

КРАТКИЕ СООБЩЕНИЯ

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ADDUCT OF 2-AMINOBENZOTHAZOLE AND 2-HYDROXY-3-NAPHTHOIC ACID
AND ITS LUMINESCENCE PROPERTIES

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The adduct of 2-aminobenzothiazole (**1**) and 2-hydroxy-3-naphthoic acid (**2**) is synthesized by the normal temperature volatilization method. The crystal belongs to the monoclinic system, $P2_1/c$ space group. It crystallizes with two independent molecules in the unit, the two independent molecules forming helices through hydrogen bonds. The luminescence property of **1**, **2**, and the adduct (**1·2**) were studied at room temperature.

Keywords: adduct of 2-aminobenzothiazole and 2-hydroxy-3-naphthoic acid, hydrogen binding, luminescence.

Supramolecular assembled chemistry and crystal engineering of organic molecules has been exploited in organ materials and active pharmaceutical ingredients by selecting building blocks and organic ligands, in which the unpredictable weak interactions are the key factor determining the properties and structures of many compounds [1–3]. Therefore, some well-established architectures designed and generated by weak interactions have recently been reported [4–5]. A number of theoretical investigations have shown that **1** can provide a site available for hydrogen bonding interactions with carboxylic acids, and **2** may experience favorable hydrogen bondings [6, 7]. In this work, the adduct constructed by hydrogen bonding with a much better luminescence property was synthesized and studied.

Experimental. Materials and physical measurements. All chemicals were of analytical reagent grade and were used directly without further purification. Elemental analyses (C, H, and N) were performed on a Finnigan NA 1112 model. Infrared spectra were recorded on a Nicolet IR-470 spectrometer using KBr pellets. Fluorescence measurements were carried out on a Perkin—Elmer LS55 fluorescence spectrofluorometer.

Synthesis of the title compound. 2-Aminobenzothiazole (0.1 mmol, 15.019 mg) was dissolved in ethanol (10 ml), and the resulting solution was then slowly added to 2-hydroxy-3-naphthoic acid (0.1 mmol, 18.818 mg) in deionized water (10 ml). After two hours stirring, the reacted mixture was allowed to stand at room temperature undisturbed for two weeks resulting in colorless crystals. Anal. Calcd for $C_{18}H_{14}N_2O_3S$: C, 63.89; H, 4.17; N, 8.28 %; Found: C, 63.91; H, 4.13; N, 8.30; IR(KBr): 3265(m), 2884(w), 2713(w), 1844(w), 1632(m), 1467(s), 1397(s), 1317(m), 1236(m), 1148(w), 1065(w), 913(w), 841(w), 741(s), 629(w), 597(w), 477(w) cm^{-1} .

X-ray crystallography analysis. Single-crystal X-ray data were collected at 113(2) K on a BRUKER SMART 1000 CCD detector with graphite monochromatized MoK_{α} radiation ($\lambda = 0.71070 \text{ \AA}$) using the ω -scan technique. The structures were solved by direct methods and refined with the full-matrix least-square fitting using the SHELXS-97 and SHELXL-97 programs [8].

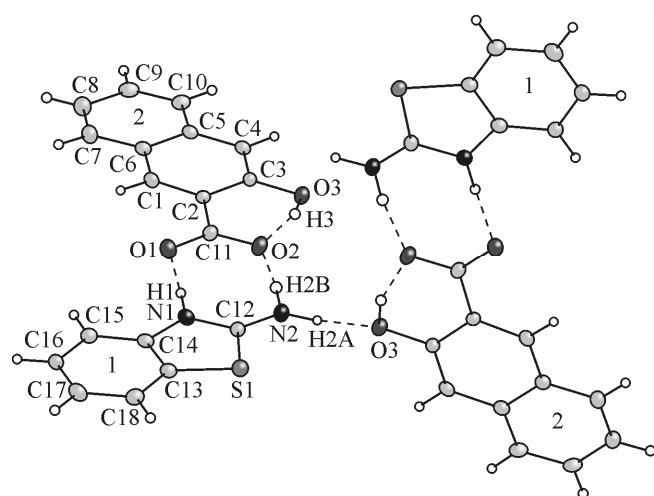
Results and discussion. The adduct is formed between **1** and **2** in a 1:1 ratio with the structure and hydrogen bond diagram depicted in Fig. 1. S1 shows the assembling of the adduct in helices. In

