

Synthesis, Crystal Structure and Fluorescent Properties of 1-(4-(Dimethylamino)benzylidene)-4-(naphthalen-1-yl) Thiosemicarbazide^①

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ABSTRACT The title compound, 1-4-(dimethylamino)benzylidene)-4-(naphthalene-1-yl) thiosemicarbazide (DMABNTS, C₂₀H₂₀N₄S, *M_r* = 348.47), was synthesized and characterized by elemental analysis, IR, ¹H NMR and MS. The crystal structure of DMABNTS with 1,4-dioxane (Diox, C₄H₈O₂) solvent molecules (DMABNTS·2Diox, C₂₈H₃₆N₄O₄S, *M_r* = 524.67) was determined by single-crystal X-ray diffraction. The crystal belongs to monoclinic system, space group *P*2₁/*c* with *a* = 14.418(4), *b* = 7.1702(19), *c* = 28.350(7) Å, β = 101.154(6)°, *V* = 2875.4(13) Å³, *Z* = 4, *D_c* = 1.212 g/cm³, *F*(000) = 1120 and μ = 0.151 mm⁻¹. A total of 6458 reflections were collected, of which 4671 were unique. The structure was solved by direct methods and refined to the final *R* = 0.0732 and *wR* = 0.2127 for 3921 observed reflections (*I* > 2σ(*I*)). There exist intermolecular hydrogen bonds (N(2)–H(2B)⋯S(1A) and N(1)–H(1A)⋯O(4B)) in the structure. The study of fluorescent properties shows that DMABNTS emits bright solid-state fluorescence in the visible region and exhibits blue photoluminescence.

Keywords: 1-(4-(dimethylamino)benzylidene)-4-(naphthalen-1-yl)thiosemicarbazide, synthesis, crystal structure, fluorescence

1 INTRODUCTION

Recently, for the fluorescent properties, Schiff base has been more and more important and widely studied in density optical memories, nonlinear optics (NLO), organic light-emitting diodes (OLED), polymer LED and electrogenerated chemiluminescence (ECL)^[1~5]. Thiosemicarbazones are a kind of Schiff bases with thiourea and good ligands easily chelating with transition metal ions. Although they have been studied extensively for a long time due to their chemical and biological activities, such as antitumor, antibacterial and antiviral^[6~8], there are only few reports concerning the solid fluorescent

properties of thiosemicarbazones^[9]. It is interesting to design and synthesize new thiosemicarbazone derivatives with solid fluorescence properties for the possible applications in these areas. Herein, we report the crystal structure of a new derivative of thiosemicarbazone containing electron donor substitute dimethylanilino, DMABNTS with 1,4-dioxane solvent molecules (DMABNTS·2Diox) and its fluorescence properties in different solvents as well as in solid state. Introduction of such a strong electron-donating moiety as *N,N*-dimethylanilino group through a double bond imparts new properties that are uncommonly observed for the parent thiourea to the resultant molecule. DMABNTS shows absorp-

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tion in the near-visible region and emission totally in the visible region with bright solid-state fluorescence. DMABNTS exhibits blue photoluminescence.

1 EXPERIMENTAL

2.1 Materials and apparatus

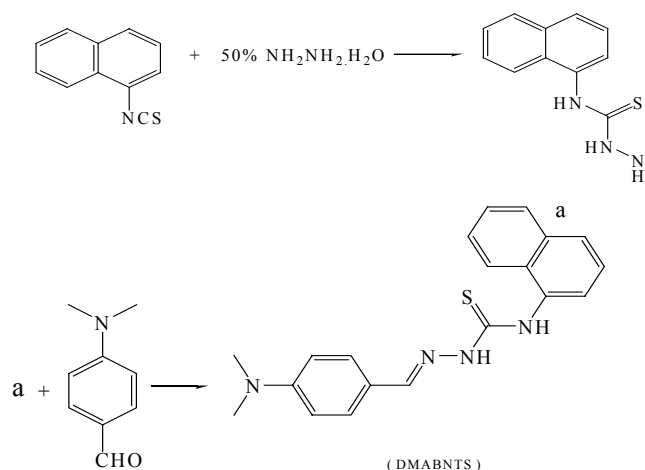
1-Naphthyl isothiocyanate was purchased from ACROS and used as received. The other analytical grade chemicals and solvents were from commercial sources. Solvents were redistilled before use to preclude the fluorescence impurities.

