Bromine Azide

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Solid State Structure of Bromine Azide

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

Covalent azides have been investigated for more than hundred years. Hydrazoic acid HN_3 for instance was synthesized for the first time by Curtius in 1890.[1] 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 on the solid state structure of the compound, which was determined by single crystal X-ray diffraction, showing that HN_3 crystallizes in a two-layer structure, in which almost planar layers, formed by intermolecular hydrogen bonds between the HN_3 molecules, are stacked parallel to (001) with a A, B, ... stacking sequence.[5]

Aside from HN_3, the halogen azides XN_3 (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. IN_3 was found to be monomeric in $CFCl_3$ solution and forms a *trans-bent* structure in the gas phase.[7] In contrast, in the solid state IN_3 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 IN_3 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 $\Delta p \geq 0.05$ Torr as well as upon crystallization.[9] However, the gas phase structure of BrN_3, which adopts a *trans-bent* structure, could be determined by electron diffraction[9] and the experimental structure parameters agreed well with those obtained from quantum chemical calculations.[10]

We became only recently interested in the synthesis of covalent azides and reported on the solid state structures of group 15-triazides ($Sb(N_3)_3$, $Pyr_2Bi(N_3)_3$),[11] a novel pentaazidoantimonite dianion $[Sb(N_3)_5^{2-}]$[12] and organoantimonydiazides $RSb(N_3)_2$.[13] Herein, we expanded these studies on the synthesis of halogen azides and report on the single crystal X-ray structure of bromine azide, BrN_3.

$$NaN_3 + Br_2 \xrightarrow[- NaBr]{(-196) - (+25)\ °C} BrN_3 \quad \mathbf{1}$$

Scheme 1. Synthesis of BrN_3

BrN_3 **1** was prepared by reaction of NaN_3 with bromine. The ^{14}N NMR spectrum of a solution of **1** in $CDCl_3$ shows three resonances for N_α (δ = -324, $\Delta\mu_{1/2}$ = 118 Hz), N_β (δ = -135, $\Delta\mu_{1/2}$ = 16 Hz) and N_γ (δ = -170, $\Delta\mu_{1/2}$ = 25 Hz). These values differ from those previously reported for a $CDCl_3$ solution of **1**,[7] but correspond well to values reported for a CH_2Cl_2 solution of **1**,[14] even though the half widths are somewhat smaller.[14] In contrast, the ^{14}N NMR spectrum of pure **1** shows broader resonances.

Table 1. ^{14}N chemical shifts of BrN_3.

Sample	N_α	N_β	N_γ	Ref.
BrN_3[a]	-324, $\Delta\mu_{1/2}$ = 118 Hz	-135, $\Delta\mu_{1/2}$ = 16 Hz	-170, $\Delta\mu_{1/2}$ = 25 Hz	this work
BrN_3[b]	-319, $\Delta\mu_{1/2}$ = 288 Hz	-134, $\Delta\mu_{1/2}$ = 22 Hz	-172, $\Delta\mu_{1/2}$ = 118 Hz	this work
BrN_3[a]	-349, $\Delta\mu_{1/2}$ = 475 Hz	-122, $\Delta\mu_{1/2}$ = 30 Hz	-157, $\Delta\mu_{1/2}$ = 90 Hz	7
BrN_3[c]	-328, $\Delta\mu_{1/2}$ = 220 Hz	-142, $\Delta\mu_{1/2}$ = 65 Hz	-178, $\Delta\mu_{1/2}$ = 80 Hz	14

[a] $CDCl_3$ [b] pure (without any solvent) [c] CH_2Cl_2

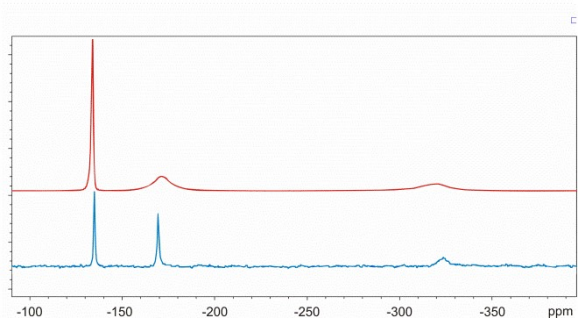

Figure 1. ^{14}N NMR spectra of the BrN_3 in solution ($CDCl_3$; bottom) and pure (without any solvent; top).

