Rahmani, M., Salimi, A., Mohammadzadeh, S., & Sparkes, H. A. (2016). The supramolecular effect of aromaticity on the crystal packing of furan/thiophene carboxamide compounds. *CrystEngComm*, 18(46), 8953-8960. <https://doi.org/10.1039/c6ce01945e>

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Supramolecular effect of aromaticity on the crystal packing of Furan/Thiophene carboxamide compounds

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Received 00th January 20xx
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

N-2-pyrazinyl-2-furancarboxamide (*I*) and *N*-2-pyrazinyl-2-thiophenecarboxamide (*II*) are compounds containing different five-membered heteroaromatic rings, furan and thiophene, respectively. They were designed and synthesized to examine the effect of an increase in aromaticity from furan to thiophene on the crystal packing. In order to explore the various features of the crystal packing motifs in more detail, single crystal X-ray diffraction, Hirshfeld surface analysis and theoretical calculations were carried out on the two compounds. The results clearly show that the heteroatom substitution of O to S in five-membered rings led to an increase in the effectiveness of π -based interactions in *II*, whereas hydrogen bond interactions are more important role in the stabilization of supramolecular architecture of *I*.

Introduction

Knowledge-based selection of building blocks that participate in creating specific molecular structures and intermolecular interactions in crystal structures are essential pillars in supramolecular chemistry.¹ Obviously the best choice of building blocks can act as a directing agent to determine the type of interactions as well as the possibility of cooperative interactions in order to create a stable supramolecular network.² The field of crystal engineering relies on considerable efforts to understand, control and predict the interaction behavior and crystal packing of specific building

blocks in order to control and design specific properties into a molecular solid.³

In this regard, aromatic structural units (such as six-membered or five-membered heteroaromatic rings) which can be engaged in various hydrogen bonding and especially π -based interactions have been widely investigated by experimental and theoretical studies.⁴ In particular, many research groups has studied the five-membered heteroaromatic systems in terms of various molecular properties such as the geometric, electronic⁵, energetic,⁶ or magnetic properties as well as aromaticity levels.⁷ The aromaticity level is one of the most important properties which has a dominant role on the π -based interactions and therefore its quantification can be a valuable feature in the assessment of likely strength and interaction nature from a crystal engineering viewpoint. In this regard, a lot of theoretical and experimental methods have been developed in order to provide a quantitative measurement of aromaticity according to various criteria, namely geometrical, energetic, magnetism, electronic and reactivity-based indices.⁸

Studies exist into the aromaticity of the five-membered heteroaromatic rings indicated that their aromaticity increases in the order furan, pyrrole to thiophene.^{9,10} In this series, the furan and thiophene with minimum and maximum aromatic

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Electronic Supplementary Information (ESI) available: Additional structural data, Cambridge Structural Database (CSD) analysis, histograms and scattergrams, NMR and IR data, Computationally binding energies of tetramer fragments. CCDC 1415044-1415045 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). See DOI: 10.1039/x0xx00000x

compound *I* suitable for X-ray analysis were obtained after 13 days. Mp: 172–173 °C. Anal Calcd for C₉H₇N₃O₂: C: 57.14, H: 3.73, N: 22.21%; Found: C: 57.16, H: 3.50, N: 22.25%

Synthesis of compound *II*

A solution with 1:1 molar ratio of 2-aminopyrazine (10.0 mmol, 0.951 g) and thiophene-2-carboxylic acid chloride (10.0 mmol, 1.07 mL) in 10.0 mL dry pyridine were produced. The resulting solution was stirred at ambient temperature for 1 h. A transparent solution resulted which was filtered. X-ray quality colorless cubic crystals were harvested by slow solvent evaporation at room temperature for 10 days with a yield of 27%. Mp: 122–123 °C. Anal Calcd for C₉H₇N₃OS: C: 52.67, H: 3.44, N: 20.47, S: 15.62%; Found: C: 52.45, H: 3.52, N: 20.26, S: 15.38%

