# PECULIARITIES OF 2-AMINO-3-R-4-ARYL-4*H*-PYRANES MULTICOMPONENT SYNTHESIS DERIVED FROM 1*H*-2,1-BENZOTHIAZIN-4(3*H*)-ONE 2,2-DIOXIDE

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#### **Supplementary materials**

Spectra <sup>1</sup>H NMR were recorded on Varian Mercury VX 200 instrument (spectrum of **8c** was recorded on Bruker AMX 500 spectrometer) using DMSO-d<sub>6</sub> as solvent and TMS as an internal standard. <sup>13</sup>C NMR experiments were performed using Bruker AMX 500 spectrometer or Varian Mercury MR-400 (for **7e** and **8a**). FID files were analyzed and reports were created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc.

IR Spectra were taken on a Perkin–Elmer 298 spectrophotometer in KBr pellets. Mass spectra were taken on a Varian 1200L DIP (EI, 70 eV).

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<sup>13</sup>C NMR spectrum of **5a**, solvent – DMSO- $d_6$ 





## EI-MS of 5a





<sup>13</sup>C NMR spectrum of **5b**, solvent – DMSO- $d_6$ 











<sup>13</sup>C NMR spectrum of **5**c, solvent – DMSO-d<sub>6</sub>





## EI-MS of 5c





<sup>13</sup>C NMR spectrum of **5d**, solvent – DMSO- $d_6$ 











<sup>13</sup>C NMR spectrum of **5**e, solvent – DMSO-d<sub>6</sub>





EI-MS of **5e** 





<sup>13</sup>C NMR spectrum of **5f**, solvent – DMSO- $d_6$ 





#### EI-MS of **5f**





All carbon atoms of anthracene core are unequal due to hindrance of rotation.





# EI-MS of **5g**





<sup>13</sup>C NMR spectrum of **7a**, solvent – DMSO-d<sub>6</sub>











<sup>13</sup>C NMR spectrum of **7b**, solvent – DMSO- $d_6$ 





#### EI-MS of 7b

















<sup>13</sup>C NMR spectrum of **7d**, solvent – DMSO- $d_6$ 



IR spectrum of 7d









IR spectrum of 7e













## EI-MS of 8a

The mass spectra of bis-adduct 8a is characterized by the presence of the heaviest fragment of ion peak ([M-326]<sup>+</sup>) corresponding to enone 11a.





<sup>13</sup>C NMR spectrum of **8b**, solvent – DMSO- $d_6$ 





## EI-MS of 8b

The mass spectra of bis-adduct **8b** is characterized by the presence of the heaviest fragment of ion peak ( $[M-326]^+$ ) corresponding to enone **11b**.





<sup>13</sup>C NMR spectrum of **8c**, solvent – DMSO-d<sub>6</sub>







<sup>13</sup>C NMR spectrum of **8e**, solvent – DMSO- $d_6$ 





## EI-MS of 8e

The mass spectra of bis-adduct 8e is characterized by the presence of the heaviest fragment of ion peak ([M-326]<sup>+</sup>) corresponding to enone 11e.



#### SINGLE CRYSTAL X-RAY DIFFRACTION STUDY of compounds 7b and 8b



Molecular and crystal structure of the compound 7b.

**Figure 1.** The molecular structure of the compound **7b** according to X-ray diffraction data. Thermal ellipsoids of atoms are shown at 50% probability levels.

The compound **7b** exists as methanol monosolvate in the crystal phase. The solvate molecule is disordered over three positions with its non-equal populations (0.5 : 0.25 : 0.25).

The benzothiazine ring adopts a *twist-boat* conformation (the puckering parameters [1] are: S = 0.65,  $\Theta = 51.4^{\circ}$ ,  $\Psi = 27.3^{\circ}$ ). Deviations of the S1 and C8 atoms from the mean plane of the remaining atoms of this ring are -0.90 Å and -0.35 Å, respectively. The pyrane ring is planar within 0.02 Å. The carboxylic fragment of the ester substituent is coplanar to the pyrane ring (the C11-C10-C12-O4 torsion angle is -5.0(2)°), that is stabilized by the N2-H2Nb...O4 intramolecular hydrogen bond (H...O 2.02 Å N-H...O 132°). The formation of hydrogen bond results in the elongation of the O4-C12 bond up to 1.227(2) Å as compared with its mean value [2] 1.210 Å. The ethyl group has *ap*-conformation relatively the C10-C12 bond and the C13-C14 and C12-O5 bonds are anti-periplanar (the C13-O5-C12-C10 and C12-O5-C13-C14 torsion angles are -179.5(1)° and 178.4(1)°, respectively). *Para*-nitrophenyl substituent adopts an axial position and is turned appreciably relatively the pyrane ring (the C7-C8-C9-C15 and C8-C9-

