Inorganica Chimica Acta 362 (2009) 3872–3876

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Note

Structure and photophysics of a Schiff base-bipyridine ligand and its rhenium(I) tricarbonylchloro complex

Tenzing Doleck [a], Jonathan Attard [a], Frank R. Fronczek [b], Amy Moskun [a], Ralph Isovitsch [a,*]

[a] *Department of Chemistry, Whittier College, 13406 Philadelphia Street, Whittier, CA 90608, United States*
[b] *Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States*

ARTICLE INFO

Article history:
Received 16 January 2009
Received in revised form 7 April 2009
Accepted 17 April 2009
Available online 3 May 2009

Keywords:
X-ray crystal structure
Rhenium(I) tricarbonylchloro
Schiff base
Bipyridine
Photophysics

ABSTRACT

A new Schiff base-bipyridine ligand, [4-(4′-methyl)-2,2′-bipyridyl)imine]-2-hydroxybenzene, was prepared, characterized and its X-ray crystal structure obtained. The rhenium(I) tricarbonylchloro complex of this novel derivative of 2,2′-bipyridine was also prepared and characterized. The photophysics of both of these compounds were explored. The absorption spectrum of the Schiff base in acetonitrile possessed bipyridine based $\pi \rightarrow \pi^*$ transitions at 246 and 278 nm along with a phenolic charge transfer absorption at 360 nm. Acetonitrile solutions of this compound were found to be luminescent at room temperature with an emission maximum at 435 nm. The rhenium(I) metal complex prepared from the Schiff base exhibited wavelength dependent metal-centered and ligand-centered emission at wavelengths shorter than the analogous rhenium(I) compound prepared from 4′-formyl-4-methyl-2,2′-bipyridine.

1. Introduction

The 2,2′-bipyridine ligand is extensively used in coordination chemistry because it produces metal complexes of noted thermal and kinetic stability [1]. Such metal complexes often possess useful photophysical and electrochemical characteristics, which arise from the interaction of the orbitals of the metal and a 2,2′-bipyridine ligand. Much work has focused on changing the functionality of the 2,2′-bipyridine ligand toward the end of predictably altering the electronic properties of metal complexes that are prepared from them [2]. The above-mentioned properties make 2,2′-bipyridine metal complexes versatile molecules that have been used in areas ranging from photocatalytic CO_2 reduction to metal–organic polymers [3,4]. Of particular interest are rhenium(I) chlorotricarbonyl complexes possessing a 2,2′-bipyridine ligand because of their applicability to materials synthesis and biomedical sensing [5–8].

Our research involves the synthesis of Schiff base ligands and the preparation of photophysically interesting metal complexes from them with the aim of applying them toward the construction of novel materials. Toward that end, we report the synthesis, structural characterization and photophysics of a unique Schiff base derivative of 2,2′-bipyridine, [4-(4′-methyl)-2,2′-bipyridyl)imine]-2-hydroxybenzene, which possesses metal binding moieties that are positioned for formation of metal–organic oligomers. The rhenium(I) tricarbonylchloro complex of this new Schiff base was synthesized and its structure and photophysics defined. The known compounds 4′-formyl-4-methyl-2,2′-bipyridine and its rhenium(I) tricarbonylchloro complex were also prepared and their photophysics explored for the first time. The new Schiff base and its rhenium(I) tricarbonylchloro complex were found to emit more intensely and at shorter wavelengths than 4′-formyl-4-methyl-2,2′-bipyridine and its rhenium(I) tricarbonylchloro complex. Both of the rhenium(I) tricarbonylchloro complexes discussed here emit at longer wavelengths than the prototypical rhenium(I) tricarbonylchloro diimine complex prepared from 2,2′-bipyridine [9].

2. Results and discussion

2.1. Synthesis and characterization of the ligands

Compound **1**, 4′-formyl-4-methyl-2,2′-bipyridine, which is prepared by SeO_2 oxidation of 4,4′-dimethyl-2,2′-bipyridine, is a versatile synthon for numerous bipyridine derivatives [10,11]. Scheme 1 illustrates the condensation reaction between **1** and 2-aminophenol performed under anhydrous conditions that resulted in the formation of **2**. Slow evaporation of the condensation reaction mixture gave analytically pure **2** as an orange–yellow microcrystalline solid in 53% yield.