Elemental analyses for C, H and N were carried out with a CE instruments EA 1110 Elemental Analyzer. The infrared spectra were recorded on a Nicolet AVATAR FT-IR360 spectrometer by using

the pressed KBr pellet. ^1H NMR spectrum was measured on a Varian Unity 500MHZ with TMS as the internal standard. Melting point was determined with an X-4 melting point apparatus. Corrected fluorescence spectra were taken on a Hitachi F-4500 fluorescence spectrophotometer and absorption spectra were scanned on a Bekeman DU-7400 absorption spectrophotometer. Quantum yields were determined using quinine bisulphate as standard^[10]. Solid-state fluorescence spectra were recorded with solid powder on a 1 cm quartz round plate with excitation and emission slits 2.5/2.5 nm. The excitation wavelength for DMABNTS was 350 nm. All experiments were conducted at room temperature of *ca.* 25 °C.

2.2 Synthesis and characterization

The synthetic route for the title compound is shown in Scheme 1.



Scheme 1. Synthesis route of the title compound DMABNTS

2.2.1 Preparation of 4-(naphthalen-1-yl)thiosemicarbazide

1-Naphthyl isothiocyanate (0.741 g, 4 mmol) was dissolved in 30 mL of ethanol, and the resulting solution was then slowly added to 50% hydrazine hydrate (1.00 g, 10 mmol) in ethanol (10 mL). The mixed solution was stirred at room temperature for 8 h, and the white solid was collected by filtration and recrystallized by ethanol.

2.2.2 Synthesis and characterization of 1-(4-(dimethylamino)benzylidene)-4-(naphthalen-1-yl)thiosemicarbazide

4-(Naphthalen-1-yl)thiosemicarbazide (0.434 g,

2 mmol) was dissolved in 20 mL of ethanol and added to a refluxing ethanol solution of 0.298 g (2 mmol) *p*-dimethylaminobenzaldehyde. The mixed solution was further refluxed for about 6 h, forming light yellow precipitate which was then filtered off under low pressure and washed several times with ethanol. The product was recrystallized from ethanol, and dried under vacuum for 4 h. Yield 0.362 g (52%). m. p: 210~211°C. Anal. Calcd. (%) for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{S}$: C, 68.94; H, 5.79; N, 16.08. Found (%): C, 69.08; H, 5.63; N, 15.95. IR (KBr): 3435.68, 3315.03 (NH, s); 3132.11, 2976.45 (CH_3 , m); 1614.27, 1520.86, 1497.51 (C = N, C = C, s);

1178.36 (C= S, s); ^1H NMR (500MHz, DMSO) δ : 2.969(s, 6H, CH_3); 6.715~7.720 (d, 8H, H2, H4, H5, H8, H14, H15, H17, H18); 7.878~7.975(t, 3H, H3, H6, H7); 8.090(s, 1H, HC=N); 10.209(s, 1H, NH); 11.680(s, 1H, N-NH); MS m/z (%): 349.0 (M^+ + 1, 100).

2. 2. 3 X-ray crystallography analysis

Crystals suitable for diffraction were obtained by recrystallizing the products from 1,4-dioxane at room temperature. A rectangular transparent crystal with dimensions of 0.52mm \times 0.48mm \times 0.42 mm was chosen and mounted at the top of a glass fiber in air. The diffraction data were collected on a Bruker Apex-2000 diffractometer equipped with a graphite-monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation by using an ω - ϕ scan mode at 173(2) K. A total of 6458 reflections were measured in the 2θ range ($1.44 \leq 2\theta \leq 25.00^\circ$) and 4671 were independent with $R_{\text{int}} = 0.0221$, of which 3921 were considered as observed ($I > 2\sigma(I)$). Lorentz-polarization and empirical absorption corrections were applied to the data. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares calculations with SHE-

LXL-97 based on F^2 ^[11]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located at the geometrically calculated positions and rode on the related atoms. The final $R = 0.0732$, $wR = 0.2127$ ($w = 1/[\sigma^2(F_o^2) + (0.1545P)^2 + 1.9479P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.043$, $(\Delta/\sigma)_{\text{max}} = 0.000$, $(\Delta\rho)_{\text{max}} = 0.812$ and $(\Delta\rho)_{\text{min}} = -0.424 \text{ e/\AA}^3$.

