方酸与 2,6-二苯并咪唑的超分子自组装及氢键实验与理论研究

胡爱彬 潘志权 程清蓉 周 红*

(武汉工程大学化学与环境工程学院, 武汉 430073)

摘要: 在氘代的二甲基亚砷的溶剂中合成了方酸与 2,6-二苯并咪唑的超分子的化合物, 并用 X 射线单晶衍射对其结构进行了表征。晶体结构分析表明: 超分子是通过 $\pi-\pi$ 堆积和分子之间氢键所形成的一维链状的聚合物。探讨了不同温度和不同浓度 CCl_4 溶剂对聚合物中氢键的影响。此外, 用密度泛函理论和分子中原子理论对其进行了理论分析, 计算结果表明分子间的键能分别是 135.65 和 $49.40 \text{ J}\cdot\text{mol}^{-1}$ 。

关键词: 分子间氢键; 变温红外; 密度泛函理论; 分子中原子理论

中图分类号: O641

Experimental and Theoretical Evidence for Supramolecular Self-Assembly and Hydrogen Bonding between Squaric Acid and 2,6-Bis(2-benzimidazolyl)pyridine

HU Ai-Bin PAN Zhi-Quan CHENG Qing-Rong ZHOU Hong*

(College of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430073, P. R. China)

Abstract: Supramolecular complex (**1**) was obtained from a mixture of squaric acid and 2,6-bis(2-benzimidazolyl)pyridine in deuterated dimethylsulfoxide (d-DMSO) and characterized by single-crystal X-ray diffraction. The crystal structure data showed that **1** was a one-dimensional chain polymer assembled through $\pi-\pi$ stacking and hydrogen bonding interactions. Infrared vibrational spectra of **1** were measured at different temperatures and sample concentrations in carbon tetrachloride. Moreover, the hydrogen bonding in the crystals was further evaluated by density functional theory (DFT) and atoms in molecules (AIM) theory. The calculated hydrogen bonding energies were about 135.65 and $49.40 \text{ J}\cdot\text{mol}^{-1}$, respectively.

Key Words: Intermolecular hydrogen bonding; Variable temperature infrared; Density functional theory; Atoms in molecules theory

1 Introduction

Hydrogen bonding is one kind of interactions between covalent bonds and van der Waals forces¹. Due to its wide existence in solid, gas, and liquid states, hydrogen bonding plays an important role in the biological, pharmaceutical materials, and chemical reactions^{2,3}. It is well known that the hydrogen bonding interactions are the key factor to maintain the double helix structure of DNA and the secondary structure of protein. To better understand

the function of hydrogen bonding in biomacromolecules and other substances, various technologies have been applied to explore hydrogen bonding in molecules⁴. Among them, X-ray single crystal diffraction can provide information about the distance between the acceptor and donor atoms of the hydrogen bonding as well as the types and the contribution of hydrogen bonding to the configuration of crystals. Infrared spectroscopy gives evidence for the hydrogen bonding formation by the shift of the vibration

Received: October 29, 2015; Revised: December 24, 2015; Published on Web: December 25, 2015.

*Corresponding author. Email: hzhouh@126.com; Tel: +86-13871359786.

The project was supported by the National Natural Science Foundation of China (21171135, 21301131).

国家自然科学基金(21171135, 21301131)资助项目

© Editorial office of *Acta Physico-Chimica Sinica*

bands^{5,6}. Both density functional theory (DFT) and quantum theory of atoms in molecules (QTAIM) have been proved to be the most powerful methods to theoretically evaluate hydrogen bonding^{7–9}.

A squaric acid molecule contains two ketonic oxygen atoms and two hydroxyl groups. It is easy to form hydrogen bond with other molecules containing donor or acceptor atoms^{10–12}. 2,6-Bis(2-benzimidazolyl)pyridine molecule contains two secondary amine and two tertiary amine, which could act as donor and acceptor in the formation of hydrogen bond. When squaric acid mixes with 2, 6-bis(2-benzimidazolyl)pyridine in a suitable solvent, abundant hydrogen bonding interactions should be formed. With the purpose of understanding the hydrogen bond interactions between imidazole-based compound and squaric acid, the crystals derived from their mixture in deuterated DMSO solution were obtained. Moreover, the essence of the hydrogen bonding was revealed through the electron density. The strength comparison of three kinds of N–H···O hydrogen bonds was performed and the reason was also analyzed. In this work, a new polymer derived from the supramolecular self-assembly of hydrogen bond was obtained and fully characterized. Moreover, the hydrogen bonding interaction was further evaluated by the computational analysis.