C15-C20 torsion angles are  $-117.7(2)^{\circ}$  and  $60.5(2)^{\circ}$ , respectively). The repulsion between vicinal ester and *p*-nitrophenyl substituents (the shortened intramolecular contact O5...C15 2.96 Å as compared with van der Waals radii sum [3] 3.00 Å) leads to the C9-C15 bond elongation (1.531(2) Å as compared with mean value 1.511 Å). The nitro group is slightly non-coplanar to the aromatic ring (the O7-N3-C18-C19 torsion angle is  $-7.0(2)^{\circ}$ ), in spite of the H17...O6 2.41 Å and H19...O7 2.45 Å attractive interactions (van der Waals radii sum is 2.46 Å) which should not be considered as hydrogen bonds due to too small bond angle value (98° and 96°, respectively). The ethyl substituent at the N1 atom is orthogonal to the planar fragment of the benzothiazine ring (the C1-N1-C21-C22 torsion angle is 92.1(2)°). The steric repulsion between this substituent and the C1...C6 aromatic ring (the shortened intramolecular contacts are: H2...C21 2.66 Å, H21b...C2 2.70 Å, H2...H21b 2.32 Å, H22a...H2 2.30 Å as compared with van der Waals radii sum 2.87 Å for C...H contact and 2.34 Å for H...H contact) causes the elongation of the C1-N1 bond up to 1.412(2) Å (mean value is 1.371 Å).

In the crystal phase the **7b** molecules are bonded with solvate methanol molecules by the N2-H2Na...O1s' intermolecular hydrogen bond (H...O 2.12 Å N-H...O 168°).

Molecular and crystal structure of the compound 8b.



**Figure 2.** The molecular structure of the compound **8b** according to X-ray diffraction data. Thermal ellipsoids of atoms are shown at 50% probability levels.

The **8b** compound corresponds to the triethylammonium salt with organic anion. The hydrogen atom at the N1s is located from the electron density difference maps. Only one peak corresponding to the hydrogen atom is observed between O1 and O4 atoms from the experimental data and it is located nearer to the O4 atom. The O1-C7 and O4-C11 bond lengths are comparable (1.309(4) Å and 1.314(4) Å, respectively) and slightly shorter than the mean value for the Csp<sup>2</sup>-OH bond (1.333 Å). Summary, only one tautomer of organic anion with negative charge at the O1 atom may exist in the crystal phase. The O4-H...O1 strong charge-assisted hydrogen bond (H...O 1.54 Å, O-H...O 177°) is formed.

The bicyclic fragments of the anion is situated very similar relatively the C9-C18 bond (the C7-C8-C9-C18 and C18-C9-C10-C11 torsion angles are -68.0(5)° and 50.05(4)°, respectively). The endocyclic double bonds are almost coplanar to each other (the C7-C8...C10-C11 pseudo-torsion angle is -13.8(4)°) what is stabilized by the O4-H...O1 hydrogen bond considered over. The benzothiazine rings adopt a *twist-boat* conformations (the puckering parameters are: S = 0.52,  $\Theta = 46.9^\circ$ ,  $\Psi = 26.0^\circ$  for the S1...C8 ring and S = 0.61,  $\Theta = 49.1^\circ$ ,  $\Psi =$ 21.4° for the S2...N2 ring). Deviations of the S1 and C8 atoms from the mean plane of the remaining atoms of the S1...C8 ring are 0.69 Å and 0.28 Å, respectively. Pseudo-symmetrical to ones S2 and C10 atoms deviate from the mean plane of the remaining atoms of the S2...N2 ring on -0.82 Å and -0.24 Å, respectively. The C7-C8 and C10-C11 bonds are elongated (1.379(5) Å and 1.360(5) Å) as compared with their mean value 1.331 Å. The aromatic ring of the substituent at the C9 atom is almost coplanar to the C8-C9 exocyclic bond (the C8-C9-C18-C19 torsion angle is -1.7(5)°) and the C9-C18 bond (1.540(5) Å) is elongated (mean value is 1.511 Å). The strong repulsion between substituents at the C9 atom and bicyclic fragment (the shortened intramolecular contacts are C8...H19 2.53 Å, C9...H19 2.64 Å, C10...H23 2.70 Å C7...C19 3.24 Å, C11...C23 3.38 Å (van der Waals radii sum is 2.87 Å for C...H contact and 3.42 Å for C...C contact)) is supposed to be reason of it. The nitro group is non-coplanar to the aromatic ring (the O7-N3-C21-C20 torsion angle is  $14.7(8)^{\circ}$ ). The ethyl substituents are situated in such way that the C24-C25 bond is orthogonal to the planar fragment of bicycle (the C1-N1-C24-C25 torsion angle is -90.2(6)°) and the C26-C27 bond has *-sc*-conformation relatively the C17-N2 bond (the C17-N2-C26-C27 torsion angle is  $-62.3(9)^{\circ}$ ). The considerable steric repulsion is observed between ethyl substituent at the N1 atom and bicyclic ring (the shortened intramolecular contacts H2...C24 2.64 Å, H2...H24b 2.31 Å, H24b...C2 2.70 Å, H2...C25 2.83 Å, H2...H25b 2.31 Å).