The Raman spectrum of BrN_3 **1** shows strong adsorption bands due to the asymmetric (ν = 2146 cm^{-1}) and symmetric N_α-N_β-N_γ stretching mode (ν = 1274 cm^{-1}) and the N_α-Br (ν = 451 cm^{-1}) stretching mode. Recording of the spectrum was limited due to a partial decomposition of **1** upon irradiation.[15]

The crystallization of **1** was performed on the diffractometer at a temperature of 150 K using a miniature zone melting procedure with focused infrared-laser-radiation.[16] The IR-laser allowed a very controlled heating of BrN_3, hence allowing optimization of the growth conditions. The successful growth of suitable crystals of **1** clearly demonstrates the promising potential of this method even for the structural characterization of heat- and shock-sensitive compounds.

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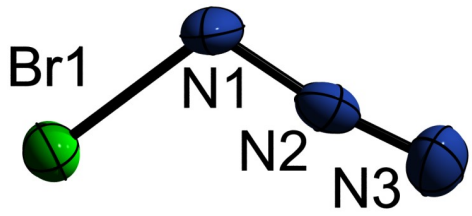


Figure 2. Representation of BrN_3 **1**. Thermal ellipsoids at 50% probability levels.

1 crystallizes in the tetragonal space group $I4_1cd$ with 16 molecules in the unit cell and adopts a trans-bent structure.[17] The N_α-N_β-N_γ bond angle (172.2(11)°) is significantly larger than the Br-N_α-N_β bond angle (108.6(7)°). The N_α-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),[18] but corresponds very well to typical values observed for neutral compounds containing a direct N-Br bond.[19] The difference in the N_α-N_β (1.265(9) Å) and N_β-N_γ (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.[9] 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,[20] and relativistic and bromine atom core-valence electron correlation effects have been determined using the Douglas-Kroll-Heß Hamiltonian.[21,22]

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

	ED[a]	SC[b]	*ab initio*
N_α-Br	1.899(6)	1.916(9)	1.894
N_α-N_β	1.231(22)	1.265(9)	1.250
N_β-N_γ	1.129(22)	1.123(12)	1.134
N_α-N_β-N_γ	170.7(24)	172.2(11)	172.6
Br-N_α-N_β	109.7(11)	108.6(7)	108.6

[a] electron diffraction [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 $^{14}N_2$ are obtained as 1.099 Å and 2359 cm^{-1} (exp values: 1.09768 Å and 2358.57 cm^{-1},[23]) while for $^{79}Br_2$ 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 *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 $^{79}Br^{14}N_3$ (187, 475, 543, 698, 1189, and 2125 cm^{-1}) agree within 23 cm^{-1} with the measured frequencies, with exception of the symmetric N_α-N_β-N_γ 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_2 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 -9.0 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 IN_3, which was found to form an endless chain-like structure via bridging iodine atoms with almost identical I-N_α 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.

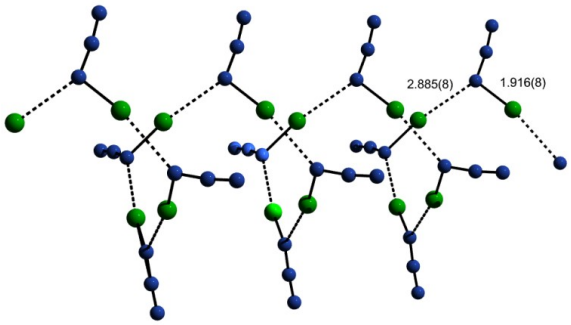


Figure 3. Helical structure as observed for **1** due to intermolecular interactions between N_α and the adjacent bromine atom. The helix is constituted via a 4_1-screw axis (y-1/2, -x+1, z+1/4).