2 Experimental

2.1 Materials and characterization

Pyridine-2,6-dicarboxylic acid (99%), *o*-phenylenediamine (98%), and squaric acid were purchased from Aladdin Industrial Corporation (China). Poly-phosphoric acid (PPA), methanol, and ethanol were analytic reagents and obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Deuterated dimethylsulfoxide (d-DMSO, 99.9%) was supplied by Cambridge Isotope Laboratories, Inc. (USA).

IR analysis was carried out using a Thermo Nicolet 8700 (USA) Fourier transform spectrometer fitted with a global source, a Ge/KBr beam splitter, and a DTGS detector. An IR spectrum in the region 400–4000 cm^{–1} was recorded at a resolution of 4 cm^{–1} with 128 co-added scans, Happ-Genzel apodized, and Fourier transformed by applying a zero filling factor of 1. The cryostat is optically coupled to the spectrometer using KRS-5 windows. All solid-state samples were studied using the KBr method.

Diffraction intensity data were obtained using a SMART-CCD (SMART APEX CCD II, Germany) area detector diffractometer at 291 K with graphite monochromatic Mo-*K*_α radiation ($\lambda = 0.071073$ nm). Data reduction and cell refinement were carried out by SMART and SAINT Programs¹³. The structures were identified by direct methods (Bruker SHELXTL) and refined on F² by full-matrix least squares (Bruker SHELXTL) using all unique data¹⁴. The non-H atoms in the structure were treated as anisotropic. Hydrogen atoms were located geometrically and refined in riding mode.

2.2 Synthesis of the supramolecule (1)

Supramolecule **1** was synthesized by the reaction of 2,6-bis(2-benzimidazolyl)pyridine (L) with 1 equivalent of squaric acid in ethanol under reflux for 0.5 h. The produced yellow crystals were purified by recrystallization in methanol. After this, the sample

was dissolved in d-DMSO and the mixture was maintained for three days. Yellow crystals suitable for the X-ray diffraction measurement were obtained.

2.3 Computational details

The initial structure (IS) was extracted from the crystal structure of supramolecule **1**. Then IS was subject to optimization, energy calculation, and wavefunction analysis. We first tried to use B3LYP, BLYP, and revPBE functionals to optimize the geometries, however, we found that the hydroxyl hydrogen atom of the center molecule transferred to the nitrogen atom opposite to it. It could be ascribed to the strong hydrogen bonding as well as the very low transfer barrier. We then tried the PM7 method in MOPAC2012 package^{15,16}, which is known to be able to reasonably deal with noncovalent interactions¹⁷. Since the result of the PM7 optimization was fully consistent with the actual situation, no hydrogen transfer was observed, we finally adopted the PM7 optimized geometry for all the following analyses. The calculation of hydrogen bond energy was performed using B3LYP-D3(BJ) functional with very high quality basis-set def2-QZVPP(-g,-f)^{18,19}. ORCA 3.0.2 program^{20,21} was used to conduct the single-point energy calculation^{22,23}. AIM topology analysis was performed by Multiwfn 3.3.6 program^{24–26}, based on the BLYP/def2-SVP level of density generated at the PM7 geometry.