The spectra of **2** had the expected characteristics of a hydroxyimine-bipyridine type compound. The IR spectrum of **2** featured a band at 1597 cm^{-1} attributable to the C=N stretching mode of the imine. Proton resonances for HC=N and OH were observed in

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* Corresponding author. Tel.: +1 5629074200x4499; fax: +1 5624644591.
E-mail address: risovits@whittier.edu (R. Isovitsch).

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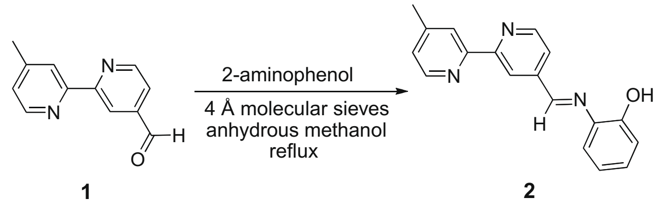
doi:10.1016/j.ica.2009.04.034



Scheme 1.

the ^{1}H NMR spectrum, while the HC=N carbon resonance was observed at 157.4 ppm in the ^{13}C NMR spectrum [12]. The elemental analysis of **2** gave acceptable C, H and N values. The structure of **2** is also supported by the HRESI-MS, which has a $[M+H]^+$ peak at $m/z = 290.1278$ (calculated mass for $[M+H]^+$ $m/z = 290.1293$). These key indicators support the formation of **2** as a pure compound.

2.2. X-ray crystal structure of 2

The structure of **2** was determined by X-ray diffraction and is shown in Fig. 1. A crystal of the required quality was grown by the slow evaporation of the reaction mixture. Selected bond lengths and angles are listed in the caption of Fig. 1; crystallographic data are presented in Section 4.

Compound **2** crystallized in the orthorhombic space group *Pbca*. The bipyridine rings were found to adopt an essentially planar, transoid arrangement due to repulsion between hydrogen atoms and steric repulsion between groups at the 4 and 4′-positions. The phenyl ring was found to be twisted (C7–N1–C2–C1 −134.38° (10)), out of the plane of the bipyridine rings. The bond lengths comprising the imine linkage between the bipyridine moiety and the phenyl ring, C10–C7 and N1–C2, were found to be between those of a single and double bond. Overall bond distances and angles were found to correspond well with those of related compounds [13].

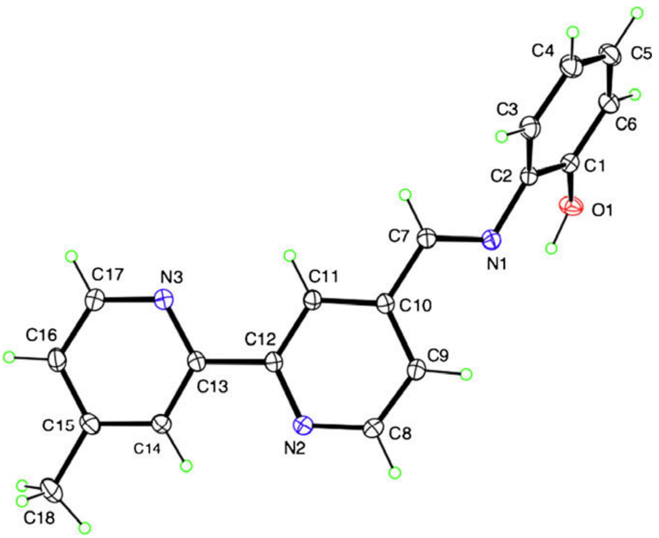


Fig. 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): C18–C15 1.5026(15), C15–C16 1.3947(15), C17–N3 1.3467(13), C13–C12 1.4951(14), C7–C10 1.4751(14), C7–N1 1.2794(13), N1–C2 1.4178(12), C2–C1 1.4093(14), C1–O1 1.3558(12), C1–C2–N1 117.61(9), N1–C7–C10 120.56(9), C2–N1–C7–C10 −178.39(10), C7–N1–C2–C1 −134.38(10).

2.3. Synthesis and characterization of the metal complexes

The rhenium(I) tricarbonylchloro compound **4** was prepared by combining equimolar portions of **2** and $Re(CO)_5Cl$ in benzene [14]. Compound **4**, which readily precipitated from its reaction mixture, was filtered from the hot reaction mixture and then washed with several portions of hot benzene to remove residual **2**. Compound **4** was isolated as a mustard yellow solid in 64% yield. Complex **3**, which is the rhenium(I) tricarbonylchloro compound of **1**, was prepared in the manner of Gholamkhass and coworkers [2].

