# Halogenotrinitromethanes

# Halogenotrinitromethanes: A Combined Study in the Crystalline and Gaseous Phase and Using Quantum Chemical Methods

Thomas M. Klapötke,<sup>\*[a]</sup> Burkhard Krumm,<sup>[a]</sup> Richard Moll,<sup>[a]</sup> Sebastian F. Rest,<sup>[a]</sup> Yury V. Vishnevskiy,<sup>[b]</sup> Christian Reuter,<sup>[b]</sup> Hans-Georg Stammler,<sup>[b]</sup> and Norbert W. Mitzel<sup>\*[b]</sup>

**Abstract:** The halogenotrinitromethanes  $FC(NO_2)_3$  (1), BrC(NO<sub>2</sub>)<sub>3</sub> (2), and IC(NO<sub>2</sub>)<sub>3</sub> (3) were synthesized and fully characterized. The molecular structures of 1–3 were determined in the crystalline state by X-ray diffraction, and gasphase structures of 1 and 2 were determined by electron diffraction. The Hal–C bond lengths in F–, Cl–, and Br–  $C(NO_2)_3$  in the crystalline state are similar to those in the gas phase. The obtained experimental data are interpreted in terms of Natural Bond Orbitals (NBO), Atoms in Molecules (AIM), and Interacting Quantum Atoms (IQA) theories. All

## Introduction

Mutual influences of atoms and functional groups in molecules are to a great extent responsible for the chemical and structural properties. Detailed analysis of these influences and the understanding of intra- and intermolecular interactions are of fundamental interest for chemical science. Especially small compounds containing the trinitromethyl moiety, with its strong electron-withdrawing property, may show special and unusual characteristics. A detailed understanding of the nature of bonding within and between these molecules is therefore highly desirable. Although the trinitromethyl moiety consists of C, N, and O atoms, its properties are comparable to those of a Group VII element. Early studies of  $\alpha$ -halogen derivatives of trinitromethane have demonstrated the pseudohalogenic nature of the trinitromethyl moiety.<sup>[1]</sup> Further experimental evidence supporting this behavior as a pseudohalogen are the discoveries of the corresponding strong acid  $HC(NO_2)_{3}$ ,<sup>[2]</sup> various metal salts like K[C(NO<sub>2</sub>)<sub>3</sub>] and Ag[C(NO<sub>2</sub>)<sub>3</sub>],<sup>[2b]</sup> pseudointerhalogen compounds such as NCC(NO<sub>2</sub>)<sub>3</sub><sup>[3]</sup> and N<sub>3</sub>C(NO<sub>2</sub>)<sub>3</sub><sup>[4]</sup> as well as its dimer hexanitroethane.<sup>[5]</sup> Furthermore, the existence

_	
[a]	Prof. Dr. T. M. Klapötke, Dr. B. Krumm, Dr. R. Moll, S. F. Rest
	Department of Chemistry, Ludwig-Maximilian University of Munich
	Butenandtstraße 5–13 (D), 81377 Munich (Germany)
	Fax: (+ 49) 89-2180-77492
	E-mail: tmk@cup.uni-muenchen.de
[b]	Dr. Y. V. Vishnevskiy, C. Reuter, Dr. HG. Stammler, Prof. Dr. N. W. Mitzel
	Inorganic and Structural Chemistry, Bielefeld University
	Universitätsstraße 25, 33615 Bielefeld (Germany)
	Fax: (+ 49) 521-106-6026
	E-mail: mitzel@uni-bielefeld.de
	Supporting information for this article is available on the WWW under
	http://dx.doi.org/10.1002/chem.201402798.

halogenotrinitromethanes show various intra- and intermolecular non-bonded interactions. Intramolecular N···O and Hal···O (Hal = F (1), Br (2), I (3)) interactions, both competitors in terms of the orientation of the nitro groups by rotation about the C–N bonds, lead to a propeller-type twisting of these groups favoring the mentioned interactions. The origin of the unusually short Hal–C bonds is discussed in detail. The results of this study are compared to the molecular structure of ClC(NO<sub>2</sub>)<sub>3</sub> and the respective interactions therein.

of the halogenotrinitromethanes  $HalC(NO_2)_3$   $(Hal\,{=}\,F,$  Cl, Br, I) confirm this assumption.

Although various syntheses of HalC(NO<sub>2</sub>)<sub>3</sub> (Hal = F (1), Cl, Br (2), I (3)) by different methods are known,<sup>[6]</sup> analytical data available in the literature are often fragmentary despite considerable efforts of various researchers. In this context, studies of the NMR spectra<sup>[7]</sup> and vibrational analyses<sup>[7a,8]</sup> have been previously reported. Furthermore, quantum chemical calculations have been performed to predict the molecular structures of the halogenotrinitromethanes.<sup>[9]</sup>

Reliable data of experimental structural investigations of 1-3 are rather limited in literature. When it comes to understand the interplay of various types of intra- and intermolecular interactions on the molecular structures, it is generally highly desirable to compare structural data of free molecules in the gas phase, without distortions from intermolecular forces, with those of molecules embedded in a crystal, the very existence of which depends on the existence of intermolecular forces. So far gas-phase structure determinations exist for CIC(NO<sub>2</sub>)<sub>3</sub><sup>[10]</sup> and BrC(NO<sub>2</sub>)<sub>3</sub>,<sup>[10b, c]</sup> but the latter are based on a data set of limited quality and is therefore reinvestigated in this work. Experimental structure data for both, gas and solid, are completely unknown for FC(NO<sub>2</sub>)<sub>3</sub>. Furthermore, a determination of the crystal structure of  $IC(NO_2)_3$  has been previously reported, but using a poor data set of X-ray diffraction data, due to decomposition of upon exposure to  $Mo_{K\alpha}$  X-ray radiation.<sup>[11]</sup> This prevented the coordinates of the light atoms carbon, nitrogen, and oxygen from being properly determined and the resulting structures show a considerable scatter for bond lengths and made a reinvestigation of the crystal structure desirable.

The molecular structure of  $CIC(NO_2)_3$  has previously been investigated in our laboratory, using X-ray diffraction and quan-

Chem. Eur. J. 2014, 20, 1–13 Wiley

Wiley Online Library



tum chemical calculations of the molecular electrostatic potential.<sup>[12]</sup> Following these studies, we describe here convenient syntheses and full characterization of the halogenotrinitromethanes  $FC(NO_2)_3$  (1),  $BrC(NO_2)_3$  (2), and  $IC(NO_2)_3$  (3) as well as their molecular structures in the gas phase and in the crystalline state. This completes our detailed investigations of  $\alpha$ -halogen derivatives of trinitromethane.

