

Halogen Azides

Solid-State Structure of Bromine Azide**

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

Dedicated to Professor Günter Schmid on the occasion of his 75th birthday

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.^[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 singlecrystal 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 an ABA 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. IN₃ was found to be monomeric in CFCl₃ 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 Xray diffraction to date. The growth of suitable single crystals of halogen azides in general is difficult owing to their extreme sensitivity towards small pressure variations. For instance, bromine azide was reported to explode when $\Delta p \ge 0.05$ Torr, and also upon crystallization.^[9] However, the gas-phase structure of BrN₃, 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 interested in the synthesis of covalent azides only recently, 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 organoantimony diazides $RSb(N_3)_2$.^[13] Herein, we expand these studies on the synthesis of halogen azides and present the single-crystal X-ray structure of bromine azide, BrN_3 (1).

 BrN_3 (1) was prepared by reaction of NaN_3 with bromine (Scheme 1). The ¹⁴N NMR spectrum of a solution of 1 in

Scheme 1. Synthesis of BrN₃.

CDCl₃ shows three resonances for N_a ($\delta = -324$ ppm, $\Delta \mu_{1/2} = 118$ Hz), N_β ($\delta = -135$ ppm, $\Delta \mu_{1/2} = 16$ Hz), and N_γ ($\delta = -170$ ppm, $\Delta \mu_{1/2} = 25$ Hz; Table 1 and Figure 1). These values differ from those previously reported for a CDCl₃

Table 1: ¹⁴N chemical shifts [ppm] of BrN₃.

Sample	Να	N _β	Νγ	Ref.
BrN ₃ ^[a]	-324 , $\Delta \mu_{1/2} = 118$ Hz	–135, Δμ _{1/2} =16 Hz	−170, Δμ _{1/2} =25 Hz	this work
BrN₃ ^[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 , $\Delta \mu_{1/2} = 220 \text{ Hz}$	-142 , $\Delta \mu_{1/2} = 65$ Hz	-178 , $\Delta \mu_{1/2} = 80$ Hz	[14]

[a] CDCl₃. [b] Pure (without any solvent). [c] CH₂Cl₂.



Figure 1. ¹⁴N NMR spectra of the BrN_3 in solution (CDCl₃; bottom) and pure (without any solvent; top). The spectra are displaced vertically for clarity.

solution of $\mathbf{1}$,^[7] but correspond well to values reported for a CH₂Cl₂ solution of $\mathbf{1}$,^[14] even though the half-widths are somewhat smaller.^[14] In contrast, the ¹⁴N NMR spectrum of pure $\mathbf{1}$ shows broader resonances.

The Raman spectrum of liquid BrN₃ shows strong adsorption bands that are due to the asymmetric ($\tilde{\nu} = 2146 \text{ cm}^{-1}$) and symmetric N_a-N_p-N_y stretching mode ($\tilde{\nu} = 1274 \text{ cm}^{-1}$) and the N_a-Br ($\tilde{\nu} = 451 \text{ cm}^{-1}$) stretching mode. The recording of the spectrum was limited by partial decomposition of **1** upon irradiation.^[15]

^[*] B. Lyhs, D. Bläser, Dr. C. Wölper, Prof. S. Schulz, Prof. G. Jansen Faculty of Chemistry, University of Duisburg-Essen Universitätsstrasse 5–7, S07 S03 C30, 45117 Essen (Germany) E-mail: stephan.schulz@uni-due.de

^[**] S.S. and B.L. 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://dx.doi.org/10.1002/anie.201108092.

The crystallization of **1** was performed directly 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 , thus 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.

