Syntheses and Fluorescence of Salicylaldimine Schiff Base Derivatives of 1,1'-Di(aminoethylaminocarbonylalkyl)-2,2'-biimidazole

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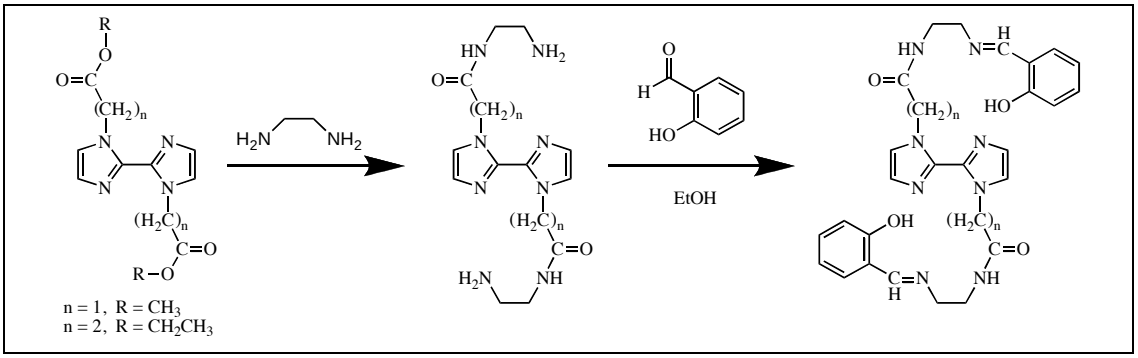

The amide-amine, 1,1'-di(aminoethylaminocarbonylethyl)-2,2'-biimidazole (DAEPB) (**1**), and subsequent Schiff base imine product, 1,1'-di(salicylaldiminoethylaminocarbonylethyl)-2,2'-biimidazole (DSEB) (**2a**), have been synthesized from the ester, 1,1'-di(ethoxycarbonylethyl)-2,2'-biimidazole (DEPB). Additionally, 1,1'-di(salicylaldiminoethylaminocarbonylmethyl)-2,2'-biimidazole (DSMB) (**2b**), was prepared from its corresponding amide-amine. All compounds were characterized with FTIR, NMR and elemental analyses. The salicylaldimines, compounds (**2a**) and (**2b**), exhibit fluorescence at 540 and 520 nm, respectively, over a broad range of excitation wavelengths.

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INTRODUCTION

Schiff base imines have been the focus of several investigations recently with facile preparation of a variety of acyclic and cyclic macromolecules and their transition metal ion complexes [1,2]. Imine macrocycles, possessing multidentate and polynuclear metal coordination sites, are of particular interest for their antifungal and antibacterial activity [1]. The macrocycles have been synthesized by reacting rigid aromatic dicarboxaldehydes and aliphatic diamines under high dilution conditions. Metal complexes of salicylaldimine derivatives having liquid crystalline properties have been prepared by reacting equimolar quantities of amine and aldehyde, yielding compounds exhibiting high birefringence, polarizability, paramagnetism and color [2].

Similarly, macromolecules containing 2,2'-biimidazole, including polymers [3-8] and macrocycles [9,10] have been described in efforts to explore relationships between structure, selective binding of metal ions, and thermal stability. Acyclic derivatives of 2,2'-biimidazole have been shown to exhibit cardiotonic [11] and antiprotozoal properties [12]. Over the past few years, new 1,1'-disubstituted-2,2'-biimidazole ester, amide-amine, and hydrazide macromolecules have been reported [13-16]. X-ray diffraction crystallography revealed these compounds assume a *trans* orientation in the crystalline state that may preclude single metal binding by both substituents.

The present study involves the synthesis of a pair of disalicylaldimines for use as macromolecular precursors for selective metal ion binding and macrocycle formation. During the course of the investigation, the compounds were observed to fluoresce brightly over a broad range of excitation wavelengths. Fluorescent compounds are of interest for their potential applications as light emitting diodes, photovoltaic devices, biological probes and sensors [17-19]. While fluorescence has been observed for 2,2'-biimidazole and a few of its derivatives [20-22], fluorescence of the biimidazole amide-amine precursors for the title compounds was not observed to an appreciable degree. However, fluorescence of salicyl-aldehyde is well known and occurs in the yellow-green region of the spectrum [25], precisely the region over which the title compounds fluoresce.

RESULTS AND DISCUSSION

The disalicylaldimines were prepared by reacting aliphatic amines with the aromatic aldehyde, salicylaldehyde. The rigidity afforded by the aldehyde is important for the chemical stabilization of the resulting

imine functional group [1]. Acid catalyst was unnecessary, as the relatively acidic proton of salicylaldehyde was sufficient for the reaction to proceed rapidly.