3 Results and discussion

3.1 X-ray study

A perspective view of the molecular unit of **1** is illustrated in Fig. 1(a) as well as some atom numbering schemes. Crystallographic data are presented in Table 1. The molecular structure of the supramolecular (**1**) contains two L, one squaric acid, and two d-DMSO molecules. The most reliable criterion of hydrogen bonding (X–H···Y) formation relies on the van der Waals radius²⁷. According to the previous reported examples, hydrogen bonding distances between X and Y atoms were shorter than the sum of their respective van der Waals radii. The van der Waals radii of the atoms, which are possibly engaged, are 0.155 nm (N) and 0.152 nm (O)²⁸. Therefore, the presence of hydrogen bonding between N and O atoms must be considered when N···O distance is shorter than 0.307 nm. Due to van der Waals radius of hydrogen atom ranging from 0.100 to 0.120 nm, the hydrogen bonding radii of H···O and H···N are 0.252–0.272 nm and 0.255–0.275 nm, respectively.

Methanol and ethanol are the two solvents, which were used in the synthesis of **1**, however, there are no methanol or ethanol molecules involved in the crystal structure, indicating that methanol and ethanol have no hydrogen bonding interaction with either squaric acid or L molecules. Although the molecule structure shows that it contains d-DMSO molecules, no hydrogen bonding involving d-DMSO exists in the crystal structure. In the molecular unit of **1**, one squaric acid molecule acts as a bridge group to connect two L molecules through three types of hydrogen bonding interactions, and two d-DMSO molecules are in the lattice (Fig. 1(a)). The squaric acid molecule also connects with the adjacent other two L molecules through three hydrogen bonding interactions (Fig. 1(b)). On account of the symmetry of a squaric acid, the six hydrogen bonding inter-

Fig.1 (a) A perspective of molecular unit of **1** with π - π stacking and hydrogen bonding interactions, where DMSO molecules are omitted for clarity, (b) the hydrogen bonding interactions between one squaric acid and four L molecules, (c) one dimensional chain polymer assembled by hydrogen bonding and π - π stacking interactions

actions associated with one squaric acid is generally the same as the counterparts. Four nitrogen atoms in benzimidazolyl groups of **L** participate in the hydrogen bonding interactions with squaric acid, acting as either a proton donor or proton acceptor. The distances in the hydrogen bonding interaction are in the region 0.176–0.201 nm

for $\text{H}\cdots\text{O}$, 0.115 nm for $\text{H}\cdots\text{N}$, and 0.265–0.302 nm for $\text{N}\cdots\text{O}$, along with the angle of the hydrogen bond no more than 170° . Selected bond lengths and angles relevant to the hydrogen bonding interactions are listed in Table 2. The length and angle of the hydrogen bonds in **1** are comparable to those reported in literature^{29,30}.

Considering the shorter $\text{H}\cdots\text{O}$, $\text{H}\cdots\text{N}$, and $\text{N}\cdots\text{O}$ distances between donor and accept atoms as well as large hydrogen bond angles in **1**, it can be concluded that there are very strong hydrogen bonding interactions between one squaric acid and the adjacent four 2,6-bis(2-benzimidazolyl)pyridine molecules. In addition, there are strong π - π stacking interactions between the aromatic groups in two adjacent **L** units, shown in Fig.1(a), N3 and the plane composed of an imidazole group from the another **L** with the distance of N3 and the center of the plane of 0.32865 nm; and three interactions of two atoms from different **L**: C7–C18 0.33409 nm; C12–N4 0.33234 nm, N3–C14 0.34001 nm, respectively. The hydrogen bonding interactions and π - π stacking interactions are the driven force to form one-dimensional chain (Fig.1(c)).

3.2 Vibrational spectra analysis

Vibrational spectra of the supramolecular (**1**) at different temperatures and different sample concentrations in CCl_4 solvent are shown in Fig.2 and Fig.3. In Fig.2, the peaks at 3343 and 3149 cm^{-1} at 25°C , which can be attributed to the stretching vibration of $\text{N}-\text{H}$, shift to 3352 and 3160 cm^{-1} at 90°C , respectively³¹. Additionally, the peak caused by the deformation vibration $\text{N}-\text{H}$

