Halogen Azides XN_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) - A Comparison of Their Solid State Structures

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Dedicated to Prof. Dr. Peter G. Jones belated on the occasion of his 60th birthday

Covalent azides are challenging inorganic compounds for inorganic and theoretical chemists. HN_3 **1**, which was synthesized for the first time by Curtius in 1890,^[1] and halogen azides XN_3 ($\text{X} = \text{F}$ **2**, Cl **3**, Br **4**, I **5**), which were prepared between 1900 (IN_3)^[2] and 1942 (FN_3)^[3], also show a remarkable chemical reactivity.^[4-7] Moreover, they have been subject to many computational studies since their simple composition of only four atoms allows the use of the highest theoretical basis sets in order to gain a detailed understanding of the nature of covalent bonding.^[8-16] Unfortunately, their structural characterization was hampered by their expressed shock and heat sensitivity and characterization techniques were almost limited to NMR,^[17-21] IR,^[8,22-25] photoelectron,^[26-28] and microwave spectroscopy^[29-32] and electron diffraction.^[8,33] In contrast, their solid state structures remained unknown except for IN_3 **5a**,^[34] which adopts a polymeric structure, and HN_3 **1**,^[35] whose structure was recently reported. Moreover, we reported on the solid state structure of bromine azide **4**,^[36] which crystallizes in a helical arrangement through formation of intermolecular $\text{Br}\cdots\text{N}_\alpha$ and $\text{N}_\beta\cdots\text{N}_\gamma$ interactions.

Herein, we report on the single crystal X-ray structures of ClN_3 **3**. Moreover, the structure of IN_3 **5a** was re-evaluated and an additional polymorph **5b** was structurally characterized. The structures of **3**, **5a** and **5b** are compared with that of BrN_3 **4** and theoretical calculations were performed in order to investigate the strength of the intermolecular interactions in detail.

3 was prepared by reaction of NaN_3 with sodium hypochloride and boronic acid and **5** by reaction of AgN_3 with iodine, respectively.

Scheme 1. Synthesis of ClN_3 **3** and IN_3 **5**.

The ^{14}N NMR spectrum of pure **3** in CDCl_3 shows three resonances for N_α ($\delta = -274$, $\Delta\mu_{1/2} = 145$ Hz), N_β ($\delta = -123$, $\Delta\mu_{1/2} =$

28 Hz) and N_γ ($\delta = -113$, $\Delta\mu_{1/2} = 36$ Hz), which correspond fairly well to values reported for solutions of **3** in CDCl_3 (-269.9 , $\Delta\mu_{1/2} = 240$ Hz, N_α ; -119.2 , $\Delta\mu_{1/2} = 20$ Hz, N_β ; -109.3 , $\Delta\mu_{1/2} = 50$ Hz, N_γ)^[20] and CD_2Cl_2 (-271.2 N_α ; -123.7 N_β , -114.1 N_γ).^[17] A solution of **5** in $\text{CH}_2\text{Cl}_2/\text{CDCl}_3$ also shows three resonances for N_α ($\delta = -359$, $\Delta\mu_{1/2} = 540$ Hz), N_β ($\delta = -127$, $\Delta\mu_{1/2} = 12$ Hz) and N_γ ($\delta = -165$, $\Delta\mu_{1/2} = 250$ Hz), which slightly differ from values reported for a CDCl_3 solution (-349.2 , $\Delta\mu_{1/2} = 450$ Hz, N_α ; -122.0 , $\Delta\mu_{1/2} = 20$ Hz, N_β ; -157.0 , $\Delta\mu_{1/2} = 85$ Hz, N_γ).^[20] Raman spectra of **3** and **5** show strong adsorption bands due to the antisymmetric ($\nu = 2062$ cm^{-1} **3**; 2072 cm^{-1} **5**) and symmetric $\text{N}_\alpha\text{-N}_\beta\text{-N}_\gamma$ stretching modes ($\nu = 1134$ cm^{-1} **3**; 1220 cm^{-1} **5**) and the $\text{N}_\alpha\text{-Cl/I}$ ($\nu = 542$ cm^{-1} **3**; 412 cm^{-1} **5**) stretching mode,^[37] which agree very well with values previously reported.^[9,10,38] The Raman spectrum of **5** in the low frequency range is somewhat more complex compared to that of **3** due to its polymeric nature.

