Covalent azides have been investigated for more than hundred years. Hydrazoic acid HN₃ for instance was synthesized for the first time by Curtius in 1890,11) Since then, its molecular structure was investigated by use of IR and microwave spectroscopy as well as electron diffraction.2-4) Only very recently, Klapötke et al. reported by solid state structure of the compound, which was determined by single crystal X-ray diffraction, showing that HN₃ crystallizes in a two-layer structure, in which almost planar layers, formed by intermolecular hydrogen bonds between the HN₃ molecules, are stacked parallel to (001) with a A, B,…, stacking sequence.5) Aside from HN₃, the halogen azides XN₃ (X = F, Cl, Br, I) are the simplest azides.6) They have been investigated experimentally and theoretically, in particular in respect to their bonding situation. IN₃ was found to be monomeric in CFC₁ solution and forms a trans-bent structure in the gas phase.7) In contrast, in the solid state IN₃ adopts a polymeric structure with disordered azide groups with almost identical I-N bond distances (2.264(23), 2.30(3) Å).8) Unfortunately, only IN₃ has been structurally characterized by single crystal X-ray diffraction, to date. The growth of suitable single crystals of halogen azides in general is difficult due to their expressed sensitivity towards small pressure variations. For instance, bromine azide was reported to explode when Δp ≥ 0.05 Torr as well as upon crystallization.9) However, the gas phase structure of BrN₃, which adopts a trans-bent structure, could be determined by electron diffraction and the experimental structure parameters agreed well with those obtained from quantum chemical calculations.10,11)

We became only recently interested in the synthesis of covalent azides and reported on the solid state structures of group 15-triazides (Sb(N₃)₃), Pyr₃Br(N₃)₃,12) a novel pentazaazadiimine diion [Sb(N₃)₅]²⁻13) and organoantimonydiazides R₂Sb(N₃)₂.13) Herein, we expanded these studies on the synthesis of halogen azides and report on the single crystal X-ray structure of bromine azide, BrN₃.

\[ \text{NaN₃ + Br}_2 \xrightarrow{(-196)^\circ C} \xrightarrow{(+25)^\circ C} \text{BrN₃} \]

Scheme 1. Synthesis of BrN₃

BrN₃ I was prepared by reaction of NaN₃ with bromine. The ¹⁴N NMR spectrum of a solution of 1 in CDCl₃ shows three resonances for N≡N (δ = -324, Δ½ = 118 Hz), N≡Br (δ = -135, Δ½ = 16 Hz) and N≡N (δ = -170, Δ½ = 25 Hz). These values differ from those previously reported for a CDCl₃ solution of 1,7) but correspond well to values reported for a CH₂Cl₂ solution of 1,14) even though the half widths are somewhat smaller.14) In contrast, the ¹⁴N NMR spectrum of pure 1 shows broader resonances.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N≡N</th>
<th>N≡Br</th>
<th>N≡N</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrN₃[4]</td>
<td>-324, Δ½ = 220 Hz</td>
<td>-135, Δ½ = 475 Hz</td>
<td>-170, Δ½ = 30 Hz</td>
<td>this work</td>
</tr>
<tr>
<td>BrN₃[4]</td>
<td>-319, Δ½ = 228 Hz</td>
<td>-134, Δ½ = 472 Hz</td>
<td>-172, Δ½ = 22 Hz</td>
<td>this work</td>
</tr>
<tr>
<td>BrN₃[4]</td>
<td>-349, Δ½ = 475 Hz</td>
<td>-122, Δ½ = 30 Hz</td>
<td>-157, Δ½ = 90 Hz</td>
<td>7</td>
</tr>
<tr>
<td>BrN₃[4]</td>
<td>-328, Δ½ = 475 Hz</td>
<td>-142, Δ½ = 30 Hz</td>
<td>-178, Δ½ = 90 Hz</td>
<td>14</td>
</tr>
<tr>
<td>[a] CDCl₃ [b]</td>
<td>-220 Hz</td>
<td>-65 Hz</td>
<td>-80 Hz</td>
<td>[c] CH₂Cl₂</td>
</tr>
</tbody>
</table>

[4] Sample N≡N, N≡Br, N≡N at 150 K in CDCl₃. [b] pure (without any solvent) [c] CH₂Cl₂

Fig. 1. ¹⁴N NMR spectra of the BrN₃ in solution (CDCl₃; bottom) and pure (without any solvent; top).

