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PII:	S1386-1425(16)30252-9
DOI:	doi: 10.1016/j.saa.2016.05.008
Reference:	SAA 14429

To appear in:

Received date:11 December 2015Revised date:27 April 2016Accepted date:9 May 2016



Please cite this article as: Ibrahim Sen, Hulya Kara, Akın Azizoglu, Substituent effects on hydrogen bonding of aromatic amide-carboxylate, (2016), doi: 10.1016/j.saa.2016.05.008

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### Substituent Effects on Hydrogen Bonding of Aromatic Amide-Carboxylate

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#### ABSTRACT

*N*-(p-benzoyl)-anthranilic acid (**BAA**) derivatives have been synthesized with different substituents (X: Br, Cl, OCH<sub>3</sub>, CH<sub>3</sub>), and their crystal structures have been analyzed in order to understand the variations in their molecular geometries with respect to the substituents by using <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR and X-ray single-crystal diffraction. The carboxylic acid group forms classic O–H···O hydrogen bonded dimers in a centrosymmetric  $R_2^2(8)$  ring motifs for **BAA-Br** and **BAA-Cl**. However, no carboxylic acid group forms classic O–H···O hydrogen bonded dimers in **BAA-OCH<sub>3</sub>** and **BAA-CH<sub>3</sub>**. The asymmetric unit consists of two crystallographically independent molecules in **BAA-OCH<sub>3</sub>**. DFT computations show that the interaction energies between monomer and dimer are in the range of 0.5 – 3.8 kcal/mol with the B3LYP/6-31+G<sup>\*</sup>, B3LYP/6-31++G<sup>\*</sup>, B3LYP/6-31++G<sup>\*\*</sup>, and B3LYP/AUG-cc-pVDZ levels of theory. The presence of different hydrogen bond patterns is also governed by the substrate. For monomeric compounds studied herein, theoretical calculations lead to two low-energy conformers; *trans* (**a**) and *cis* (**b**). Former one is more stable than latter by about 4 kcal/mol.

Keywords: Hydrogen bonding, Crystal structure, Computational methods, DFT

#### **1. Introduction**

The basis of crystal engineering is to understand the relationship between the crystal structure and molecular structure. This can be achieved by studying the most prominent intermolecular interactions in the crystals, mainly the hydrogen bonds [1]. Hydrogen bonding has considerable interest in many fields within chemistry and material science because of its fundamental role in the vital biological, chemical processes and crystal engineering [2]. Among the most widely investigated ones are the strong O-H…O, O-H…N, N-H…N, and N-H…O non-covalent interactions in various organic compounds, which have already found extensive applications in molecular recognition and self-assembly [3].

Amides tends to form modestly intermolecular and intramolecular N-H···O hydrogen bonding. To exploit weak intramolecular N-H···O-H hydrogen bonding in amide derivatives, the more competitive intermolecular N-H···O=C interaction needs to suppressed. Several techniques have been developed to investigate weak inter- or intramolecular hydrogen bonding in solution and/or in the solid phase. The NMR spectroscopy is promising for studies in solution [4], the IR spectroscopy can be used to detect samples in both the solution and solid state [5]. The computational studies can provide useful information about the effects of discrete factors on the stability of the H-bonds, [6, 7b] which are particularly valuable when experimental evidences are not available.

Controlling the crystal structure provides to understand the strength and directional preferences of hydrogen bonds and intermolecular interactions. The energies for the strongest O-H···O hydrogen bonds are within 8-11 kcal/mol ranges and weaker than covalent bonds, the former can be easily deformed by packing forces and exhibit variable geometry in crystals [8].

Comparing the energies of different conformers of a compound helps us to understand inter and intramolecular influences on a particular crystal form. Computational techniques are used for studying intermolecular interactions between different molecules of co-crystalline materials and help to determine the influence of nearest neighbor molecules in a crystal on the molecular polarization [9].

In this report, X-ray crystallographic, NMR studies, and theoretical calculations at DFT levels were used to probe the effects of substituent groups on the stabilization

of amide N-H···O hydrogen bonds. The importance of substituents in amide hydrogen bonding has been demonstrated using a series of small-organic molecule models derived from 2-benzamidobenzoic acids (Scheme 1).