### **Results and Discussion**

The general and established procedure for the preparation of the halogenotrinitromethanes  $HalC(NO_2)_3$  (Hal = F (1), Br (2), I (3)) implies direct halogenation of trinitromethane or its anion (Scheme 1).



Scheme 1. Synthesis of the halogenotrinitromethanes  $FC(NO_2)_3$  (1),  $BrC(NO_2)_3$  (2), and  $IC(NO_2)_3$  (3).

Fluorination of trinitromethanide in aqueous solution enables separation of the pure product by evaporation and furnishes 1 as a colorless stable liquid, immiscible with water. The use of Selectfluor (1-chloro-methyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2]octane bis(tetrafluoroborate)) as a fluorinating agent significantly simplifies the experimental effort compared with the experimental setup required for elemental fluorine. In case of 2, the immiscibility with water facilitates the separation of the product. The use of elemental bromine in the synthesis of 2 cannot be applied to that of 3 by an analogous reaction of trinitromethane or its salt with elemental iodine. Therefore, iodine monochloride, due to its high polarity as a source of I<sup>+</sup>, is needed for a successful reaction. At ambient temperature, compound 3 is the only solid halogenotrinitromethane derivative, and in analogy to 1 and 2 is not miscible with water. It decomposes slowly at ambient temperature and/or when exposed to daylight, forming elemental iodine.

For comparison of analytic data, an authentic sample of chlorotrinitromethane was also synthesized, according to a procedure in the literature.<sup>[6]</sup>

#### NMR Spectroscopy

All compounds were thoroughly characterized by multinuclear NMR spectroscopy (Table 1). The  ${}^{13}$ C NMR spectra of 1–3 and the authentic sample of CIC(NO<sub>2</sub>)<sub>3</sub> show the resonances for the

	$(NO_2)_3$ in $CDCI_3$ ( $O$ [	ppm], J [H2]).		
	1 FC(NO <sub>2</sub> ) <sub>3</sub> <sup>[a]</sup>	CIC(NO <sub>2</sub> ) <sub>3</sub> <sup>[b]</sup>	2 BrC(NO <sub>2</sub> ) <sub>3</sub>	<b>3</b> IC(NO <sub>2</sub> ) <sub>3</sub>
<sup>13</sup> C	113.7 ${}^{1}J_{C-14N} = 12.1$ ${}^{1}J_{C-F} = 333.4$	126.3 <sup>1</sup> J <sub>C-14N</sub> =9.3	121.9 <sup>1</sup> J <sub>C-14N</sub> =8.1	106.7 <sup>1</sup> J <sub>C-14N</sub> =6.4
<sup>15</sup> N	$-40.7$ ${}^{2}J_{N-19F} = 14.2$	-35.7	-34.8	-30.8
[a] <sup>19</sup> F: CIC(NO <sub>2</sub>	$\delta = -87.3$ (sept, ) <sub>3</sub> .	$^{2}J_{\rm F-14N}$ = 10.2 Hz)	[b] Authentic	sample of

sole carbon atom between  $\delta = 126.3 - 106.7$  ppm. In general, an increasing number of electron-withdrawing groups in the vicinity of a carbon atom lead to a downfield shift. Therefore, the carbon resonance of CIC(NO<sub>2</sub>)<sub>3</sub> at  $\delta = 126.3$  ppm and that of **2** at  $\delta = 121.9 \text{ ppm}$  is found downfield relative to the carbon resonance of **3** at  $\delta = 106.7$  ppm (Table 1). The fluorine compound 1 has a special position among this series of halogenotrinitromethanes. The <sup>13</sup>C NMR resonance of **1** at  $\delta =$ 113.7 ppm is surprisingly much more highfield shifted than expected for the electronegative fluorine substituent. All resonances of the carbon atoms of 1-3 and CIC(NO<sub>2</sub>)<sub>3</sub> are split into septets due to coupling with the <sup>14</sup>N nuclei, whereas for 1 a doublet of septets is observed due to additional coupling with fluorine. The coupling constants  ${}^{1}J_{C-14N}$  are 12.1 (1), 9.3 (CIC(NO<sub>2</sub>)<sub>3</sub>), 8.1 (2), and 6.4 Hz (3), a constant decrease along the series of decreasing electronegativity, respectively, with increasing molecular weight of the halogen atom (Table 1). The  ${}^{1}J_{C-F}$  coupling constant for **1** at 333.4 Hz is similar to the previously reported value.<sup>[7c]</sup> The <sup>15</sup>N NMR spectroscopic resonances are found in the typical range of  $\delta = -30$  to -40 ppm for trinitromethyl derivatives.<sup>[13]</sup> In case of **1** the coupling constants  ${}^{2}J_{F}$  $_{14N}$  and  $^{2}J_{15N-F}$  are determined with values of 10.2 and 14.2 Hz.

#### Vibrational spectroscopy

IR and Raman spectra of 1, 2, CIC(NO<sub>2</sub>)<sub>3</sub> in the liquid state and of 3 in the solid state were measured. Vibrational analyses of 1-3 and an authentic sample of CIC(NO<sub>2</sub>)<sub>3</sub> show the characteristic asymmetric NO<sub>2</sub> stretching vibration at 1622–1583 cm<sup>-1</sup> (Table 2), which is in agreement with previously reported other values and nitro group-containing compounds.<sup>[8a, 13a, b, d, e, 14]</sup> The symmetric NO<sub>2</sub> stretching vibration is found for these compounds in the typical range of 1298-1272 cm<sup>-1</sup>. The CN stretching vibrations of **1–3** and ClC(NO<sub>2</sub>)<sub>3</sub> occur at 857-837 cm<sup>-1</sup>, whereas the frequency decreases with heavier halogens (Table 2). The general low-frequency absorptions of these vibrations are surprising but explainable with the low C-N bond order in the trinitromethyl moiety,<sup>[14a, 15]</sup> in agreement with the corresponding elongated C-N bonds observed in the crystal structures (see below). The Hal-C stretching vibrations for  $1\mathchar`-3$  and  $\mbox{CIC}(NO_2)_3$  were observed at higher frequencies than commonly found, indicating shorter Hal-C bonds (Table 2).<sup>[14a]</sup> The C–F stretching vibration of 1 is difficult to locate and is very likely overlapped with the symmetric