The Br-N_α (1.916(9) Å) and Br-N_α' (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)[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 **1** the ring is transformed into a helix. Unlike in the solid state structure of HN_3, the interactions of this arrangement in **1** 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.[24] **1** not only shows Br···N contacts but also N···N contacts (3.094(16) Å). *Klapötke et al.* attributed a weak bonding nature to these contacts due to opposite formal charges of N_β and N_γ 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 **1** where they cannot be related to hydrogen bonds, a weak attractive interaction seems possible. Furthermore, they are not observed in the IN_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 BrN_3 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 HN_3 (Figure 4c in [5]) also has its counterpart in the packing of **1**. Four BrN_3 molecules form a ring with two fold symmetry. As was observed in HN_3, 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).

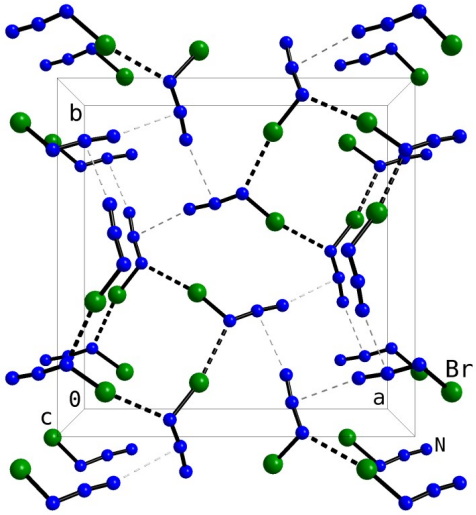
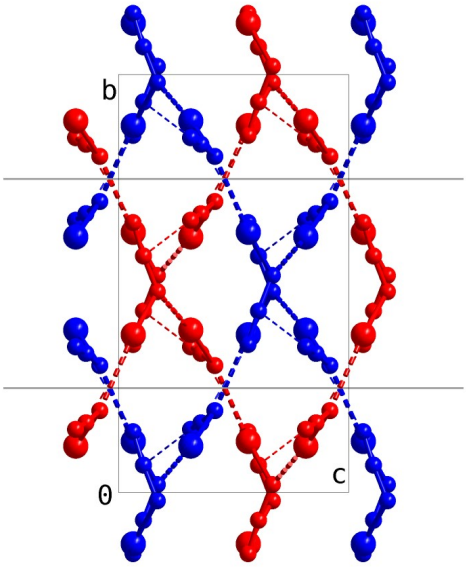


Figure 4. Packing of **1**. Br···N interactions in thick dashed lines. N···N contacts of uncertain nature in thin dashes lines. The helices formed by the Br···N interactions are primitively packed parallel to the *c*-axis. If regarding the N···N contacts bonding, these connect the helices to form a three dimensional network. The N···N contacts themselves constitute a helix via 4_1 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).



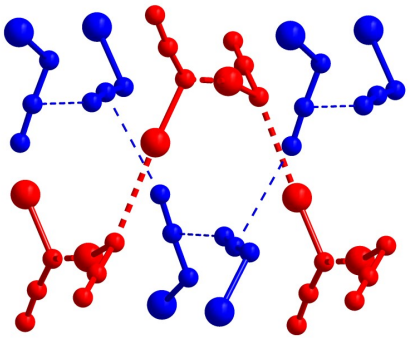


Figure 5. Top*:* Interleaved networks in the packing of **1**. One of the networks is depicted in blue the other one in red. The grey lines mark the positions of the 4_1 screw axes in the centre of the helices. The networks are related via *c* glide plane symmetry. ***Bottom****:* Detail of the interleaved 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).