#### Scheme 1

#### 2. Materials and Methods

#### 2.1. General Procedure for the preparation of target compounds

The procedure to synthesize the target compounds is known in the literature [7]. To a solution of anthranilic acid (1.1 mmol) in anhydrous THF (5 ml) was added 1.0 mmol of the appropriate benzoyl chloride at room temperature. After cooling the solution with ice bath, 1.2 mmol of triethylamine was added dropwise and reaction was stirred at room temperature for additional 3-10 h. The mixture was poured into a 25 mL cold solution of 1.0 M HCl, and precipitates were collected by filtration. Recrystallization from acetonitrile afforded the desired compound in quantitative yields. Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), m (multiplet). <sup>1</sup>H-NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer at 400 MHz. It is also recommended to acquire <sup>1</sup>H NMR spectra in DMSO- $d_6$ , where otherwise exchangable protons such as those of COOH, NH, and NH<sub>2</sub> are usually visible [10]. All chemical reagents and solvents were purchased from Merck or Aldrich Co. and used without further purification. Analytical grade solvents were used for the crystallization experiments. FT-IR spectra were measured with a Perkin-Elmer Model Bx 1600 instrument with the samples as KBr pellets in the 4000–400  $\text{cm}^{-1}$  range.

**2-(4-Bromobenzamido)benzoic acid (BAA-Br):** IR : v 3317 (N-H), 3102 (Ar-H), 3024 (Ar-H), 2643 (OH-C=O), 1689 (C=O), 1661 (C=O, first amide band), 1585 (C=O, secondary amide band), 1485-1468 (C=C) cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO  $d_6$ ):  $\delta$ =13.2 (s, 1H), 12.1 (s, 2H), 8.7 (dd, *J*=8.2, 1.1 Hz, 2H), 8.1 (dd, *J*=7.9, 1.5 Hz, 2H), 7.9 (d, *J*=8.4 Hz), 7.4-7.3 (m), 7.2 (td, *J*=8.0, 1.0 Hz).

**2-(4-Chlorobenzamido)benzoic acid (BAA-Cl):** IR: v 3311 (N-H), 3102 (Ar-H), 3024 (Ar-H), 2650 (OH-C=O), 1692 (C=O), 1659 (C=O, first amide band), 1587

(C=O, secondary amide band), 1488-1468 (C=C), cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO *d*<sub>6</sub>): δ=13.4 (s, 1H), 12.1 (s, 2H), 8.7 (dd, *J*=8.3, 1.1 Hz, 2H), 8.0 (dd, *J*=8.0, 1.5 Hz, 2H), 7.9 (d, *J*=8.7 Hz), 7.7-7.6 (m), 7.2 (td, *J*=8.0, 1.2 Hz).

**2-(4-Methoxybenzamido)benzoic acid (BAA-OCH<sub>3</sub>):** IR: v 3317 (N-H), 3127 (Ar-H), 2368 (OH-C=O), 1685 (C=O), 1647 (C=O), first amide band), 1585 (C=O, secondary amide band), 1508-1458 (C=C), cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO  $d_6$ ):  $\delta$ =13.4 (s, 1H), 12.1 (s, 2H), 8.7 (d, *J*=8.2 Hz, 2H), 8.1 (dd, *J*=8.1, 1.5 Hz, 1H), 7.7 (d, *J*=8.3 Hz), 7.6-7.5 (m), 7.3-7.2 (m), 6.9 (d, *J*=8.5 Hz), 3.7 (s, 3H).

**2-(4-Methylbenzamido)benzoic acid (BAA-CH<sub>3</sub>):** IR: v 3317 (N-H), 3124 (Ar-H), 2345 (OH-C=O), 1654 (C=O, first amide band), 1542 (C=O, secondary amide band), 1508-1449 (C=C), cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO *d*<sub>6</sub>): δ=12.2 (s, 1H), 8.7 (d, *J*=8.1 Hz, 1H), 8.1 (d, *J*=8.0 Hz, 1H), 7.9 (d, *J*=8.1 Hz, 2H), 7.7 (t, *J*=8.0 Hz, 1H), 7.4 (d, *J*=8.0 Hz, 2H), 7.2 (t, *J*=7.7 Hz, 1H), 2.4 (s, 4H).

#### 2.2. Crystal structure determination

Diffraction measurements were made on a Bruker ApexII kappa CCD diffractometer using graphite monochromated Mo–K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å) at 100 K for **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub>. The intensity data were integrated using the APEXII program [11]. Absorption corrections were applied based on equivalent reflections using SADABS [12]. The structures were solved by direct methods and refined using full-matrix least-squares against F<sup>2</sup> using SHELXL [13]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealized positions with isotropic displacement parameters constrained to 1.5 times the U<sub>equiv</sub> of their attached carbon atoms for methyl hydrogens, and 1.2 times the U<sub>equiv</sub> of their attached carbon atoms for all others. All of the crystallographic computations were carried out using Shelxtl, Mercury 3.3 [14] and Ortep-3 [15] programs. Details of the data collection parameters and crystallographic information for the complexes are summarized in Table 1. Ortep diagrams of BAAs are depicted in Figure 1, and packing diagrams are displayed Figure 2, Figure 3, Figure 4, and Figure 5.

