Brief Communications

X-ray diffraction analysis and luminescence spectral study of crystal solvates of *N*-(*N´*-tosylanthranoyl)anthranilic acid with acetic acid and dimethylformamide

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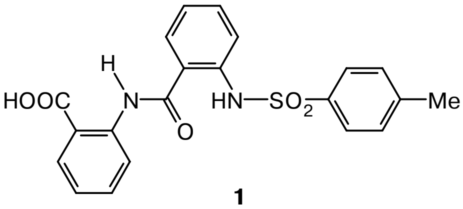
Two crystal modifications of *N*-(*N´*-tosylanthranoyl)anthranilic acid were studied by X-ray diffraction analysis and luminescence spectroscopy. One crystal modification is a crystal solvate with acetic acid and is characterized by green fluorescence. Another modification is a crystal solvate with DMF and exhibits blue fluorescence. The modifications differ in the melting point.

Key words: luminescence, crystal structure, fluorescence, derivatives of anthranilic acid, hydrogen bond.

When performing recrystallization of *N*-(*N´*-tosylanthranoyl)anthranilic acid (**1**) from acetic acid and DMF, we found that acid **1** formed crystals exhibiting different fluorescence, *viz.*, green (**1a**) and blue (**1b**). Crystal modifications **1a** and **1b** differ also in the melting point (206 and 197 °C, respectively). With the aim of establishing the structures of both crystal modifications and revealing the reasons for the difference in their luminescence properties, we studied these single crystals by X-ray diffraction analysis.



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Results and Discussion

According to the X-ray diffraction data, molecule **1a** (Fig. 1) is nonplanar. Benzene rings *A* and *B* are rotated about the C(1)—N(2) bond by 18.1°. Benzene rings *B* and *C* are rotated about the N(1)—S bond by 106.7°. In crystal solvate **1b** (Fig. 2), the central fragment of molecule **1** is virtually planar. Benzene rings *A* and *B* are rotated about the C(1)—N(2) bond by 4.6°, and benzene rings *B* and *C* are rotated about the N(1)—S bond by 9.8°. The carboxyl group of molecule **1a** is involved in two intermolecular hydrogen bonds with the molecule of acetic acid: the O(5)...O(7) and H(23)...O(7) interatomic distances are 2.694(3) and 1.88(2) Å, respectively (the H(23)—O(5) bond length is 0.82(2) Å), the O(5)—H(23)—O(7) angle is 173.5(2)°, the O(4)...O(6) and H(24)...O(4) distances are 2.728(3) and 2.00(2) Å, respectively (the H(24)—O(6) bond length is 0.73(2) Å),

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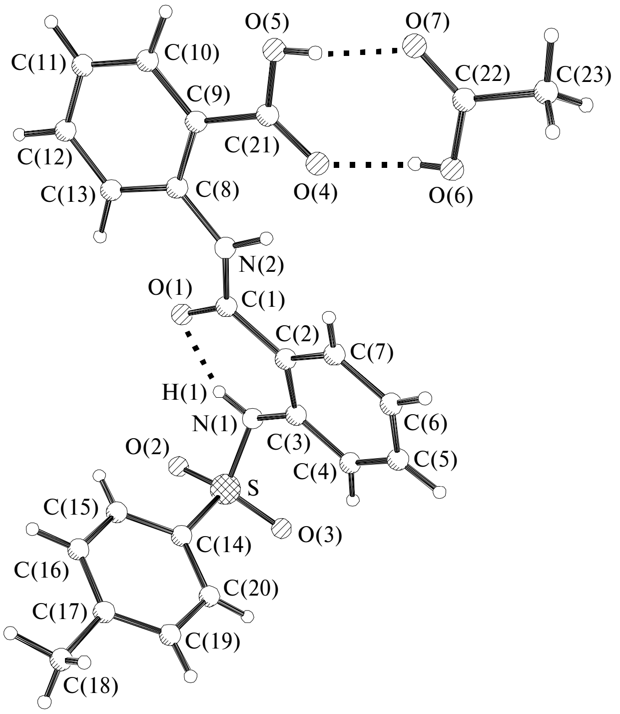

Fig. 1. Overall view of crystal solvate **1a**.

