Dominant Role of C–Br····N Halogen Bond in Molecular Self-Organization. Crystallographic and Quantum-Chemical Study of Schiff-Base-Containing Triazoles

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Three Schiff-base-containing triazole derivatives have been synthesized and investigated by X-ray crystallography. Structural motifs (*zigzag* or linear chains) formed in the solid state are stabilized by C–Br•••N halogen bond interactions, while hydrogen bonds do not seem to play a significant role in the molecular self-organization of studied compounds. Quantum-chemical studies confirm that these interactions are sufficient to account for both the arrangement of structural motifs and very short Br•••N distances observed experimentally. It is also shown that Br•••N interactions can lead to generally shorter donor–acceptor distances than Cl•••N contacts.

Introduction

Weak intermolecular interactions play important roles in many chemical phenomena, such as molecular recognition, conformational transformation, and molecular packing in crystals.¹ Hydrogen bonding is the most frequently used tool to assemble organic molecules in solid, liquid, or gas phases.² On the other hand, it is well-known that carbon-bound halogen atoms can act as electron acceptors and form short contacts with atoms containing lone pairs (e.g., nitrogen, phosphorus, oxygen, and sulfur).³ This electron donor–acceptor interaction has been called "halogen bonding"⁴ to emphasize its similarity with hydrogen bonding. The highly directional character of this interaction as well as the interpenetrating of van der Waals volumes of halogen and nitrogen atoms has been reported. This noncovalent interaction can be strong enough to control the aggregation of organic molecules.^{3–7}

Recently, particular attention has been focused on the interaction between haloperfluorocarbons and aromatic dinitrogen hydrocarbons^{3a,5} and between organic nitriles and halogen atoms.^{6b,7} On the other hand, studies on the nitrogen-halogen interactions involving nitrogen-rich heterocycles are relatively rare.^{8–10} These investigations concern crystal structure studies on aromatic compounds containing the N=C-X subunit where X = Cl or Br. In the structures of bromotetrazole⁹ and 3-chloro-1,2,4-triazole,¹⁰ both the N···X intermolecular interactions and strong N-H···N hydrogen bonds (D···A distance equal to 2.757 Å and 2.865 Å, respectively) are responsible for the formation of two-dimensional arrays of molecules. Presumably, the hydrogen bonds, which must be much stronger than N····X interactions, are of greater importance in determining the crystal packing. At this point it is necessary to mention that weak N····X-C interactions are observed in binary structures, 8c,d while their presence in crystals of a single chemical species is less common.^{8b} Our aim is to design and prepare such a unary crystal with distinct C=N····X-C halogen bonds. To prevent the formation of strong hydrogen bonds between heterocycles, we

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have prepared 4-(4-*H*-1,2,4-triazol-4-yl)-n-Br-phenylmethanimine where n = 4 (1) or n = 3 (2) and 4-(4-*H*-1,2,4-triazol-4-yl)-4-Br-phenylmethylmethanimine, (3) (Figure 1). Detailed analysis of the crystal structures of 1-3 was performed. Due to the fact that the structures of molecules 1-3 seem to be stabilized by the C-Br···N interaction, it was interesting to characterize them by means of advanced theoretical methods: the topological analysis of the electron density¹¹ and SAPT interaction energy decomposition scheme.¹² The urge for theoretical support is partially motivated by recent work of Dance,¹³ who pointed out that the distance criterion need not always be indicative of the presence of attractive forces between atoms. Indeed, close contact between atoms may be energetically destabilizing, but when forced by several stronger interactions may yield a net gain in stability.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls and KBr pellets on a Bruker IFS 113V FT-IR spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of this university. ¹H NMR spectra were recorded on a Bruker AM300 spectrometer in CD₃CN. ESI MS were performed on a mass spectrometer Finnigan Mat type TSQ700.

Starting Materials. Commercially available solvents, hydrazine monohydrate, formic acid, 4-bromobenzaldehyde, 3-bromobenzaldehyde (Fluka), and 4-bromoacetophenon (Aldrich) were used without further purification. The 4-amino-1,2,4-triazole was prepared according to literature method.¹⁴

Synthesis of 4-(4-*H*-1,2,4-triazol-4-yl)-4-Br-phenylmethanimine, (1). Ethanolic solution (30 mL) of 4-bromobenzaldehyde (3.70 g, 20 mM) was added to a warm ethanolic solution (25 mL) of 4-amino-1,2,4-triazole (1.69 g, 20 mM) and the resulting solution was refluxed for 4 h. Upon standing overnight at the room temperature, the solution deposited white crystals that were isolated by filtration, washed with a small amount of ethanol and diethyl ether, and dried under vacuum. For 1: yield 2,1 g, 41.8%, Mp: 197 °C. MS (m/e) 251.1. Anal. calcd. for C₉H₇N₄Br: C, 43.05; H, 2.81; N, 23.31; Br, 31.82. Found: C,



Figure 1. Numbering scheme and overall conformation of 1-3.