#### **2.3.** Computational Details

The initial geometries of **BAAs** have been calculated with density functional theory (DFT) [16] using the combined Becke's three-parameter exchange functional and the gradient-corrected functional of Lee, Yang and Parr (B3LYP functional) [17] at the 6-31+G\* level. This functional has been demonstrated to predict reliable geometries for hydrogen bonded systems [18]. Single point calculations at the B3LYP/6-31+G\*, B3LYP/6-31++G\*\* and B3LYP/AUG-cc-pVDZ [19] level were performed on the fully optimized geometries using the B3LYP/6-31+G\* method. All calculations in the gas phase are achieved using the Gaussian03 program [20].

#### **3. Results and discussion**

#### **3.1. Description of the crystal structure of BAAs**

Crystals of **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub> have analogous structures with different substituents. Intramolecular N–H···O hydrogen bonds are observed in **BAAs**. The carboxylic acid group forms classic O–H···O hydrogen bonded dimers in a centrosymmetric  $R_2^2(8)$  ring motifs which link the molecules into pairs around inversion centers in a supramolecular assembly in the unit cell of **BAA-Br** and **BAA-Cl**.

#### Fig. 1

#### Table.1

In the crystalline architecture of **BAA-Br**, the dimers are involved in N1– $H1\cdots O3$  interactions generating an open ended chain structure along the *b* axis (Fig. 2a). These chains form zig-zag packing structure in the *bc* plane (Fig. 2b). The parallel arrangement of the almost planar dimeric units in columns is indicated by the projection in Fig. 2c.

#### Fig. 2

In the crystalline architecture of **BAA-Cl**, intermolecular C5–H5…O3 weak hydrogen bonds link the dimers generating  $R_2^2(14)$  motifs (Figure 3a). The dimers linked by C–H…Cl [21] and C–H…O [22] weak intermolecular interactions to form infinite 3D structure of **BAA-Cl** (Figure 3b and Figure 3c). This hydrogen bonded polymeric networks lie in the *ab*-plane and stacks along to the *c*-axis (Figure 3b). The parallel arrangement of the almost planar dimeric units in columns is indicated by the projection in the *bc*-plane and stacks along to the *a*-axis (Fig. 3c). Besides that there is an intermolecular C11-H11… $\pi$  contact [H…Cg2 = 2.88 Å, C11… $\pi$  = 3.5303 Å, C11-H… $\pi$  = 127°, Cg2 = C9-C10-C11-C12-C13-C14, xiii = 1-x,-1/2+y,1/2-z] in 2.  $\pi \dots \pi$ stacking is not discernible due to the large distances between adjacent arene moieties (d > 4 Å) for **BAA-Br** and **BAA-Cl**.

#### Fig. 3

The atomic size, polarization, and radial anisotropy increase in the order Cl < Br < I, whereas electronegativity changes are in the reverse order [23]. While  $Cl \cdots H$  interaction is seen for **BAA-Cl**, Br $\cdots$ H interaction not appears for **BAA-Br** (Table 2).

#### Table 2

The carboxylic acid group don't form classic O–H…O hydrogen bonded dimers BAA-OCH<sub>3</sub> and BAA-CH<sub>3</sub>. The asymmetric unit in consists of two crystallographically independent molecules in BAA-OCH<sub>3</sub> (Figure 1c). In the crystalline architecture of **BAA-OCH<sub>3</sub>**, intermolecular O2–H2…O7/O6–H6…O3 and C21-H21···O1/C6-H6···O5 hydrogen bonds link the molecules, generating  $R_2^2(10)$ motifs and also the O2/O6 atom of carboxylate group form bifurcated weak hydrogen bond with methyl group of aromatic ring which produce  $R_2^{(2)}(8)$  motifs via C3-H3···O4/C18-H18···O8 and C15-H15B···O2/C30-H30B···O6 weak interactions which leads to form 2D sheet in bc plane. C30-H30A...O1 weak intermolecular interaction connect the molecules in the structure of BAA-OCH<sub>3</sub> which form to channels in 3D network of hydrogen bonds. This polymeric networks lie in the acplane and stacks along to the b-axis (Figure 4b). Besides that  $\pi \cdots \pi$  interactions