Computational methods

The most stable (probable) *syn* and *anti*-conformations for each of title compounds were obtained *via* the full optimization using DFT calculations (B3LYP method with 6-311+G(d,p) basis set) without any restriction condition and the frequency analysis showed the absence of imaginary frequencies in any state. The binding energies of the all molecules pairs (dimer) were calculated based on M06-2X and M06¹⁹ and B3LYP-D3 as a DFT dispersion-corrected method²⁰ along with 6-311+G (d, p) basis set to investigate the energy of non-covalent interactions involved in supramolecular architectures of title compounds. Since, the calculation of non-covalent interactions from the DFT-D3 new method is particularly reliable where the dispersion component has a significant contribution,^{20c} the interaction energies of reasonable double pairs or quaternary fragments (tetramer) were calculated based on B3LYP-D3 method. The corrections for basis set substitution error (BSSE) were performed using the counterpoise method.²¹ We have taken the fragment structural coordinates directly from the crystal structure data with H atoms at their neutron distances (1.08 Å for C–H and 1.00 Å for N–H) as input geometries in the single point energy calculations. All the calculations were performed in the GAMESS program package.²²

In this study, the electrostatic surface potential (ESP) for individual molecules were mapped on the Hirshfeld surface over the range –0.015 au (red), through 0 (white), to 0.015 au (blue). For this purpose, *ab initio* wave functions were obtained at B3LYP method and 6-31G(d, p) basis set. The molecular Hirshfeld surfaces²³ presented in this paper were generated using Crystal Explorer 3.1.²⁴

Results and discussion

Crystal structure description

Compound *I* crystallizes in the orthorhombic space group *Fdd2* with one independent molecule in the asymmetric unit (*Z* = 16,

see Table 1). Due to the limited flexibility of *I*, a plate structure is predictable but the twist angle between planes calculated through the two rings is 24.8(1)° illustrated a curved-like structure. In this structure, the molecules pack to form the variable intermolecular interactions, such as N–H...N, C–H...N, C–H...O, C–H...π and π–π stacking interactions (Figure 2 and Table 2). The N1–H1...N3 hydrogen bond (HB) forms a stable classical HB-based molecular pair (*R*₂²(8) graph-set with *head-to-tail* configuration) and it can be considered as suitable repetitive species in the crystal packing (Figure 2.*up-right*). In this pair, there are also two C–H...O weak hydrogen bonds between the C9–H9 of pyrazine ring and oxygen atom of furan ring via the formation of the *R*₂²(16) pattern. The repetition of main fragment accompanied by C–H...N/C–H...O hydrogen bonds (C3–H3...N2(pyrazine) and C8–H8...O2(amide) with *R*₂²(8) graph-set) develops the 2D supramolecular sheets along *ab*-plane (Figure 2.*down*). Additional reinforcement between molecules in the sheet is provided by the C1–H1A...O2(amide) (Figure 2.*right*) and the C2–H2...N2(pyrazine) (Figure 2.*left*) hydrogen bonds. Consequently, the sheets are packed *via* C–H...π and π...π stacking interactions in *c*-direction to create a three-dimensional architecture.

The Cambridge Structural Database (CSD) analysis of C–H...π interactions in five-membered furan ring reveals that all geometrical parameters of C9–H9...π_{Furan} interactions between adjacent sheets (H...Cg contact distance and C–H...Cg angle are 2.964 Å, 158.83°) are in the normal range (for more details see **Supporting information**). Moreover, π...π stacking interactions in the form of homosynthons (similar stack rings as π_{Furan}...π_{Furan} and π_{pyz}...π_{pyz}) have been taken place in *c*-direction (Figure 2.*up-left* and Table 2). A CSD survey for π_{Furan}...π_{Furan} and π_{pyz}...π_{pyz} interactions revealed that the parameters associated with *I* all coincide with the maximum frequency of occurrence for such interactions in the CSD (for more details see **Supporting information**). Compound *II* crystallizes in the monoclinic space group *P2₁/n* with *Z* = 4. The angle between the ring planes is 5.35(4)° indicating that the structure is approximately planar. A detailed study of packing diagram revealed that a 3D supramolecular organic framework structure is formed through complex intermolecular interactions such as N–H...N, C–H...O, C–H...N, C–H...S and π...π interactions (Figure 3). In this way, one of the major molecular pairs is formed through suitable π...π stacking interactions in which the aromatic rings packed in a *head-to-tail* parallel fashion with a short distance of π_{Thio}...π_{pyz} and a limited slippage (Figure 3.*up-right* and Table 2). Additionally, the presence of homosynthons π_{Thio}...π_{Thio} interactions, between thiophene rings in adjacent mentioned π-based dimer species, leads to stacking of this dimers as 1D tapes in the *ab*-plane (Figure 3.*up-left* and Table 2). Our analysis of the CSD for π...π interactions between thiophene rings revealed that the geometrical parameters of this homosynthon lie in a limited number of cases which can be considered as a strong π...π interaction (for more details see **Supporting information**).