Table 1 Crystallographic data of supramolecule **1**

Parameter	Value
chemical formula	$\text{C}_{46}\text{H}_{27}\text{D}_{12}\text{N}_{10}\text{O}_6\text{S}_2$
M_r	904.06
crystal system	triclinic
space group	$P1$
a/nm	8.378(2)
b/nm	10.342(3)
c/nm	13.372(4)
$\alpha/^\circ$	95.281(5)
$\beta/^\circ$	90.596(5)
$\gamma/^\circ$	112.369(4)
V/nm^3	1.0656(5)
Z	1
$D_c/(\text{g}\cdot\text{cm}^{-3})$	1.409
$\mu(\text{Mo } K_\alpha)/\text{nm}^{-1}$	0.188
$F(000)$	465
q range for data collection/ $^\circ$	1.5–28.4
index range	$-9 \leq h \leq 8$ $-7 \leq k \leq 12$ $-15 \leq l \leq 14$
reflections collected/unique (R_{int})	7889/5265 (0.049)
R_1, wR_2 ($I > 2\sigma(I)$)	0.0662, 0.1596
R_1, wR_2 (all data)	0.0817, 0.1653
goodness of fit on F^2	1.117
largest difference peak and hole/ $(e\cdot\text{nm}^{-3})$	260, -270

Table 2 Bond lengths (R) and angle of hydrogen bond in **1**

$\text{X}-\text{H}\cdots\text{Y}$	$R(\text{H}\cdots\text{Y})/\text{nm}$		$R(\text{X}\cdots\text{Y})/\text{nm}$		$\angle\text{X}-\text{H}\cdots\text{Y}/^\circ$	
	calc.	expt.	calc.	expt.	calc.	expt.
$\text{N1}-\text{H1}\cdots\text{O2}$	0.2015	0.2126(1)	0.3023	0.3022(2)	170.2	165.1
$\text{N4}-\text{H4}\cdots\text{O2}$	0.1768	0.1857(1)	0.2782	0.2782(2)	173.7	172.1
$\text{O3}-\text{H3A}\cdots\text{N5}$	0.1151	0.1746(2)	0.2650	0.2651(2)	174.0	156.0

Fig.2 IR spectra of **1** at 25 and 90 °C

Fig.3 IR spectra of **1** in CCl_4 solvent with the concentrations of 0.25 and 0.50 $\text{mg} \cdot \text{mL}^{-1}$

shifts from 1481 at 25 °C to 1488 cm^{-1} at 90 °C. The blue-shift caused by the increase of the temperature can be ascribed to the decrease in the hydrogen bonding interactions^{32,33}. As the temperature increases, the intensity of intermolecular hydrogen bond becomes weaker and the intensity of the related covalent N—H bond increases, resulting in the increases of the bond energy and wavenumber. Fig.3 shows the IR spectra of the sample **1** at 0.25 and 0.50 $\text{mg} \cdot \text{mL}^{-1}$ in CCl_4 , respectively. The characteristic absorption peak intensity increases with the increase of concentration, which reflects the concentration changes on the intensity of the absorption peak. However, no change has been found in the wavenumber of the characteristic peaks as the concentration of the sample increases, suggesting that there is no difference of hydrogen bonding interaction in sample with lower or higher concentration.

3.3 Energy analysis for hydrogen-bond

To clearly illustrate the interaction between the center squaric acid unit with the adjacent four 2,6-bis(2-benzimidazolyl)pyridine molecules, the assembly structure of **1** has been divided into five parts, denoted as C, F1 to F4, shown in Fig.4. In this structure, C is the center molecule while F1, F2, F3, and F4 stand for four pieces. Hydrogen bonding energy was calculated using Eq.(1)³⁴:

$$E_{(\text{F1-C})} = E_{(\text{CF1})} - E_{\text{C}} - E_{\text{F1}} \quad (1)$$

where $E_{(\text{F1-C})}$ is the hydrogen bonding energy between F1 and C, $E_{(\text{CF1})}$ is the total energy of CF1, $E_{(\text{C})}$ and $E_{(\text{F1})}$ are the individual energies of C and F1, respectively. The hydrogen bonding energies of the center

Fig.4 Divided region diagram for the hydrogen bonding interactions of one squaric acid with the adjacent four L molecules in **1**

molecule and four adjacent molecules (F1–F4) are listed in Table 3.