between the aromatic rings  $(Cg2\cdots Cg2^{xiii} = 3.8525 \text{ Å}, Cg3\cdots Cg3^{xiv} = 3.6702 \text{ Å}, Cg4\cdots Cg4^{iii} = 3.7778 \text{ Å}, [Cg2=C9-C10-C11-C12-C13-C14, Cg3=C16-C17-C18-C19-C20-C21, Cg4=C24-C25-C26-C27-C28-C29, iii = 2-x,1-y,-z, xiii = -x,-y,1-z, xiv = 2-x,-y,-z]$  are also observed in the hydrogen bonded assembly of **BAA-OCH**<sub>3</sub>.

#### Fig. 4

The geometrical parameters show that  $N-H\cdots O$  interactions should be stronger than C-H···O interactions if we assume that the proton···acceptor distance is an approximation of hydrogen bonding strength. Additionally, the N-H···O bond for crystal structure **BAA-OCH**<sub>3</sub> should be the strongest of all of the interactions of this type. The geometrical parameters for the O-H···N intramolecular H bond also show that this is the strongest interaction for all H bonds existing within the crystal structures investigated here [24].

In the crystalline architecture of **BAA-CH**<sub>3</sub>, intermolecular O2–H2···O3 and C6–H6···O1 hydrogen bonds link the molecules generating  $R_2^2(10)$  motifs which leads to form hydrogen bonded one-dimensional chain structure of **BAA-CH**<sub>3</sub> along *a* axis. Also the O1 atom of carboxylate group form bifurcated C10–H10···O1 weak intermolecular hydrogen bond which leads to form 2D sheet in *bc* plane (Figure 5b). This polymeric 2D networks lie in the *ac*-plane and stacks along to the *b*-axis (Figure 5c).  $\pi \cdots \pi$  stacking is not discernible due to the large distances between adjacent arene moieties (d > 4 Å) for **BAA-CH**<sub>3</sub>.

#### Fig. 5

#### **3.2 DFT Calculations**

The energetic of hydrogen bonds in the solid state cannot be directly measured, and this type of bonding leaves upon questions in many structural works. Computational chemistry, on the other hand, generates theoretical results on hydrogen bond energies at an inflationary rate, many obtained at high levels [25] and even more in rather routine computations using black-box methods. Density functional theory (DFT) is very appealing due to its excellent performance to cost ratio, and DFT

methods, very successful in modeling hydrogen bonded systems, are widely used in the computational chemistry community [26]. Hence, we wish to determine the strength of hydrogen-bonding in BAA-Br, BAA-Cl, BAA-OCH<sub>3</sub>, and BAA-CH<sub>3</sub> with the help of DFT calculations using various diffuse functions. The geometries of monomers and dimers of title compounds were initially optimized at the B3LYP/6-31G\* level of theory. Then, single point calculations were achieved at B3LYP/6-31+G\*, B3LYP/6-31++G\*, B3LYP/6-31++G\*\*, and B3LYP/AUG-cc-pVDZ levels. The interaction energy of  $\Delta E$  of dimers, defined as the difference between the energy of the complex and that of isolated monomers (in the geometry of the complex), was calculated using the formula;  $\Delta E_{int} = E_{dimer} - 2E_{monomer}$  (Table 3). The trends in interaction energy are similar at all levels of theory except for B3LYP/AUG-cc-pVDZ level. Moreover, the geometrical parameters in the crystalline architecture of BAA-OCH<sub>3</sub> show that N-H…O interactions should be stronger than C-H…O interactions if we assume that the proton...acceptor distance is an approximation of hydrogen bonding strength. This experimental finding is only proved by diffuse double-ζ basis function AUG-cc-pVDZ, which shows the highest interaction energy for dimer BAA-OCH<sub>3</sub>. Baruah et al. stated that the importance of such small interaction energies in crystal lattice is well documented with the help of AUG-cc-pVDZ basis set [25b]. The dimeric structure in **BAA-OCH**<sub>3</sub> should help reduce the torsion of the amide unit from the attached phenyl ring. It is also reasonable to indicate that the inter- and intramolecular interactions actually stabilized each other to result in the final crystal structures.