The IR spectrum of **4** had the three carbonyl bands that are characteristic of rhenium(I) tricarbonylchloro bipyridine metal complexes at 2020, 1913 and 1887 cm^{-1}. The ^{1}H NMR spectrum of **4** showed a general downfield shift of proton resonances when compared to **2**. The identification of **4** is supported by an elemental analysis and a HRESI-MS which had a prominent $[M-Cl]^+$ peak at $m/z = 560.0611$ (calculated mass for $[M-Cl]^+$ $m/z = 560.0620$). The low solubility of the metal complex prohibited the acquisition of an acceptable ^{13}C NMR spectrum. Spectra of **4** corresponded to those found in the literature [2].

2.4. Photophysical characterization

Table 1 summarizes acetonitrile solution absorption and emission data for compounds **1**–**5**. The absorption spectrum of **1** possesses bands characteristic of bipyridine $\pi \rightarrow \pi^*$ transitions at 279 and 308 nm [15]. Dilute acetonitrile solutions ($\sim 1.1 \times 10^{-5}$ M) of **1** excited at 279 nm were weakly emissive at room temperature with a broad, featureless maximum at 465 nm.

The absorption spectrum of compound **2**, shown in Fig. 3, had bipyridine $\pi \rightarrow \pi^*$ absorptions at 246 and 278 nm along with a unique absorption at 360 nm, which was assigned to a phenolic charge transfer transition on the hydroxyimino moiety of **2** [15,16]. Acetonitrile solution and solid state room temperature emission spectra of **2** are also shown in Fig. 3. Excitation of dilute acetonitrile solutions ($\sim 4.6 \times 10^{-4}$ M) of **2** at 360 nm resulted in emission with a maximum at 435 nm and poorly resolved fine structure at longer wavelengths [17]. This fine structure is more clearly resolved in the solid state emission spectrum of **2**.

Prominent features in the absorption spectrum of compound **4** in acetonitrile, which is shown in Fig. 4, include bipyridine $\pi \rightarrow \pi^*$ transitions at 258 and 295 nm, and an MLCT observed at 400 nm. The absorption bands of **4** are characteristic of similar compounds with the only difference being that its MLCT is more intense [9,15].

Table 1
Acetonitrile solution absorption and emission data for compounds **1-5**.

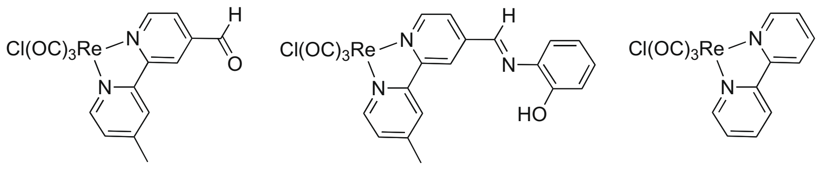
Compound	Absorption wavelength λ_{max} nm (ε)[a]	Emission wavelength λ_{max} nm (λ_{ex} nm)
1	225 (22 300) 279 (10 700) 308 (6220)	465 (279)
2	246 (22 800) 278 (20 900) 360 (11 000)	435 (360) 449[b] 466[b]
3	246 (21 100) 310 (11 100) 402 (4050)	550 (254) 550, 730[c] (400) 730[c] (450)
4	258 (22 600) 295 (18 800) 400 (15 600)	500, 655 (400) 630 (345) 655 (258)
5[d]	370 (3420)	622

[a] Extinction coefficient units M^{-1} cm^{-1}.

[b] Vibrational structure maxima.

[c] An approximated value at the less sensitive red end of the R928P photomultiplier tube.

[d] See Ref. [9].



3 **4** **5**

Fig. 2. The rhenium(I) tricarbonylchloro complexes prepared from **1** and **2** and Re(CO)3(bpy)(Cl), compound **5**.