The cation and anion are bonded by the N1s-H...O2' (H...O 1.95 Å, N-H...O 152°) intermolecular hydrogen bond in the crystal phase. It causes the elongation of the S1-O2 bond (1.458(3) Å as compared with mean value 1.428 Å).

#### Experimental part. X-ray diffraction study.

The crystals of **7b** (C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub>S · CH<sub>3</sub>OH) are monoclinic. At 100 K a = 21.5619(7), b = 11.3694(4), c = 18.9777(7) Å, b $\beta$  = 93.367(3)<sup>oo</sup>, V = 4642.4(3) Å<sup>3</sup>, Mr = 500.77, Z = 1, space groupC2/c, d<sub>calc</sub>= 1.433 g/cm<sup>3</sup>, mµ(MoKa $\alpha$ ) = 0.194 mm<sup>-1</sup>, F(000) = 2096. Intensities of 24414 reflections (6761 independent, R<sub>int</sub> = 0.029) were measured on the«Xcalibur-3» diffractometer (graphite monochromated MoK<sub> $\alpha$ </sub> radiation, CCD detector,  $\omega$ -scaning, 2 $\Theta_{max}$  = 60°).

The crystals of **8b** (C<sub>6</sub>H<sub>15</sub>NH<sup>+</sup> · C<sub>27</sub>H<sub>24</sub>N<sub>3</sub>O<sub>8</sub>S<sub>2</sub><sup>-</sup>) are orthorhombic. At 293 K a = 13.1522(7), b = 23.496(2), c = 11.0242(5) Å, V = 3406.8(3) Å<sup>3</sup>, Mr = 684.81, Z = 4, space group Pna2<sub>1</sub>, d<sub>calc</sub>= 1.335 g/cm<sup>3</sup>, mµ(MoKa $\alpha$ ) = 0.212 mm<sup>-1</sup>, F(000) = 1448. Intensities of 33893 reflections (9887 independent, R<sub>int</sub> = 0.053) were measured on the«Xcalibur-3» diffractometer (graphite monochromated MoK<sub> $\alpha$ </sub> radiation, CCD detector,  $\omega$ -scaning, 2 $\Theta_{max}$  = 60°).

The structures were solved by direct method using SHELXTL package [4]. Position of the hydrogen atoms were located from electron density difference maps and refined by "riding" model with  $U_{iso} = nU_{eq}$  of the carrier atom (n = 1.5 for methyl and hydroxyl groups and for water molecule and n = 1.2 for other hydrogen atoms). Full-matrix least-squares refinement of the

structures against F<sup>2</sup> in anisotropic approximation for non-hydrogen atoms using 6714 (**7b**), 9840 (**8b**) reflections was converged to:  $wR_2 = 0.131$  ( $R_1 = 0.048$  for 5324 reflections with F>4 $\sigma$ (F), S = 1.046) for structure **7b** and  $wR_2 = 0.189$  ( $R_1 = 0.067$  for 4692 reflections with F>4 $\sigma$ (F), S = 0.918) for structure **8b**. The final atomic coordinates, and crystallographic data for molecules **7b** and **8b** have been deposited to with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition numbers CCDC 1405511 for **7b** and CCDC 1405512 for **8b**).

#### Literature.

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