The crystallization of halogen azides is typically complicated by their expressed sensitivity toward small pressure and temperature differences. However, use of a miniature zone melting procedure with focused infrared-laser-radiation,^[39] which was successfully applied for the growth of a BrN_3 crystal,^[36] allowed the growth of a single crystal of **3** on the diffractometer at a temperature of 150 K. Suitable crystals of **5a,b** were obtained by slow sublimation.

Figure 1. Representation of ClN_3 **3**. Thermal ellipsoids at 50% probability levels.

ClN_3 **3** crystallizes in the orthorhombic space group $\text{Cmc}2_1$ with four molecules (all four atoms are placed in a mirror-plane)^[40] in the unit cell and adopts - like the other halogen azides - a trans-bent structure. The $\text{N}_\alpha\text{-N}_\beta\text{-N}_\gamma$ ($170.1(5)^\circ$) and $\text{Cl-N}_\alpha\text{-N}_\beta$ bond angles ($108.7(4)^\circ$) are comparable to those observed in BrN_3 **4**. The $\text{N}_\alpha\text{-Cl}$ bond ($1.748(5)$ Å) is shorter than the $\text{N}_\alpha\text{-Br}$ bond length in **4** ($1.916(9)$ Å) as was expected due to the smaller covalent radius of Cl compared to Br, but slightly longer than the sum of the covalent radii as reported by Pyykkö et al. (1.70 Å)^[41] and of compounds containing a terminal N-Cl bond.^[42] The $\text{N}_\alpha\text{-N}_\beta$ ($1.258(6)$ Å) and $\text{N}_\beta\text{-N}_\gamma$ ($1.115(7)$ Å) bond lengths differ significantly, clearly proving the covalent-bonding character. The bond angles and bond lengths are in excellent agreement with values obtained from microwave spectroscopy studies ($\text{N}_\alpha\text{-Cl}$ 1.745 Å, $\text{N}_\alpha\text{-N}_\beta$ 1.252 Å, $\text{N}_\beta\text{-N}_\gamma$ 1.133 Å; $\text{N}_\alpha\text{-N}_\beta\text{-N}_\gamma$ 171.56° , $\text{Cl-N}_\alpha\text{-N}_\beta$ 108.40°)^[31] and computational

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calculations.^[9-12] **3** adopts a chain-like polymeric structure constituted via a two-fold screw axis due to the formation of Cl $\cdots$ Cl interactions (see Figure 2). This chain is comparable to the "herring bone" arrangement in the solid state structures of the elemental halogens X₂. The solid state structure of Cl₂ shows additional Cl $\cdots$ Cl interactions at the "opposite end" of the molecule, which were not observed in the packing of **3**. The corresponding N $\gamma\cdots$ N γ distance of 3.121(13) Å (N3 $\cdots$ N3[-x, -y+1, z+1/2]) is longer than the sum of the *van der Waals* radii, hence indicating no attractive interaction. In addition the centrosymmetric nature of the Cl₂ molecule leads to crystallization in the corresponding centrosymmetric space group *Cmca*, whereas **3** crystallizes in *Cmc2*₁. The arrangement of the chains is governed by closest packing since no contacts suggesting further directed interaction can be found.

Figure 2. Chain in the packing of **3** formed via 2₁ screw axis (-x, -y+2, z+1/2).

Figure 3. Chain polymer as observed in both polymorphs of **5**. The azide molecule is evenly disordered over two positions (one depicted with pale colors). The polymer is formed via translation parallel to the *c* axis.

The two polymorphs of IN₃ **5a,b** both crystallize in the orthorhombic space group *Pbam* with both iodine and the nitrogen atoms on special positions (mirror-planes). The azide unit is disordered over two positions in both polymorphs.^[40] Both polymorphs of IN₃ form one-dimensional polymeric structures in the solid state. The N γ of both positions of the azide groups share the same site in both polymorphs as a structural consequence of the disorder. Even though the constitution of the chains in **5a** and **5b** are nearly identical, their relative arrangement in the packing is different (*vide infra*). The difference becomes most obvious when choosing a projection parallel to the *c* axis (see Fig. 4). In this projection, stacks of the chain polymer parallel to (-120) in **5a** and (100) in **5b** are

found. Even though these arrangements are fundamentally different, the polymorphs can be transformed to the other by rotating the chains of every second stack about the *c* axis by approx. 90° followed by minor adjustment for closest packing. Since the intermolecular interactions are identical in both polymorphs and their densities are almost equal, the difference in energy is expected to be rather low.