2

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



CHEMISTRY A European Journal Full Paper

	1 FC(	NO <sub>2</sub> ) <sub>3</sub>	CIC(N	$ O_2 _3^{[a]}$	<b>2</b> BrC	(NO <sub>2</sub> ) <sub>3</sub>	3 IC(1	NO <sub>2</sub> ) <sub>3</sub>
	Raman	IR	Raman	IR	Raman	IR	Raman	IR
$v_{as}NO_2$	1622 (16)	1606 (vs)	1620 (18)	1602 (vs)	1615 (14)	1595 (vs)	1616 (5)/1597 (35)	1597 (s)/1583 (vs)
$v_{s}NO_{2}$	1298 (28)	1288 (s)	1279 (12)	1272 (s)	1294 (8)	1277 (s)	1298 (7)/1287 (5)	1290 (s)/1278 (s)
νCN	857 (100)	856 (m)	845 (100)	843 (s)	840 (88)	838 (s)	839 (97)	837 (s)
$\nu$ HalC <sup>[b]</sup>	1298 (28) <sup>[c]</sup>	1288 (s) <sup>[c]</sup>	1027 (5)	1024 (s)	981 (3)	979 (m)	947 (5)	944 (m)

stretching vibration  $\nu_s NO_2$  in the region around 1290 cm<sup>-1</sup>. The corresponding vibrations of **2**, **3** and ClC(NO<sub>2</sub>)<sub>3</sub> are in agreement with previous investigations,<sup>[8b]</sup> however, there also exists very disputable assignments at much lower frequencies.<sup>[8a, 11]</sup> Evidence on bond shortening is described in more detail below in the gas and crystal structure section.

#### Gas-phase structure

Gas electron diffraction (GED) was used to determine the structure of the free molecules of  $FC(NO_2)_3$  (1) and  $BrC(NO_2)_3$  (2). The structure including atom labeling is shown in Figure 1. The



Figure 1. Molecular structure of  $FC(NO_2)_3$  (1) and analogously  $BrC(NO_2)_3$  (2) in the gas phase.

refined experimental equilibrium structure parameter values along with the quantum chemically calculated ones are listed in Table 3. Thermally averaged values for the bond lengths of **1** are:  $r_g(F-C) = 1.308(11)$ ,  $r_g(N-C) = 1.532(4)$ ,  $r_g(N1-O1) = r_g(N1-O2) = 1.216(1)$  Å; those of **2** are:  $r_g(Br-C) = 1.878(6)$ ,  $r_g(N-C) =$ 1.548(3),  $r_g(N1-O1) = 1.215(1)$ ,  $r_g(N1-O2) = 1.218(1)$  Å. The radial distribution curves (Figure 2 and Figure 3), which can be interpreted as spectra of interatomic distances, show that the C-Br bond contribution in **2** is in a separate peak whereas that of the C-F bond in **1** is under the same feature as that of the N-O bonds and therefore correlated. Thus the experimentally **Table 3.** Experimental and calculated structural parameters  $(r_{er} \not\approx_e)$  of FC(NO<sub>2</sub>)<sub>3</sub> (1) and BrC(NO<sub>2</sub>)<sub>3</sub> (2). Levels of theory: 1: MP2/cc-pVTZ, 2: MP2/SDB-cc-pVTZ (distances [Å], angles [°]).

	1 FC(NO <sub>2</sub>	2) <sub>3</sub>	2 BrC(NO <sub>2</sub>	)3
	GED <sup>[a]</sup>	MP2	GED <sup>[a]</sup>	MP2
<i>r</i> (Hal–C1) <sup>[b]</sup>	1.300(11) <sup>1</sup>	1.304	1.869(6) <sup>1</sup>	1.866
<i>r</i> (C1–N1)	1.517(4) <sup>2</sup>	1.517	1.529(3) <sup>2</sup>	1.533
<i>r</i> (N1–O1)	1.210(1) <sup>3</sup>	1.220	1.209(1) <sup>3</sup>	1.217
<i>r</i> (N1–O2)	1.211(1) <sup>3</sup>	1.221	1.214(1) <sup>3</sup>	1.221
$\alpha$ (Hal-C1-N1) <sup>[b]</sup>	110.2(6) <sup>4</sup>	110.5	112.5(3) <sup>4</sup>	112.2
α(C1-N1-O1)	114.1(3) <sup>5</sup>	114.2	115.7(2) <sup>5</sup>	115.4
α(C1-N1-O2)	116.3(3)5	116.4	115.9(2) <sup>5</sup>	115.7
α(01-N1-O2)	129.5(6) <sup>[d]</sup>	129.4	128.3(4) <sup>[d]</sup>	128.8
α(N-C1-N)	108.7(6) <sup>[d]</sup>	108.5	106.3(3) <sup>[d]</sup>	106.6
arphi (Hal-C1-N1-O1) <sup>[b]</sup>	-37.9(22) <sup>6</sup>	-39.9	-38.3(13) <sup>6</sup>	-44.2
arphi (Hal-C1-N1-O2) <sup>[b]</sup>	143.9(31) <sup>[d]</sup>	141.2	139.6(24) <sup>[d]</sup>	137.8
o(01,C1-N1-O2) <sup>[c]</sup>	-1.6(20) <sup>[d]</sup>	-1.0	1.9(18) <sup>[d]</sup>	-1.9
o(02,C1-N1-O1) <sup>[c]</sup>	1.5(20) <sup>[d]</sup>	1.0	-1.9(18) <sup>[d]</sup>	1.9
R <sub>str</sub> [%]	6.28	-	5.29	-

[a] Superscript numbers indicate independent groups of parameters in the least-squares (LSQ) analyses. In groups with more than one parameter the differences between parameter values were fixed at theoretical values to avoid strong correlations. In those cases the threefold standard deviations given in parentheses correspond to groups and not to parameters independently. [b] Hal = F(1), Br (2). [c] Out-of-plane angle (A,B-C-D) calculated as the angle between the A–C bond and the B-C-D plane. [d] Dependent parameter.

determined C–F bond length is considerably less precise than that of C–Br. In addition, the difference curves (Figure 2 and 3) show relative high overall quality of the refined structures.

A discussion of structural parameters will be given in direct comparison with the data obtained from the crystalline state by X-ray diffraction below.