#### Table 3

Understanding the relationship between molecular structure and crystal structure is the basis aspect in crystal engineering. Carboxylic acids play important roles in many processes in chemistry and biology [27]. There should be two forms for the monomer of studied carboxylic acids; *trans* (**a**) and *cis* (**b**). The former has the carboxylic -OH group pointing toward the amide group, while the latter has the two pointing away from each other. A 180° rotation about the C-O single bond would transform one isomer into the other. To understand the structural geometry of the N–H···O hydrogen bond, conformational search calculations were performed at the B3LYP/6-31+G\* level. The theoretical calculations resulted in two low-energy

conformers for compounds **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub> (Fig. 6). In conformer **a** and **b**, N-H bond lengths of **BAA-Br**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub> remained unchanged. However, it is only shorter by 0.01 Å in the *trans* conformer of **BAA-Cl**. In conformer **b**, O····H distances are found to be 1.85 Å for **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub>, whereas in conformer **a**, these values are determined to be 1.82, 1.81, 1.83, 1.83 Å respectively. The relative energies realized through calculations predicted *trans* conformers of **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub>, whereas of **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub>, whereas of **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub>, whereas of **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub>, to be more stable by 4.18, 4.44, 4.04, and 4.01 kcal/mol, respectively.

# Fig. 6

#### 4. Conclusions

In this study, the roles of intermolecular interactions of a series of four amide derivatives (**BAAs**) have been analyzed through single crystal studies and DFT computations. These compounds demonstrate the formation N–H····O=C as a primary structural motif, which constitute the key supramolecular synthon essential for the formation of the crystal packing. The analysis of the interaction energy of the molecular pairs via quantum chemical calculations suggests the presence of significant stabilization from strong as well as weak interactions in the crystal packing, where it has been observed for **BAA-Br** and **BAA-Cl** that the centrosymmetric N–H···O supramolecular synthon has a significant contribution toward the overall stabilization.

DFT calculations about monomer and dimer of **BAAs** to determine the strength of intermolecular hydrogen bonds show that the lowest interaction energy with  $B3LYP/6-31+G^*$ ,  $B3LYP/6-31++G^*$ , and  $B3LYP/6-31++G^{**}$  basis sets is determined in the compound **BAA-CH**<sub>3</sub>, whereas that with the AUG-cc-pVDZ basis set is found in the compound **BAA-Br**. We have also demonstrated with the help of quantum chemical calculations that intramolecular N-H···O=C hydrogen bonds exist in title compounds when the competing intramolecular N-H···O-H hydrogen bond is inhibited with the energy barriers of ~4 kcal/mol.

#### Acknowledgments

The authors are indebted to the Scientific and Technical Research Council of Turkey (TUBITAK) and Balikesir Uinversity for their financial support. Prof. Kara would like to thank TUBITAK for NATO-B1 and the Royal Society short visit fellowship for financial support and Prof. Guy Orpen (School of Chemistry, University of Bristol, UK) for his hospitality. The authors are also very grateful to Dr. Mairi F. Haddow (The School of Chemistry, University of Bristol) for the X-ray measurements.

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#### References

[1] (a) Y. Dimitrova, L.I. Daskalova, Spectrochim. Acta A 71 (2009) 1720.

(b) E. Selvakumar, G. Anandha babu, P. Ramasamy, Rajnikant, T. Uma Devi, R. Meenakshi, A. Chandramohan, Spectrochim. Acta A 125 (2014) 114-119.

(c) B. Sridhar, J. B. Nanubolu, K. Ravikumar, CrystEngComm. 14 (2012) 7065.

[2] (a) S. Scheiner, Hydrogen Bonding: A Theoretical Perspective, Oxford University Press, 1997.

(b) G. A. Jeffrey, An Introduction to Hydrogen Bonding; Oxford University Press: New York, 1997.

(c) J. W. Steed, J. L. Atwood, Supramolecular Chemistry; John Wiley&Sons: Chichester, 2000.

[3] (a) S. H. Gellman, Acc. Chem. Res. 31 (1998) 173.

(b) T. Steiner, Angew. Chem. Int. Ed. 41 (2002) 48.

(c) M. Karabacak, E. Kose, A. Atac, Spectrochim. Acta A 91 (2012) 83.

(d) D. Tzeli, I. D. Petsalakis, G. Theodorakopoulos, D.Ajami, J. Jr. Rebek, Int. J. Quant. Chem. 113 (2013) 734.

(e) Z. Moosavi-Tekyeh, S. F. Tayyari, Spectrochim. Acta A 135 (2015) 820.

[4] R. G. N. Manjunatha, K. M. V. Vasantha, Row, G. T. N. Suryaprakash, N. Phys. Chem. Chem. Phys. 12 (2010) 13232

[5] A. C. Legon, Chem. Soc. Rev. 19 (1990) 197.