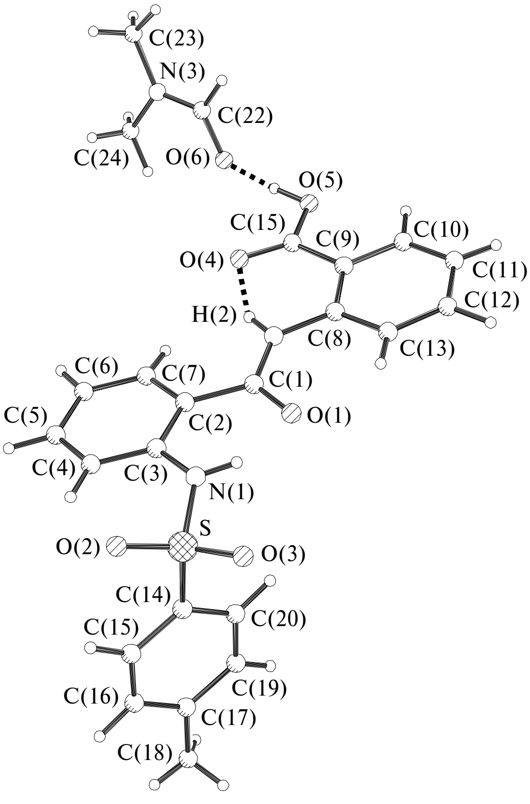

Fig. 2. Overall view of crystal solvate **1b**.

and the O(4)—H(24)—O(6) angle is 171.0(2)°. The carboxyl group in **1b**, unlike that in **1a**, is involved only in one, and yet stronger, intermolecular hydrogen bond with the O atom of the carbonyl group of DMF: the O(5)...O(6) and H(51)...O(6) interatomic distances are 2.576(3) and 1.45(2) Å, respectively (the H(51)—O(5) bond length is 1.15(2) Å), the O(5)—H(51)—O(6) angle is 165.5(2)°. The O(4) atom of the carbonyl group in crystal **1b** is not involved in intermolecular hydrogen bonding (the C(21)—O(4) bond length is 1.218(3) Å), whereas this atom in crystal **1a** participates in hydrogen bonding (the C(21)—O(4) bond length is 1.225(2) Å). The involvement of the O(6) atom of the carbonyl bond of the DMF molecule in intermolecular hydrogen bonding leads to substantial elongation of the C(22)—O(6) bond (1.237(3) Å). The DMF molecule in crystal **1b** is virtually perpendicular to the central fragment of molecule **1**. The angle between the plane of the DMF molecule and the plane passing through the atoms of the central fragment of molecule **1** is 107.8(2)°. The O(1) and O(4) atoms of the carbonyl groups in crystals **1a** and **1b** form intramolecular hydrogen bonds with the amide H(1) and H(2) atoms, respectively. The parameters of the above-listed intramolecular hydrogen bonds are given in Table 1. The O(1)...N(1) distance in **1a** is increased due to rotation of benzene rings *A* and *B* about the C(1)—N(1) bond.

Apparently, a higher degree of nonplanarity of molecule **1a** (green fluorescence), which is stabilized in the crystal (Fig. 3) by intermolecular hydrogen bonds between the COOH groups of molecules **1** and CH_3COOH, and the resulting weakening of N—H...O intramolecular hydrogen bonds leads to the fact that the excited molecule (after absorption of an exciting photon) adopts a coplanar form favorable for more efficient π-conjugation. This, in turn, leads to a decrease in the energy of the lower excitation level and, as a consequence, to a decrease in the energy of the emitted luminescence photon. After emission of the photon, the molecule reverts to the ground state and then changes once again to regain its initial geometrical configuration. These changes, which occur in nonplanar molecule **1a** and which are absent in molecule **1b**, result not only in the bathochromic shift of the fluorescence band of the "green" form by 22 nm compared to that of the "blue" form (the fluorescence maxima are observed at 504 and 482 nm, respectively) (Fig. 4), but also in the hypsochromic shift of the long-wavelength excitation band of the molecules in crystal **1a**.

Table 1. Parameters of hydrogen bonds in crystals **1a** and **1b**

Parameter	**1a**	**1b**
Interatomic distance	*d*/Å	
O(1)...N(1)	2.611(3)	2.532(3)
O(1)...H(1)	1.88(2)	1.80(2)
O(4)...N(2)	2.641(3)	2.634(3)
O(4)...H(2)	1.82(2)	1.90(2)
Bond angle	ω/deg	
O(1)—H(1)—N(1)	142.8(2)	144.1(2)
O(4)—H(2)—N(2)	146.0(2)	147.2(2)