Figure 4. Arrangement of the polymer chains in **5**. One stack of chains is highlighted. View parallel to *c* along the polymer chains. The N γ of each component of the disorder share the same site. **Left:** Packing of **5a**. **Right:** Packing of **5b**.

Table 1. Selected structural parameters of covalent azides XN₃ (X = Cl **3**, Br **4**, I **5a,b**). Bond lengths [Å] and angles [°] in **5a** and **5b** of the azide group are of low significance due to the disorder.

	ClN ₃ 3	BrN ₃ 4	IN ₃ 5a	IN ₃ 5b
N α -X	1.747(5)	1.916(9)	2.266(5), 2.276(4)	2.264(4), 2.276(4)
N α -N β	1.258(6)	1.265(9)	1.220(13), 1.242(12)	1.211(11), 1.244(11)
N β -N γ	1.116(6)	1.123(12)	1.093(9), 1.069(9)	1.169(10), 1.059(9)
N α -N β -N γ	170.1(7)	172.2(11)	178.9(10), 177.2(9)	175.8(9), 177.6(10)
X-N α -N β	108.7(4)	108.6(7)	118.0(2), 114.8(2)	117.9(2), 114.8(2)

Figure 5. Helical structure of the one dimensional polymer in **4** generated via a 4_1 screw axis ($y-1/2, -x+1, z+1/4$).

The most obvious difference between the structures of the halogen azides is the change of the intermolecular interactions. **3** shows Cl $\cdots$ Cl interactions as was observed in elemental chlorine, whereas **4** and **5a,b** prefer the formation of intermolecular X $\cdots$ N interactions. This is rather unexpected since halogen $\cdots$ halogen interactions typically become stronger with increasing atomic number of the halogen. Moreover, the intermolecular interactions as observed in BrN₃ **4** and both IN₃ polymorphs **5a,b** are different despite their topological identity. The one-dimensional polymer in **5a** and **5b** adopt flat chain-like arrangements with almost equidistant I-N bonds (Fig. 4), whereas **4** adopts a helical structure (Fig. 5), in which the intramolecular Br-N bond (1.916(9) Å) is significantly shorter than the intermolecular one (2.885(8) Å). It cannot definitely be decided if these structural differences between **4** and **5** result from the existence (**4**) respectively non-existence (**5a,b**) of N $\beta\cdots$ N γ interactions or from the larger atomic radius of iodine compared to bromine, which leads to different conditions for the closest packing.

Since the crystal of ClN₃ **3** is composed of molecular units, we have determined its gas phase structure and harmonic frequencies with explicitly correlated coupled cluster theory at the CCSD(T)-F12a level for comparison.^[44] Core-valence electron correlation of the chlorine atom and relativistic effects at the Douglas-Kroll-Hess level of theory were also estimated employing CCSD(T).^[45,46] We have previously used the very same methodology to determine the structures and harmonic frequencies of BrN₃, Br₂, and N₂ and found excellent agreement with the experimental values.^[36] We now obtained a Cl-Cl bond distance of 1.981 Å and a harmonic frequency of 563.7 cm⁻¹ for the Cl₂ molecule, which compare well with the corresponding experimental spectroscopic values of 1.987 Å and 559.7 cm⁻¹, respectively.^[47] Neglecting core-valence electron correlation and relativistic effects leads to a slightly elongated bond (by 0.015 Å) and a red-shift of the harmonic frequency by 5 cm⁻¹. Table 2 summarizes the results of our calculations of **3** and previous results by Palmer et al. (MP2 TZVP 82, B3LYP TZVP 83) as well as various experimental structure parameters.

Table 2. Comparison of selected structural parameters of ClN₃ **3** [single crystal X-ray analysis (SC), microwave spectroscopy (MW)^[31] and computational calculation (MP2, B3LYP,^[48] CCSD(T)-F12 (this work)].