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Figure 2. A representation of part of the unit cell contents of I, viewed in various projections. Different colors are shown for different dimer motifs for clarity of various intermolecular interactions.

Figure 3. A representation of part of the unit cell contents of II viewed in various projections. Different colors are shown for different dimer motifs for clarity of various intermolecular interactions.

These results show that there is a strong tendency to form $\pi\cdots\pi$ stacking synthons between adjacent aromatic rings, in addition of N1-H1...N3 classical hydrogen bond (with the C(5) supramolecular synthon), as well as C3-H3...N3 hydrogen bond (with the R¹₂(7) motif), to further stabilize the packing (Figure 3.*down* and Table 2). The C-H...O hydrogen bonded synthons (C1-H1A...O1, C8-H8...O1 with the C(6) and C(8) patterns, respectively) cause the expansion of the crystal structure in a three-dimensional architecture (Figures 3.*left* and *right*, Table 2).

Comparison of I and II

The structural definition based on the geometry of aromaticity by numerical identifiers has attracted a lot of attention. In this respect, a measure based on the geometry of the π electrons delocalization (aromaticity harmonic oscillator model HOMA) is one of the most effective indexes used to describe the aromaticity.^{8a} Therefore, in this work a detailed study of the local aromaticity was performed using the HOMA indices²⁵ for the five-membered heterocycle and pyrazine rings which are 0.0911 and 0.9757, respectively in compound *I*, while the respective values for *II* were 0.8498 and 0.9855. The values indicate that heteroatom substitution from oxygen to sulfur increases the π -electron delocalization level of five-membered ring, considerably.

The specific consequence of this alteration can be observed in the molecular conformation of title compounds. Obviously, the orientation of furan (O) and thiophene (S) toward the oxygen of carbonyl group in *I* and *II* (as the *anti* and *syn* conformations, respectively) leading to the presence of N-H...O_{Furan} and lack of significant S_{Thiophene} intramolecular interactions. Reasonably, this evidence can be related to the more localization of electron density (non-bonding pair) on oxygen heteroatom of furan ring with low aromaticity index to participate in the intramolecular hydrogen bonding (and *vice versa* for aromatic thiophene ring). This progressive withdrawal of the n-pair on the heteroatom into the ring from oxygen to sulfur has been also observed in the literature.²⁶ In order to gain more insight into the stabilization effect of intermolecular hydrogen bond, two probable conformations (*anti* and *syn*) of each compound were considered theoretically. The full optimization results showed that the compound *I* in the *anti*-conformation including an N-H...O interaction is more stable than *syn* geometry by as much as 15.90 kJ.mol⁻¹ that is consistent with experimental structure. On the other hand, the stabilisation energy of the *syn* conformation of *II* is slightly more than the *anti* geometry included N-H...S interaction (1.34 kJ.mol⁻¹). This was confirmed by the geometry of compound *II* from the X-ray structure

which showed that the intramolecular interaction of the sulfur atom in the aromatic thiophene ring is not significant enough to be observed in the experimental structure (Figure S1).