The Raman spectrum of BrN₃ I shows strong adsorption bands due to the asymmetric (ν = 2146 cm⁻¹) and symmetric νN=N-N≡N stretching mode (ν = 1274 cm⁻¹) and the νN=Br (ν = 451 cm⁻¹) stretching mode. Recording of the spectrum was limited due to a partial decomposition of I upon irradiation.15)

The crystallization of I was performed on the diffractometer at a temperature of 150 K using a miniature zone melting procedure with focused infrared-laser-radiation.10) The IR-laser allowed a very controlled heating of BrN₃, hence allowing optimization of the growth conditions. The successful growth of suitable crystals of I clearly demonstrates the promising potential of this method even for the structural characterization of heat- and shock-sensitive compounds.

Dedicated to Prof. Dr. G. Schmid on the occasion of his 75th birthday

Benjamin Lyhs, Dieter Bläser, Christoph Wölper, Stephan Schulz*, Georg Jansen

Faculty of Chemistry, University of Duisburg-Essen
Universitätsstr. 5-7, S07 S03 C30, D-45117 Essen
Fax: (+) 201-183 3830
E-mail: stephan.schulz@uni-due.de

B. Lyhs, D. Bläser, Dr. C. Wölper, Prof. S. Schulz*, Prof. G. Jansen
Faculty of Chemistry, University of Duisburg-Essen
Universitätsstr. 5-7, S07 S03 C30, D-45117 Essen
Fax: (+) 201-183 3830
E-mail: stephan.schulz@uni-due.de

S. Schulz and B. Lyhs gratefully acknowledge the Fonds der Chemischen Industrie (FCI) for financial support and a doctoral fellowship (B.L.).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
I crystallizes in the tetragonal space group $I4_1/acd$ with 16 molecules in the unit cell and adopts a trans-bent structure.\cite{17} The N$_r$-N$_l$-N$_a$ bond angle (172.2(11)$^\circ$) is significantly larger than the Br-N$_r$-N$_a$ bond angle (108.6(7)$^\circ$). The N$_r$-Br bond length (1.916(9) Å) is slightly longer than the sum of the covalent radii as reported by Pyykkö et al. (1.85 Å).\cite{18} but corresponds very well to typical values observed for neutral compounds containing a direct N-Br bond.\cite{19} The difference in the N$_r$-N$_a$ (1.265(9) Å) and N$_l$-N$_a$ (1.123(12) Å) bond lengths clearly proves its covalent-bonded nature. The bond angles and bond lengths correspond very well with those obtained from an electron diffraction study as well as with values previously obtained from HF-MO and MP2 calculations.\cite{19,20} Here, we have further increased the level of theory to that of coupled cluster theory with iterative single and double and perturbative triple excitations (CCSD(T)). The complete basis set limit has been nearly reached with the explicitly correlated CCSD(T)-F12a method.\cite{20} and relativistic and bromine atom core-valence electron correlation effects have been determined using the Douglas-Kroll-Hülle Hamiltonian.\cite{21,22}

**Table 2.** Selected structural parameters of 1.

<table>
<thead>
<tr>
<th></th>
<th>ED\textsuperscript{[a]}</th>
<th>SC\textsuperscript{[b]}</th>
<th>\textit{ab initio}</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_r$-Br</td>
<td>1.899(6)</td>
<td>1.916(9)</td>
<td>1.894</td>
</tr>
<tr>
<td>N$_l$-N$_a$</td>
<td>1.231(22)</td>
<td>1.265(9)</td>
<td>1.250</td>
</tr>
<tr>
<td>N$_l$-N$_r$</td>
<td>1.129(22)</td>
<td>1.123(12)</td>
<td>1.134</td>
</tr>
<tr>
<td>N$_r$-N$_a$-N$_l$</td>
<td>170.7(24)</td>
<td>172.2(11)</td>
<td>172.6</td>
</tr>
<tr>
<td>Br-N$_r$-N$_a$</td>
<td>109.7(11)</td>
<td>108.6(7)</td>
<td>108.6</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} electron diffraction \textsuperscript{[b]} single crystal determination