	RSA	MW	MP2	B3LYP	CCSD(T)-F12
N α -X	1.747(5)	1.745(5)	1.766	1.794	1.736
N α -N β	1.258(6)	1.252(10)	1.256	1.244	1.254
N β -N γ	1.116(6)	1.133(10)	1.147	1.131	1.133
N α -N β -N γ	170.1(7)	171.56(30)	171.6	172.0	172.4
X-N α -N β	108.7(4)	108.40(30)	109.0	109.7	108.7

The CCSD(T)-F12 structural parameters agree very well (within 0.01 Å and better than 1 degree) and usually slightly better than the previous quantum chemical data with the microwave data and crystal structure data.^[48] The largest discrepancies were found between calculated and crystal structure data for the N β -N γ distance (less than 0.02 Å) and the N α -N β -N γ angle (about 2 degree). When relativistic and core-valence correlation effects are neglected, the structural parameters hardly change with exception of an elongation of the N-Cl bond by 0.009 Å.

The harmonic vibration frequencies for ³⁵Cl¹⁴N₃ were calculated to be 214, 533, 565, 736, 1178, and 2137 cm⁻¹, respectively. These

values are 13 – 75 cm⁻¹ larger than the Raman frequencies as determined here (*vide supra*), which certainly has to be attributed to anharmonic effects. The decomposition of ClN₃ into Cl₂ and N₂ was calculated to occur with a release of energy by -791.8 kJ/mol at 0 K, i.e., nearly twice as much as the corresponding value of -403.5 kJ/mol for BrN₃.^[36] The harmonic zero-point vibrational energy contributes -18.4 kJ/mol to the former one, while the combined effect of relativity and core-valence electron correlation is only -1.0 kJ/mol.

Figure 6. Intermolecular interactions between ClN₃ molecules.

The energy of interaction of a ClN₃ molecule (white molecule in Fig. 6) with its nearest neighbors as found in the crystal structure of **3** has been calculated with the same CCSD(T)-F12 methodology as used to determine the structure of an isolated ClN₃ molecule. The weakest interaction with -3.0 kJ/mol is found for the in-plane N γ -N γ contact (blue, neighbor A), while our best estimate for the Cl-Cl contact is -5.2 kJ/mol (green, neighbor B), in good agreement with the interaction energy for a T-shaped dimer of the chlorine molecule.^[49] The interaction with an in-plane parallel displaced dimer (red, neighbor C) is slightly stronger (-5.7 kJ/mol), but the strongest interaction occurs between molecules of the neighboring planes (black, neighbor D), which was calculated to -12.2 kJ/mol. These values are hardly influenced when relativistic and core-valence correlation effects are neglected with exception for that of the Cl-Cl contact, whose magnitude is diminished by 0.2 kJ/mol.

Fig. 7 displays the results of an analysis of these interactions in terms of the energy contributions as obtained by symmetry-adapted perturbation theory combined with density-functional theory (DFT-SAPT).^[50,51] The interaction energy E_{int} is obtained as the sum of the electrostatic, E_{el} , induction, E_{ind} , and dispersion, E_{disp} , contributions, along with corresponding exchange corrections, which take the overall repulsive effect of electron exchange between the overlapping monomers into account. While the first-order exchange term, E_{exch} , as the most important exchange term is explicitly shown in Fig. 7, the exchange-dispersion correction is contained in E_{disp} , and the exchange-induction correction in E_{ind} . It should be noted that the total DFT-SAPT interaction energies of -3.0, -5.5, -6.0, and -12.1 kJ/mol for the interaction with neighbors A, B, C, and D, respectively, agree within 0.3 kJ/mol with the coupled-cluster results. In all cases the dispersion energy represents the largest of the attractive energy contributions, and it becomes particularly large for the interaction with neighbor D. The second largest contribution in all cases is the repulsive first-order exchange contribution, while the electrostatic and induction contributions modulate the interaction energy, but do not play a dominant role. This is in agreement with the outcome of a natural population analysis for the ClN₃ molecule,^[52] yielding fairly low charges of +0.12 and +0.03 e for the

terminating Cl and N_γ atoms, while the charges for the N_α (-0.34 e) and N_β (+0.19 e) atoms are somewhat larger. All in all, the interactions between the ClN₃ molecules in the crystal resemble rather typical *van-der-Waals* interactions, and in particular the interactions between molecules in neighboring planes stabilize the crystal.