3 RESULTS AND DISCUSSION

3. 1 Crystal structure

The ^1H NMR, IR, MS and elemental analysis for the product are in good agreement with DMABNTS. The non-hydrogen atomic coordinates and equivalent isotropic thermal parameters of DMABNTS·2Diox are listed in Table 1, and selected bond lengths and bond angles in Table 2. The single-crystal X-ray diffraction analysis exhibits that there are coordinating Diox solvent molecules in the crystal with the molar ratio of DMABNTS:Diox being 1:2. The crystal structure and intermolecular hydrogen bond diagram of the title compound are shown in Fig. 1.

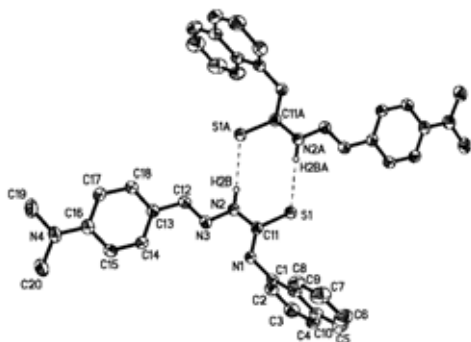
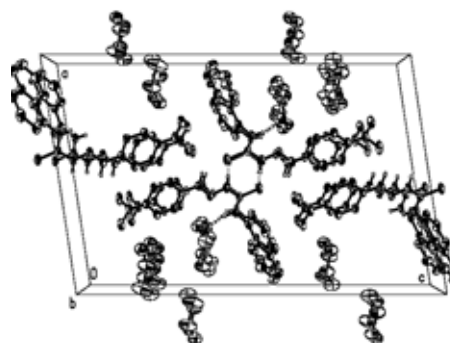
Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S(1)	4398(1)	7789(1)	382(1)	36(1)	C(15)	3312(2)	7436(4)	-2552(1)	32(1)
N(1)	3411(2)	5946(3)	-370(1)	30(1)	C(16)	3734(2)	8663(4)	-2836(1)	32(1)
N(2)	4428(2)	8172(4)	-537(1)	32(1)	C(17)	4405(2)	9931(4)	-2594(1)	34(1)
N(3)	4102(2)	7847(3)	-1018(1)	31(1)	C(18)	4642(2)	9945(4)	-2098(1)	35(1)
N(4)	3503(2)	8632(4)	-3328(1)	40(1)	C(19)	3939(2)	9953(5)	-3604(1)	46(1)
C(1)	2922(2)	4885(4)	-68(1)	29(1)	C(20)	2873(2)	7247(5)	-3579(1)	46(1)
C(2)	3204(2)	3114(4)	60(1)	37(1)	C(21)	-1326(3)	9100(8)	2861(3)	107(2)
C(3)	2718(2)	2044(5)	352(1)	45(1)	C(22)	-1958(3)	7705(7)	2975(2)	86(2)
C(4)	1959(2)	2787(5)	507(1)	43(1)	C(23)	-750(3)	5528(7)	3060(2)	91(2)
C(5)	860(2)	5413(6)	539(1)	51(1)	C(24)	-119(3)	6945(8)	2948(3)	103(2)
C(6)	566(2)	7164(6)	407(2)	59(1)	C(25)	2284(3)	3971(6)	3744(2)	79(1)
C(7)	1028(2)	8203(6)	103(2)	55(1)	C(26)	2890(3)	2533(6)	3590(2)	65(1)
C(8)	1789(2)	7488(5)	-55(1)	40(1)	C(27)	1680(3)	371(6)	3539(2)	59(1)
C(9)	2123(2)	5688(4)	80(1)	31(1)	C(28)	1084(3)	1805(7)	3708(2)	72(1)
C(10)	1645(2)	4607(5)	382(1)	37(1)	O(1)	-386(2)	8734(5)	3089(2)	133(2)
C(11)	4046(2)	7258(4)	-206(1)	28(1)	O(2)	-1688(2)	5918(4)	2841(1)	81(1)
C(12)	4507(2)	8808(4)	-1300(1)	31(1)	O(3)	1311(2)	3607(4)	3561(1)	75(1)
C(13)	4234(2)	8718(4)	-1819(1)	30(1)	O(4)	2644(2)	733(3)	3723(1)	48(1)
C(14)	3554(2)	7463(4)	-2059(1)	30(1)					