43.02; H, 2.74; N, 22.04; Br, 31.96. ¹H NMR (CD₃CN, RT, [ppm] (multiplicity, assignment)): 8.76 (s, C-H_{im}), 8.69 (s, 2C-H_{tr}), 7.73 (4H, m, *o*-, *m*-Ph).

Synthesis of 4-(4-*H*-1,2,4-triazol-4-yl)-3-Br-phenylmethanimine, (2). The compound 2 was prepared in a similar manner by using 3-bromobenzaldehyde instead of 4-bromobenzaldehyde. For 2: yield 2.04 g, 40.6%, Mp: 185-188 °C. MS (*m/e*) 251.1. Anal. calcd. for C₉H₇N₄Br: C, 43.05; H, 2.81; N, 23.31; Br, 31.82. Found: C, 43.26; H, 2.82; N, 22.30; Br, 32.00. ¹H NMR (CD₃CN, RT, [ppm] (multiplicity, assignment)): 9.03 (s, C-H_{im}), 8.74 (s, 2C-H_{tr}), 8.09-7.49 (4H, m, *o-,o'-*, *m-*, *p*-Ph).

Synthesis of 4-(4-H-1,2,4-triazol-4-yl)-4-Br-phenylmethylmethanimine, (3). Ethanolic solution (30 mL) of 4- bromoacetophenon (3.98 g, 20 mM) was added to a warm ethanolic solution (25 mL) of 4-amino-1,2,4-triazole (1.69 g, 20 mM) and the resulting solution was refluxed for 4 h, then the reaction mixture was cooled to the room temperature. Subsequently, the volume of the reaction mixture was reduced to 5 mL on a rotary evaporator resulting in precipitation of a white solid. The solid was filtered off and then dissolved in diethyl ether. The solution was allowed to stand overnight in a refrigerator, resulting in formation of well-shaped colorless crystals that were separated by filtration, washed with a small amount of diethyl ether, and dried in air. For 3: yield 1.59 g, 30.0%, Mp: 76-78 °C. MS (m/e) 265.0. Anal. calcd. for C₁₀H₉N₄Br: C, 45.31; H, 3.42; N, 21.13; Br, 30.14. Found: C, 45.86; H, 3.65; N, 19.16; Br, 30.21. ¹H NMR (CDCl₃, RT, [ppm] (multiplicity, assignment)): 8.29 (s, $2C-H_{tr}$), 7.71 (4H, dd, *o-*, *m*-Ph, J = 8.6 Hz), 2.39 (3H, CH₃)

Crystallographic Data Collection and Structure Determination. Crystal data³² for 1, 2, and 3 are given in Tables S1-S3 of the Supplementary Information, together with refine-



Figure 2. Top: the chain of molecules linked by the C–Br···N bonds in **1**. Middle: two chains of molecules linked by the C–Br···N bonds in **2**. Weak C–H···Br interchain interactions are also shown. Bottom: two neighbor chains of molecules linked by the C–Br···N bonds in **3**.

ment details, while the most important features of the structures are presented in Figures 1-2. All measurements were performed on a Kuma KM4CCD k-axis diffractometer with graphitemonochromated MoKa radiation at 100 K using an Oxford Cryosystem adapter. Crystals were positioned at 65 mm from the KM4CCD camera. Using a counting time of 20 s, 612 frames were measured at 0.75°. The data were corrected for Lorentz and polarization effects. An analytical absorption correction was also applied.¹⁵ Data reduction and analysis were carried out with the Oxford Diffraction Poland (formerly Kuma Diffraction Wrocław, Poland) programs. All structures were solved by direct methods (program SHELXS97¹⁶) and refined by the full-matrix least-squares method on all F² data using the SHELXL97¹⁷ program. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from geometry of molecules or $\Delta \rho$ maps and were refined with isotropic displacement parameters.

