

## The Interaction of Mesoionic Benzo[*c*]tetrazolo[2,3-*a*]cinnolinium-2-olate with Hydroxy Groups

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**Keywords:** mesoionic compounds, co-crystals, pseudo-polymorphism, crystal structure, intermolecular interaction

Mesoionic compounds have characteristic electronic states, and are classified into five groups, among which class 5 mesoionic compounds are particularly interesting because they exhibit more polarized properties than other mesoionic compounds.<sup>1,2</sup> Experimental studies of class 5 mesoionic compounds, however, are strictly limited. Class 5 mesoionic compounds are normally stabilized by forming hydrogen bond between the exocyclic atom and a donor group.<sup>3</sup> We have found that benzo[*c*]tetrazolo[2,3-*a*]cinnolinium (BTCs) is a class 5 mesoionic compound that can be handled stably under ambient conditions.<sup>4</sup> We report here that synthesis of BTC olate **1** and a variety of solvated crystals of **1** with several small molecules including methanol, formic acid, acetic acid, propionic acid and trifluoro acetic acid. In addition, these crystals were analyzed using single crystal X-ray structure analysis and symmetry-adapted perturbation theory (SAPT) calculations.

BTC·H<sub>2</sub>O **1aa** was isolated by reprecipitation from a solution of anhydride **1** in acetonitrile-H<sub>2</sub>O, and X-ray-suitable crystals were obtained through slow volatilization from a CH<sub>2</sub>Cl<sub>2</sub>/EtOH solution of **1aa** (Fig. 1), while from a solution containing a small amount of Et<sub>3</sub>N, BTC·H<sub>2</sub>O **1ab** with different space groups was obtained (**1aa**: orthorhombic, **1ab**: monoclinic). A series of pseudo-polymorphic crystals **1b-f** were isolated from solutions of **1** in methanol, formic acid, acetic acid, propionic acid, or trifluoro acetic acid, and their single-crystal X-ray structure analysis revealed that hydrogen bonds form between the tetrazolium olate group and the hydroxy groups (Table 1). The interaction energy analysis of **1a-f** at the SAPT0/jun-cc-pVDZ level proposed relatively large electrostatic interaction in **1c**, **1d** and **1f**.

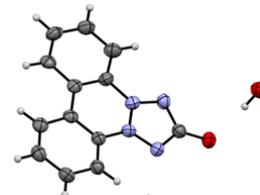
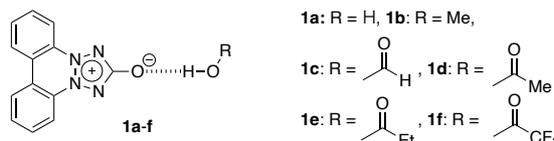


Fig. 1 **1aa**

Table 1. Hydrogen bond geometry and SAPT0 interaction energy of BTC olate **1** with hydroxy groups.



Mol.	Solvate	Hydrogen bond geometry <sup>a</sup>		Intermolecular interaction energy <sup>b</sup>	
		D-A distance [Å]	D-H-A angle [°]	$E_{elst}$ [kcal/mol]	$E_{total}$ [kcal/mol] <sup>c</sup>
<b>1aa</b>	H <sub>2</sub> O (orthorhombic)	2.809(7)	147.75	-13.03	-9.16
<b>1ab</b>	H <sub>2</sub> O (monoclinic)	2.810(4)	174.87	-14.17	-10.34
<b>1b</b>	methanol	2.7483(14)	176.68	-11.13	-7.44
<b>1c</b>	formic acid	2.5826(19)	164.79	-21.56	-15.16
<b>1d</b>	acetic acid	2.564(2)	175.07	-23.42	-15.94
<b>1e</b>	propionic acid	2.561(3)	169.32	-16.90	-9.72
<b>1f</b>	TFA	2.457(3)	168.76	-26.90	-16.59

<sup>a</sup> Measurement by X-ray diffraction of single crystal structure analysis. <sup>b</sup> Calculation at SAPT0/jun-cc-pVDZ level. <sup>c</sup>  $E_{total} = E_{elst} + E_{exch} + E_{ind} + E_{disp}$

<sup>1</sup> W. P. Oziminski, C. A. Ramsden, *Tetrahedron* **2015**, *71*, 7191. <sup>2</sup> C. A. Ramsden, *Prog. Heterocycl. Chem.* **2016**, *28*, 1. <sup>3</sup> C. A. Ramsden, W. P. Oziminski, *Tetrahedron Lett.*, **2019**, *60*, 150876. <sup>4</sup> M. Nakata, T. Hirashita, 99<sup>th</sup> Annual Meeting of the Chemical Society of Japan, Japan, 2PB-177, **2019**.