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
S(1)–C(11)	1.691(3)	N(2)–C(11)	1.344(3)	N(4)–C(16)	1.371(3)
N(1)–C(11)	1.332(4)	N(2)–N(3)	1.375(3)	N(4)–C(20)	1.438(4)
N(1)–C(1)	1.429(3)	N(3)–C(12)	1.277(4)	N(4)–C(19)	1.447(4)
Angle	(°)	Angle	(°)	Angle	(°)
C(11)–N(1)–C(1)	123.5(2)	C(16)–N(4)–C(19)	119.6(2)	N(2)–C(11)–S(1)	119.5(2)
C(11)–N(2)–N(3)	120.1(2)	C(20)–N(4)–C(19)	118.9(2)	N(3)–C(12)–C(13)	122.9(2)
C(12)–N(3)–N(2)	114.8(2)	N(1)–C(11)–N(2)	116.6(2)		
C(16)–N(4)–C(20)	121.4(3)	N(1)–C(11)–S(1)	123.9(2)		

**Fig. 1. Molecular structure and intermolecular hydrogen bonds of DMABNTS****Fig. 2. Packing diagram of DMABNTS·2Diox in a unit cell**

The title compound molecule is composed of *p*-dimethylaminobenzyl, thiosemicarbazone and naphthyl and has two planes. In *p*1, the phenyl ring does not show any unusual features and the bond lengths and bond angles are within the normal ranges^[12]. The interatomic distance for C(12)–N(3) is 1.277(4) Å, showing it is a normal C=N double bond^[13]. The sum of the bond angles S(1)–C(11)–N(1), S(1)–C(11)–N(2), N(1)–C(11)–N(2) and C(19)–N(4)–C(16), C(20)–N(4)–C(16), C(20)–N(4)–C(19) is 360.0°, indicating the C(11) and N(4) atoms are of *sp*² hybridization. The atoms C(11), C(12), C(19), C(20), N(1), N(2), N(3), N(4), S(1) and the phenyl ring (C(13)~C(18)) are coplanar (plane1) with plane equation 10.598*x*–4.861*y*–4.131*z* = 0.9348, and the mean deviation from the least-squares plane is 0.0486 Å. Furthermore, the atoms C(11), C(12), N(1), N(2), N(3), N(4), S(1) and the phenyl ring form a conjugated system so the C(11)–N(1) and C(11)–N(2) bonds (1.332 and 1.344 Å, respectively) are shorter than the normal C–N bond (1.47 Å)^[14]. The C=S bond (1.691(3) Å) is slightly longer than

the C=S double bond (1.646 Å)^[15] and the bond distance of N(4)–C(16), 1.371 Å, is shorter than that of N(4)–C(19) and N(4)–C(20) (1.447 and 1.438 Å, respectively). In *p*2 (C(1)~C(10)), the bond lengths and bond angles are generally normal in the naphthalene ring. The least-squares plane of the naphthalene ring has the mean deviation of 0.0125 Å (plane 2 equation: 6.618*x* + 2.621*y* + 20.005*z* = 3.0534) and forms a dihedral angle of 85.0° between two planes. *P*-Dimethylaminophenyl at C(12) and 1-naphthyl thiourea at N(3) are located on opposite sides of the C(12)=N(3) double bond, so the compound is in a *trans* form.

As shown in Fig. 1, in the title compound there exist intermolecular hydrogen bonding interactions of N(2)–H(2B)···S(1A)ⁱ (*i*: –*x*+1, –*y*+2, –*z*) listed in Table 3. There are hydrogen bond acceptor and donor in every molecule, and a centrosymmetric dimer with an 8-membered ring is produced by the intermolecular hydrogen bonds.

Packing diagram of the molecule in a unit cell is shown in Fig. 2. The intermolecular hydrogen bond

of N(1)–H(1A)⋯O(4B)ⁱⁱ (ii: $x, -y+1/2, z-1/2$) in the crystal has been observed between the title compound and 1,4-dioxane solvent molecules with

O(4) from Diox and N(1) from DMABNTS. The hydrogen bond lengths and bond angles are listed in Table 3.