Compound **1** crystallizes in the tetragonal space group $I\bar{4}cd$ with 16 molecules in the unit cell and adopts a *trans-bent* structure (Figure 2).^[17] The N_{α} - N_{β} - N_{γ} angle (172.2(11)°) is



Figure 2. Solid-state structure of BrN_3 (1). Ellipsoids set at 50% probability.

significantly larger than the Br-N_{α}-N_{β} angle (108.6(7)°). The N_a -Br bond (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 $N_{\alpha} – N_{\beta}$ (1.265(9) Å) and $N_{\beta} – N_{\gamma}$ (1.123(12) Å) bond lengths clearly shows its covalently bonded nature. The bond lengths and angles correspond very well with those obtained from an electron-diffraction study and also with values previously obtained from HF-MO and MP2 calculations.^[9] Herein, we have further increased the level of theory to that of coupled-cluster theory with iterative single, double, and perturbative triple excitations (CCSD(T)). The complete basis set limit was nearly reached with the explicitly correlated CCSD(T)-F12a method,^[20] and relativistic and bromine atom core-valence electron correlation effects were determined using the Douglas-Kroll-Heß Hamiltonian.^[21,22]

Geometry optimizations and calculations of harmonic frequencies with numerical first and second derivatives for the nitrogen and bromine molecules demonstrate the accuracy of this method: a bond distance and harmonic frequency for ¹⁴N₂ of 1.099 Å and 2359 cm⁻¹ were obtained (experimental values: 1.09768 Å and 2358.57 cm⁻¹),^[23] while for $^{79}Br_2$ values of 2.278 Å and 328.5 cm^{-1} (exptl values: 2.28105 Å and 325.321 cm⁻¹) were obtained. Without inclusion of relativity effects and bromine core-valence correlation, the Br₂ bond is 0.019 Å longer and has a harmonic frequency that is lower by 2 cm^{-1} . The geometrical parameters obtained for BrN₃ are shown in Table 2. 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-zerotemperature vibrational averaging in case of the electron diffraction data and also 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

Table 2: Selected structural parameters of 1.

	ED ^[a]	SC ^[b]	ab initio
N _a —Br	1.899(6)	1.916(9)	1.894
$N_{\alpha} - N_{\beta}$	1.231 (22)	1.265 (9)	1.250
Ν _β -Ν _γ	1.129(22)	1.123(12)	1.134
$N_{\alpha} - N_{\beta} - N_{\gamma}$	170.7(24)	172.2(11)	172.6
$Br-N_{\alpha}-N_{\beta}$	109.7(11)	108.6(7)	108.6

[a] Electron diffraction. [b] single-crystal determination.

most significant changes upon neglect of relativistic and corevalence 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 to 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 cannot 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 BrN₃ to Br₂ and N₂ (–403.5 kJ mol⁻¹, at 0 K) was calculated including zero-point vibrational energy correction (ZPE). The latter (in the harmonic approximation) contributes –9.0 kJ mol⁻¹ to this value, while the contribution of relativistic and core–valence correlation effects amounts to -0.9 kJ mol⁻¹.

In remarkable contrast to the solid state structure of IN₃, which was found to form an endless chain-like structure by bridging iodine atoms with almost identical $I-N_{\alpha}$ bond lengths (2.264(23), 2.30(3) Å), BrN₃ forms a helical structure in the solid state (Figure 3). This structural motif has not been observed in covalent azide chemistry to date.



Figure 3. Helical structure as observed for 1 owing to intermolecular interactions between N_{α} and the adjacent bromine atom. The helix is constituted by a 4_1 screw axis (y-1/2, -x+1, z+1/4).

The Br–N_{α} (1.916(9) Å) and Br–N_{$\alpha'} (2.885(8) Å) bonds$ differ by about 0.9 Å, but the value of 2.885(8) Å is clearlysmaller than 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 acrystallographic point of view. Compared to the otherstructurally characterized simple covalent azide, namelyHN₃, some striking similarities can be found. While BrN₃forms a helix with a 4₁ screw axis, HN₃ has the same structuralmotif with (approximately) fourfold symmetry bar the trans-</sub>

Angewandte munications

lational component. As a consequence, an eight-membered ring consisting of four HN₃ molecules (see Figure 4a in Ref. [5]) is formed rather than the helix observed for BrN₃. 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 HN₃, the interactions of this arrangement in 1 are less certain. Weak, but indisputably existent, hydrogen bonds connect the molecules in the HN₃ structure accompanied by N···N contacts just less the sum of the van-der-Waals radii,^[24] whereas in 1 Br...N contacts and N...N contacts (3.094(16) Å) were found. Klapötke et al. attributed a weak bonding nature to these contacts to be due to opposite formal charges of N_{β} and N_{γ} in one mesomeric structure, even though this mesomeric form is most likely not the most important one. Furthermore, these contacts might be random side effects of the weak hydrogen bonds. However, as 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 IN₃ structure, which thus might explain why BrN3 forms helices instead of chains. Unfortunately, attempts 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 could not be resolved experimentally.