Figure 7. Electrostatic, E_{el} , exchange, E_{exch} , induction, E_{ind} , and dispersion, E_{disp} DFT-SAPT contributions to the total interaction energy, E_{int} , for the interaction with different neighbor molecules.

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- [40] Bruker AXS SMART diffractometer with APEX2 detector (MoK α radiation, $\lambda = 0.71073$ Å; **3**: T = 143(1) K, **5a**, **5b**: T = 100(1) K). The structures were solved by Direct Methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, 46, 467) and refined by full-matrix least-squares on F². Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). All atoms were refined anisotropically. Single crystals of **3** were formed by an *in-situ* zone melting process inside a quartz capillary using an IR-laser. The experimental setup does only allow for ω scans with χ set to 0°. Any other orientation would have partially removed the capillary from the cooling stream and thus led to a melting of the crystals. This limits the completeness to 65% to 90% depending on the crystal system. **3**: ClN₃, M = 77.48, yellow needle (0.43 x 0.08 x 0.05 mm); orthorhombic, space group *Cmc*₂₁; $a = 5.6456(7)$, $b = 11.7515(14)$, $c = 4.3077(7)$ Å; $\alpha = \beta = \gamma = 90^\circ$, $V = 285.79(7)$ Å³; $Z = 4$, $\rho_{\text{calc}} = 1.031$ g cm⁻³; $\rho_{\text{exp}} = 1.801$ g cm⁻³; 2023 reflexes ($2\theta_{\text{max}} = 60^\circ$), 340 unique ($R_{\text{int}} = 0.0319$); 25 parameters, 1 restraint; largest max./min. in the final difference Fourier synthesis 0.451/-0.693 eÅ⁻³; max./min. transmission 0.75/0.48; $R_1 = 0.0425$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0984. Flack absolute structure parameter 0.0(2) in the final structure factor calculation (a) H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, 39, 876-881. b)

G. Bernadinelli, H. D. Flack, *Acta Crystallogr. Sect. A* **1985**, *41*, 500-511.). Redetermination of **5a**^[34]: IN₃, M = 168.93, dark brown needle (0.37 x 0.03 x 0.03 mm); orthorhombic, space group *Pbam*; *a* = 6.5551(3), *b* = 12.7764(5), *c* = 3.9837(2) Å; $\alpha = \beta = \gamma = 90^\circ$, *V* = 333.64(3) Å³; *Z* = 4; $\mu = 9.338 \text{ mm}^{-1}$; $\rho_{\text{ber.}} = 3.363 \text{ g cm}^{-3}$; 7808 reflexes ($2\theta_{\text{max}} = 60^\circ$), 550 unique ($R_{\text{int}} = 0.0288$); 37 parameters; largest max./min. in the final difference Fourier synthesis 2.148 [0.68 Å from I(1)]/-1.250 eÅ⁻³; max./min. transmission 0.75/0.61; $R_1 = 0.0223$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0582. **5b**: IN₃, M = 168.93, dark brown needle (0.42 x 0.03 x 0.03 mm); orthorhombic, space group *Pbam*; *a* = 8.4583(7), *b* = 9.7872(8), *c* = 3.9894(3) Å; $\alpha = \beta = \gamma = 90^\circ$, *V* = 330.25(5) Å³; *Z* = 4; $\mu = 9.434 \text{ mm}^{-1}$; $\rho_{\text{ber.}} = 3.398 \text{ g cm}^{-3}$; 6312 reflexes ($2\theta_{\text{max}} = 61^\circ$), 570 unique ($R_{\text{int}} = 0.0383$); 37 parameters; largest max./min. in the final difference Fourier synthesis 1.701 [0.75 Å from I(1)]/-0.782 eÅ⁻³; max./min. transmission 0.75/0.42; $R_1 = 0.0253$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0603. Details of the crystal structure determination of **3**, **5a** and **5b** may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de,) on quoting the deposition number CSD-424502 (**3**), CSD-424504 (**5a**), and CSD-424503 (**5b**).

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Halogen Azides

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Halogen Azides XN_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) - A Comparison of Their Solid State Structures

ClN_3 adopts a polymeric structure in the solid state with short intermolecular $\text{Cl}\cdots\text{Cl}$ distances as was observed for the elemental halogens.

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