[6] (a) J. D. Dunitz, ChemBioChem. 5 (2004) 614.

(b) Z. Liu, R. C. Remsing, D. Liu, G. Moyna, V. Pophristic, J. Phys. Chem. B 113 (2009) 7041.

- [7] (a) D. T. Zentmyer, E. C. Wagner, J. Org. Chem. 14 (1949) 967.
- (b) B. U. Emenike, A. T. Liu, E. P. Naveo, J. D. Roberts, J. Org. Chem. 78 (2013) 11765.
- [8] (a) T. Kozlecki, P. M. Tolstoy, A. Kwocz, M. A. Vovk, A. Kochel, I. Polowczyk, P. Y.

Tretyakov, A. Filarowski, Spectrochim. Acta A 149 (2015) 254–262.

- (b) K. J. Kolonko, H. J. Reich, J. Am. Chem. Soc. 130 (2008) 9668.
- (c) Y. Y. Zhu, H. P. Yi, C. Li, X. K. Jiang, Z. T. Li, Cryst. Growth Des. 8 (2008) 1294.
- [9] M. L. Peterson, M. K. Stanton, R. C. Kelly, R. Staples, A. Cheng, CrystEngComm. 13 (2011) 1170.
- [10] P. Wiklund, J. Bergman, Tetrahedron Lett. 45 (2004) 969.
- [11] Bruker–AXS SAINT V7.60A.

[12] G. M. Sheldrick, SADABS V2008/1, University of Göttingen, Germany.

[13] G. M. Sheldrick, SHELXTL Version 5.1, *Program for the Solution and Refinement of Crystal Structures*, Bruker AXS, Inc., Madison, WI, USA, 1999.

[14] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock,L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, J. Appl. Crystallogr.41 (2008) 466.

[15] L. J. Farrugia, J. Appl. Cryst. 30 (1997) 565.

[16] (a) J. Ireta, J. Neugebauer, M. Scheffler, J. Phys. Chem. A 108 (2004) 5692.

(b) P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.

[17] (a) A. D. Becke, J. Chem. Phys. 98 (1993) 5648. (b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 37 (1988) 785.

[18] (a) A. Dkhissi, L. Adamowicz, G. Maes, Chem. Phys. Lett. 324 (2000) 127.

(b) I. Sen, C.B. Yildiz, H. Kara, A. Azizoglu, Phosphorus Sulfur Silicon Rel. Elem. 11 (2013) 1621.

(c) A. Dkhissi, L. Adamowicz, G. Maes, J. Phys. Chem. A 104 (2000) 2112.

(d) U. Korkmaz, A. Bulut, Spectrochim. Acta Part A 130 (2014) 376.

[19] D. E. Woon, T. H. Jr. Dunning, J. Chem. Phys. 98 (1993) 1358.

[20] Gaussian03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. E. Montgomery, J. A. Peralta Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, R. Staroverov, V. N Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B.

Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian Inc., Wallingford, 2003. [21] C. B. Aakeröy, T. A. Evans, K. R. Seddon, I. Palinko, New J. Chem. (1999) 145-152.

[22] T. Steiner, Crystallogr. Rev. 9 (2003) 177.

[23] S. K. Nayak, M. K. Reddy, T. N. G. Row, D. Chopra, Cryst. Growth Des. 11 (2011)1591.

[24] A. J. Rybarczyk-Pirek, S. J. Grabowski, J. Nawrot-Modranka, J. Phys. Chem. A 107 (2003) 9236.

[25] (a) U. Lourderaj, K. Giri, N. Sathyamurthy, J. Phys. Chem. A 110 (2006) 2709.

(b) D. Singh, P. K. Bhattacharyya, J. B. Baruah, Cryst. Growth Des. 10 (2010) 348.

[26] (a) D. Tzeli, G. Theodorakopoulos, I. D. Petsalakis, D. Ajami, J. Jr. Rebek, J. Am. Chem. Soc. 133 (2011) 16977.

- (b) J. Tonannavar, Y. B. Chavan, J. Yenagi, Spectrochim. Acta A 149 (2015) 860.
- (c) Z. Moosavi-Tekyeha, S. F. Tayyari, Spectrochim. Acta A 135 (2015) 820.
- [27] (a) Y. Y. Zhu, L. Jiang, , Z.-T. Li, CrystEngComm. 11 (2009) 235.
- (b) N. Saracoglu, O. Talaz, A. Azizoglu, W. H. Watson, M. Balci, J. Org. Chem. 70 (2005) 5403.