It can be seen that the energy value of C-F1 is same with that of C-F3, so are those of C-F2 and C-F4, resulting from the symmetric system of **1**. There are two O—H···N hydrogen bonds between C-F2 and C-F4. The average energy of hydrogen bond is 49.4 $\text{kJ} \cdot \text{mol}^{-1}$, which is around 28.4 $\text{kJ} \cdot \text{mol}^{-1}$ higher than that of hydrogen bond in water dimer (21 $\text{kJ} \cdot \text{mol}^{-1}$)³⁵, suggesting the presence of hydrogen bond. The hydrogen bonding energies of C-F1 and C-F3 reach up to 135 $\text{kJ} \cdot \text{mol}^{-1}$, which is much higher than that of the general hydrogen bonding. It could be attributed to strong hydrogen bonding with some covalent bond characteristics. The high hydrogen bonding energy can be assigned to π -conjugation of the hydrogen bonding acceptor atom (N) in the fragment, which greatly increases the electron density of the atom in the receptors. It belongs to charge auxiliary hydrogen bonding (resonance assisted hydrogen bonding, RAHB)^{36,37}. To verify the results, BLYP/def2-SVP was used to optimize CF1. The corresponding hydrogen bonding energy calculated by Eq.(1) is 119 $\text{kJ} \cdot \text{mol}^{-1}$. It has no significant difference from the results obtained from DFT calculation, indicating that the calculation results are reasonable.

3.4 Topological analysis of electronic density

Topology analysis was performed on the basis of the data obtained before using Multiwfn 3.3.6 program. The topology analysis image was drawn by VMD, presented in Fig.5. As shown in Fig.5, the orange yellow ball represents for bond critical point (BCP), and the violet lines stand for bond path. It can be seen that the hydrogen bonds associated with the center molecule have corresponding BCP and bond path. There is only one hydrogen bond in both C-F1 and C-F3, hence, it owns a bond path. Both of C-F2 and C-F4 have two hydrogen bonds, they have two bond paths. Besides, the center and the surrounding molecules have other types of bond paths, such as the bond path between the carbon atoms of the center molecule and the hydrogen atoms of

Table 3 Hydrogen bonding (HB) energies of the center molecule C and four adjacent molecules (F1–F4)

	$E_{\text{C}}/(\text{a.u.})$	$E_{\text{F}}/(\text{a.u.})$	$E_{\text{CF}}/(\text{a.u.})$	HB energy/ ($\text{kJ} \cdot \text{mol}^{-1}$)
C-F1	-454.41249	-1005.56428	-1460.02837	135.49
C-F2	-454.41249	-1005.56456	-1459.99587	49.40
C-F3	-454.41249	-1005.56424	-1460.02827	135.34
C-F4	-454.41249	-1005.56465	-1459.99589	49.24

Fig.5 Topology analysis diagram for 1
color on web version

the surrounding molecules, which can be attributed to the interaction between π -hydrogen bond interaction³⁸. However, the strength of the mutual interaction is very weak because of its long distance and the small positive charge, therefore, this kind of interaction can be ignored. It was reported that the topology of the electron density at BCP is an indicator of the strength of intermolecular interactions³⁹. The hydrogen bonds in C-F1 and C-F3 have relatively large electron densities (0.0924 – 0.0922 a.u.), which are much stronger than those in C-F2 and C-F4 with ρ_{BCP} in range of 0.0223 – 0.0349 a.u. It is in agreement with the geometrical findings, the hydrogen bond contacts in the former are evidently shorter than those in the later.

We can learn from Table 4 that C-F1 and C-F3 are equivalent, so are C-F2(1) and C-F4(1). AIM analysis indicates that the hydrogen bond of C-F1 or C-F3 is very strong. According to the data obtained from the literature, the ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ values of hydrogen bond are in the range of 0.002–0.04 and 0.02–0.15 a.u., respectively^{40–42}. And the bigger ρ_{BCP} and the smaller $\nabla^2\rho_{\text{BCP}}$, the stronger the hydrogen bond. The ρ_{BCP} and the $\nabla^2\rho_{\text{BCP}}$ of C-F1 were 0.092 and 0.003 a.u., respectively, which are much larger beyond the strength range of than the corresponding ones of the general hydrogen bond, indicating that the hydrogen bond strength is very strong. Generally, the values of $\nabla^2\rho_{\text{BCP}}$ and H_{BCP} in van der Waals forces are positive values