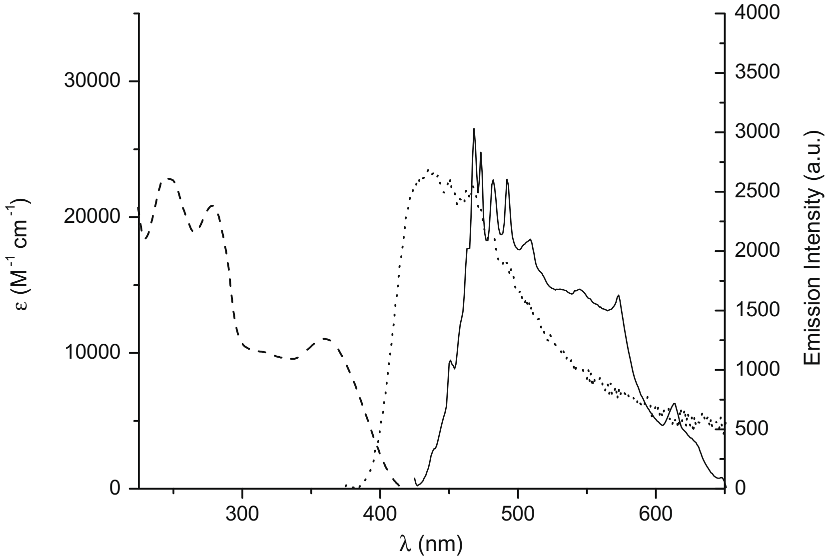


Fig. 3. Electronic absorption and emission spectra of compound **2**. (———) absorption spectrum in acetonitrile, (••••) room temperature emission spectrum in acetonitrile (λ_{exc} = 360 nm), (—) room temperature solid state emission spectrum (λ_{exc} = 360 nm).

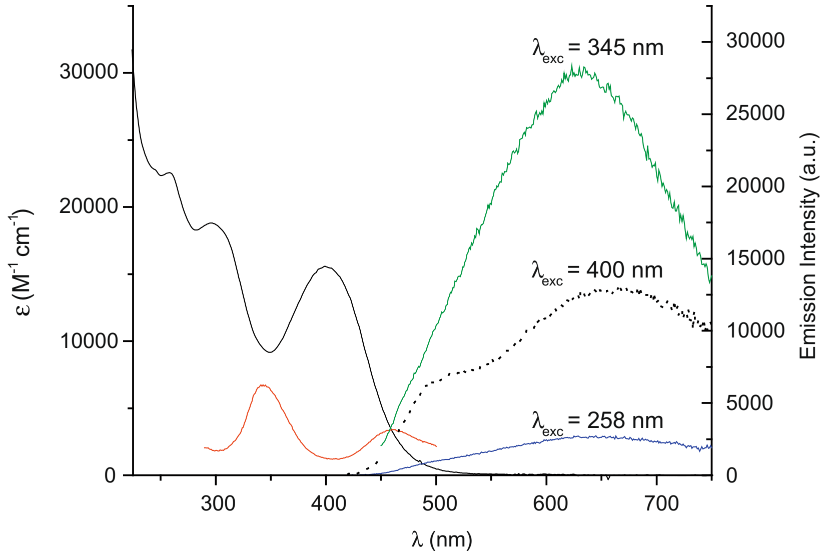


Fig. 4. Electronic absorption and emission spectra of compound **4** in acetonitrile. (—) Absorption spectrum, (——) room temperature excitation spectrum (λ_{obs} = 625 nm), (——) room temperature emission spectrum (λ_{exc} = 258 nm), (......) room temperature emission spectrum (λ_{exc} = 400 nm), (——) room temperature emission spectrum (λ_{exc} = 345 nm).

Excitation of compound **4** in its different absorption bands lead to the observation of dual metal-centered and ligand-centered emission bands as shown in Fig. 4. Such dual emission is not common, but examples have been documented [18–20]. For example, excitation at 400 nm led to the observation of emission with maxima at 500 nm (ligand-centered) and 655 nm (metal-centered). The metal-centered emission is similar to other Re(I) tricarbonylchloro diimine complexes [9,21].