Finally, the third motive identified in the packing of HN_3 (Figure 4c in Ref. [5]) also has its counterpart in the packing of **1**. Four BrN_3 molecules form a ring with twofold 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 (Figure 4), of which two, related by *c*-glide-plane symmetry, interleave (Figure 5).



Figure 4. Packing of 1. Br…N interactions are shown as thick dashed lines, and N…N contacts of uncertain nature in thin dashed lines. The helices formed by the Br…N interactions are primitively packed parallel to the *c* axis. The N…N contacts (assuming they are bonding interactions) connect the helices to form a three-dimensional network. The N…N contacts themselves constitute a helix with 4_1 symmetry. A series of stacked rings can be observed along the twofold axes parallel to *c*, for example, in the center of the *ab* plane (others only partially shown).



Figure 5. Top: Interleaved networks in the packing of 1. One network is depicted in blue and the other in red. Gray lines mark the positions of the 4_1 screw axes in the center of the helices. The networks are related by *c* glide plane symmetry. Bottom: Detail of the interleaved networks. One helix formed by Br…N interactions (red) is interpenetrated by another formed by N…N contacts (blue) of the other network (interactions/contacts indicated as above).

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 neighbors in the crystal was determined by CCSD(T)-F12a calculations using the same ab initio methods 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 $-13.1 \text{ kJ mol}^{-1}$, while for a dimer with an N···N contact a value of -6.1 kJ mol^{-1} was found, thus demonstrating that the latter indeed stabilizes the crystal. Relativistic and core-valence correlation effects contribute -0.8 kJ mol^{-1} to the former value, while their influence is completely negligible for the N···N contact. The intermolecular Br…N interaction is fairly large, amounting to about 60% of the 21 kJ mol⁻¹ found for the hydrogen bond in the water dimer.^[26] These strong interactions are the main factor for the stability of the crystal.

To understand the reasons for the strength of these interactions DFT-SAPT calculations, that is, symmetryadapted intermolecular perturbation theory based on a density functional theory description of the monomers,^[27] were carried out. In this case the interaction energy is calculated as the sum of electrostatic, induction, and dispersion energy contributions, along with their repulsive exchange corrections that take the energetic consequences of the antisymmetry principle into account.^[28] 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_a contact is determined to be $-12.6 \text{ kJ mol}^{-1}$, which is in good agreement with the non-relativistic CCSD(T) value of $-12.3 \text{ kJ mol}^{-1}$. While the partial charges as determined with a natural population analysis with +0.19e for the Br atom and -0.39e for the N_a atom suggest that a strong electrostatic interaction could provide the main contribution,^[29] Figure 6 shows that the dispersion contribution is even slightly more important. This reflects the large polarizability



Figure 6. Electrostatic (E_{el}), exchange (E_{exch}), induction (E_{ind}), and dispersion (E_{disp}) DFT-SAPT contributions to the total interaction energy (E_{int}) for dimers with Br···N_{α} and N_{β}···N_{γ} contacts in the geometry of the crystal structure.

of the bromine atom, which also becomes apparent in the importance of the induction contribution. For the dimer with an N_β···N_γ contact, the total DFT-SAPT interaction energy is -6.0 kJ mol^{-1} , 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 decreased compared to that of the Br···N_α contact. It is still an attractive contribution owing to the incomplete screening of the attraction between electrons and nuclei from the different molecules through repulsive electron–electron and nucleus–nucleus interactions. Nevertheless, dispersion clearly is the dominant stabilizing contribution in case of the N_β···N_γ contact.