Table 4 Information of the corresponding critical point for each hydrogen bond

	<i>R</i> /nm	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	V_{BCP}	H_{BCP}	ELF_{BCP}
C-F1	0.2650	0.0924	0.0033	−0.0901	−0.0447	0.587
C-F2(1)	0.2782	0.0349	0.1337	−0.0258	0.0038	0.116
C-F2(2)	0.3023	0.0224	0.0624	−0.0146	0.0005	0.102
C-F3	0.2651	0.0922	0.0041	−0.0897	−0.0444	0.586
C-F4(1)	0.2782	0.0349	0.1336	−0.0258	0.0038	0.115
C-F4(2)	0.3024	0.0223	0.0623	−0.0146	0.0005	0.102

ρ_{BCP} , $\nabla^2\rho_{\text{BCP}}$, V_{BCP} , H_{BCP} , and ELF_{BCP} are the electron density, laplace function of electron density of BCP, electronic potential energy density, electronic energy density, electron localization function of BCP, respectively.

All of the above quantities of units are a.u. as a unit.

while the ones of $\nabla^2\rho_{\text{BCP}}$ and H_{BCP} in covalent interaction were negative⁴³. For **1**, the $\nabla^2\rho_{\text{BCP}}$ value of C-F1 is positive and the H_{BCP} is negative, which explains that this hydrogen bonding has the property of partial covalent interaction. Rybarczyk-Pirek³⁹ studied the nature of N—H···O with AIM analysis, the results indicated that the hydrogen bond of N—H···O is partial covalent interaction when $\nabla^2\rho_{\text{BCP}}$ and H_{BCP} values of N—H···O are positive and negative, respectively, which are consistent with our results. The value of V_{BCP} is related to hydrogen bonding intensity^{9,44}.

The potential energy density of BCP can be used to estimate the bond energy of hydrogen bond using Eq.(2):

$$E_{\text{HIB}} = -V_{\text{BCP}}/2 \quad (2)$$

Hence, the hydrogen bonding energy is estimated to be 118.3 kJ·mol^{−1}, which is comparable to the calculated data of 135 kJ·mol^{−1}. Thus, the potential energy density also reveals that the hydrogen bonding is very strong. ELF is a very important function to evaluate the intensity of covalent interaction. ELF values of BCP for weak interaction is usually quite small, however, the value of ELF_{BCP} for C-F1 is more than 0.5, which also shows certain characteristics of covalent bonding.

From the point of numerical value, the hydrogen bond of C-F2(2) is stronger than that of C-F2(1) but weaker than that of C-F1. The results agree well with the information reflected by the length of hydrogen bonds. The values of ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ are in the range of general hydrogen bonding. Their values of H_{BCP} are positive and the values of ELF_{BCP} are very small, indicating that they are ordinary closed shell interactions with no covalent interaction character. According to the Eq.(2), the bonding energies of two hydrogen bonds are 34 and 19 kJ·mol^{−1} respectively. The sum of the two hydrogen bond energy is 53 kJ·mol^{−1}, which is comparable to the calculated values of 49 kJ·mol^{−1}. In addition, comparing the hydrogen bond parameters between calculated values and the crystal data, listed in Table 2, it was found that the calculated distances X···Y of X—H···Y are same with those in the relative ones, however, the calculated distances H···Y are different from the relative crystal data. The two hydroxyl groups in squaric acid molecule and the surrounding molecules can form two extremely strong hydrogen bonds. Meanwhile, two carbonyl oxygen atoms in squaric acid molecule and the surrounding molecules generate four hydrogen bonds that have ordinary strength, where two of them are a little bit stronger than the others. The bond energy calculation is consistent with the results obtained from AIM analysis.