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Crystal Data and Structure Refinement for the Title Compound

| | |
|---|---|
| Empirical formula | C ₁₈ H ₁₄ N ₂ O ₃ S |
| CCDC deposit No | 658579 |
| Formula weight | 338.37 |
| Wavelength, Å | 0.71073 |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg. | 11.758(6), 9.781(4), 14.422(7); 111.253(6) |
| Volume, Å ³ | 1545.9(12) |
| <i>Z</i> | 4 |
| <i>D</i> _{calc} , mg/m ³ | 1.454 |
| Absorption coefficient, mm ⁻¹ | 0.229 |
| <i>F</i> (000) | 704 |
| Crystal size | 0.12×0.10×0.08 |
| θ Range for data collection, deg. | 1.86—25.00 |
| Index ranges | −13 ≤ <i>h</i> ≤ 13, −11 ≤ <i>k</i> ≤ 11, −17 ≤ <i>l</i> ≤ 17 |
| Reflections collected | 15242 |
| Independent reflections, <i>R</i> _{int} | 2720 |
| Data / restraints / parameters | 2720 / 0 / 233 |
| <i>S</i> | 1.075 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> 1 = 0.0681, <i>wR</i> 2 = 0.1458 |
| <i>R</i> indices, all data | <i>R</i> 1 = 0.0946, <i>wR</i> 2 = 0.1614 |
| Largest diffraction peak and hole, e/Å ³ | 1.444 and −0.377 |

Fig. 1, the structure analysis shows that **1** and **2** formed one unit linked by the N(2) H(2A) O(3') hydrogen bond. The adduct revealed the expected supramolecular features assembled via hydrogen bonding. They are N(1) H(1) O(1), N(2) H(2B) O(2), and N(2) H(2A) O(3') intermolecular hydrogen bonds driving the formation of the helices, as shown in S1, and N(1) H(1) O(1), N(2) H(2B) O(2) form rings with a graph-set [9] motif of $R_2^2(8)$. Also, an analysis of the intermolecular hydrogen distances involved in the $R_2^2(8)$ interactions shows that the equivalent 2-amino nitrogen/carboxylate oxygen distances are slightly longer (2.9 Å) [10, 11], however, there is a decrease in the distances being 2.685 and 2.728 Å in our adduct. One intramolecular O(2)H(3)O(3) hydrogen bond is shown in Fig. 1. **2** exhibits unusual features with a longer C=O bond (1.272 Å), as compared to the usual delocalized carboxylate Car—C ~ O₂⁻ anions (1.255).



carboxylate Car—C ~ O₂⁻ anions (1.255).

The luminescence spectrum of **1**, **2**, and the adduct in the solid state at room temperature is shown in Fig. 2. It can be observed that the adduct exhibits intense green luminescence with an emission maximum at 498 nm upon excitation at 391 nm, while no clear luminescence is observed for **1** and **2** under the same condition. This emission band may be assigned to the emission of the

Fig. 1. Part of the adduct structure shown with the thermal ellipsoids drawn at the 25 % probability level and hydrogen bonds shown as dashed lines

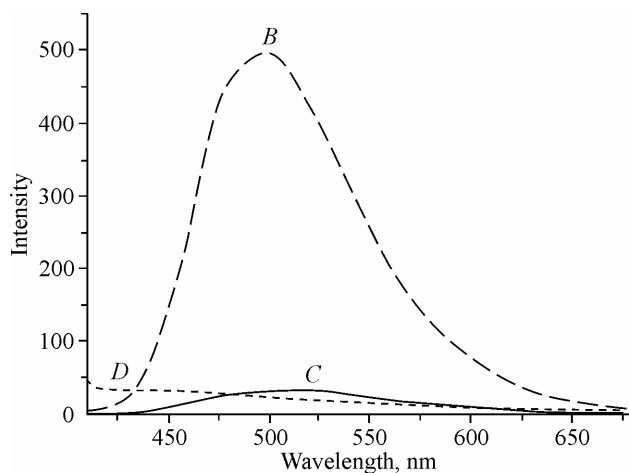


Fig. 2. Emission spectra of **1**, **2**, and the adduct in solid state at room temperature ($\lambda_{ex} = 391$ nm) (B = the adduct, C = 2-aminobenzothiazole, D = 2-hydroxy-3-naphthoic acid)

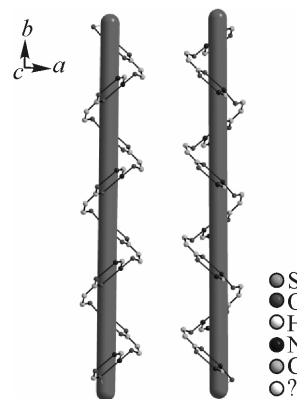


Fig. 3. Helices constructed by hydrogen bonding interactions (some atoms omitted for clarity)

ligand-to-ligand charge transfer. This observation indicates that the title compound can be an excellent candidate for potential photoactive materials.

Conclusion. The adduct has been synthesized and characterized. The luminescence property was studied at room temperature in comparison with that of **1** and **2**. The emission band may be assigned to the emission of the ligand-to-ligand charge transfer. This observation indicates that the title compound can be an excellent candidate for potential photoactive materials.

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