#### Crystal structure analysis

Single crystals suitable for X-ray diffraction measurements were obtained by crystallization of the neat melt (1, 2) or from solution in *n*-hexane (3). Crystals of 1 and 2 were grown in situ in a capillary directly on the X-ray diffractometer. This was achieved by first establishing a solid–liquid equilibrium close to the melting point, then melting all solid but a tiny crystal seed (by using a thin copper wire as external heat source) followed by very slowly lowering the temperature until the whole capillary was filled with a single crystalline specimen. In contrast to the literature,<sup>[11]</sup> crystals of **3** did not show decomposition upon exposure to Mo<sub>Ka</sub> radiation and a good data set could

These are not the final page numbers! 77

www.chemeurj.org

Chem. Eur. J. 2014, 20, 1-13



ChemPubSoc

Europe

Figure 2. Experimental (O) and model (------) radial distribution functions of FC(NO<sub>2</sub>)<sub>3</sub> (1). The difference curve is shown below. Vertical bars indicate interatomic distances in the model.



BrC(NO<sub>2</sub>)<sub>3</sub> (2). The difference curve is shown below. Vertical bars indicate interatomic distances in the model.

be recorded. A full list of the crystallographic refinement parameters and structure data for compounds 1-3 is shown in

Chem. Eur. J. 2014, 20, 1-13

www.chemeurj.org

4

angles are listed in Table 5.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

**FF** These are not the final page numbers!

the Experimental Section (Table 8). All halogenotrinitromethanes 1-3 crystallize in the monoclinic crystal system, in the space group Cc(1),  $P2_1/c(2, 3)$ , respectively, each with four formula units per unit cell. The molecular structures of 1-3 are shown in Figures 4–6.

### Comparative discussion of molecular structures

In discussion of geometrical parameters below the traditional representations of their experimental errors in parentheses are used:  $1\sigma$  for values from XRD and  $3\sigma$  for the values from GED. The quantum chemically optimized structures at the levels



Figure 4. Molecular structure of 1 in the crystal. Selected distances and angles are listed in Table 5.





Figure 6. Molecular structure of 3. Selected distances and angles are listed in Table 5.

MP2/cc-pVTZ for F–, Cl– and MP2/SDB-cc-pVTZ for Br– and l– C(NO<sub>2</sub>)<sub>3</sub> agree well with experimentally determined values. Therefore, the wavefunctions obtained with these approximations were further used in Natural Bond Orbital (NBO)<sup>[16]</sup> and Atoms in Molecules (AIM)<sup>[17]</sup> calculations and a discussion of the various molecular features is in the Supporting Information. Additionally, Interacting Quantum Atoms (IQA)<sup>[18]</sup> calculations were performed by using RHF/cc-pVTZ (for **1** and CIC(NO<sub>2</sub>)<sub>3</sub>) and RHF/6-311G(d) (**2**, **3**) wavefunctions, which were computed for the MP2 geometries obtained with the same basis sets. The IQA theory allows a separation of the molecular energy into terms corresponding to atoms (in the form of the QTAIM atomic basins) and their pairs [Eq. (1)].

$$E_{\rm mol} = \sum_{\rm A} E_{\rm (A)} + \sum_{\rm A} \sum_{\rm B} E_{\rm (A,B)} \tag{1}$$

In Equation (1),  $E_{mol}$  is the total molecular energy,  $E_{(A)}$  is the energy of atom A and  $E_{(A,B)}$  is the interaction energy of atoms A and B. The summation is carried out over all atoms and their pairs. Thus, there is a possibility to identify stabilizing and destabilizing pairwise atom-atom interactions. The most important results of IQA calculations for the F–, Cl–, Br– and l– C(NO<sub>2</sub>)<sub>3</sub> molecules are summarized in Table 4 and used in the discussion below.

Relative to the conformation of the gas-phase structures, for which propeller-like  $C_3$  symmetry was assumed in the refinement of the electron diffraction data and confirmed by the good fit of these models to the experimental data, the crystal structures display the lower  $C_1$  symmetry. However, the trinitromethyl moieties of **1–3** reveal an approximate threefold axis of symmetry along the Hal–C bond.

The C–N bonds of **1–3** in the solid are between 1.501(7) and 1.548(7) Å (Table 5), similar to the equilibrium values obtained from the gas phase at 1.517(4) Å for **1** and 1.529(3) Å for **2**. All these values are remarkably larger than those for typical C–N

<b>Table 4.</b> Results of NBO, AIM, and IQA analyses of $HalC(NO_2)_3$ molecules (charges, volumes, and energies in atomic units).							
	1 FC(NO <sub>2</sub> ) <sub>3</sub>	CIC(NO <sub>2</sub> ) <sub>3</sub>	2 BrC(NO <sub>2</sub> ) <sub>3</sub>	3 IC(NO <sub>2</sub> ) <sub>3</sub>			
q <sub>NBO</sub> (Hal)	-0.29	0.15	0.27	0.42			
$q_{\rm NBO}({\rm C})$	0.73	0.29	0.20	0.10			
$q_{\rm NBO}({\rm N})$	0.59	0.60	0.59	0.59			
$q_{\rm NBO}({\rm O})^{[a]}$	-0.37	-0.37	-0.37	-0.38			
$q_{\text{AIM}}(\text{Hal})$	-0.72	0.01	0.17	0.35			
$q_{\text{AIM}}(C)$	1.70	0.97	0.85	0.74			
$q_{AIM}(N)$	0.52	0.54	0.54	0.54			
$q_{\text{AIM}}(\text{O})^{[a]}$	-0.43	-0.44	-0.44	-0.45			
V(Hal) <sup>[b]</sup>	1789	3962	4613	5205			
<i>V</i> (C) <sup>[b]</sup>	23	32	35	40			
E(Hal, C1)	-0.985	-0.251	-0.204	-0.198			
E(Hal, O1)	0.054	-0.011	-0.032	-0.052			
E(Hal, O2)	0.045	-0.003	-0.018	-0.031			
E <sub>(Hal, N1)</sub>	-0.088	-0.008	0.015	0.033			
E <sub>(C1, N1)</sub>	-0.059	-0.134	-0.177	-0.197			
E <sub>(N, N)</sub>	0.033	0.037	0.026	0.024			
E <sub>(O, O)</sub> <sup>[c]</sup>	0.027	0.029	0.027	0.028			
E <sub>(N, O)</sub> [c]	-0.049	-0.054	-0.049	-0.049			

Full Paper

[a] Average value. [b] Atomic basin volumes. [c] For the non-bonded pair with shortest interatomic distance.

bonds ( $\approx$ 1.47 Å).<sup>[19]</sup> Elongated C–N bonds in trinitromethyl moieties are not unusual and have been reported earlier.<sup>[12-13,20]</sup> In terms of NBO theory this can be explained by orbital interactions of two types. First is the  $lp(Hal) \rightarrow \sigma^*(C-N)$  interaction, in which in the NBO notation lp is one of the lone pairs of electron on a halogen atom and  $\sigma^*$  corresponds to an antibonding orbital of a C-N bond. The NBO second order perturbation theory analysis shows that the  $E^{(2)}$  energies of such interactions can be as large as 19.7, 17.5, 13.6 and 9.9 kcalmol<sup>-1</sup> for F-, Cl-, Br- and I- derivatives, respectively. The second type of orbital interactions relevant to the elongation of the C-N bonds is  $lp(O) \rightarrow \sigma^*(C-N)$  within independent C-NO<sub>2</sub> units. The corresponding  $E^{(2)}$  values are even somewhat larger than for those described above of the first type, the largest ones are 26.9, 26.5, 25.5 and 24.9 kcal mol<sup>-1</sup> along the same series of molecules. Both types of interactions lead to significantly increased occupations (0.22 e in average for all compounds) of anti-bonding  $\sigma^*(C-N)$  orbitals and, as a consequence, to a weakening and elongation of the corresponding C-N bonds.