Solid-state fluorescence was observed for both compounds in their crystalline form. Both compounds exhibited fluorescence in the green-yellow visible region of the spectrum over a broad range of excitation wavelengths. DSEB (**2a**) and DSMB (**2b**) had emission maxima at 540 and 520 nm respectively (Figures 1 and 2). UV-visible absorption also occurred over a broad range, encompassing the excitation and remaining visible region. When melted into an amorphous mass, fluorescence was lost; however, after recrystallization, fluorescence was restored. The compounds exhibited fluorescence in suspension, but in solution, fluorescence was quenched. These observations suggest solid-state morphology is an important contributing factor for fluorescence.

NMR studies indicate intramolecular hydrogen bonding of the phenol proton as evidenced by the characteristic downfield location of its chemical shift. Several intramolecular hydrogen bonding interactions are possible for the disalicylaldimines (Scheme I.) Fluorescence of salicylaldehyde [25] and 2-(2-hydroxyphenyl)imidazo-[1,2-*a*]pyridine analogues [23,24] exhibiting hydrogen bonding similar to that shown between the salicylaldimino

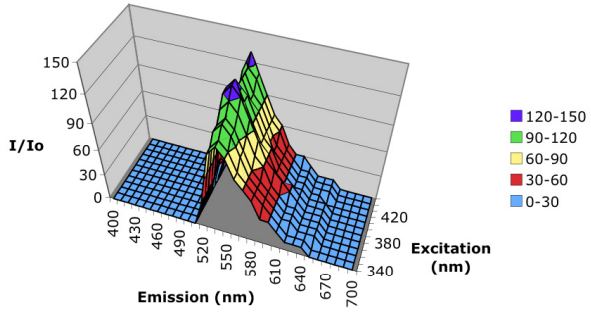


Figure 1. Fluorescence spectrum of DSEB with emission maxima at 540 nm.

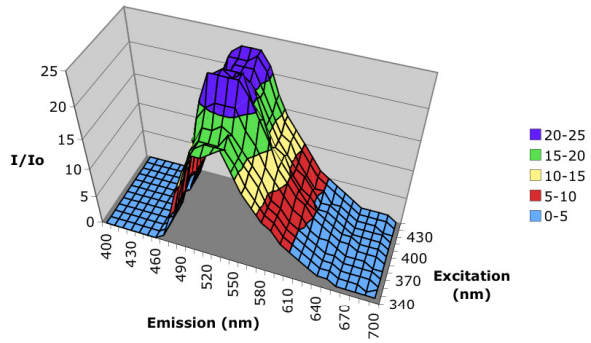
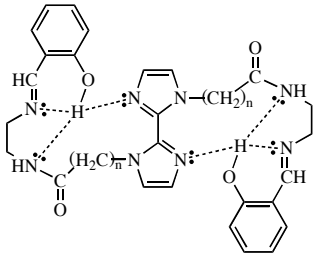


Figure 2. Fluorescence spectrum of DSMB with emission maxima at 520 nm.

Scheme I



nitrogen and phenolic proton in Scheme I, have been reported to involve excited state intramolecular proton transfer [23,24], in which the nitrogen atom (oxygen atom in the case of salicylaldehyde) serves as a proton acceptor during the fluorescing process. As neither of the amide-amine precursors was noted to fluoresce, the fluorescence exhibited by the title compounds is likely due entirely to the salicylaldimine moiety. Disruption of the hydrogen bonding of this specific morphological state accounts for the disappearance and quenching of visible fluorescence in the melt and solution.

EXPERIMENTAL

Melting points were determined using an Electro-thermal Capillary Melting Point Apparatus and are uncorrected. Infrared spectra were obtained from a Nicolet Nexus 470 Fourier Transform Infrared Spectrometer using pressed potassium bromide pellets. ^{1}H NMR spectra were obtained using a Varian Unity Inova High Resolution 400 MHz Fourier Transform Pulsed Nuclear Magnetic Resonance spectrometer. In the case of D_2O, sodium trimethylsilylpropionate was used as a reference. Elemental analyses were conducted using a Perkin Elmer 2400 CHN Elemental Analyzer. Fluorescence specta were obtained with a Perkin Elmer LS-5 Fluorescence Spectrophotometer. Absorbance spectra were obtained with a Cary 100 Bio UV-Visible Spectrophotometer with solids attachment. 1,1'-Di(aminoethylacetamido)-2,2'-biimidazole [13] (DAEAB) and 1,1'-di(ethoxypropionato)-2,2'-biimidazole [15] (DEPB) were prepared according to published procedures. All other reagents were obtained from Aldrich Chemical Co., and used as received.