In order to quantify the stabilizing or destabilizing role of the N···N and Br···N contacts, the energy of interaction of a BrN_3 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···N_α contact is obtained as -12.6 kJ/mol, in good agreement with the non-relatvistic 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 N_α 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 N_β···N_γ 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 N_β and N_γ atoms of +0.18 and +0.02 e,[30] respectively, the electrostatic interaction energy is strongly reduced compared to that of the Br···N_α contact. It still represents an attractive contribution due to the incomplete screening of the

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 $N_\beta \cdots N_\gamma$ contact.

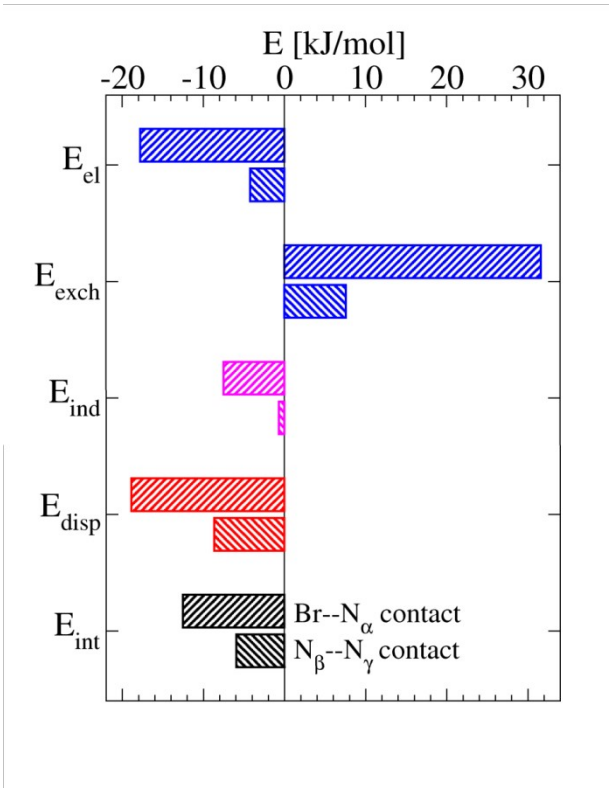


Figure 6. Electrostatic, E_{el}, exchange, E_{exch}, induction, E_{int}, and dispersion, E_{disp} DFT-SAPT contributions to the total interaction energy, E_{int}, for dimers with $Br\cdots N_\alpha$ and $N_\beta\cdots N_\gamma$ contacts in the geometry of the crystal structure.

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 traps constructed from FEP tubes. Volatile materials were handled in a stainless steel-Teflon-FEP vacuum line, nonvolatile materials under Ar in a glove box. $CDCl_3$ was dried over molecular sieve (3 Å) and degassed prior to use. The ^{14}N NMR spectrum was recorded on a Bruker Avance 300 spectrometer at 25 °C at 21.7 MHz and referenced to external CH_3NO_2 ($\delta(^{14}N)$ = 0). Raman spectra were recorded with a Bruker FT-Raman spectrometer RFS 100/S using the 1064 nm line of a Nd:YAG laser. The backscattered (180°) radiation was sampled and analysed (Stoke range: 0 to 3500 cm^{-1}). The liquid sample was measured in a sealed capillary (400 scans and a resolution of 2 cm^{-1}) using a laserpower of 40 mW. Unfortunately, an attempt to obtain a Raman spectrum of solid BrN_3 on the diffractometer resulted in an explosion of the sample immediately upon radiation.

BrN_3 *(1).* 0.14 g (2.15 mmol) NaN_3 was loaded in the glovebox into a FEP reaction trap. 80 µL (1.55 mmol) of pure Br_2 was condensed to NaN_3 at -196 °C. The trap was then slowly warmed to ambient temperature. The reaction mixture was kept at ambient temperature for 30 min and then slowly cooled to -15 °C. The resulting BrN_3 was condensed in another FEP trap at -80 °C. This procedure was repeated twice to finally yield pure BrN_3.
Raman (40 mW, 25 °C, 400 Scans): ν = 2146, 1273, 451, 303, cm^{-1}. $^{14}N\{^1H\}$ ($CDCl_3$): δ = -135 (s, N_β, $\Delta\nu_{1/2}$ = 16 Hz), -170 (s, N_γ, $\Delta\nu_{1/2}$ = 25 Hz), -324 (s, N_α, $\Delta\nu_{1/2}$ = 118 Hz). $^{14}N\{^1H\}$ (pure BrN_3): δ = -134 (s, N_β, $\Delta\nu_{1/2}$ = 22 Hz), -172 (s, N_γ, $\Delta\nu_{1/2}$ = 182 Hz), -319 (s, N_α, $\Delta\nu_{1/2}$ = 288 Hz).

