Halogen Azides

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A Comparison of the Solid-State Structures of Halogen Azides XN_3 (X = Cl, Br, I)**

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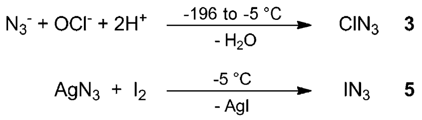
Dedicated to Professor Peter G. Jones on the occasion of his 60th birthday

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 (X = 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 because their simple composition of only four atoms allows the use of the most advanced theoretical methods 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] Their solid-state structures remained unknown except for IN_3 (**5a**),[34] which adopts a polymeric structure, and HN_3 (**1**),[35] the structure of which 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 $Br\cdots N_\alpha$ and $N_\beta\cdots N_\gamma$ 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 to investigate the strength of the intermolecular interactions in detail.

Compound **3** was prepared by reaction of NaN_3 with sodium hypochlorite and boric acid and **5** by reaction of AgN_3[43]with iodine (Scheme 1). The ^{14}N NMR spectrum of pure **3** shows three resonances for N_α ($\delta = -274$ ppm, $\Delta\mu_{1/2} = 145$ Hz), N_β ($\delta = -123$ ppm, $\Delta\mu_{1/2} = 28$ Hz), and N_γ ($\delta = -113$ ppm, $\Delta\mu_{1/2} = 36$ 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 $CH_2Cl_2/CDCl_3$ also shows three resonances for N_α ($\delta = -359$ ppm, $\Delta\mu_{1/2} = 540$ Hz), N_β ($\delta = -127$ ppm, $\Delta\mu_{1/2} = 12$ Hz), and N_γ ($\delta = -165$ ppm, $\Delta\mu_{1/2} = 250$ 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 owing to the antisymmetric ($\tilde{\nu} = 2062\ cm^{-1}$ **3**; $2072\ cm^{-1}$ **5**) and symmetric N_α-N_β-N_γ stretching modes ($\tilde{\nu} = 1134\ cm^{-1}$ **3**; $1220\ cm^{-1}$ **5**) and the N_α-Cl/I ($\tilde{\nu} = 542\ cm^{-1}$ **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** owing to its polymeric nature.



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

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.

ClN_3 (**3**) crystallizes in the orthorhombic space group $Cmc2_1$ with four molecules (all four atoms are on a mirror plane)[40] in the unit cell and adopts, like the other halogen azides, a *trans*-bent structure (Figure 1). The N_α–N_β–N_γ (170.1(5)°) and Cl–N_α–N_β angles (108.7(4)°) are comparable to those observed in BrN_3 (**4**). The N_α–Cl bond (1.748(5) Å) is shorter than the N_α–Br bond length in **4** (1.916(9) Å), as was expected owing 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 N_α–N_β (1.258(6) Å) and N_β–N_γ (1.115(7) Å) bond lengths differ significantly,

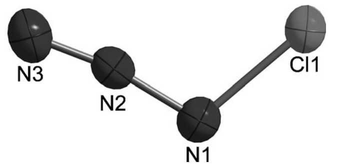


Figure 1. Representation of ClN_3 (**3**). Ellipsoids are set at 50% probability.

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clearly proving the covalent bonding character. The angles and bond lengths are in excellent agreement with values obtained from microwave spectroscopy studies (N_α–Cl 1.745 Å, N_α–N_β 1.252 Å, N_β–N_γ 1.133 Å; N_α–N_β–N_γ 171.56°, Cl–N_α–N_β 108.40°)[31] and calculations.[9–12] Compound **3** adopts a chain-like polymeric structure formed by a two-fold screw axis owing to the formation of Cl···Cl interactions (Figure 2). This chain is comparable to the herring-bone arrangement in the solid-state structures of the elemental halogens X_2. The solid state structure of Cl_2 shows additional Cl···Cl interactions at the "opposite end" of the molecule, which were not observed in the packing of **3**. The corresponding N_γ···N_γ distance of 3.121(13) Å (N3···N3 [$-x, -y+1, z+1/2$]) is longer than the sum of the van der Waals radii, thus indicating no attractive interaction. Furthermore, the centrosymmetric nature of the Cl_2 molecule leads to crystallization in the corresponding centrosymmetric space group *Cmca*, whereas **3** crystallizes in *Cmc*2_1. The arrangement of the chains is governed by closest packing since no contacts suggesting further directed interaction can be found.

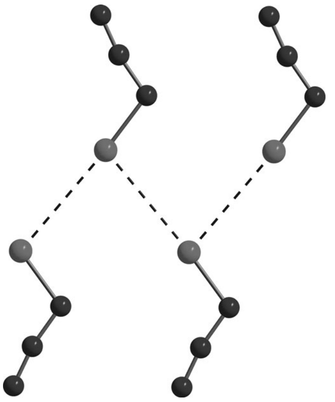

Figure 2. The chain in the packing of **3** formed by the 2_1 screw axis ($-x$, $-y+2$, $z+1/2$).