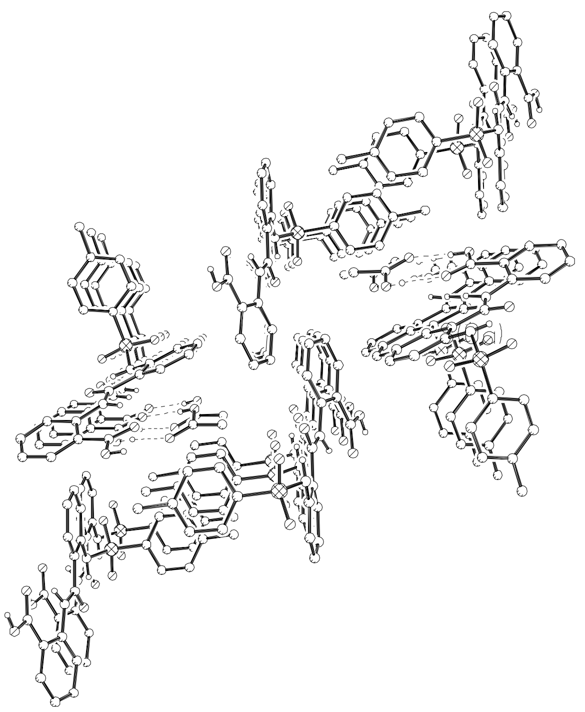

Fig. 3. Fragment of the stacked packing of molecules **1** in crystal **1a**.

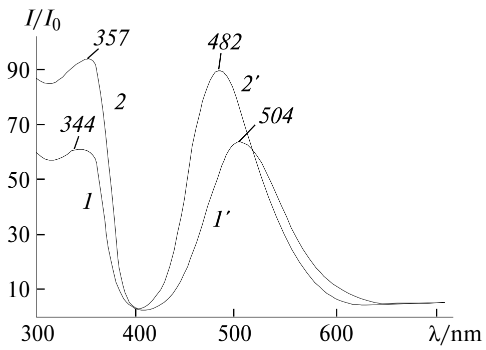

Fig. 4. Excitation (*1*, *2*) and fluorescence (*1′*, *2′*) spectra of crystalline powders of **1a** (*1*, *1′*) and **1b** (*2*, *2′*).

Experimental

Principal crystallographic data for 1a: $C_{21}H_{18}N_2O_5S \cdot CH_3COOH$, M = 470.43, monoclinic system, space group $P2_1/c$, $a = 8.573(2)$, $b = 16.368(3)$, $c = 16.195(3)$ Å, $\beta = 92.48(3)°$, $V = 2270.4(8)$ Å^3, $d_c = 1.345$ g cm^{-3}, $Z = 4$; for **1b**: $C_{21}H_{18}N_2O_5S \cdot (CH_3)_2NCOH$, M = 483.45, monoclinic system, space group $P2_1/n$, $a = 23.290(5)$, $b = 11.050(2)$, $c = 9.458(2)$ Å, $\beta = 101.30(3)°$, $V = 2386.9(8)$ Å^3, $d_c = 1.345$ g cm^{-3}, $Z = 4$. The intensities of 4843 (**1a**) and 4974 (**1b**) independent reflections with $I > 2\sigma(I)$ were measured on an automated four-circle KM-4 diffractometer (Mo-Kα radiation). Both structures were solved by the direct method (SHELX-86)[1] and refined anisotropically by the full-matrix least-squares method (SHELXL-93).[2] The H atoms in the structure of **1a** were located from the Fourier synthesis and only their positional parameters were refined. In the structure of **1b**, the H atoms of the methyl groups were placed in geometrically calculated positions and all other atoms were revealed from the Fourier synthesis. The final values of the *R* factor were 0.046 (**1a**) and 0.047 (**1b**). The atomic coordinates and interatomic distances were deposited with the Cambridge Structural Database.

The fluorescence spectra were recorded on an LS-5 (Perkin—Elmer) spectrofluorimeter with 2.5-nm slits of both monochromators (a flash xenon lamp as the excitation source (~100 Hz), the scan rate was 60 nm min^{-1}, the response time was 1 s, the amplification was 1, the 3% attenuator). The excitation and fluorescence spectra were corrected taking into account the sensitivity of the photoelectric multiplier to different wavelengths. The excitation spectra were measured at the fluorescence maximum. The fluorescence spectra were excited with light with the wavelength 365 nm.

***N*-(*N′*-Tosylanthranoyl)anthranilic acid (1).** Water (2 mL) was added to a solution of 2-(2-tosylaminophenyl)-4*H*-3,1-benzooxazin-4-one (5 g) in pyridine (70 mL). The reaction mixture was refluxed for 1 h, cooled, poured into water (300 mL), and acidified with HCl to pH 6. The precipitate that formed was filtered off, thoroughly washed with water, and dried at ~20 °C. Crystals of **1a** (m.p. 206 °C) were prepared by crystallization from glacial acetic acid. Crystals of **1b** (m.p. 196 °C) were obtained by crystallization from aqueous DMF.

References

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