Table 3. Hydrogen-bonding Geometry (Å and °)

Donor–H⋯accepter	D–H	H⋯A	D⋯A	D–H⋯A
N(2)–H(2B)⋯S(1A)	0.88	2.53	3.341(3)	153.8
N(1)–H(1A)⋯O(4B)	0.88	2.05	2.859(3)	153.2

A: $-x+1, -y+2, -z$; B: $x, -y+1/2, z-1/2$

Table 4. Solvatochromic Data of DMABNTS

Solvent (ϵ) ^a	$\lambda_{\max}^{\text{Flu}}/\text{nm}$ [ν/cm^{-1}]	Φ_{Flu} ^c	$\lambda_{\max}^{\text{abs}}/\text{nm}$ [ν/cm^{-1}]	Stokes shift $\Delta\nu\text{cm}^{-1}$	ϵ_{\max} ^b
Diox (2.21)	419 [23866]	0.038	365 [27397]	3531	4.6
THF (7.58)	428 [23364]	0.016	369 [27100]	3736	4.8
EtOH (24.55)	443 [22573]	0.014	366 [27322]	4749	4.9
MeCN (37.50)	445 [22471]	0.015	364 [27472]	5001	4.9

^a Dielectric constant (ϵ , from ref [16])

^b Molar absorption coefficient ($\times 10^4 \text{ mol}^{-1} \text{ l cm}^{-1}$)

^c Fluorescence quantum yield, calculated using quinine bisulphate 350 nm as standard

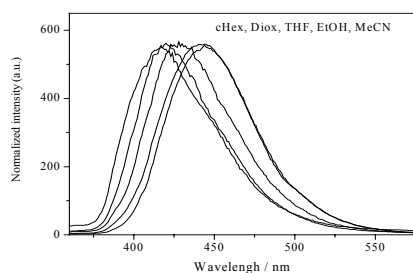


Fig. 3. Normalized fluorescence spectra of DMABNTS in different solvents

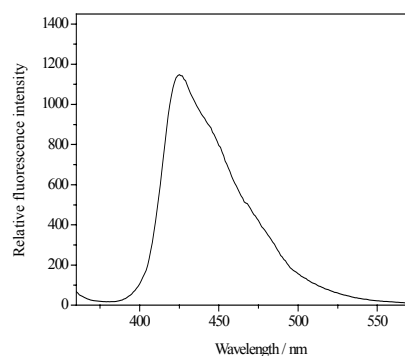


Fig. 4. Fluorescence spectrum of DMABNTS in solid state excited at 350 nm with excitation and emission slits of 2.5/2.5nm

3.2 Fluorescent properties of DMABNTS

The UV-vis and fluorescence spectra of DMABNTS ($1.29 \times 10^{-5} \text{ M}$) in different solvents were recorded. The values of the spectra are listed in Table 4 and the fluorescence spectra are shown in Fig. 3. It can be seen that the $\pi-\pi^*$ transitions for DMABNTS appear close to the visible region. DMABNTS shows the longest wavelength absorption maximum in near-visible region and emits blue fluorescence in different solvents, although its quantum yield is not high in all kinds of solvents. DMABNTS exhibits Stokes shift from 3531 cm^{-1} in

Diox to 5001 cm^{-1} in MeCN, implying more prominent charge transfer in the excited state. The absorption maxima recorded in various solvents reveal almost no shift from Diox to MeCN upon increasing the polarity of the solvent. There is a well-pronounced increase in the Stokes shift and decrease in emission quantum yield with the increase of polarity of the solvent. As shown in Fig. 3, the maximum of emission wavelength shifts from 419 nm in Diox to MeCN (445 nm) upon increasing the solvent polarity.

Bright emission of DMABNTS upon shining light

on solid sample is observed. The emission spectrum from solid powder is shown in Fig. 4. It can be seen from Figs. 3 and 4 that the solution fluorescence spectral maxima were almost the same with that of solid state. That the solid-state emission spectrum exhibits very close consistency with the solution

fluorescence spectra indicates the solid emission from monomer. The characteristics are very useful in opening up new prospects and promises for novel organic materials, ECL, OLED, and other optoelectronic applications.

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