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. CDCl₃ was dried over molecular sieves (3 Å) and degassed prior to use. The ¹⁴N NMR spectrum was recorded on a Bruker Avance 300 spectrometer at 25 °C at 21.7 MHz and referenced to external CH₃NO₂ (δ (¹⁴N) = 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 back-scattered (180°) radiation was sampled and analyzed (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 laser power of 40 mW. Unfortunately, an attempt to obtain a Raman spectrum of solid BrN₃ on the diffractometer (80 mW power) resulted in an explosion of the sample immediately upon radiation.

BrN₃ (1): NaN₃ (0.14 g, 2.15 mmol) was loaded in the glovebox into a FEP reaction trap. Pure Br₂ (80 µL, 1.55 mmol) was condensed onto NaN₃ 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 BrN₃ was 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): $\tilde{\nu}$ = 2146, 1273, 451, 303 cm⁻¹. ¹⁴N{¹H} NMR (21.7 MHz, CDCl₃): δ = -135 (s, N_β, $\Delta \nu_{1/2}$ = 16 Hz), -170 (s, N_γ, $\Delta \nu_{1/2}$ = 25 Hz), -324 ppm (s, N_α, $\Delta \nu_{1/2}$ = 118 Hz). ¹⁴N{¹H} NMR (pure BrN₃): δ = -134 (s, N_β, $\Delta \nu_{1/2}$ = 22 Hz), -172 (s, N_γ, $\Delta \nu_{1/2}$ = 182 Hz), -319 ppm (s, N_α, $\Delta \nu_{1/2}$ = 288 Hz).

Received: November 17, 2011 Published online: January 16, 2012

Keywords: ab initio computations · bromine azide · covalent azides · solid-state structures

- N. N. Greenwood, A. Earnshaw in *Chemistry of the Elements*, Pergamon Press, Amsterdam, **1984**, p. 12.
- [2] E. H. Eyster, J. Chem. Phys. 1940, 8, 135-142.
- [3] E. Amble, B. P. Daley, J. Chem. Phys. 1950, 18, 1422-1422.
- [4] V. R. Schomaker, A. Spurr, J. Am. Chem. Soc. 1942, 64, 1184– 1187.
- [5] J. Evers, M. Göbel, B. Krumm, F. Martin, S. Medvedyev, G. Oehlinger, F. X. Steemann, I. Troyan, T. M. Klapötke, M. I. Eremets, J. Am. Chem. Soc. 2011, 133, 12100–12105.
- [6] I. C. Tornieporth-Oetting, T. M. Klapötke, Angew. Chem. 1995, 107, 559-568; Angew. Chem. Int. Ed. Engl. 1995, 34, 511-520, and references therein.
- [7] P. Geissler, T. M. Klapötke, H.-J. Kroth, Spectrochim. Acta Part A 1995, 51, 1075–1078.
- [8] P. Buzek, T. M. Klapötke, P. von R. Schleyer, I. C. Tornieporth-Oetting, P. S. White, Angew. Chem. 1993, 105, 289–290; Angew. Chem. Int. Ed. Engl. 1993, 32, 275–277.
- M. Hargittai, I. C. Tornieporth-Oetting, T. M. Klapötke, M. Kolonits, I. Hargittai, *Angew. Chem.* 1993, 105, 773-774; *Angew. Chem. Int. Ed. Engl.* 1993, 32, 759-761.
- [10] a) M. Otto, S. D. Lotz, G. Frenking, *Inorg. Chem.* 1992, 31, 3647–3655; b) A. Schulz, I. C. Tornieporth-Oetting, T. M. Klapötke, *Inorg. Chem.* 1995, 34, 4343–4346.
- [11] S. Schulz, B. Lyhs, G. Jansen, D. Bläser, C. Wölper, *Chem. Commun.* 2011, 47, 3401–3403.
- [12] B. Lyhs, G. Jansen, D. Bläser, C. Wölper, S. Schulz, *Chem. Eur. J.* 2011, *17*, 11394–11398.
- [13] B. Lyhs, D. Bläser, C. Wölper, S. Schulz, *Chem. Eur. J.* 2011, 17, 4914–4920.
- [14] T. M. Klapötke, Polyhedron 1997, 16, 2701-2704.
- [15] Details are given in the Supporting Information.
- [16] "In Situ Crystallisation Techniques": R. Boese, M. Nussbaumer in Organic Crystal Chemistry (Ed.: D. W. Jones), Oxford University Press, Oxford, 1994, pp. 20–37.