The electrostatic potential has been mapped over the Hirshfeld surface of title compounds (Figure 4). A clear separation of the electropositive and electronegative areas was observed over the flat surfaces. However, electronegative regions on the oxygen atom of amide group and nitrogen atoms of pyrazine ring are very similar in two molecules, there is a significant difference in the electrostatic potential region of five-membered heteroaromatic rings. Interestingly, the electropositive and electronegative regions on the furan ring show the alternate fashion which is related to the positive and negative charge accumulation on the C1-C4 and C2-C3, O1 atoms, respectively. This issue supports the observation of offset homosynthon $\pi_{\text{Furan}}\cdots\pi_{\text{Furan}}$ stacking as an electrostatic interaction between these regions (Figure 2.*up-left*). Nevertheless, the electronegative region on the thiophene ring is almost uniformly around all atoms, resulting in electrostatic complementarity to the electropositive region on the pyrazine ring, leading to the formation of the significant $\pi_{\text{Thio}}\cdots\pi_{\text{Pyz}}$ stacking heterosynthon (Figure 3. *up-left*). Additionally, the orientation of the ring oxygen and sulfur atoms to the oxygen of carbonyl group affects the area of electropositive and electronegative regions on the side of title molecules which have high potential for electrophilic and nucleophilic attack, respectively in various hydrogen bond interactions in the crystal packing.²⁷

Figure 4. The Hirshfeld surface for *I* and *II* mapped with electrostatic potential (ESP) over the range -0.015 au (red) through 0.0 (white) to 0.015 au (blue).

Table 2. Experimental (X-ray) geometrical parameters of interactions involved in all molecular pairs of compounds I and II and the binding energies calculated at the DFT-D, M06-2X and M06 methods (Dimers were labeled based on the energy relevance)

Molecular pair No.	Symmetry code	Involved Interactions	X-ray Geometry (Å/deg)*	Binding energy, E _{calc} (kJ/mol)		
				DFT-D	M06-2X	M06
Compound I						
D1(HB)	1/2-x,1/2-y,z	N1-H1...N3	2.266(2)/3.117(3)/163	-44.20	-37.87	-35.03
		C9-H9...O1	2.480(2)/3.011(2)/115			
D2(π...π)	x,y,-1+z	π _{furan} ...π _{furan}	3.791(2)/ 27.32/ 0.00	-28.04	-29.51	-23.88
		pyzπ...pyzπ	3.791(2)/ 27.32/ 0.00			
D3(HB)	1/4-x,-1/4+y,-1/4+z	C3-H3...N2	2.831(2)/ 3.763(3)/ 167	-19.88	-15.68	-14.80
		C8-H8...O2	2.673(2)/ 3.575(2)/ 159			
D4(HB)	-1/4+x,1/4-y,-1/4+z	C1-H1A...O2	2.623(2)/ 3.537(3) /161	-13.76	-10.84	-10.03
D5(HB)	1/4+x,1/4-y,-3/4+z	C2-H2...N2	2.696(2)/3.350(3)/126	-13.75	-10.64	-9.93
D6(HB)	1/4-x,1/4+y,1/4+z	C8-H8...O2	2.786(2)/3.211(2)/108	-11.40	-8.81	-8.66
D7(HB)	1/2-x,1/2-y,1+z	C9-H9...π _{pyz}	2.964(3)/2.436(2)/159	-7.31	-2.61	-1.50
D8(HB)	1/2-x,-y,-1/2+z	C2-H2...π _{pyz}	3.515(3)/2.567(2)/144	-5.76	-3.22	-2.94
Compound II						
D1(π...π)	1-x,1-y,-z	π _{thio} ...π _{pyz}	3.488(3)/18.79/7	-39.44	-34.32	-34.32
D2(HB)	1/2+x,1/2-y,1/2+z	N1-H1...N3	2.193(2)/3.055(2)/166	-32.08	-24.98	-24.98
		C3-H3...N3	2.445(2)/3.350(3)/159			
D3(π...π)	-x,1-y,-z	π _{thio} ...π _{thio}	3.579(3)/18.09/0.00	-27.38	-24.17	-24.17
D4(HB)	1/2-x,1/2+y,1/2-z	C1-H1A...O1	2.452(2)/3.225(3)/138	-15.68	-11.71	-11.71
D5(HB)	1/2-x,-1/2+y,1/2-z	C8-H8...O1	3.221(3)/3.834(3)/124	-13.77	-9.08	-9.08
D6(π...π)	1-x,-y,-z	pyzπ...pyzπ	4.327(3)/40.83/3	-10.35	-7.39	-7.39
D7(HB)	1/2-x,1/2+y,-1/2-z	C2-H2...N2	2.753(2)/3.496(3)/136	-9.08	-5.26	-5.26
D8(HB)	-1/2+x,1/2-y,1/2+z	C9-H9...S1	3.144(2)/3.995(3)/150	-6.25	-2.90	-2.90
D9(HB)	-1/2+x,1.5-y,-1/2+z	C2-H2...S1	3.224(3)/4.145(3)/164	-4.55	-1.24	-1.24