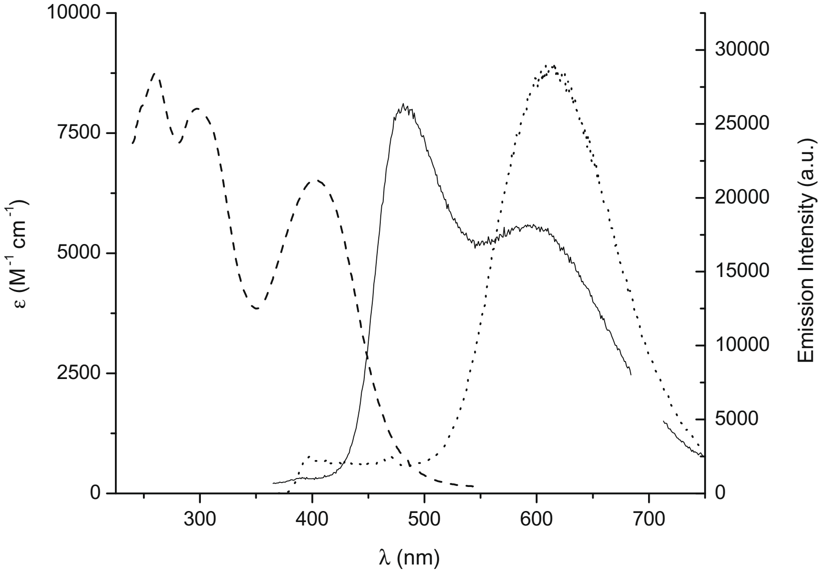


Fig. 5. Electronic absorption and emission spectra of compound **4**. (———) absorption spectrum in propionitrile (—), room temperature emission spectrum in propionitrile (λ_{exc} = 350 nm), (●●●●) emission spectrum in propionitrile glass at 77 K (λ_{exc} = 350 nm).

Excitation scans in both emission bands of **4** revealed a highly emissive absorption feature at 345 nm. This feature dominates excitation spectral probing below 550 nm and is not directly observed in the absorption spectrum of **4**. It resembles the phenolic charge transfer observed at 360 nm in the absorption spectrum of **2**, which can be seen in Fig. 3. Excitation of **4** at 345 nm produced intense metal-centered emission at 630 nm that was approximately five times more intense than emission that resulted from excitation into any other absorption band.

The low temperature emission properties of **4** were investigated in propionitrile glass. Fig. 5 shows the absorption and emission spectra of **4** in propionitrile solution at room temperature and the emission spectrum in propionitrile glass at 77 K. The absorption spectrum in is essentially the same as in acetonitrile with maxima at 260, 298 and 404 nm. Excitation of a dilute solution (~3.0×10^{-4} M) of **4** at 350 nm resulted in the observation of the dual ligand- and metal-centered emission observed when **4** is dissolved in acetonitrile. The dual emission was shifted to shorter wavelengths and was relatively more intense as compared to **4** in acetonitrile, with maxima at 482 and 598 nm, respectively. In a proprionitrile glass at 77 K, the emission spectrum of **4** had one shifted maximum at 612 nm that we attribute to the ligand-centered emission [18].

Acetonitrile solutions of compound **3** had absorptions similar to those of **4** in that they exhibited absorptions at 246 and 310 nm, which were assigned as bipyridine $\pi \rightarrow \pi^*$ transitions. The MLCT was observed at 402 nm. Dilute acetontitrile solutions (~1.6×10^{-4} M) of **3** exhibited dual luminescence with ligand-centered and metal-centered transitions. Excitation of **3** at 254 nm produced ligand-centered emission at 550 nm, while excitation in the red-edge of the MLCT produced metal-centered emission at approximately 730 nm. Excitation of **3** at 400 nm, the center of the MLCT absorption, resulted in dual ligand-centered and metal-centered emission at 550 nm and approximately 730 nm, respectively.

3. Conclusions

The novel Schiff base compound **2** and its rhenium(I) tricarbonylchloro compound **4** were prepared and structurally characterized. Acetonitrile solutions of these compounds were found to luminescent at room temperature, with **4** exhibiting both ligand-centered and metal-centered emission that was excitation wavelength dependent. The excitation spectrum of compound **4**, observing in both of its emission bands, revealed a phenolic ligand-centered charge transfer absorption that, when irradiated, was very efficient in inducing metal-centered luminescence. The known compounds **1** and **3** were prepared and their photochemistry explored for the first time. Acetonitrile solution of both were weakly luminescent at room temperature. Compound **3** exhibited similar excitation wavelength dependent dual ligand-centered and metal-centered luminescence that compound **4** did. The room temperature emission of **1** and **3** is comparatively weaker and at longer wavelengths than that of **2** and **4**. The rhenium(I) tricarbonylchloro compounds that were discussed in this work emit at longer wavelengths than compound **5** [9] (Fig. 2).

4. Experimental

4.1. General methods

All manipulations were carried out under an atmosphere of argon using standard techniques. Reagents and anhydrous solvents were used as received. Compound **3** was prepared utilizing the literature procedure. Melting points were determined in open capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra were acquired on a Joel ECX 300 MHz spectrometer using TMS as the internal standard. IR spectra were recorded as KCl disks on a JASCO 460 FT-IR. Elemental analyses were performed by M–H–W Laboratories of Tucson Arizona. Mass spectrometry was provided by the Washington University Mass Spectrometry Resource with support from the NIH National Center for Research Resources (Grant No. P41RR0954).