(c) A. G. Osborne, Z. Goolamali, Spectrochim. Acta A 56 (2000) 1079.

(d) T. Joselin Beaula, A. Packiavathi, D. Manimaran, I. Hubert Joe, V.K. Rastogi, V. Bena Jothy, Spectrochim. Acta A 138 (2015) 723.

### FIGURE CAPTIONS

Fig. 1. The ORTEP illustrations of BAA-Br, BAA-Cl, BAA-OCH<sub>3</sub>, and BAA-CH<sub>3</sub>.

Fig. 2. (a) Hydrogen bonded dimers are involved in N-H...O intermolecular interactions generating an open ended chain structure of **BAA-Br**. (b) The zig-zag chain structure of **BAA-Br** in the *bc*-plane. (c) View of the same dimers in 1 **BAA-Br** as in Figure 2b after a 90° rotation, showing the planar sheet (view down crystallographic axis *b* direction). (d) Space filling representation of **BAA-Br** as in Figure 1c.

**Fig. 3.** (a) Hydrogen bonded dimers are involved in C–H····Cl weak interactions generating a 2D sheet in the structure of **BAA-Cl**. (b) The packing structure of **BAA-Cl** in the *ab*-plane (view down crystallographic axis *c* direction). (c) View of the same dimers in **BAA-Cl** as in Figure 3b after a 90° rotation, showing the planar sheet in the *bc*-plane (view down crystallographic axis *a* direction). (d) Space filling representation of **BAA-Cl** as in Figure 3c.

Fig. 4. (a) Hydrogen bonded 2D sheet in the structure of **BAA-OCH**<sub>3</sub> in bc plane. (b)  $C-H\cdots O$  weak intermolecular interaction connect the molecules in the structure of **BAA-OCH**<sub>3</sub> which form to channels in 3D network of hydrogen bonds (view down crystallographic axis *b* direction). (c) Space filling representation of **BAA-OCH**<sub>3</sub> as in Figure 3c.

Fig. 5. (a) Hydrogen bonded one-dimensional chain structure of BAA-CH<sub>3</sub>. (b) C-H···O weak intermolecular hydrogen bond form 2D sheet in bc plane. (c) View of the same 2D sheets in BAA-Cl as in Figure 5b after a 90° rotation, the polymeric 2D networks lie in the ac-plane and stacks along to the b-axis. (d) Space filling representation of BAA-CH<sub>3</sub> as in Figure 5c.

**Fig. 6.** Low-energy conformers and the relative energy for the title compounds **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub> at B3LYP/6-31+G\* level. The selected O <sup>...</sup> H and N-H distances are given in Å.

Scheme 1 Synthesis of title compounds; BAA-Br, BAA-Cl, BAA-OCH<sub>3</sub>, and BAA-CH<sub>3</sub>.











(a)







(**d**)













### TABLE CAPTIONS

Table 1 Crystal data and structure refinement of compounds BAA-Br, BAA-Cl, BAA-OCH<sub>3</sub>, and BAA-CH<sub>3</sub>.

Table 2 Intramolecular and intermolecular hydrogen bond geometry (bond length in Å, bond angle and in °) of compounds BAA-Br, BAA-Cl, BAA-OCH<sub>3</sub>, and BAA-CH<sub>3</sub>.

**Table 3** Interaction Energies ( $\Delta E_{int} = E_{dimer} - 2E_{monomer}$ ) of **BAA-Br**, **BAA-Cl**, **BAA-OCH**<sub>3</sub>, and **BAA-CH**<sub>3</sub> (in kcal/mol).