* Geometrical parameters of HB-bond: H...A/ D...A/<D-H...A, $\pi\cdots\pi$ stacking: $d_{\text{cent}}/ <\text{cc-p}/<\text{p-p}$, C-H... π : $d_{\text{cent}}/ d_{\text{pin}}/ \alpha$

It is noteworthy that the privileged formation of $\pi_{\text{thio}}\cdots\pi_{\text{pyz}}$ interaction in I can be also explained based on the “aromatic donor-acceptor” description term suggested by Martinez and Iverson in which stacking between aromatics with differential polarization was described as the interaction of relatively electron-deficient and electron-rich aromatic molecules in an alternating fashion.^{4b} In this regard, pyrazine ring as an electron-acceptor and thiophene ring as a donor group formed this significant interaction. Consequently, the more electron donor character of thiophene in comparison of furan revealed the different role of these heteroaromatic rings in the π -based interactions.

In order to gain more insight into the exact effect of aromaticity level on the crystal packing structures, the cohesive energy of all the molecular pairs (dimer fragments) in the molecular coordination shell of title compounds were calculated and ranked in order of energetic relevance (Figure 5

and Table 2). The results showed that the supramolecular associations in I as dimer species D1 and D3-D8 are based on the hydrogen bond (HB) interactions, whereas D2 is only formed by $\pi\cdots\pi$ interaction. Obviously, the D1^(HB) (IE = -44.20 kJ/mol) is the most stable molecular pair presented in I which is created by the formation of strong N-H...N hydrogen bonds as well as C-H...O interactions (Table 2). The investigation of other dimers showed that D2^($\pi\cdots\pi$) (IE = -28.04 kJ/mol) formed via homosynthon $\pi\cdots\pi$ interactions lies in second place with significant reduction in IE. The other dimers created by the weak hydrogen bonds such as C-H...N and C-H...O synthons, showed less stabilisation energies.

On the other hand, the energy ranking in II emphasized that the most stable dimer D1^($\pi\cdots\pi$) (IE = -39.44 kJ/mol) is created by the formation of two $\pi_{\text{thio}}\cdots\pi_{\text{pyz}}$ heterosynthons. While, the second most stable dimeric motif, D2^(HB) (IE = -32.09 kJ/mol), results from directional N-H...N and C-H...N hydrogen bonding,

Figure 5. Stacking patterns observed for all the molecular pairs (dimers) which are labeled based on the interaction energy ranking in *I* and *II*

the homosynthon $\pi_{\text{Thio}} \cdots \pi_{\text{Thio}}$ interaction presented in the $D3(\pi \cdots \pi)$ results in strong $\pi \cdots \pi$ stacking of as much as -27.38 kJ/mol per interaction in the crystal packing *II*. The rest of the dimeric motifs in *II* are formed by the various C-H...N, C-H...O and C-H...S interactions.