Angewandte ommunications

- [17] Bruker AXS SMART diffractometer with APEX2 detector (Mo K_a radiation, $\lambda = 0.71073$ 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 multiscans (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 only allows 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: BrN₃, $M_r = 121.94$, yellow crystal ($0.27 \times 0.05 \times$ 0.03 mm³); tetragonal, space group $I\bar{4}cd$; a = 13.1873(12), b =13.1873(12), c = 7.266(3) Å; V = 1263.6(5) Å³; Z = 16; $\mu =$ 12.736 mm⁻¹; $\rho_{\text{calcd}} = 2.564 \text{ g cm}^{-3}$; 3541 reflexes $(2\theta_{\text{max}} = 54^{\circ})$, 586 unique ($R_{int} = 0.1904$); 37 parameters, 1 restraint; largest max./min. in the final difference Fourier synthesis $0.620 \text{ e} \text{ Å}^{-3}$ / $-0.613 \text{ e} \text{\AA}^{-3}$; max./min. transmission 0.75/0.17; $R_1 = 0.0423 (I > 1000)$ $2\sigma(I)$), 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. Bernardinelli, H. D. Flack, Acta Crystallogr. Sect. A 1985, 41, 500-511). Further details on the crystal structure investigations for 1 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 number CSD-423741.
- [18] P. Pyykkö, M. Atsumi, Chem. Eur. J. 2009, 15, 186-197.
- [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.
- [20] a) T. B. Adler, G. Knizia, H.-J. Werner, J. Chem. Phys. 2007, 127, 221106; b) G. Knizia, T. B. Adler, H.-J. Werner, J. Chem. Phys. 2009, 130, 054104.
- [21] G. Jansen, B. A. Heß, Phys. Rev. A 1989, 39, 6016-6017.
- [22] CCSD(T)-F12a and F12b calculations were carried out with an augmented triple-zeta valence Gaussian orbital basis set (aug-ccpVTZ; see: R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, J. Chem. Phys. 1992, 96, 6796-6806) and the appropriate auxiliary basis sets for the density fitting and resolution of the identity approximations involved (a) F. Weigend, Phys. Chem. Chem. Phys. 2002, 4, 4285-4291; b) F. Weigend, A. Köhn, C. Hättig, J. Chem. Phys. 2002, 116, 3175-3183). They were made with the Molpro program package (MOLPRO, version 2010.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, 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 corevalence 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-pVTZ-DK, also correlating 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-ccpVTZ result to the CCSD(T)-F12a value. Full details and (nearly identical) CCSD(T)-F12b results can be found in the Supporting Information.

- [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] A. D. Buckingham, J. E. Del Bene, S. A. C. McDowell, *Chem. Phys. Lett.* 2008, 463, 1–10, and references cited therein.
- [27] a) G. Jansen, A. Heßelmann, J. Phys. Chem. A 2001, 105, 11156–11157; b) A. Heßelmann, G. Jansen, Phys. Chem. Chem. Phys. 2003, 5, 5010–5014; c) A. J. Misquitta, R. Podeszwa, B. Jeziorski, K. Szalewicz, J. Chem. Phys. 2005, 123, 214103.
- [28] DFT-SAPT calculations were carried out using the densityfitting approximation as implemented in Molpro (A. Heßelmann, G. Jansen, M. Schütz, J. Chem. Phys. 2005, 122, 014103) 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 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 $E_{\rm disp}$, 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 $E_{\rm el}$ and $E_{\rm exch}$ denote the first-order electrostatic and exchange contributions, E_{ind} stands for the sum of the secondorder induction and exchange-induction and the $\delta(HF)$ 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 HN₃, whereas this effect hardly shows up in the partial charges of BrN₃.