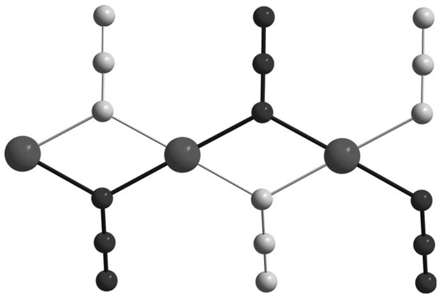

Figure 3. A chain polymer as observed in both polymorphs of **5**. The azide molecule is evenly disordered over two positions (one is depicted with pale colors). The polymer is formed by translation parallel to the *c* axis.

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**.

The two polymorphs of IN_3 **5a,b** crystallize in the orthorhombic space group *Pbam* with iodine and the nitrogen atoms on special positions (mirror planes). The azide unit is disordered over two positions in both polymorphs.[40] **5a,b** both form one-dimensional polymeric structures in the solid state (Figure 3). 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. The difference becomes most obvious when choosing a projection parallel to the *c* axis (Figure 4). In this projection, stacks of the chain polymer parallel to ($\bar{1}$20) 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. As the intermolecular interactions are identical in both polymorphs and their densities are almost equal, the difference in energy is expected to be rather low.

The structural parameters for molecules of halogenazides **3–5** are compared in Table 1.

The most obvious difference between the structures of the halogen azides is the change of the intermolecular interactions. Compound **3** has Cl···Cl interactions as was observed in elemental chlorine, whereas **4** and **5a,b** prefer the formation of intermolecular X···N interactions. This is rather unexpected as halogen···halogen interactions typically become stronger with increasing atomic number of the halogen. Moreover, the intermolecular interactions as observed in BrN_3 (**4**) and both IN_3 polymorphs **5a,b** are different despite their topological

Table 1: Selected structural parameters of covalent azides XN_3 **3–5**.

	ClN_3 (**3**)	BrN_3 (**4**)	IN_3 (**5a**)[a]	IN_3 (**5b**)[a]
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)

[a] Bond lengths [Å] and angles [°] in **5a** and **5b** of the azide group are of low significance owing to the disorder.

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identity. The one-dimensional polymer in **5a** and **5b** adopt flat chain-like arrangements with almost equidistant I–N bonds (Figure 4), whereas **4** adopts a helical structure (Figure 5), in which the intramolecular Br–N bond (1.916(9) Å) is significantly shorter than the intermolecular bond (2.885(8) Å). It cannot definitely be established whether these structural differences between **4** and **5** result from the existence (**4**) respectively non-existence (**5a**,**b**) of $N_\beta{\cdots}N_\gamma$ interactions or from the larger atomic radius of iodine compared to bromine, which leads to different conditions for the closest packing.

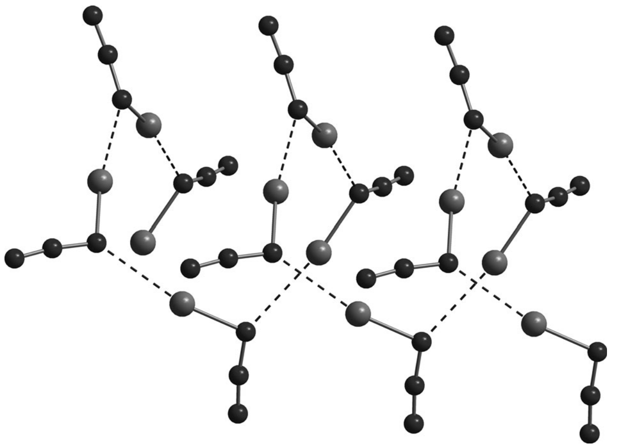

Figure 5. The helical structure of the one-dimensional polymer in **4** generated by a 4_1 screw axis ($y-1/2$, $-x+1$, $z+1/4$).

As the crystal of ClN_3 **3** is composed of molecular units, we determined the 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 method to determine the structures and harmonic frequencies of BrN_3, Br_2, and N_2 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 Cl_2 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)[48] as well as various experimental structure parameters.

Table 2: Comparison of selected structural parameters of **3**.

			Calculations		
	SC[a]	MW[b]	MP2[48]	B3LYP[48]	CCSD(T)-F12[c]
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

[a] Single-crystal X-ray analysis. [b] Microwave spectroscopy.[31] [c] This work.

The CCSD(T)-F12 structural parameters agree very well (within 0.01 Å and better than 1°) 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°). When relativistic and core–valence correlation effects are neglected, the structural parameters hardly change, with the exception of an elongation of the N–Cl bond by 0.009 Å.

The harmonic vibration frequencies for $^{35}Cl^{14}N_3$ 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 (see above), which certainly has to be attributed to anharmonic effects. The decomposition of ClN_3 into Cl_2 and N_2 was calculated to occur with a release of energy by -791.8 kJ mol^{-1} at 0 K, that is, nearly twice as much as the corresponding value of -403.5 kJ mol^{-1} for BrN_3.[36] The harmonic zero-point vibrational energy contributes -18.4 kJ mol^{-1} to the former energy, while the combined effect of relativity and core–valence electron correlation is only -1.0 kJ mol^{-1}.

