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Synthesis of new substituted benzaldazine derivatives, hydrogen bonding-induced supramolecular structures and luminescent properties

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ABSTRACT

Syntheses of three benzaldazine compounds **1**–**3** with the general formula $Ar_1(CH=N–N=HC)Ar_2$ ($Ar_1 = Ar_2 = 2\text{-OH-}3,5\text{-}^tBu_2C_6H_2$ (**1**), $Ar_1 = Ar_2 = 2\text{-}BrC_6H_4$ (**2**), Ar_1 = *ortho*-$C_6H_4(NHC_6H_3\text{-}Me_2\text{-}2,6)$, $Ar_2 = C_6H_4F\text{-}2$ (**3**)) are described. All compounds were characterized by elemental analysis, ^1H NMR, ^{13}C NMR, IR spectroscopy and single-crystal X-ray crystallography. The different supramolecular structures were obtained through different weak interactions (C – H···O, O – H···N and π···π interactions for **1**; C – H···Br and Br···Br interactions for **2**; C – H···F and C – H···N interactions for **3**). Compound **1** shows solvent-dependent fluorescent properties with blue to green emission on the increasing of the solvent polarity. Compounds **2**, **3** show blue photoluminescence in different solvents.

1. Introduction

Noncovalent interactions such as hydrogen bonding, π–π interactions, Van der Waals contacts and other weak forces play crucial roles in several fields, such as supramolecular chemistry, molecular recognition, biochemistry and materials science [1–3]. Many research efforts have focused on systematically studying a variety of noncovalent forces to observe the interesting cooperative effects in the formation and function of supramolecular architectures. As is well known, O – H···O/N, C – H···O/N, C – H···π interactions and aromatic π-stacking interactions are used to construct a range of supramolecular architectures, because of their strength, selectivity and directionality [4]. More importantly, highly ordered molecular assemblies into chains, sheets and networks as efficient strategies in achieving desired supramolecular architectures are of current interest [5,6].

Schiff-base compounds have been extensively investigated over the past few decades, and therefore attracted considerable attention due to their intriguing properties and the potential applications, such as catalysis, magnetics, nonlinear optics and drug design [7–11]. The bidentate Schiff-base ligands with —CR = N–N = CR— acceptor groups have been reported to generate supramolecular systems with interesting host-guest chemistry [12]. The bidentate and multidentate Schiff-base ligands with terminal pyridyl groups have also been investigated to generate coordination polymers with novel network patterns, and the multidentate Schiff-base ligands have contributed to one-dimensional metal-organic nanometer tube which are further linked together through weak C – H···X bonds [13]. Considering the ligand structure features, salicylaldazines are suitable candidates for investigating the possibilities for intramolecular hydrogen bonding and intramolecular proton transfer process between two groups, due to the high degree of conjugation and the presence of OH groups close to the azine nitrogens [14]. Our research interest has focused on investigating the nature of noncovalent interactions in determining the supramolecular structures of new benzaldazine derivatives and clarifying the relationship of the corresponding structure and fluorescent properties. Herein we wish to report synthesis and characterization of three compounds

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1–**3** with the general formula $Ar_1(CH=N–N=HC)Ar_2$ ($Ar_1 = Ar_2$ = 2-OH-3,5-^{t}Bu$_2$C$_6$H$_2$ (**1**), $Ar_1 = Ar_2$ = 2-BrC$_6$H$_4$ (**2**), Ar_1 = *ortho*-C$_6$H$_4$(NHC$_6$H$_3$-Me$_2$-2,6), Ar_2 = 2-FC$_6$H$_4$ (**3**)). The luminescent properties of these benzaldazine derivatives **1**–**3** were studied both in solution and in the solid state. The effect of the functional groups on molecular packing and fluorescent properties in the solid state and solution with different solvents was also investigated.

2. Experimental

2.1. General

All solvents and reagents were commercially obtained and used as received. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde was synthesized according to the literature method [15]. ^{1}H NMR and ^{13}C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The elemental analyses were performed on a Perkin-Elmer 2400 analyzer. UV–vis absorption spectra were recorded on an UV-3100 spectrophotometer. Fluorescent measurements were carried out on a RF-5301PC. All melting points were determined by an X-5 micr-melting point apparatus and are uncorrected.

2.2. Synthesis of 3,5-di-^{t}Bu-2-OHC$_6$H$_4$(CH = N–N = HC)C$_6$H$_4$-OH-2-^{t}Bu-di-5,3 (1)

3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.40 g, 2.00 mmol) was added to hydrazine hydrate (0.05 g, 1.00 mmol) in 5 mL ethanol. The resulting bright yellowish mixture was refluxed for 2 h. Upon cooling the reaction mixture to room temperature, yellow solids were precipitated. The obtained solid product was washed with cold ethanol, then dried in vacuo to give the desired product in excellent yield. Yield: 0.45 g (96%). M.p. 219.2–221.4 °C. Anal. Calcd. for $C_{30}H_{44}N_2O_2$ (464.68): C 77.54, H 9.54, N 6.03. Found: C 77.48, H 9.62, N 6.10. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.89 (s, 2H), 8.76 (s, 2H), 7.46 (d, J = 2.0 Hz, 2H), 7.17 (d, J = 2.0 Hz, 2H), 1.47 (s, 18H), 1.32 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 156.8, 141.3, 136.9, 128.2, 126.9, 116.7, 31.4, 29.4 ppm. IR (KBr, cm^{-1}): υ 2960, 1623, 1592, 1439, 1390, 1362, 1251, 1201, 1173, 963, 717.