There is a trend for the N-C-N angles to be slightly smaller for the HalC(NO<sub>2</sub>)<sub>3</sub> molecules with larger and less electronegative Hal from both the crystal and gas-phase data and the average solid state values nicely match with the gas-phase data (Table 5). As expected, the spatially more demanding bromine and iodine atoms in **2** and **3** lead to wider Hal-C-N and subsequently to narrower N-C-N angles. Due to the small fluorine atom, the conformation of **1** shows the most tetrahedronlike surrounding of the central carbon atom. An argument in the same direction can be derived from the view of the simple VSEPR model. The higher the electronegativity of Hal, the more polarized is the Hal–C bond towards Hal and consequently this bond requires less space at the carbon atom and allows the nitro groups to move further apart.

······································
······································

Che

5

# These are not the final page numbers! **77**



**Table 5.** Comparison of selected bond lengths and angles of HalC(NO<sub>2</sub>)<sub>3</sub> (Hal = F (1), Cl, Br (2), I (3)) in the crystal and gas-phase structures (distances [Å], angles [°]). Due to the higher symmetry in the gas phase, parameter values corresponding to groups of parameters in the crystal structures are provided (estimated standard deviations (esd) quoted are  $1\sigma$  for XRD and  $3\sigma$  for GED).

	1 FC(NO	,) <sub>3</sub>	1 CIC(NC	<b>D</b> <sub>2</sub> ) <sub>3</sub>	2 BrC(NO <sub>2</sub> )	3	<b>3</b> IC(NO <sub>2</sub> ) <sub>3</sub>
	XRD	GED <sup>(b)</sup>	XRD <sup>[12]</sup>	GED <sup>[10][c]</sup>	XRD	GED <sup>(b)</sup>	XRD
C1–Hal <sup>[a]</sup>	1.297(3)	1.300(11)	1.694(2)	1.712(12)	1.853(5)	1.869(6)	2.097(4)
C1N1	1.524(3)		1.543(2)		1.548(7)		1.533(5)
C1–N2	1.530(3)	1.517(4)	1.544(2)	1.513(9)	1.547(7)	1.529(3)	1.540(6)
C1–N3	1.520(3)		1.538(2) <sup>J</sup>		1.501(7)		1.531(6)
N1-01	1.204(3)		1.214(2)		1.214(7)		1.211(5)
N2-03	1.205(3)	1.210(1)	1.205(2)	1.213(3)	1.183(8)	1.209(1)	1.206(5)
N305	1.209(3)		1.209(2) <sup>J</sup>		1.198(7)		1.204(5)
N102	1.218(3)		1.211(2)		1.219(7)		1.212(5)
N2-04	1.209(3)	1.211(1)	1.216(2)	1.213(3)	1.208(8)	1.214(1)	1.208(5)
N306	1.217(3)		1.215(2) <sup>J</sup>		1.229(7)		1.207(5)
Hal-C1-N1	110.8(2)		112.3(2)		112.8(3)		112.4(3)
Hal-C1-N2	110.2(2)	110.2(6)	112.7(2)	112.1(15)	111.5(3)	112.5(3)	112.2(3)
Hal-C1-N3	110.3(2)		112.5(2) <sup>J</sup>		113.4(3)		113.8(3)
N1-C1-N2	108.1(2)		106.0(2)		105.2(4)		106.3(3)
N2-C1-N3	109.3(2)	108.7(6)	106.0(2)	106.7(16) <sup>[d]</sup>	106.3(5)	106.3(3)	105.8(3)
N3-C1-N1	108.3(2) <sup>J</sup>		106.8(2) <sup>J</sup>		107.0(4)		105.8(3)
Hal-C1-N-O	36.3(3) <sup>[e]</sup>	37.9(22)	42.2(2) <sup>[e]</sup>	49.3(1)	42.2(7) <sup>[e]</sup>	38.3(13)	44.8(4) <sup>[e]</sup>
[a] For compa	ison: Average Hal–C	<sup>3</sup> bond lengths: F–C	: 1.43 Å, Cl–C: 1.85 Å	, Br—C: 1.97 Å, I—C: 2.16	6 Å. <sup>[19a]</sup> [b] r <sub>e</sub> values. [c]	] Presumably r <sub>a</sub> value	es are given

in ref. [10c]. [d] The value of the parameter and error propagation were calculated from the data given in ref. [10c]. [e] Averaged value of Hal-C1-N-O1/3/5.

Expectedly, all C-NO<sub>2</sub> groups of 1-3 are essentially planar in the solid and gas phases. The nitro groups are arranged in a propeller-like twisted array (Figure 1 and Figure 7). In this context, the Hal-C-N-O dihedral angles are indicative for the rotation of the nitro groups out of the Hal C N plane. These dihedral angles are in the range of  $27.8-48.8^{\circ}$  in the crystal (for 1-**3**;  $CIC(NO_2)_3$ :<sup>[12]</sup> 37.0–46.6°) and in a narrow range of 37.9– 38.3  $^{\circ}$  in the gas-phase structures (for 1 and 2; CIC(NO<sub>2</sub>)<sub>3</sub>:<sup>[10a]</sup> 49.3°), which are all quite common values and comparable to various other trinitromethyl compounds.<sup>[10,13,20]</sup> The calculated NBO and AIM charges of nitrogen and oxygen atoms for the series F-, Cl-, Br-, and I-C(NO<sub>2</sub>)<sub>3</sub> are collected in Table 4. Both types of charges show high constancy along this series of compounds. In terms of the primitive model of charged atoms, the partial charge distributions of nitrogen ( $\delta^+$ ) and oxygen atoms  $(\delta^{-})$  in the nitro groups optimize propeller-like twisting intramolecular non-bonded N···O attractions while minimizing the