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Compound No	BAA-Br	BAA-Cl	BAA-OCH <sub>3</sub>	BAA-CH <sub>3</sub>			
Chemical Formula	$C_{14}H_{10}BrNO_3$	$C_{14}H_{10}ClNO_3$	C <sub>15</sub> H <sub>13</sub> NO <sub>4</sub>	C <sub>15</sub> H <sub>13</sub> NO <sub>3</sub>			
$M_{\rm w}$	320.13	275.68	283.26	255.26			
Crystal system Space group Unit cell dimensions $V / Å^3$ T / K Z $\rho_{calc} / g cm^{-3}$	monoclinic C2/c a=27.3559(12) Å b=4.9265(2) Å c=20.8382(10) Å a=90 ° $\beta=117.954(2)$ ° $\gamma=90$ ° 2480.7(2) 100(2) 8 1.714	monoclinic P21/c a=6.6989(5) Å b=7.2140(6) Å c=25.1489(18) Å a=90 ° $\beta=92.624(4)$ ° $\gamma=90$ ° 1214.07(16) 100(2) 4 1.508	triclinic P-1 a=7.1716(11) Å b=12.971(2) Å c=13.828(3) Å a=83.900(9) ° $\beta=81.801(9)$ ° $\gamma=78.948(9)$ ° 1245.3(4) 100(2) 4 1.511	monoclinic P21/c a=11.7376(6) Å b=14.7540(9) Å c=7.3524(4) Å a=90 ° $\beta=100.234(3)$ ° $\gamma=90$ ° 1253.01(12) 100(2) 4 1.353			
$\mu/\mathrm{mm}^{-1}$	3.317	0.317	0.106	0.095			
Reflections collected	30344	11505	12983	10665			
Independent reflections	2849	2669	4699	2148			
$R_1 \left[ I > 2\sigma(I) \right]$	0.0210	0.0316	0.0722	0.0405			
WR <sub>2</sub> (all data)	0.0558	0.0867	0.2608	0.1055			

### Table 1

Table 2					
	D-H···A*	D-H	Н…А	D····A	<i>D-H···A</i>
BAA-Br	N1-H101	0.80	2.06	2.676	133
	N1-H1···O3 <sup>1</sup>	0.80	2.54	3.128	132
	$O2-H2\cdots O1^n$	0.84	1.81	2.646	177
BAA-Cl	N1-H1A····O1	0.81	1.99	2.671	141
	$O2-H2\cdots O1^{m}$	0.84	1.83	2.670	176
	$C5-H5\cdots O3^{N}$	0.95	2.45	3.357	160
	C3–H3····Cl1 <sup>v</sup>	0.95	2.84	3.737	157
BAA-OCH <sub>3</sub>	N1-H1O1	0.80	1.94	2.645	145
	$O2-H2\cdots O7^{vi}$	0.82	1.82	2.638	180
	N2-H2AO5	0.80	1.95	2.649	146
	O6-H6A…O3	0.82	1.86	2.645	160
	$C3-H3\cdots O4^{i}$	0.93	2.56	3.421	153
	С6-Н6…О5	0.93	2.60	3.439	150
	C18–H18…O8 <sup>vii</sup>	0.93	2.54	3.390	151
	C21–H21…O <sup>viii</sup>	0.93	2.52	3.367	152
	C15-H15BO2 <sup>vii</sup>	0.93	2.69	3.575	154
	C30–H30B…O6 <sup>i</sup>	0.96	2.66	3.550	154
	C30-H30AO1 <sup>ix</sup>	0.96	2.72	3.568	148
BAA-CH <sub>3</sub>	N1–H1A…O1	0.82	1.92	2.638	145
	O2−H2…O3 <sup>x</sup>	0.82	1.82	2.639	178
	C6–H6····O1 <sup>xi</sup>	0.95	2.60	3.491	155
(	C10–H10…O1 <sup>xii</sup>	0.95	2.67	3.397	134

\*D: Donor, A: Acceptor; Symmetry codes: (i) [x,1+y,z], (ii) [1/2-x,3/2-y,-z], (iii) [2-x,1-y,-z], (iv) [-x,-y,-z], (v) [x,1/2-y,1/2+z], (vi) [-1+x,y,1+z], (vii) [x,-1+y,z], (viii) [1+x,y,-1+z], (ix) [1-x,1-y,1-z], (x) [-x,1/2+y,1/2-z], (xi) [-x,-1/2+y,1/2-z], (xii) [x,1/2-y,-1/2+z]

#### Table 3

Table 3					
	$(\Delta E_{int})$				
Basis sets	BAA-Br	BAA-Cl	BAA-OCH <sub>3</sub>	BAA-CH <sub>3</sub>	
6-31+G*	-3.58	-2.54	-2.99	-1.97	
6-31++G*	-3.76	-2.64	-3.17	-2.23	
6-31++G**	-3.76	-2.47	-3.03	-1.99	
AUG-cc-pVDZ	-0.51	-1.78	-2.71	-1.68	
AUG-CC-PVDZ	-0.51	-1.78	-2.71	-1.00	
		)			
		7			
X					

#### **GRAPHICAL ABSTRACT**



### HIGHLIGHTS

- ► *N*-(p-benzoyl)-anthranilic acid derivatives have been analyzed and characterized.
- ► N-H···O=C hydrogen bonds are more stable than N-H···O-H hydrogen bonds.
- ► The interaction energy values of monomers are more stable than dimers.
- ► The research shows intra and inter-molecular interactions in the title compound.

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