The binding energies of pairs in *I* and *II* are in the 5-44 and 5-39 kJ/mol ranges for B3LYP-D3 method, respectively. M06-2X and M06 quantities are somewhat smaller between 1-37 and 1-34 kJ/mol for *I* and *II*, respectively. Regarding to the presence of multi-interactions in each pairs, they are in the normal ranges

of HB (*ca.* 1-160 kJ/mol) and π -stacking (*ca.* 2-50 kJ/mol) interaction energies.²⁸

In light of the dimeric motifs binding energies, we have chosen the forty most stable double pairs of compounds *I* and *II* as tetramer fragments (see **Supporting information**) and calculated the complexation energies to give a relative weight of interaction energies (HB and π stacking) influence on the formation of supramolecular aggregations in the self-assembly processes.

Investigation of these tetramer motifs also provided useful information on the additive and non-additive effects of the HB-

bonding and $\pi\cdots\pi$ stacking in title structures. In this regard, the magnitude of cooperativity was calculated by deducting all pair wise interactions from the total complexation energy of the tetramer. The total binding energy, the contribution of cooperativity, HB and $\pi\cdots\pi$ stacking energies as the magnitude and percentage of total binding energy, as well as the weighted contribution of cooperativity, HB and $\pi\cdots\pi$ stacking as a percentage of the overall total binding energies of the studied fragments, the summation of the weighted contribution of cooperativity, HB and $\pi\cdots\pi$ stacking for all most stable tetramer fragments of *I* and *II* are gathered in **Tables S1 and S2**, respectively.

The binding energies range between -51.84 and -160.27 kJ/mol for *I*. The most stable tetramer fragment of *I* (Tet1) is formed by the participation of strong dimers D1^(HB), D2^($\pi\cdots\pi$) and D7^(HB) with an interaction energy of about -160.27 kJ/mol with additional stability of -1.18 kJ/mol as an additive effect in this cooperation. The highest cooperativity in the studied complexes of *I* is related to the Tet19 in which dimers D1^(HB), D2^($\pi\cdots\pi$) and D5^(HB) result in a positive cooperative effect of -4.65 kJ/mol. Twelve cases of anticooperativity are observed in ranging from 0.07 kJ/mol in Tet37 to 1.45 kJ/mol in Tet34 of *I*. The range of total binding energies in the thiophene-based compound is between -46.04 and -140.76 kJ/mol. Combination of dimers D1^($\pi\cdots\pi$), D2^(HB), D5^(HB), D7^(HB), and D9^(HB) created Tet1 that is in the first place of the tetramer list with the additive effect of -2.39 kJ/mol. Tet17 containing dimers, D2^(HB) lead to the highest additive cooperativity of -5.80 kJ/mol. Additionally, there were 15 cases with non-additive effect between interactions in which Tet39, made by partnership of $\pi\cdots\pi$ based dimers, had the largest negative cooperative effects of 2.31 kJ/mol.

Regarding to the summation of the weighted contribution of HB and $\pi\cdots\pi$ stacking interactions in the most stable tetramer fragments, one can concluded that the tendency to form the HB-based molecular pairs (ca. **75%**) is much higher than $\pi\cdots\pi$ stacking motifs (ca. **24%**) in compound *I* which can be related to the low aromatic index of furan ring. Although, these results emphasized that there is the much more tendency to form π -based synthons (ca. **49%**) based on the aromatic thiophene ring in compound *II*, hydrogen bond interactions still play an important role to stabilize the packing structure.

Conclusions

Two carboxamide compounds containing furan or thiophene ring have been synthesized and investigated for the effect of different aromaticity level of five-membered ring on the supramolecular aggregations using a combination of experimental and computational studies. The energetic study of the noncovalent interactions in the molecular pairs (dimer) and doubly pairs (tetramer) are responsible of the supramolecular assemblies observed in the solid state. It is observed that the increase in the aromaticity of thiophene ring in compound *II* encourages the molecule of the opportunities to precipitate in the strong $\pi\cdots\pi$ stacking interactions as much as hydrogen bonding. However, this balance significantly

changes in favor of strong hydrogen bonding due to the decrease of aromaticity of furan ring in compound *I*. This study shows that the aromaticity parameter can be utilized as a directing agent to design the favorable supramolecular synthons in the context of crystal engineering.

Acknowledgements

The authors gratefully acknowledge the financial support by the Ferdowsi University of Mashhad, Mashhad, Iran (**Grant No. 3/25631**).