corresponding O···O repulsions. This interpretation is supported by results of the IQA calculations since the  $E_{(N,O)}$  and  $E_{(O,O)}$ values are negative and positive, respectively, in all discussed compounds. These N···O attractive interactions of two adjacent nitro groups in the trinitromethyl moieties are found for 1-3 in the range between 2.50 and 2.64 Å (Table 6), which are significantly lower than the sum of the van der Waals radii of nitrogen and oxygen (3.07 Å).<sup>[21]</sup> Very similar distances have been measured also by GED in the gas phase. Very strong attractive N···O interactions would be expected to lead to a pyramidalization of nitrogen atoms, but this is neither observed in the gas nor in the solid state. It can thus be concluded that the effect of N---O interactions is of minor influence on the molecular structures. The structure motif of twisted nitro groups with attractive N···O interactions is also found in the crystal structures of the comparable compounds  $HC(NO_2)_3^{[20c]}$  and  $CIC(NO_2)_3^{[12]}$ Similar to  $CIC(NO_2)_{3}^{[12]}$  the oxygen atoms in 1-3 involved in

these intramolecular N····O contacts are those most distant to the halogen atom (Figure 7).

The other oxygen atoms in 1– **3** display short distances to the corresponding halogen atoms in the range of 2.56 to 2.62 Å (crystal) and 2.58 Å (gas phase) for **1**, 2.99 to 3.01 Å (crystal) and 2.98 Å (gas phase) for **2**, and 3.16 to 3.20 Å (crystal) for **3**. These values are substantially lower than the sum of the van der Waals radii for these atom pairs ( $r_{(F+O)}=2.99$ ,  $r_{(Br+O)}=3.37$ , and  $r_{(I+O)}=3.50$  Å),<sup>[21]</sup> but this

**Figure 7.** Intramolecular Hal···O (Hal = F (1), Br (2), I (3)) and N···O interactions of 1 (left), 2 (center) and 3 (right), displayed by dashed lines. Thermal ellipsoids are drawn at the 25 (1), 8 (2), and 12% (3) probability level for clarity. Selected distances [Å]: FC(NO<sub>2</sub>)<sub>3</sub> (1): F1···O1 2.609(3), F1···O3 2.563(3), F1···O5 2.616(3), N1···O4 2.637(3), N2···O6 2.615(3), N3···O2 2.604(3); BrC(NO<sub>2</sub>)<sub>3</sub> (2): Br1···O1 3.007(5), Br1···O3 2.984(7), Br1···O5 3.002(8), N1···O4 2.518(9), N2···O2 2.539(9), N3···O4 2.504(11); IC(NO<sub>2</sub>)<sub>3</sub> (3): I1···O1 3.158(4), I1···O3 3.194(5), I1···O5 3.204(4), N1···O4 2.554(6), N2···O6 2.542(6), N3···O2 2.556(5).

Chem. Eur. J. 2014, 20, 1-13

www.chemeurj.org

# © 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

6



	1 FC(	(NO <sub>2</sub> ) <sub>3</sub>	1 CIC(NO <sub>2</sub> ) <sub>3</sub> <sup>[12]</sup>	<b>2</b> BrC(	NO <sub>2</sub> ) <sub>3</sub>	3 IC(NO <sub>2</sub> ) <sub>3</sub>
	XRD	GED	XRD	XRD	GED	XRD
N····O <sub>intra</sub> <sup>[a]</sup>	2.637(3)	)	2.571(2)	2.518(9)	]	2.554(6)
	2.615(3)	2.611(7)	2.547(2)	2.539(9)	2.543(4)	2.542(6)
	2.604(3)	J	2.554(2)	2.504(11)	ļ	2.556(5)
HalO <sub>intra</sub> <sup>[a]</sup>	2.609(3)	1	2.939(2)	3.007(5)	1	3.158(4)
	2.563(3)	2.576(6)	2.897(2)	2.984(7)	2.980(4)	3.194(5)
	2.616(3)	J	2.903(2)	3.002(8)		3.204(4)
HalO <sub>inter</sub> [a]	2.782(3)	_	2.950(2)	3.035(5)	-	2.930(3)
$C-Hal{O_{inter}}$	141.0(2)	-	172.8(1)	165.3(2)	-	172.8(2)

does not necessarily indicate attractive interactions between the oxygen and halogen atoms. Due to the particularly high electron-withdrawing properties of the trinitromethyl moiety, the C-Hal bonds are shorter than usual, and consequently, sterically overcrowded structures are observed.

The electron-withdrawing strength can be estimated using the Taft parameter ( $\sigma^*$ ), which reflects polar (inductive, field, and resonance) effects.<sup>[22]</sup> The trinitromethyl moiety has a very large value of that polar substituent constant of  $\sigma^* = 4.54$ ,<sup>[23]</sup> compared with the smaller ones for fluorine (3.19), chlorine (2.94), bromine (2.80), and iodine (2.22).<sup>[24]</sup> Consequently, conventional (electrostatic) properties of the halogen atoms are expected to change under the action of the trinitromethyl moiety, even the strongly electronegative fluorine atom.

Electronegativity can also be attributed to composition of  $\sigma$ bonding orbitals. NBO calculations of BrC(NO<sub>2</sub>)<sub>3</sub> have shown that  $\sigma(Br-C)$  can be described as being composed of  $0.68(sp^{6.7})_{Br}$  + 0.73(sp<sup>2.8</sup>)<sub>C</sub>. The polarization coefficients 0.73 > 0.68 can serve as indicators of electronegativity and show that in 2 bromine is less electronegative than the carbon atom due to the nitro-substituent effect. For comparison we have performed similar calculations for the BrC(CH<sub>3</sub>)<sub>3</sub> molecule. In this case the inverted picture was obtained: The composition of the  $\sigma(\text{Br-C})$  orbital was  $0.73(\text{sp}^{6.1})_{\text{Br}} + 0.68(\text{sp}^{5.7})_{\text{C}}$  indicating a normal situation in which bromine is more negative than the carbon atom. The same relationship has been found for  $\sigma$ (Hal– C) orbital composition in the I-, but not for the CI-, and especially for the F- derivatives. Nevertheless, the trend of decreasing halogen electronegativity with respect to that of the carbon atom upon transition from Hal-C(CH<sub>3</sub>)<sub>3</sub> to Hal-C(NO<sub>2</sub>)<sub>3</sub> was observed for all types of halogen atoms. Another observation is the much higher s contribution in the carbon hybrid to the Br–C bond in BrC(NO<sub>2</sub>)<sub>3</sub> (sp<sup>2.8</sup>) than in BrC(CH<sub>3</sub>)<sub>3</sub> (sp<sup>5.7</sup>), again explaining the shorter bond in the first. It may thus be concluded that electronegativity plays an important role in shortening of the Hal-C bonds in the HalC(NO<sub>2</sub>)<sub>3</sub> molecules.