2.3. Synthesis of ortho-C$_6$H$_4$Br(CH = N–N = HC)C$_6$H$_4$Br-ortho (2)

Similarly, 2-bromo-benzaldehyde (0.37 g, 2.00 mmol) and hydrazine hydrate (0.05 g, 1.00 mmol) in ethanol afforded compound **2** as yellow solid. Yield: 0.34 g (94%). M.p. 173.2–173.4 °C. Anal. Calcd. for $C_{14}H_{10}N_2Br_2$ (366.05): C 45.94, H 2.75, N 7.65. Found: C 45.98, H 2.82, N 7.54. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.02 (s, 2H), 8.23 (d, J = 1.8 Hz, 2H), 8.20 (d, J = 1.8 Hz, 2H), 7.42–7.29 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4, 133.2, 132.7, 132.4, 128.6, 127.6, 125.8 ppm. IR (KBr, cm^{-1}): υ 1613, 1559, 1431, 1316, 1270, 1024, 953, 751, 640, 439.

2.4. Synthesis of ortho-C$_6$H$_4$F(CH = N–N = HC)C$_6$H$_4$(NHC$_6$H$_3$-Me$_2$-2,6)-ortho (3)

Compound *ortho*-C$_6$H$_4$F(CH = N–N = HC)C$_6$H$_4$F-*ortho* was synthesized by the similar procedure as compound **1**. Hydrazine hydrate (0.05 g, 1.00 mmol) and 2-fluorobenzaldehyde (0.25 g, 2.00 mmol) in ethanol afforded compound *ortho*-C$_6$H$_4$F(CH = N–N = HC)C$_6$H$_4$F-*ortho* as yellow solid. Yield: 0.24 g (98%). M.p. 132.3–132.8 °C. Anal. Calcd. for $C_{14}H_{10}N_2F_2$ (244.24): C 68.85, H 4.13, N 11.47. Found: C 68.94, H 4.25, N 11.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.93 (s, 2H), 8.13 (t, J = 6.9 Hz, 2H), 7.48–7.42 (m, 2H), 7.23–7.10 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 155.4, 150.6, 150.6, 127.8, 127.7, 122.5, 122.5, 119.3, 119.2, 116.6, 116.4, 110.9, 110.6 ppm. IR (KBr, cm^{-1}): υ 1627, 1483, 1457, 1233, 1096, 959, 814, 753, 653, 462.

A solution of *n*-BuLi (1.40 mL, 1.90 mmol) in *n*-hexane was added to a solution of 2,6-dimethylaniline (0.22 mL, 1.80 mmol) in THF (20 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for additional 2 h. The resulting solution was transferred into a solution of *ortho*-C$_6$H$_4$F(CH = N-N = HC)C$_6$H$_4$F-*ortho* (0.40 g, 1.60 mmol) in THF (10 mL) at 25 °C. After stirring for 2 h, the reaction was quenched with H_2O (20 mL). The layers were separated and the water layer was washed with Et_2O (2 × 30 mL). The combined organic phase was dried over anhydrous $MgSO_4$ for 2 h, and filtered. The organic phase was evaporated to dryness to give the crude product as brown oil. The crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:5 in volume) as eluent to give the pure product as yellowish crystals. Yield: 0.48 g (85%). M.p.: 117.6–118.3 °C. Anal. Calcd. for $C_{22}H_{20}N_3F$ (345.41): C 76.50, H 5.84, N 12.17. Found: C 76.42, H 5.90, N 12.13. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.89 (s, 1H), 8.86 (s, 1H), 8.13 (t, J = 6.6 Hz, 1H), 7.50–7.33 (m, 2H), 7.24–7.05 (m, 6H), 6.72 (t, J = 7.4 Hz, 1H), 6.26 (d, J = 8.3 Hz, 1H), 2.24 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 153.8, 136.5, 134.4, 132.4, 132.2, 132.1, 128.2, 127.4, 127.3, 126.2, 124.2, 124.1, 115.8, 115.8, 115.6, 114.9, 111.6, 18.2. IR (KBr, cm^{-1}): υ 2922, 1622, 1576, 1456, 1318, 1198, 1099, 768, 754, 465.

2.5. X-ray structure determinations of 1, 2 and 3

The block-shaped single yellow crystals for X-ray analysis of **1** and **2** were obtained from a tetrahydrofuran solution and diethyl ether solution upon cooling to 0 °C, respectively. Single crystals of **3** suitable for X-ray structural analysis were obtained from slow evaporation of a methanol solution. Diffraction data were collected at 226(2) K (for **1**) or at 293 K (for **2** and **3**) on a Bruker Smart diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) for all compounds. The structures were solved by direct methods [16] and refined by full-matrix least-squares on F2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL [17] crystallographic software packages. Details of the crystal data, data