.97, 129.05, 128.92, 127.97, 127.74, 127.59, 127.52, 127.30, 127.24, 126.98, 126.73, 126.44 (two C's), 126.36, 125.05. Mass (ESI) calcd. for $C_{24}H_{14}N_2$ $[M+H]^+$ 331, found 331. *Anal* Calcd. for $C_{24}H_{14}N_2$•$0.5H_2O$: C, 84.93; H, 4.45; N, 8.25. Found: C, 85.00; H, 4.44; N, 8.23.

Benzo[*b*]anthraceno[2,1-*j*]-1,10-phenanthroline (2hH) The same procedure described for **2gH** was employed with **2fH** (38.2 mg, 0.1 mmol) afforded 36 mg (96%) of pale yellow solid: mp 310 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 10.42 (s, 1H, H1'), 8.801 (d, 1H, *J* = 8.4 Hz, H11), 8.798 (s, 1H, H7), 8.62 (s, 1H, H4), 8.45 (dd, 1H, J = 8.4, 1.0 Hz, H8), 8.41 (s, 1H, H4'), 8.11 (overlapped d, 2H, *J* = 8.4 Hz), 7.96-7.92 (m, 2H), 7.90-7.84 (AB quartet, 2H), 7.76 (d, 1H, *J* = 9.0 Hz), 7.72 (d, 1H, *J* = 9.0 Hz), 7.65-7.62 (m, 2H). Mass (ESI) calcd. for $C_{28}H_{16}N_2$ $[M+H]^+$ 381, found 381. *Anal* Calcd. for $C_{28}H_{16}N_2$•H_2O: C, 84.40; H, 4.55; N, 7.03. Found: C, 84.50; H, 4.54; N, 7.00.

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6. Dihedral angles between benzo[*b*]-1,10-phenanthroline and phenyl ring are 0°, 20° (15°), 55° (49°), and 80° (59°), for **2aH**, **2bH**, **2cH**, **2dH**, and **2eH**, respectively, measured from Dreiding and Fieser Models. The values in parenthesis are calculated from CS Chem Draw.
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