QTAIM calculations support this view by comparing the charges and basin volumes of halogen atoms in HalC(NO<sub>2</sub>)<sub>3</sub> and HalC(CH<sub>3</sub>)<sub>3</sub> molecules. The values for HalC(NO<sub>2</sub>)<sub>3</sub> are given in Table 4. The AIM charges of the halogen atoms in HalC(CH<sub>3</sub>)<sub>3</sub> molecules are -0.69, -0.31, -0.20, and -0.07 e in the series of F-, Cl-, Br-, and I- derivatives, respectively. These results show the systematically smaller values of charges of all halogen atoms in HalC(CH<sub>3</sub>)<sub>3</sub> compared with those in HalC(NO<sub>2</sub>)<sub>3</sub>. This is consistent with the conclusions on electronegativity made before.

The AIM basin volumes of halogen atoms in HalC(CH<sub>3</sub>)<sub>3</sub> are 1624, 3486, 4294, and 4937 Bohr<sup>3</sup>, and in HalC(NO<sub>2</sub>)<sub>3</sub> the corresponding basin volumes are systematically larger (Table 4). This indicates that in  $HalC(NO_2)_3$  the halogen atoms

are more diffuse. Also interesting is to compare basin volumes of the central carbon atoms in both series of compounds. Table 4 shows these quantities for the HalC(NO<sub>2</sub>)<sub>3</sub> molecules. The corresponding values for HalC(CH<sub>3</sub>)<sub>3</sub> molecules are 36, 44, 44, and 47 Bohr<sup>3</sup>. Thus, the carbon atoms are more compact in all HalC(NO<sub>2</sub>)<sub>3</sub> derivatives, in agreement with the concept of electronegativity and explaining the shortening of the Hal-C bonds in these molecules. Therefore, these bonds in 1-3, F-C 1.297(3) Å (crystal), 1.300(11) Å (gas phase); Br-C 1.853(5) Å (crystal), 1.869(6) Å (gas phase); I-C 2.097(4) Å (crystal), respectively, are remarkably shorter than average Hal-C<sub>sp</sub><sup>3</sup> bond lengths (F-C: 1.43 Å, Br-C: 1.97 Å, I-C: 2.16 Å).<sup>[19a]</sup>

Gas-phase equilibrium structures determined by GED allow a direct comparison with theoretically calculated structures. Interestingly, the previously predicted length of the C-F bond in  $FC(NO_2)_3$  (1.305 Å on the B3LYP/6-311  $+\,G(d,p)$  level)  $^{[9b]}$  agrees well with the value measured in this work at 1.300(11) Å. However, the same combination of DFT functional and basis set gives overestimated lengths for the C-Br bond (1.894 Å)<sup>[9b]</sup> versus the experimental value of 1.869(6) Å. The corresponding thermally averaged  $r_a$  value found in this work (1.876(6) Å) is also slightly smaller, in fact, almost equal to the  $r_a$  values from previous GED measurements (1.885(9) and 1.894(9) Å).<sup>[10a,c]</sup>

Concerning the Hal-O contacts in HalC(NO<sub>2</sub>)<sub>3</sub> according to the simplest model, the calculated AIM charges, predict repulsion for the pair F···O and attraction for the pairs Br···O, and I---O. The CI---O contact is on the border between repulsion and attraction due to the almost neutral charge of the chlorine atom (0.01 e). Indeed, the  $E_{(Hal,O)}$  energies (Table 4) from the more advanced IQA theory show that the F···O contacts destabilize the molecule, the Cl-O contacts play only a minor role, whereas the Br---O and I---O should stabilize the respective molecules. The opposite trend is observed for the Hal...N contacts, in which F···N stabilizes the molecule, whereas Br···N and I···N are destabilizing. The Cl-N contacts show only very weak interactions as in the case of the Cl-O contacts. Thus, the shortening of the all Hal-C bonds in each of HalC(NO<sub>2</sub>)<sub>3</sub> cannot be explained by a single model based on the analysis of intramolecular contacts of atoms.

Previously performed calculations showed the surfaces of the halogen atoms in F-, Cl- and Br-C(NO<sub>2</sub>)<sub>3</sub> to be entirely

Chem. Eur. J. <b>2014</b> , 20, 1 – 13	www.chemeurj.org
These are not the	final page numbers! 77

7



positive, with the most positive site on the extension of the C-Hal bond.<sup>[12]</sup> The presence and magnitude of a positive halogen potential depends upon both the halogen and electronwithdrawing strength of the remainder of the molecule.<sup>[25]</sup> In this work we have calculated the total electrostatic potential (ESP) for the I- derivative and, for consistency, for all other discussed molecules (Figure 8). Since the computed ESP values in

#### Intermolecular interactions in the crystals

Besides intramolecular interactions, various intermolecular interactions determine the arrangement of the molecules within their crystals. Intermolecular N···O contacts with values only slightly lower than the sum of the van der Waals radii for these atoms (3.07 Å)<sup>[21]</sup> suggest weak, but attractive interactions. The shortest intermolecular N····O



Figure 8. Total electrostatic potentials of the F-, CI-, Br-, and I-C(NO<sub>2</sub>)<sub>3</sub> molecules mapped on the isosurfaces of electron density (0.001 eBohr<sup>-3</sup>). Contour plots are total electrostatic potentials in the planes of three atoms Hal. C1, and O1. Blue color displays positive values, red color displays negative values.

the previous work<sup>[12]</sup> were for points of only one isosurface of electron density (0.001 eBohr<sup>-3</sup>) and to extend our knowledge about this property of the molecules, we have also calculated contour plots of ESP for the planes at which Hal, C, and O atoms reside. Figure 8 clearly shows that the ESPs on the lines (and regions) between halogen and oxygen atoms are entirely positive and cannot serve as indicators of attractive interactions between Hal and O atoms. In fact, the total ESP is positive in areas between all pairs of bonded and non-bonded atoms. However, the bonded atoms, as well as some pairs of non-bonded atoms, demonstrate stabilizing interactions as we already know from the IQA calculations (Table 4). Thus, total ESPs are hardly useful in the discussion of intramolecular properties of these small molecules, but could rather be helpful in the discussion of intermolecular interactions.

drawing. Therefore, the  $\sigma$ -hole is least positive for the fluorine compound 1 and most positive for the iodine compound 3. The  $\sigma$ -hole bonding R–X···B (B=Lewis base), in this context also commonly called halogen bonding, is the resulting noncovalent interaction that may occur with a negative site.<sup>[25,27]</sup> The interaction is highly directional, along the extension of the covalent bond, giving rise to the  $\sigma$ -hole.