1,1'-Di(aminoethylaminocarbonylethyl)-2,2'-biimidazole (1). To 0.25 g (0.75 mmol) 1,1'-di(ethoxycarbonylethyl)-2,2'-biimidazole (DEPB) was added 3.0 mL anhydrous 1,2-diaminoethane. The mixture was stirred at room temperature and dissolved rapidly to form a pale yellow solution. Over a period of 24 hours, the product evolved as a white suspension. The reaction contents were poured into 20 mL acetonitrile, the white solid collected *via* gravity filtration, recrystallized from acetonitrile and dried *in vacuo* to yield white powdery product, 0.17 g (63%), mp 154-155°C; ir: *v* 3132, 3117, 3045 (Ar-H), 1654, 1561 (CON) cm^{-1}; ^{1}H nmr (D_2O): δ 2.6 (m, 8H, CH_2), 3.2 (t, 4H, CH_2), 4.5 (t, 4H, CH_2), 7.2 (s, 2H, H_5, $H_{5'}$), 7.3 (s, 2H, H_4, $H_{4'}$). *Anal.* Calcd. for $C_{16}H_{26}N_8O_2$: C, 53.01; H, 7.24; N, 30.92; O, 8.83. Found: C, 52.90; H, 7.21; N, 30.64.

General Procedure for the Preparation of Salicylaldimine Schiff Base Derivatives of 1,1'-Di(aminoethylamino-carbonylalkyl)-2,2'-biimidazole. To 0.25 g (0.75 mmol) of either 1,1'-di(aminoethyl-aminocarbonylmethyl)- or 1,1'-di-(aminoethylamino-carbonylethyl)-2,2'-biimidazole (**1**) was added 5.0 mL salicylaldehyde. The mixtures were stirred at room temperature and the amines dissolved over the course of two minutes to form yellow solutions. After several minutes, the solutions became opaque as pale yellow precipitate formed. To each of these stirred mixtures was added 5 mL ethanol and heating applied *via* heating mantle to effect solution. Once the transparent yellow solutions formed, heating was discontinued and the reaction contents were allowed to cool with stirring. Upon cooling, yellow suspensions were observed. The yellow solids were collected by gravity filtration, recrystallized twice from ethanol (0.2 g product to 15 mL ethanol) with chilling, and dried *in vacuo*.

1,1'-Di(salicylaldiminoethylaminocarbonylethyl)-2,2'-biimidazole (2a). Bright yellow needles, 0.23 g (58%), mp 170-171°C; ir: *v* 3431 (O-H), 3336 (N-H), 3066 (Ar-H), 2974, 2927 (C-H), 1639 (C=O), 1614 (C=N), 1541 (II, N-H) cm^{-1}; ^1H nmr (d_7-DMF): δ 2.7 (t, 4H, CH_2-C=O), 3.4-3.6 (m, 4H, CON-CH_2), 3.6-3.7 (t, 4H, CH_2-N=C), 4.7 (t, 4H, Im-CH_2), 6.9 (m, 4H, Ar-H), 7.0 (s, 2H, Im-$H_{5,5'}$), 7.2-7.3 (s, 2H, Im-$H_{4,4'}$), 7.3-7.4 (t, 2H, Ar-H), 7.4-7.5 (d, 2H, Ar-H), 8.2 (t, 2H, HN-C=O), 8.4-8.5 (s, 2H, N=CH), 13.3 (s, 2H, OH). *Anal.* Calcd. for $C_{30}H_{34}N_8O_4$: C, 63.13; H, 6.02; N, 19.64; O, 11.21. Found: C, 62.83; H, 5.78; N, 19.28.

1,1'-Di(salicylaldiminoethylaminocarbonylmethyl)-2,2'-biimidazole (2b). Fine pale yellow needles, 0.25 g (62%), mp 206-207°C; ir: *v* 3429 (O-H), 3302 (N-H), 3080 (Ar-H), 2933, 2873 (C-H), 1660 (C=O), 1632 (C=N), 1560 (II, N-H) cm^{-1}; ^1H nmr (d_7-DMF): δ 3.4-3.6 (m, 4H, CON-CH_2), 3.6-3.7 (t, 4H, CH_2-N=C), 5.3 (s, 4H, Im-CH_2), 6.9 (m, 4H, Ar-H), 6.9-7.0 (s, 2H, Im-$H_{5,5'}$), 7.2-7.3 (s, 2H, Im-$H_{4,4'}$), 7.3-7.4 (t, 2H, Ar-H), 7.4-7.5 (d, 2H, Ar-H), 8.4 (t, 2H, HN-C=O), 8.5 (s, 2H, N=CH), 13.3 (s, 2H, OH). *Anal.* Calcd. for $C_{28}H_{30}N_8O_4$: C, 61.97; H, 5.58; N, 20.65; O, 11.79. Found: C, 61.68; H, 5.34; N, 20.32.

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