Computational Methodology. Large number of atoms in the crystallographic unit cell prevents performing detailed ab initio calculations by using the periodic Hartree-Fock method. Therefore, several models of increasing simplification have been chosen for our computational study. First, model dimers of 1, 2, and 3 have been chosen with geometrical structures taken from the bulk solid. The assumed complexes named 4, 5, and 6, respectively, are presented in Figure 4. Geometry optimization using the LANL2DZ approximation¹⁸ was carried out for 4, 5, and $\mathbf{6}$ at the density-functional B3LYP¹⁹⁻²¹ computational level with the Gaussian 98 program.²² DFT theory is nowadays routinely applied to organic systems, which is also the case for halogen-bonded intermolecular complexes.3b,c,8c However, when dispersion energy is significant, one must treat its results with care. Therefore, more involved computational models will also be invoked further in this study as tools for assessing the accuracy of the DFT approach for the systems under consideration. To obtain a more detailed insight into the nature of the $C-X \cdots N$ (X = Cl, Br, and I) molecular interaction additional calculations have been performed for model complexes consisting of 4-amino-4H-1,2,4-triazole and 4-X-benzaldehyde (X =



Figure 3. Weak intermolecular interactions in 1, 2, and 3 (top, middle, and bottom respectively). The dark molecules are linked via the Br···N interactions. The open dashed lines represent weak intermolecular CH···A (A = N, Br) interactions. Lengths of the hydrogen bonds are no longer than the sum of respective van der Waals radii.²⁹



Figure 4. Model dimers 4, 5, and 6 taken from crystals of compounds 1, 2, and 3.

Cl, Br, I) abbreviated as **7**, **8**, and **9** respectively (see Figure 5). Geometry optimization with $C-X\cdots N$ linearity and overall system planarity constraint was carried out for these structures at the same level of theory as mentioned above. $C-X\cdots N$





Figure 6. Dimers 10 and 11, the smallest models for N···X interactions.

interactions for 7-9 structures were investigated with Bader's Atoms in Molecules analysis of electron density¹¹ using AIMPAC²³ and AIM2000²⁴ programs. Finally, the simplest models of C-X···N interaction were constructed as complexes of methanimine with chloro- and bromomethanimine (denoted 10 and 11 respectively - see Figure 6). The reason for the high simplification of models is the necessity to treat them with more sophisticated theoretical methods. Their structures were fully optimized at MP2 and MP4(SDQ) correlated ab initio levels using a series of three basis sets (6-31G(d, p), aug-cc-pVDZ and mixed basis set with aug-cc-pVTZ on interacting N····X atoms and aug-cc-pVDZ for the remaining atoms). The mixed basis set was also applied in B3LYP DFT geometry optimizations of 10 and 11. The Gaussian 98 package was used for this part of the calculations. Interaction energy for N-Cl and N-Br systems (10, 11) and mixed basis set (cc-pVTZ for C-X···N, cc-pVDZ for the rest of the molecule) was partitioned according to symmetry-adapted perturbation theory¹² (SAPT) using SAPT2002 program.²⁵

Results and Discussion

X-ray Crystal and Molecular Structure. The numbering scheme and overall conformation of the studied compounds are shown in Figure 1. Bond lengths, valence, and torsion angles in studied compounds are presented in Tables S1–S3 of the Supplementary Information.

In principle, the aroyl Schiff bases of 4-amino-1,2,4-triazoles show a tendency to retain the planar conformation with a rather flat surface of potential energy as calculated for rotation around the N(3)–N(4) and C(1)–C(2) bonds.²⁶ A common feature for this group of compounds is the tendency for creating hydrogen bond systems with the C–H groups as donors [C(8) and/or C(9)] and nitrogen atoms [N(1) and/or N(2)] or phenyl rings as acceptors. These interactions control molecular arrangement in all reported crystal structures of the aroyl Schiff bases of 4-amino-1,2,4-triazoles.^{27,28}

The molecular structures of **1** and **2** are essentially planar with angles between the best planes calculated for phenyl and triazole rings of 13.7(2) and $7.6(2)^\circ$, respectively. The presence of a methyl group at the C(1) atom changes the geometry of **3** toward a twisted conformation. In a crystal of **3**, two symmetry-

TABLE 1: Lengths (Å) and Angles (°) of the C–Br…N Interactions in Crystals of 1, 2, and 3

C-Br····N	Br····N	∠C−Br ··· N
compound 1 $C(5)-Br(1)\cdots N(1^{i})$ compound 2	3.240(4)	172.38(13)
$C(6)-Br(1)\cdots N(1^{ii})$ compound 3	3.192(4)	168.94(13)
$C(5) - Br(1) \cdots N(52^{iii})$	3.199(3)	164.40(11)
$C(55) - Br(2) \cdots N(2^{iv})$	3.324(3)	161.35(12)

Symmetry codes: (i) -1.5 + x, 0.5 - y, 0.5 + z; (ii) 2 + x, y, 1 + z; (iii) 1 + x, y, 1 + z; (iv) 1 + x, y, z.