Geometry optimizations and calculations of harmonic frequencies with numerical first and second derivatives for the nitrogen and bromine molecules demonstrate the accuracy of this methodology: Bond distance and harmonic frequency for $^1$N$_2$ are obtained as 1.099 Å and 2359 cm$^{-1}$ (exp values: 1.09768 Å and 2358.57 cm$^{-1}$\cite{23}) while for $^7$Br$_2$ 2.278 Å and 328.5 cm$^{-1}$ (exp values: 2.28105 Å and 325.321 cm$^{-1}$) were obtained. Without inclusion of relativity effects and bromine core-valence-correlation, the Br$_2$ bond is found to be 0.019 Å longer and to possess a harmonic frequency lower by 2 cm$^{-1}$. The geometrical parameters obtained for BrN$_3$ are shown in Table 2. Please note that the \textit{ab initio} bond distances and angles refer to the equilibrium structure, while the experimental data as shown in Table 2 contain effects of non-zero temperature vibrational averaging in case of the electron diffraction data and, in addition, interactions with the environment for the single crystal measurements. Despite this, the bond distances agree within 0.02 Å and the angles within 2°. The most significant changes upon neglect of relativistic and core-valence correlation effects are an elongation of the N-Br bond by 0.006 Å and a widening of the Br-N-N angle by 0.3°.

The harmonic vibration frequencies for $^{79}$Br$^8$N$_3$ (187, 475, 543, 698, 1189, and 2125 cm$^{-1}$) agree within 23 cm$^{-1}$ with the measured frequencies, with exception of the symmetric N$_r$-N$_l$-N$_a$ stretching mode, which was found to be 85 cm$^{-1}$ lower in the calculations. The disagreement can't be attributed to relativistic or core-valence correlation effects, which change the frequencies by less than 5 cm$^{-1}$, but is rather due to inharmonic corrections. The reaction energy for the breakup of BrN$_3$ to Br and N$_2$ (-403.5 kJ/mol, 0 K) was calculated including zero point vibrational energy correction (ZPE). The latter (in the harmonic approximation) contributes -0.9 kJ/mol to this value, while the contribution of relativistic and core-valence correlation effects amounts to -0.9 kJ/mol.

In remarkable contrast to the solid state structure of HN$_3$, which was found to form an endless chain-like structure via bridging iodine atoms with almost identical I-N$_a$ bond lengths (2.264(23), 2.30(3) Å), BrN$_3$ forms a helical structure in the solid state. This structural motif is unforeseen in covalent azide chemistry, to date.

The Br-N$_r$ (1.916(9) Å) and Br-N$_a$ (2.885(8) Å) bond distances differ by about 0.9 Å, but the value of 2.885(8) Å is clearly below the sum of the van-der-Waals radii of Br and N (3.38 Å)\cite{20} and can thus be regarded as an interaction from a crystallographic point of view. Compared to the other structurally characterized simple covalent azide, HN$_3$, some striking similarities can be found. While BrN$_3$ forms a helix via a 4$_1$ screw axis, HN$_3$ displays the same structural motif with (approximately) fourfold symmetry bar the translational component. As a consequence, an eight-membered ring consisting of four HN$_3$ molecules (Figure 4a in ref. [5]) is formed rather than a helix as observed for BrN$_3$. The same is true for the structural motif shown in Figure 4b in ref. [5]. Again, in the packing of I the ring is transformed into a helix. Unlike in the solid state structure of HN$_3$, the interactions of this arrangement in I are less certain. Weak, but indisputably existing, hydrogen bonds connect the molecules in the HN$_3$ structure accompanied by N···N contacts just below the sum of the van-der-Waals radii of N and N$_3$ (3.094 Å).\cite{24} I not only shows Br···N contacts but also N···N contacts (3.094(16) Å). Klaposke et al. attributed a weak bonding nature to these contacts due to opposite formal charges of N$_l$ and N$_a$ in one mesomeric structure, even though this mesomeric form is likely not the most important one. In addition, these contacts might be random side effects of the weak hydrogen bonds. However, since these contacts also appear in I where they cannot be related to hydrogen bonds, a weak attractive interaction seems possible. Furthermore, they are not observed in the HN$_3$ structure and hence might explain why BrN$_3$ is forming...
helices instead of chains. Unfortunately, the attempt to obtain further information on these contacts by recording a Raman spectrum of the BrN₃ crystal led to an immediate explosion of the sample on irradiation with the Raman laser. Therefore, the character of these contacts couldn't be resolved experimentally.