Notes and references

- (a) J.-M. Lehn, *Supramolecular chemistry*, Vch, Weinheim, 1995. (b) G. R. Desiraju, *Nature*, 2001, **412**, 397-400. (c) J. W. Steed and J. L. Atwood, *Supramolecular chemistry*, John Wiley & Sons, 2013.
- (a) Lehn, J.-M., *Chem. Soc. Rev.* **2007**, *36*, 151-160; (b) Sarmah, B. J.; Dutta, D. K., *Cryst. Growth Des.* **2009**, *9*, 1643-1645; (c) Matsidik, R.; Martin, J.; Schmidt, S.; Obermayer, J.; Lombeck, F.; Nübling, F.; Komber, H.; Fazzi, D.; Sommer, M., *J. Org. Chem.* **2015**, *80*, 980-987; (d) Ali, A.; Hundal, G.; Gupta, R., *Cryst. Growth Des.* **2012**, *12*, 1308-1319.
- (a) Desiraju, G. R., *J. Am. Chem. Soc.* **2013**, *135*, 9952-9967; (b) Desiraju, G. R.; Vittal, J. J.; Ramanan, A., *Crystal engineering: a textbook*. ed.; World Scientific: 2011; (c) Desiraju, G. R., *Angew. Chem. Int. Ed.* **2007**, *46*, 8342-8356; (d) Braga, D.; Desiraju, G. R.; Miller, J. S.; Orpen, A. G.; Price, S. L., *CrystEngComm* **2002**, *4*, 500-509.
- (a) Wu, J. I.; Jackson, J. E.; Schleyer, P., *J. Am. Chem. Soc.* **2014**, *136*, 13526-13529; (b) Martinez, C. R.; Iverson, B. L., *Chem. Sci.* **2012**, *3*, 2191-2201; (c) Khavasi, H. R.; Mir Mohammad Sadegh, B., *Dalton Trans.* **2015**, *44*, 5488-5502; (d) Khavasi, H. R.; Azizpoor Fard, M., *Cryst. Growth Des.* **2010**, *10*, 1892-1896; (e) Khavasi, H. R.; Salimi, A. R.; Eshtiagh-Hosseini, H.; Amini, M. M., *CrystEngComm* **2011**, *13*, 3710-3717; (f) Khavasi, H. R.; Azhdari Tehrani, A., *Inorg. Chem.* **2013**, *52*, 2891-2905; (g) Khavasi, H. R.; Mir Mohammad Sadegh, B., *Cryst. Growth Des.* **2012**, *12*, 4798-4804.
- Cooper, D. L.; Wright, S. C.; Gerratt, J.; Raimondi, M., *J. Chem. Soc., Perkin Trans. 2* **1989**, 263-267.
- Rodríguez-Ropero, F.; Casanovas, J.; Alemán, C., *J. Comput. Chem.* **2008**, *29*, 69-78.
- Rosenberg, M.; Dahlstrand, C.; Kilså, K.; Ottosson, H., *Chem. Rev.* **2014**, *114*, 5379-5425.
- (a) Krygowski, T. M.; Szatyłowicz, H.; Stasyuk, O. A.; Dominikowska, J.; Palusiak, M., *Chem. Rev.* **2014**, *114*, 6383-6422; (b) Sun, J.-Y.; Wang, L.; Zhang, D.-J.; Li, D.; Cao, Y.; Zhang, L.-Y.; Zeng, S.-L.; Pang, G.-S.; Fan, Y.; Xu, J.-N.; Song, T.-Y., *CrystEngComm* **2013**, *15*, 3402-3407.
- Horner, K. E.; Karadakov, P. B., *J. Org. Chem.* **2013**, *78*, 8037-8043.
- Najmidin, K.; Kerim, A.; Abdirishit, P.; Kalam, H.; Tawar, T., *J. Mol. Model.* **2013**, *19*, 3529-3535.
- (a) Ma, Y.; Ma, H.; Yang, Z.; Ma, J.; Su, Y.; Li, W.; Lei, Z., *Langmuir* **2015**, *31*, 4916-4923; (b) Bravaya, K. B.; Epifanovsky, E.; Krylov, A. I., *J. Phys. Chem. Lett.* **2012**, *3*, 2726-2732.
- Khan, I.; Panini, P.; Khan, S. U.; Rana, U. A.; Andleeb, H.; Chopra, D.; Hameed, Sh.; Simpson, J., *Cryst. Growth Des.* **2016**, *16*, 1371-1386.
- Bauzá, A.; Mooibroek, T. J.; Frontera, A., *CrystEngComm*, **2016**, *18*, 10-23.