 TABLE 2: Geometry of Weak Intermolecular CH···A

 Interactions in Crystals of 1, 2, and 3

D-H···A	D•••A [Å]	H•••A [Å]	∠D−H•••A [°]
compound 1			
$C(1) - H(1) N(2^{i})$	3.463(5)	2.50(5)	164(4)
$C(4) - H(4) Br(1^{ii})$	3.954(4)	3.07(5)	158(4)
$C(8) - H(8) N(2^{i})$	3.654(6)	2.71(5)	162(4)
$C(9) - H(9) Br(1^{iii})$	3.931(4)	3.01(5)	167(4)
compound 2			
$C(4) - H(4) Br(1^{iv})$	3.857(4)	2.91(6)	157(5)
$C(1) - H(1) N(2^{v})$	3.529(7)	2.56(7)	159(5)
compound 3			
C6-H6N1(vi)	3.454(4)	2.54(5)	174(4)
C9-H9N51(vii)	3.468(5)	2.56(5)	164(4)
C54-H54N4(viii)	3.535(5)	2.69(5)	144(4)
C56-H56Br1(^{ix})	3.717(4)	3.04(5)	124(3)
C57–H57Br1(^{ix})	3.722(4)	3.03(4)	126(3)

See Figure 3 for graphical representation. Symmetry codes: (i) 2.5 -x, 0.5 +y, -0.5 - z; (ii) -x, 1 - y, -z; (iii) 1 - x, -y, -z; (iv) 1 - x, -0.5 + y, 1 - z; (v) -2 - x, -0.5 + y, -z; (vi) 1 + x, y, z; (vii) x, y, 1 + z; (viii) 1 - x, -y, 1 - z; (ix) x, y, -1 + z.

independent molecules are observed with different interplanar angles equal to 45.37(12) and 68.06(14)°. The bond lengths and valence angles observed in the structures are in the normal ranges. Surprisingly, the detailed analysis of intermolecular interactions for all compounds under investigations showed, in the absence of significant short C-H···N interactions, *zigzag* (in 1 and 2) or linear (in 3) chains of molecules (Figure 2) held together by the weak attractive intermolecular C-Br...N interactions with Br ... N distances in the range of 3.192(4)-3.324(3) Å (Table 1). Within the estimated error (3 esd's), these are shorter than the sum of the van der Waals radii (3.44 Å).²⁹ The short C-Br...N contacts are nearly linear with the C-Br...N angles in the range of 160.17(11)-172.38(13)°. The geometrical parameters found in this study are comparable to other recently reported Br ... N(sp2) contacts that exhibit high directional penetrations of electronegative atoms into the van der Waals volumes of halogen atoms.6b There are, however, also some weak, near-linear C-H···A interactions (Table 2, Figure 3) that can influence the arrangement of 1-3 molecules in the solid phase. Of these, we think that the C-H···N pincer interactions could in principle constitute additional forces directing molecular aggregation. The N····H distances ranging from 2.50 to 2.71 Å are found in 1-3. However, the pincer C-H···N interaction is present only in 1 and 2. In the case of 3, the C-H···N bond is rather more likely to control the tilt of the phenyl ring with respect to the molecular backbone, while the C-Br...N interactions control formation of infinite chains. As is evident from Figure 3, even in case of 1 and 2 the C-H···N interactions do not act in close synergy with halogen bonds, while C-H···Br seems to cooperate with C-Br···N. We suggest, therefore, that the halogen bonds are primary sources of the particular arrangement of investigated structures. There

 TABLE 3: Selected Results of Geometrical Optimization of the Model Complexes 4–9

parameter	4 –Br	5 –Br	6 –Br	7 –Cl	8 –Br	9 – I
R(X…N) [Å]	3.150	3.147	3.153	3.260	3.129	3.089
$\rho(r_{\rm c}) \ [{\rm e} \ a_0^{-3}]$				0.007	0.011	0.015
$\Delta E [\text{kcal mol}^{-1}]^a$	-1.28	-1.18	-1.25	0.38	-1.27	-3.37

^{*a*} Bonding energy (relative to isolated monomers) corrected for BSSE, computed at B3LYP level with LANL2DZ pseudopotential and basis set.

is one more point to this part of the discussion. One can argue that the role of a single but weak halogen bond must be surely masked by other, generally weaker, but more numerous, van der Waals interactions (in this case, mainly C–H···H). However, we would like to point out the directionality of the halogen bond^{3c} as opposed to general nondirectional dispersion forces. The presence of a halogen bond is often a sufficient impulse for directional molecular aggregation,^{3–7} as witnessed in our case by characteristic *zigzag* or chain motifs.