Finally, the third motive identified in the packing of HN₃ (Figure 4c in [5]) also has its counterpart in the packing of 1. Four BrN₃ molecules form a ring with two fold symmetry. As was observed in HN₃, two weak and two strong interactions connect the molecules. Whether the N···N contacts are attractive or not, combined with the Br···N interactions they constitute a three dimensional network (Fig. 4), of which two, related via a c-glide plane symmetry, interleave (Fig. 5).

In order to quantify the stabilizing or destabilizing role of the N···N and Br···N contacts, the energy of interaction of a BrN₃ molecule with its nearest neighbours in the crystal has been determined by CCSD(T)-F12a calculations using the same ab initio technology as already employed to study the monomer properties.[25] We calculated the energy of interaction of a dimer with a Br···N contact exactly in the geometry as observed in the crystal to be -13.1 kJ/mol, while for a dimer with an N···N contact -6.1 kJ/mol were found, thus demonstrating that the latter are indeed stabilizing the crystal. Relativistic and core-valence correlation effects contribute -0.8 kJ/mol to the former value, while their influence is completely negligible for the N···N contact. Note that the intermolecular Br···N interaction is fairly large, amounting to about 60% of the 21 kJ/mol found for the hydrogen bond in the water dimer.[26] These strong interactions are the main factor for the stability of the crystal.

In order to understand the reasons for the strength of these interactions DFT SAPT calculations, i.e. symmetry-adapted intermolecular perturbation theory based on a density functional theory description of the monomers,[27] were carried out. Here the interaction energy is calculated as the sum of electrostatic, induction and dispersion energy contributions, along with their repulsive exchange corrections which take the energetic consequences of the antisymmetry principle into account.[28] Note that in DFT-SAPT no multipole approximation is used to calculate these contributions, which are rather determined from electron densities, density matrices, and corresponding static and dynamic response properties. Neglecting relativistic effects the interaction energy of the dimer structure with a Br···N₂ contact is obtained as -12.6 kJ/mol, in good agreement with the non-relativistic CCSD(T) value of -12.3 kJ/mol. While the partial charges as determined with a natural population analysis with +0.19 e for the Br atom and -0.39 e for the N₂ atom suggest that a strong electrostatic interaction could provide the main contribution,[29] Fig. 6 shows that the dispersion contribution is even slightly more important. This reflects the large polarizability of the bromine atom, which also becomes visible in the importance of the induction contribution. For the dimer with an N₂···N₂ contact the total DFT-SAPT interaction energy is obtained as -6.0 kJ/mol, in excellent agreement with the CCSD(T) result. As to be expected from the charges on the N₂ and N₂ atoms of +0.18 and +0.02 e,[30] respectively, the electrostatic interaction energy is strongly reduced compared to that of the Br···N₂ contact. It still represents an attractive contribution due to the incomplete screening of the

---

**Figure 5. Top:** Interleaved networks in the packing of 1. One of the networks is depicted in blue the other one in red. The grey lines mark the positions of the 41 screw axes in the centre of the helices. The networks are related via c glide plane symmetry. **Bottom:** Detail of the interleaved networks. One helix formed by Br···N interactions (red) is interpenetrated by another one formed by N···N contacts (blue) of the other network (interactions/contacts displayed as above).

---

**Figure 4.** Packing of 1. Br···N interactions in thick dashed lines. N···N contacts of uncertain nature in thin dashes lines. The helices formed by the Br···N interactions are primitively packed parallel to the c-axis. If regarding the N···N contacts bonding, these connect the helices to form a three dimensional network. The N···N contacts themselves constitute a helix via 41 symmetry. A series of stacked rings can be observed along the two fold axes parallel to c, e.g. in the centre of the ab-plane (others only partially shown).
attraction between electrons and nuclei from the different molecules through repulsive electron-electron and nuclear-nuclear interactions. Nevertheless, dispersion clearly is the dominant stabilizing contribution in case of the N–N contact.

condensed in another FEP trap at -80 °C. This procedure was repeated twice to finally yield pure BrN3.

Raman (40 mW, 25 °C, 400 Scans): ν = 2146, 1273, 451, 303, cm⁻¹.

'NN' (CDCl₃): δ = -135 (s, N₃, Δν12 = 16 Hz), -170 (s, N₃, Δν12 = 25 Hz), -324 (s, N₃, Δν12 = 118 Hz). 'NN' (pure BrN₃): δ = -134 (s, N₃, Δν12 = 22 Hz), -172 (s, N₃, Δν12 = 192 Hz), -319 (s, N₃, Δν12 = 288 Hz).