- 14 (a) Martin, A. D.; Britton, J.; Easun, T. L.; Blake, A. J.; Lewis, W.; Schroder, M., *Cryst. Growth Des.* **2015**, *15*, 1697-1706; (b) Martin, A. D.; Hartlieb, K. J.; Sobolev, A. N.; Raston, C. L., *Cryst. Growth Des.* **2010**, *10*, 5302-5306; (c) Tarahhomi, A.; Pourayoubi, M.; Golen, J. A.; Zargar, P.; Elahi, B.; Rheingold, A. L.; Ramírez, L.; Mancilla Percino, T., *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* **2013**, *69*, 260-270; (d) Yousefi, Z.; Eshtiagh-Hosseini, H.; Salimi, A.; Janiak, A., *J. Mol. Struct.* **2015**, *1083*, 460-470.
- 15 CrysAlisPro, ed.; Oxford: 2011.
- 16 Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A.; Puschmann, H., *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 59-75.
- 17 Sheldrick, G. M., *Acta Crystallogr. Sect. A Found. Adv.* **2007**, *64*, 112-122.
- 18 Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H., *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
- 19 Zhao, Y.; Truhlar, D. G., *Theor Chem Account*, **2008**, *120*, 215-241.
- 20 (a) Grimme, S., *J. Comput. Chem.* **2004**, *25*, 1463-1473. (b) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787-1799. (c) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., *J. Chem. Phys.*, **2010**, *132*, 154104.
- 21 Boys, S. F.; Bernardi, F. d., *Mol. Phys.* **1970**, *19*, 553-566.
- 22 Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., *J. Comp. Chem.* **1993**, *14*, 1347-1363.
- 23 (a) McKinnon, J. J.; Fabbiani, F. P. A.; Spackman, M. A., *Cryst. Growth Des.* **2007**, *7*, 755-769; (b) Spackman, M. A., McKinnon, J. J.; Jayatilaka, D., *CrystEngComm* **2008**, *10*, 377-388; (c) Spackman, M. A.; Jayatilaka, D., *CrystEngComm* **2009**, *11*, 9-32
- 24 Wolff, S.; Grimwood, D.; McKinnon, J.; Turner, M.; Jayatilaka, D.; Spackman, M., *University of Western Australia* **2012**.
- 25 Chattaraj, P. K.; Das, R.; Duley, S.; Giri, S., *Chemical Modelling: Applications and Theory* **2011**, *8*, 45.
- 26 (a) Galan, J. F.; Tang, C. N.; Chakrabarty, S.; Liu, Z.; Moyna, G.; Pophristic, V., *Phys. Chem. Chem. Phys.* **2013**, *15*, 11883; (b) Sánchez-García, E.; Mardukov, A.; Studentkowski, M.; Montero, L. A.; Sander, W., *J. Phys. Chem. A* **2006**, *110*, 13775-13785; (c) Kaur, D.; Khanna, S., *Struct. Chem.* **2011**, *23*, 755-764; dHuang, D.-M.; Wang, Y.-B.; Visco, L. M.; Tao, F.-M., *Chem. Phys. Lett.* **2005**, *407*, 222-226.
- 27 Smith, M. G.; Forbes, R. P.; Lemmerer, A., *Cryst. Growth Des.* **2015**, *15*, 3813-3821.
- 28 (a) Steiner, T., *Angew. Chem., Int. Ed.*, **2002**, *41*, 48-76. (b) Bishop, R. *CrystEngComm* **2015**, *17*, 7448-7460.