Computational Results and Discussion

Crystal structures of 1, 2, and 3 seem to be stabilized by the C-Br ... N interaction. Theory should help explain whether such an interaction alone can be responsible for the observed structural motifs and distance ranges. As described in the Computational Methodology section, we start by examining dimers that are cut out of the experimental crystal structure, systems 4-6 (Figure 4). Results of the geometry optimization (Table 3) show that the experimental Br····N distance is closely reproduced by the DFT approach. The complexes rearrange only slightly during the optimization; they attain more planar structures and linear C-Br ··· N arrangement as compared to the experiment. Bonding energies of 4-6 are ca. -1.2 kcal/mol. In the case of such a low stabilization, the performance of DFT methods should be verified, which is one of the aims of the following theoretical studies. The Br ... N interaction region was investigated in the framework of AIM theory and in all of the 4-6 dimers a bond critical point (BCP) accompanied by the bond path linking the N and Br atoms were found. According to Bader's criteria^{11a} for the definition of a chemical bond, this signifies the presence of bonding interaction, especially in the view of the fact that there are no other close contacts in the **4**–**6** systems. However, the electron density at the BCP ($\rho(r_c)$) is small (ca. 0.01 e a_0^{-3}) and its Laplacian is positive, which indicates weak interaction (similar to weak hydrogen bonds). We can conclude that for 4-6 the B3LYP functional is able to reproduce, at least semiquantitatively, the geometry (bond length and directionality) of the Br ... N interaction, and that this interaction is strong and directional enough to arrange the gasphase 4-6 dimers similarly to 1-3. This does not exclude the presence of other forces in the crystals of 1-3, but combined with the analysis given above indicates the importance of the halogen bond for the crystal structure of the studied systems. Now let us proceed to verify the accuracy of the DFT theoretical model in more detail.

Model systems of **7–9** (Figure 5) enable us to study the influence of halogen atoms on C–X···N interaction (Table 3). This will enable us to define the systems for which the B3LYP/ LANL2DZ level is applicable. Interestingly, the X···N distance increases with rising electronegativity of the X atom implying that the more polarizable the atom, the stronger the X···N interaction. This conclusion is supported by the magnitude of the interaction energy ΔE . The complex **7** with the Cl atom is slightly unstable (signifying failure of the DFT approach), but

 TABLE 4: Parameters of C-X···N Bridge and Binding Energies of 10 and 11 Systems

parameter	ab initio 10 –Cl	<i>ab initio</i> 11 –Br	<i>DFT</i> 10 –Cl	<i>DFT</i> 11 –Br
X•••N [Å] ^a	3.098-3.245	3.022-3.161	3.386	3.304
$<(C-X.N)[^{0}]$	165.0-170.2	169.2-170.0	171.3	175.4
$E [\text{kcal/mol}]^b$	-1.551	-2.201	-0.227	-0.726
E _{DISP} [kcal/mol] ^c	-2.146	-3.078		

^{*a*} Ab initio: Range of results from different basis sets (6-31G(d, p), aug-cc-pVDZ, and mixed basis set: aug-cc-pVTZ for N···X, aug-cc-pVDZ for the rest of the complex) at MP2 and MP4(SDQ) level with frozen-core or all-electron correlation included. *DFT*: Results obtained with B3LYP DFT functional and the mixed basis set. ^{*b*} Bonding energy corrected for BSSE, computed with mixed basis set (see above) at both the all-electron MP2 level and B3LYP DFT functional. ^{*c*} Dispersion energy calculated within SAPT approximation and mixed basis set: cc-pVTZ for N···Cl-C, cc-pVDZ for the rest of the complex.