Received: ((will be filled in by the editorial staff))
Published online on (will be filled in by the editorial staff))

**Keywords:** Covalent Azide · XRD · Bromine Azide · ab initio Computations

![Figure 6](image-url)

**Experimental Section**

Bromine azide is potentially toxic and can decompose explosively under various conditions! It should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs). Teflon containers should be used, whenever possible, to avoid hazardous fragmentation. Ignoring safety precautions can lead to serious injuries. Reactions were carried out in safety shields, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs). Teflon containers should be used, whenever possible, to avoid hazardous fragmentation. Ignoring safety precautions can lead to serious injuries. Reactions were carried out in safety shields, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs). Teflon containers should be used,

---


[15] Details are given in the supporting information file.


[17] Bruker AXS SMART diffractometer with APEX2 detector (MoKα radiation, λ = 0.71073 Å; F = 150(1) K). The structure was 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 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 γ 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. 

---

4
A. K. Wilson, pwCVTZ-DK (B. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning, Jr., relativistic Hamiltonian, replacing the basis set for bromine with aug-cc-CCSD(T) calculations employing the second-order Douglas-Kroll-Heß bromine atom core-valence-correlation have been determined from standard Wolf, see http://www.molpro.net.). The combined effects of relativity and Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Nicklass, D. P. O'Neill, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, B. A. Heßelmann, G. Jansen, M. Schütz, J. Chem. Phys. 2005, 122, 014103-1-17.) with the aug-cc-pVTZ and aug-cc-pVQZ orbital basis sets and their appropriate auxiliary basis sets as described above. Dispersion and exchange-dispersion energies were obtained with orbitals from the asymptotically corrected Perdew-Burke-Ernzerhof exchange-correlation (xc) potential (PBEAC) in combination with the adiabatic local density approximation (ALDA) for the xc kernel, the DFT-SAPT contributions and partial atomic charges were calculated with the corresponding hybrid modifications containing 25% of exact exchange (PBE0AC, see A. Hesselmann, G. Jansen, Chem. Phys. Lett. 2002, 357, 464-470; A. Hesselmann, G. Jansen, Chem. Phys. Lett. 2002, 362, 319-325.). Second-order dispersion and exchange-dispersion energies were summed to the contribution $E_{\text{disp}}$ which was extrapolated to the complete basis set limit using the standard 1'X two-point formula for $X = 3$ and 4 (A. Halkier, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Wolf, see http://www.molpro.net.). The combined effects of relativity and bromine atom core-valence-correlation have been determined from standard CCSD(T) calculations employing the second-order Douglas-Kroll-Heß relativistic Hamiltonian, replacing the basis set for bromine with aug-cc-pwCVTZ-DK (B. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning, Jr., A. K. Wilson, Theor. Chem. Acc. 2011, 128, 69-82.) and that for nitrogen with aug-cc-pVQZ-DK, correlating also the 3d shell of bromine, and finally adding the variation of the considered property as compared to the corresponding non-relativistic, valence-only CCSD(T)/aug-cc-pVTZ result to the CCSD(T)/F12a value. Full details and (nearly identical) CCSD(T)-F12b results can be found in the Supplementary Information.


By the term "contact" we refer to any distance in the range of or below the sum of the van-der-Waals radii.

The basis set superposition error has been taken into account through application of the counterpoise correction (S. F. Boys, F. Bernardi, Mol. Phys. 1970, 19, 553-566.).


[19] A Cambridge Structure Database (CSD) search (version 5.32 update August 2011) with ConQuest (version 1.13) gave 41 compounds (30 neutral, 11 ionic) containing a N-Br bond with an average bond lengths of 1.89 Å.


[17] Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on August 2011 with ConQuest (version 1.13) gave 41 compounds (30 neutral, 11 ionic) containing a N-Br bond with an average bond lengths of 1.89 Å.

[27] The basis set superposition error has been taken into account through application of the counterpoise correction (S. F. Boys, F. Bernardi, Mol. Phys. 1970, 19, 553-566.).


[28] Both the mesomeric structure with opposite formal charges on N and N$_2$ was postulated by Klapötke et al. to play a major role for the structure of HN$_3$. Whereas this effect hardly shows up in the partial charges of BrN$_3$.
Helical structure of BrN₃ in the solid state – an unforeseen structural element in covalent p-block azide chemistry.