4.2. Photochemical measurements

Emission and absorption spectra were recorded at room temperature in spectrophotometric grade acetonitrile and propionitrile utilizing a Horiba Jobin Yvon FluoroMax-4 fluorometer and a Hewlett Packard 8453 diode array spectrometer. All solutions were degassed with argon prior to luminescence measurements. All emission spectra were corrected for detector response utilizing a correction curve supplied by the fluorometer manufacturer. Emission maxima observed at greater than 700 nm are at the less sensitive, red end of the R928P photomulitplier tube that is in our fluorometer and are thus approximated.

*4.3. Synthesis of **2***

4′-Formyl-4-methyl-2,2′-bipyridine **1** (0.189 g, 0.959 mmol) and 2-aminophenol (0.105 g, 0.959 mmol) were added to anhydrous methanol (25 mL) with anhydrous 4 Å molecular sieves. The reaction was refluxed overnight (under a drying tower). The reaction mixture was filtered hot and allowed to slowly evaporate which gave **2** [0.145 g (53%)] as yellow–orange microcrystals. m.p. 179 °C. *Anal.* Calc. for $C_{18}H_{15}N_3O$: C, 74.71; H, 5.24; N, 14.53. Found: C, 74.72; H, 5.14; N 14.51%. IR (KBr disk) 3401, 3063, 1597 cm^{-1}. ^1H NMR (300 MHz, acetone-*d*6): 2.45 (s, 3H), 6.94 (m, 2H), 7.26 (m, 2H), 7.51 (m, 1H), 8.06 (dd, 1H), 8.27 (s, 1H), 8.33 (m, 1H), 8.56 (d, 1H), 8.77 (d, 1H), 8.90 (m, 1H), 8.99 (s, 1H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): 21.0, 115.3, 116.2, 120.2, 120.3, 121.3, 121.9, 125.1, 130.2, 134.7, 143.50, 148.4, 149.1, 149.9, 153.0, 155.2, 155.4, 157.4 ppm. ESI-MS $[M+H]^+$ $m/z = 290.1278$. Calc. mass for $[M+H]^+$ $m/z = 290.1293$.

*4.4. Synthesis of **4***

0.050 g (0.173 mmol) of **2** was added to 0.057 g (0.157 mmol) of $Re(CO)_5Cl$ in 15 mL benzene. The mixture was refluxed for 1 h. The precipitate that formed was collected by vacuum filtration and washed with hot benzene several times to give analytically pure **3 [**0.057 g (64%)] as a mustard yellow powder. m.p. dec. >260 °C. *Anal.* Calc. for $C_{21}H_{15}N_3O_4ClRe$: C, 42.38; H, 2.52; N, 7.06. Found: C, 42.20; H, 2.75; N, 6.83%. IR (KCl disk) 2020, 1913, 1887 cm^{-1}. ^1H NMR (300 MHz, acetone-*d*6): 2.62 (s, 3H), 6.97 (m, 2H), 7.28 (m, 1H), 7.52 (dd, 1H), 7.62 (d, 1H), 8.23 (dd, 1H), 8.32 (s, 1H), 8.62 (s, 1H), 8.92 (d, 1H), 9.08 (s, 1H), 9.17 (d, 1H), 9.21 (s, 1H). ESI-MS $[M-Cl]^+$ $m/z = 560.0611$. Calc. mass for $[M-Cl]^+$ $m/z = 560.0620$.

4.5. Structure determination for 2

An X-ray quality crystal of **2** was used for data collection at $T = 90$ K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystems Cryostream chiller and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The θ range for data collection was 2.5–32.4°, yielding 98 009 data, of which 5461 were independent and 3841 had $I > 2\sigma(I)$. Structure solution was by direct methods, and all H atoms were visible in difference maps. The OH hydrogen atom position was refined, while others were placed in calculated positions, with a torsional parameter refined for the methyl group. *Crystal data:* $C_{18}H_{15}N_3O$, $M = 289.33$, orthorhombic, $a = 16.9331(14)$, $b = 7.5584(5)$, $c = 22.447(2)$ Å, $V = 2872.9(4)$ Å^3, $T = 90$ K, space group *Pbca*, $Z = 8$, $R_{int} = 0.026$, $R_1/wR_2 = 0.045/0.137$, Goodness-of-fit on $F^2 = 1.06$.

Acknowledgements

The authors would like to thank the Fletcher Jones Foundation for funds that allowed the purchase of the fluorometer. Whittier College is acknowledged for the funds that supported this research and provided summer support for Tenzing Doleck. Dr. Andrew Maverick is acknowledged for helpful discussion.

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