the observed order of energy values is consistent with decreasing X ···· N distance. Moreover, the stabilization rises monotonically for 8 and 9. This sequence of energies was theoretically observed by Valerio et al.^{3b} for the simple model of $CF_3X \cdots NH_3$ (X = Cl, Br, I), where DFT interaction energies ranged from -2.3kcal/mol for chlorine species to -6.4 for iodine system. The lack of stability found for 7 should not suggest that there is no stabilizing C-Cl···N interaction that would be in contradiction to experimental proofs.^{5a,30} One should remember that the results presented here are based on the model systems and describe only the gas-phase heterodimer. However, we note that intermolecular X ···· N distances in 7 and 8 are similar to those found both in earlier literature studies³⁻¹⁰ and in compounds 1 to 3. Thus, we suggest that the B3LYP functional can fail for the Cl····N halogen bond, while it can provide a reasonable description of the bonding for heavier halogens. We will return to this assumption in the paragraph dealing with SAPT results.

The topological analysis of the electron density^{11a,31} for **7–9** shows a picture similar to that already obtained for the **4–6** systems. Electron densities at the bond critical point increase from **7** to **9**, but their magnitudes (ca. 0.01 e a_0^{-3}) and positive sign of a Laplacian confirm that the bonding is of the closed-shell, noncovalent type. However, the complex formation together with calculated geometrical and electron density parameters, and finally the presence of bond critical points accompanied by proper bond paths, indicate strongly that the short distances found experimentally in **1–3** are not forced contacts, but rather proper manifestations of "halogen bonding".

The final test to confirm this thesis involved MP2 and MP4 perturbational computations, schemes that are regarded as less error-prone than the density functional theory in case of weak interactions. Selected results of the investigations on two simple dimers 10 and 11 (Figure 6) are shown in Table 4. These systems are probably the simplest to exhibit C-X...N interactions and had been used previously for theoretical modeling of halogen bonding.8 It was seen in our results that bromine systems can indeed form shorter N····X distances than chlorinecontaining species, as observed already for compounds 7-9. The directionality of the "halogen bonding" is seen in the range of calculated C-X···N angles, which are very close to the linear arrangement and are consistent among various methods used, while the calculated N····X distances are ca. 0.1 Å shorter than found experimentally (cf. Table 1). Note that these distances are rather strongly dependent on the level of theory applied (basis set, correlation scheme), but the largest separations, which are closest to the experimental findings, were obtained with the best computational methods. The DFT bond lengths are larger by 0.2 Å, which is consistent with much smaller stabilization

predicted by DFT with respect to the ab initio results. The simplified systems 10 and 11 do not contain aromatic rings, which increase polarization effects and help the DFT method to perform well for 4-9. The stability of chlorine-containing 10 computed by DFT is particularly too small, supporting our earlier notion. Interaction energy partitioning with the SAPT scheme indicates that virtually all stabilization energy in complex 10 and 11 is due to the dispersion contribution, while other major components (polarization, induction, and exchange energies) basically cancel each other. However, these components are responsible for the directionality of the halogen bond. DFT recovers most of these components and therefore it is successful for systems containing heavier, easily polarizable halogen atoms (Br or I). The SAPT results are consistent with the observed strength of C-X···N interactions, which can be easily dominated by hydrogen bonds and only rarely are able to become the dominant factors in shaping crystal structures. Our analysis indicates that the crystals of 1, 2, and 3 belong to the group of structures with internal arrangement directly governed by the N····Br interactions.

Conclusions

This paper describes synthesis, structural characterization, and theoretical investigations on a series of 4-(4-H-1,2,4-triazol-4yl)-bromophenylmethanimines (1, 2, and 3). The most striking feature of their unary crystal structures is the lack of hydrogen bonds and the presence of short intermolecular N····Br contacts (3.19–3.32 Å). Planarity of these molecules is retained only in the absence of a bulky methyl substituent at the imine carbon atom. Theoretical calculations were used to get insight into the importance of N····Br interactions. The presence of bond critical points between the N and Br atoms in 4, 5, and 6 dimers implies that those atoms are in contact. The calculations on compounds 7-9 show that the N···X separation decreases with growing polarizability of the halogen atom. This notion is supported by calculations for the 10 and 11 models. SAPT interaction energy partitioning scheme, employed for 10 and 11, explains their stability in terms of the dispersion forces dominating over repulsion terms. Theoretical description of clearly defined, directional interactions of C-X ··· N type in gas-phase calculations indicates that these forces play a decisive role in crystal structures of compounds 1-3.

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Supporting Information Available: Tables containing crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for compounds 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) CCDC contains the supplementary crystallographic data for this paper under the following deposit numbers: 211333 for compound 1, 211334 for 2, and 211335 for 3. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.