4 Conclusions

One-dimensional chain polymer assembled by the hydrogen bonding and π — π stacking interactions was obtained from the mixture of squaric acid and 2,6-bis(2-benzimidazolyl)pyridine molecules in d-DMSO. It could be concluded that two kinds of oxygen atoms in a squaric acid molecule can form hydrogen bonding with the nitrogen atom in 2,6-bis(2-benzimidazolyl)pyridine. However, the strength of the formed hydrogen bond is different. The hydrogen bond formed between oxygen atom of hydroxyl group and nitrogen atom in 2,6-bis(2-benzimidazolyl)

pyridine is much stronger than that of the oxygen atom in carbonyl from a squaric acid as an acceptor.

References

- (1) Majerz, I. *J. Phys. Chem. A* **2012**, *116* (30), 7992. doi: 10.1021/jp300942n
- (2) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.
- (3) Scheiner, S. *Hydrogen Bonding: a Theoretical Perspective*; Oxford University Press: New York, 1997.
- (4) Ebrahimi, A.; Habibi Khorassani, S. M.; Delarami, H. *Chemical Physics* **2009**, *365* (1–2), 18. doi: 10.1016/j.chemphys.2009.09.013
- (5) Herrebout, W. A.; Clou, K.; Desseyn, H. O. J. *J. Phys. Chem. A* **2001**, *105* (20), 4865. doi: 10.1021/jp004396c
- (6) Tonan, K.; Ikawa, S. I. *J. Am. Chem. Soc.* **1996**, *118* (29), 6960. doi: 10.1021/JA953380A
- (7) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99* (24), 9747. doi: 10.1021/j100024a016
- (8) Bader, R. F. W. *Chem. Rev.* **1991**, *91* (5), 893. doi: 10.1021/cr00005a013
- (9) Bader, R. F. W. *Atoms in Molecules a Quantum Theory*; Clarendon Press: Oxford, 1994.
- (10) Ranganathan, A.; Kulkarni, G. U.; Rao, C. N. R. *J. Phys. Chem. A* **2003**, *107* (31), 6073. doi: 10.1021/jp030465m
- (11) Takasu, I.; Izuoka, A.; Sugawara, T. *J. Phys. Chem. B* **2004**, *108* (18), 5527. doi: 10.1021/030961a
- (12) dos Reis, F. D.; Gatti, I. C.; Garcia, H. C.; de Oliveira, V. E.; de Oliveira, L. F. C. *J. Phys. Chem. A* **2014**, *118* (49), 11521. doi:10.1021/jp509502w
- (13) *Smart and Saint, Area Detector Control and Integration Software*; Siemens Analytical XSystems, Inc.: Madison, WI, USA, 1996.
- (14) Sheldrick, G. M. *SHELXTL V5.1 Software Reference Manual*; Bruker AXS Inc.: Madison, 1997.
- (15) Maia, J. D. C.; Carvalho, G. A. U.; Manguiera, C. P., Jr.; Santana, S. R.; Cabral, L. A. F.; Rocha, G. B. *J. Chem. Theory Comput.* **2012**, *8* (9), 3072. doi: 10.1021/ct3004645
- (16) McNaught, I. J. *J. Chem. Educ.* **2011**, *88* (4), 421. doi: 10.1021/ed900038a
- (17) Stewart, J. J. P. *J. Mol. Model.* **2013**, *19* (2), 1. doi: 10.1007/s00894-012-1667-x
- (18) Stewart, J. J. P. *J. Comput. Chem.* **2011**, *32* (7), 1456. doi: 10.1002/jcc.21759
- (19) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132* (15), 154104. doi: 10.1063/1.3382344
- (20) Song, J. S.; Klein, E. L.; Neese, F.; Ye, S. F. *Inorg. Chem.* **2014**, *53* (14), 7500. doi: 10.1021/ic500829p
- (21) Atak, K.; Golnak, R.; Xiao, J.; Suljoti, E.; Pfluger, M.; Brandenburg, T.; Winter, B.; Azi, E. F. *J. Phys. Chem. B* **2014**, *118* (33), 9938. doi: 10.1021/jp505129m