The energy of interaction of a ClN_3 molecule (white molecule in Figure 6) with its nearest neighbors as found in the crystal structure of **3** has been calculated with the same CCSD(T)-F12 method as used to determine the structure of an isolated ClN_3 molecule. The weakest interaction (-3.0 kJ mol^{-1}) is found for the in-plane $N_\gamma{\cdots}N_\gamma$ contact (neighbor A), while our best estimate for the Cl···Cl contact is -5.2 kJ mol^{-1} (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 (neighbor C) is slightly stronger (-5.7 kJ mol^{-1}), but the strongest interaction occurs between molecules of the neighboring planes (neighbor D), which was calculated to be -12.2 kJ mol^{-1}. These values are hardly influenced when relativistic and core–valence correlation effects are neglected, with exception of that of the Cl···Cl contact, the magnitude of which is diminished by 0.2 kJ mol^{-1}.

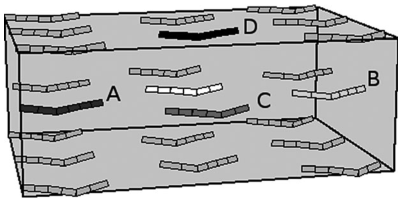

Figure 6. Intermolecular interactions between neighboring ClN_3 molecules in the solid state.

Figure 7 shows 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},

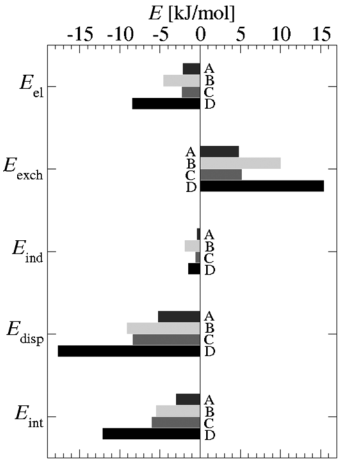

Figure 7. Electrostatic (E_{el}), exchange (E_{exch}), induction (E_{ind}), and dispersion (E_{disp}) DFT-SAPT contributions to the total interaction energy (E_{int}) for the interaction with different neighbor molecules.

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 Figure 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^{-1} for the interaction with neighbors A, B, C, and D, respectively, agree within 0.3 kJ mol^{-1} with the coupled-cluster results. In all cases, the dispersion energy is 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 ClN_3 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 ClN_3 molecules in the crystal resemble rather typical van der Waals interactions, and in particular the interactions between molecules in neighboring planes stabilize the crystal.

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[40] Bruker AXS SMART diffractometer with APEX2 detector (MoKα 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*, 467–473) and refined by full-matrix least-squares on F^2. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multiscans (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 only allows 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**: ClN_3, $M_r = 77.48$, yellow needle ($0.43 \times 0.08 \times 0.05$ mm); orthorhombic, space group $Cmc2_1$; $a = 5.6456(7)$, $b = 11.7515(14)$, $c = 4.3077(7)$ Å; $V = 285.79(7)$ Å^3; $Z = 14$ $\mu = 1.031$ mm^{-1}; $\rho_{calcd} = 1.801$ g cm^{-3}; 2023 reflections ($2\theta_{max} = 60°$), 340 unique ($R_{int} = 0.0319$); 25 parameters, 1 restraint; largest max./min. in the final difference Fourier synthesis 0.451/−0.693 e Å^{-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: H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881; G. Bernadinelli, H. D. Flack, *Acta Crystallogr. Sect. A* **1985**, *41*, 500–511.). Redetermination of **5a**:[34] IN_3, $M_r = 168.93$, dark brown needle ($0.37 \times 0.03 \times 0.03$ mm); orthorhombic, space group *Pbam*; $a = 6.5551(3)$, $b = 12.7764(5)$, $c = 3.9837(2)$ Å; $V = 333.64(3)$ Å^3; $Z = 4$; $\mu = 9.338$ mm^{-1}; $\rho_{calcd} = 3.363$ g cm^{-3}; 7808 reflections ($2\theta_{max} = 60°$), 550 unique ($R_{int} = 0.0288$); 37 parameters; largest max./min. in the final difference Fourier synthesis 2.148 [0.68 Å from I(1)]/−1.250 e Å^{-3}; max./min. transmission 0.75/0.61; $R_1 = 0.0223$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0582. **5b**: IN_3, $M_r = 168.93$, dark brown needle ($0.42 \times 0.03 \times 0.03$ mm); orthorhombic, space group *Pbam*; $a = 8.4583(7)$, $b = 9.7872(8)$, $c = 3.9894(3)$ Å; $V = 330.25(5)$ Å^3; $Z = 4$; $\mu = 9.434$ mm^{-1}; $\rho_{calcd} = 3.398$ g cm^{-3}; 6312 reflections ($2\theta_{max} = 61°$), 570 unique ($R_{int} = 0.0383$); 37 parameters; largest max./min. in the final difference Fourier synthesis 1.701 [0.75 A from I(1)]/−0.782 e Å^{-3}; max./min. transmission 0.75/0.42; $R_1 = 0.0253$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0603. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-424502 (**3**), CSD-424504 (**5a**), and CSD-424503 (**5b**).

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