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[17] Bruker AXS SMART diffractometer with APEX2 detector (MoKα radiation, λ = 0.71073 Å; T = 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 F^2. 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 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. **1**: BrN_3, M = 121.94, yellow crystal (0.27 x 0.05 x 0.03 mm); tetragonal, space group $I4_1cd$; a = 13.1873(12), b = 13.1873(12), c = 7.266(3) Å; $\alpha = \beta = \gamma = 90°$, V = 1263.6(5) $Å^3$; Z = 16; μ = 12.736 mm^{-1}; $\rho_{ber.}$ = 2.564 g cm^{-3}; 3541 reflexes ($2\theta_{max}$ = 54°), 586 unique (R_{int} = 0.1904); 37 parameters, 1 restraint; largest max./min. in the final difference Fourier synthesis 0.620 $eÅ^{-3}$/–0.613 $eÅ^{-3}$; max./min. transmission 0.75/0.17; R_1 = 0.0423 (I > 2σ(I)), wR_2 (all data) = 0.0616. Flack absolute structure parameter 0.11(6) 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.).
Details of the crystal structure determination of **1** 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-423741.
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[23] K. P. Huber, G. Herzberg, "Constants of Diatomic Molecules" (data prepared by J. W. Gallagher and R. D. Johnson, III) in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P. J. Linstrom, W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov.
[24] By the term "contact" we refer to any distance in the range of or below the sum of the van-der-Waals radii.
[25] 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.).
[26] See the following and references cited therein: A. D. Buckingham, J. E. Del Bene, S. A. C. McDowell, *Chem. Phys. Lett*. **2008**, *463*, 1-10.
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[28] DFT-SAPT calculations were carried out using the density-fitting approximation as implemented in Molpro (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 other DFT-SAPT contributions and partial atomic charges were calculated with the corresponding hybrid modifications containig 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_{disp} which was extrapolated to the complete basis set limit using the standard $1/X^3$ two-point formula for X = 3 and 4 (A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A. K. Wilson, *Chem. Phys. Lett.* **1998**, *286*, 243-252). The remaining contributions were directly taken from the aug-cc-pVQZ results. While E_{el} and E_{exch} denote the first-order electrostatic and exchange contributions, E_{int} stands for the sum of the second-order induction and exchange-induction and the δ(HF) estimate of higher-order contributions.
[29] a) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys*. **1985**, *83*, 735-746; b) A. E. Reed, L. A. Curtis, F. Weinhold, *Chem. Rev*. **1988**, *88*, 899-926.
[30] The mesomeric structure with opposite formal charges on N_β and N_γ 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.

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Bromine Azide

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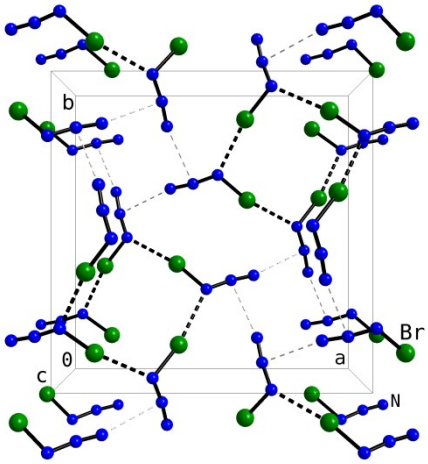
Solid State Structure of Bromine Azide



Helical structure of BrN_3 in the solid state – an unforeseen structural element in covalent p-block azide chemistry.

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