- (22) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. *Chem. Phys.* **2009**, *365* (1–3), 98. doi: 10.1016/j.chemphys.2008.10.036
- (23) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297. doi: 10.1039/b50841a
- (24) Yang, Y. *J. Phys. Chem. A* **2010**, *114* (50), 13257. doi: 10.1021/jp109278v
- (25) Zou, W. L.; Nori-Shargh, D.; Boggs, J. E. *J. Phys. Chem. A* **2013**, *117* (1), 207. doi: 10.1021/jp3104535
- (26) Lu, T.; Chen, F. W. *J. Phys. Chem. A* **2013**, *117* (14), 3100. doi: 10.1021/jp4010345
- (27) Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadle, J. *Pure Appl. Chem.* **2011**, *83*, 1619. doi: 10.1351/PAC-REP-10-01-01
- (28) Hibbert, F.; Emsley, H. *Adv. Phys. Org. Chem.* **1991**, *26*, 255. doi: 10.1016/S0065-3160(08)60047-7
- (29) Akhrieff, Y.; Server-Carrio, J.; Garcia-Lozano, J.; Folgado, J. V.; Sancho, S.; Escrivá, E.; Vitoria, P. *Crystal Growth Design* **2006**, *6* (5), 1124. doi: 10.1021/cg050543q
- (30) Silva, C. E.; Dos Santos, H. F.; Speziali, N. L.; Diniz, R.; de Oliveira, L. F. C. *J. Phys. Chem. A* **2010**, *114* (37), 10097. doi: 10.1021/jp105346h
- (31) Inkaya, E.; Günnaz, S.; Özdemir, N.; Dayan, O.; Dinçer, M.; Çetinkaya, B. *Spectrochim. Acta A* **2013**, *103*, 255. doi: 10.1016/j.saa.2012.11.039
- (32) Schwager, F.; Marand, E.; Davis, R. M. *J. Phys. Chem.* **1996**, *100* (50), 19268. doi: 10.1021/jp9613448
- (33) Desseyn, H. O.; Clou, K.; Keuleers, R.; Miao, R.; Van Doren, V. E.; Blaton, N. *Spectrochim. Acta A* **2001**, *57* (2), 231. doi: 10.1016/S1386-1425(00)00370-X
- (34) Hao, M. H. *J. Chem. Theory Comput.* **2006**, *2* (3), 863. doi: 10.1021/ct0600262
- (35) Lane, J. R. *J. Chem. Theory Comput.* **2013**, *9* (1), 316. doi: 10.1021/ct300832f
- (36) Lipkowski, P.; Grabowski, S. J.; Robinson, T. L.; Leszczynski, J. *J. Phys. Chem. A* **2004**, *108* (49), 10865. doi: 10.1021/jp048562i
- (37) Grabowski, S. J.; Dubis, A. T.; Palusiak, M.; Leszczynski, J. *J. Phys. Chem. B* **2006**, *110* (12), 5875. doi: 10.1021/jp055334v
- (38) Grabowski, S. J. *J. Phys. Org. Chem.* **2013**, *26* (6), 452. doi: 10.1002/poc.3109
- (39) Rybarczyk-Pirek, A. *J. Struct. Chem.* **2012**, *23* (6), 1739. doi: 10.1007/s11224-012-9980-7
- (40) Chou, P. T.; Ching, Y. W.; Hung, F. T. *J. Phys. Chem. B* **1997**, *101* (44), 9119. doi: 10.1021/jp971824e
- (41) Latosińska, J. N.; Latosińska, M.; Seliger, J.; Zagar, V.; Maurin, J. K.; Kazimierzczuk, Z. *J. Phys. Chem. A* **2012**, *116* (5), 1445. doi: 10.1021/jp210322p
- (42) Latosińska, J. N.; Latosińska, M.; Maurin, J. K.; Orzeszko, A.; Kazimierzczuk, Z. *J. Phys. Chem. A* **2014**, *118* (11), 2089. doi: 10.1021/jp411547z
- (43) Rozas, I.; Alkorta, I.; Elguero, J. *J. Am. Chem. Soc.* **2000**, *122* (45), 11154. doi: 10.1021/ja0017864
- (44) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, *285* (3–4), 170. doi: 10.1016/S0009-2614(98)00036-0