The strongest halogen bonding of all halogenotrinitromethanes shows the iodine compound 3 due to the most positive  $\sigma$ -hole and the C–Hal···O angle of 172.8(1)<sup> $\circ$ </sup> close to the ideal value of 180°. This leads even to significantly shorter intermolecular than intramolecular Hal--O contacts (Table 6 and Figure 9). The influence of this interaction on the general bonding situation decreases along the series from the iodine compound (3) to the fluorine compound (1). Therefore,

www.chemeurj.org

8

## © 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

The positive character of this

more polarizable and less elec-

tronegative halogens, and when

the remainder of the molecule becomes more electron-with-

# **KR** These are not the final page numbers!





**Figure 9.** Intermolecular Hal···O (Hal = F (1), Br (2), I (3)) interactions of 1 (left), 2 (center) and 3 (right), displayed by dashed lines. Thermal ellipsoids are drawn at the 25 (1), 8 (2), and 12% (3) probability level for clarity. Selected intermolecular distances [Å]:  $FC(NO_{2})_{3}$  (1): F···O 2.782(3);  $BrC(NO_{2})_{3}$  (2): Br···O 3.035(5);  $IC(NO_{2})_{3}$  (3): I···O 2.930(3).

**1** shows an unfavorable C–Hal···O angle of 141.0(2)  $^{\circ}$  and much longer intermolecular than intramolecular Hal···O contacts (Table 6 and Figure 9). Computational investigations predicted that halogen bonding is also likely to affect the Hal–C bond length, whereas both longer and shorter ones are possible, depending on the properties of the donor and acceptor.<sup>[28]</sup> Calculated values for ClC(NO<sub>2</sub>)<sub>3</sub> revealed no relevant contribution of the halogen bonding to the Cl–C bond length.<sup>[12]</sup>

### Conclusion

The molecular structures of the halogenotrinitromethanes  $HalC(NO_2)_3$  (Hal = F (1), Br (2), and I (3)), have been determined in the crystalline state by X-ray diffraction, as well as for the free molecules in the gas phase by electron diffraction. The gas-phase structures are gualitatively in agreement with structures in the crystal phase. All halogenotrinitromethanes 1-3, as well as the previously described CIC(NO<sub>2</sub>)<sub>3</sub>, illustrate various intramolecular non-bonded interactions in the free molecules and intermolecular interactions in the crystal structures. The intramolecular N···O, O···O, and Hal···O interactions, both competitors for the degree of rotation of the nitro groups about the C-N bonds, lead to propeller-type conformations favoring these interactions. The Hal-O interactions are repulsive in the view of electrostatic potentials between the atoms, while stabilizing in all cases but Hal = F(1) in the equilibrium geometries according to Interacting Quantum Atoms (IQA) calculations. The high electronegativity of the halogenotrinitromethyl moiety leads to unusually short Hal-C (Hal = F (1), Br (2), I (3)) bonds. This can be rationalized by different models: 1) A high s contribution to the carbon hybrid involved in the Hal-C bonds and 2) a high contribution of  $Ip(Hal) \rightarrow \sigma^*(C-N)$  interactions in terms of the NBO view, as well as 3) a small atomic basin of the carbon atom in the QTAIM view. Intermolecular attractive Hal-O interactions in the halogenotrinitromethanes can be explained in terms of the halogen bonding concept based on a positive  $\sigma$ -hole on the far side with respect to the Hal–C bond.

### **Experimental Section**

### General procedures

The solvents carbon tetrachloride and *n*-hexane were dried by standard methods and freshly distilled prior to use. Bromine (Fluka), iodine monochloride and Selectfluor fluorinating reagent (both Sigma–Aldrich) were used as received. An aqueous solution of trinitromethane (30%, stabilized with urea; Aerospace Propulsion Products B.V.) was extracted and purified by precipitation of its potassium salt and subsequent acidification. Potassium trinitromethanide

was synthesized by reaction of trinitromethanide with potassium hydroxide in water at ambient temperature. Raman spectra were recorded with a Bruker MultiRAM FT-Raman instrument fitted with a liquid nitrogen cooled germanium detector and a Nd:YAG laser  $(\lambda = 1064 \text{ nm}, 300 \text{ mW})$ . Infrared (IR) spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSampl/R II ATR device. All spectra were recorded at ambient temperature; the samples were neat liquids or solids. NMR spectra were recorded at 25 °C with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me<sub>4</sub>Si (<sup>1</sup>H, 400.2 MHz; <sup>13</sup>C, 100.6 MHz), MeNO<sub>2</sub> (<sup>15</sup>N, 40.6 MHz), and CCl<sub>3</sub>F (<sup>19</sup>F, 376.5 MHz). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (EI+). All fragments are referred to the isotope with the highest natural abundance. Elemental analyses (C/N) were performed with an Elementar vario EL analyzer.

### Quantum chemical calculations

Geometry optimizations using MP2 approximation<sup>[29]</sup> with cc-pVTZ and SDB-cc-pVTZ have been carried out by using Firefly QC package,<sup>[30]</sup> which is partially based on the GAMESS (US) source code.<sup>[31]</sup> Calculations of vibrational frequencies and numeric cubic force fields were done on the same level of theory with the Gaussian 03 program package.<sup>[32]</sup> The 6–311G(d) basis set<sup>[33]</sup> for the iodine atom has been taken from the EMSL Basis Set Library.<sup>[34]</sup> The QTAIM and IQA calculations were performed using the AIMAII program.<sup>[35]</sup>

#### Gas-phase electron-diffraction experiment

The electron diffraction patterns were recorded on the heavily improved Balzers Eldigraph KD-G2 gas-phase electron diffractometer<sup>[36]</sup> at the University of Bielefeld. The experimental details (Table 7) are presented elsewhere.<sup>[36]</sup> The electron diffraction patterns were measured on the Fuji BAS-IP MP 2025 imaging plates, which were scanned using a calibrated Fuji BAS-1800II scanner. The intensity curves (Figure S1 and S2 of the Supporting Information) were obtained by applying the method described earlier.<sup>[37]</sup> Sector function and electron wavelengths were refined<sup>[38]</sup> using

Chem.	Eur. J.	<b>2014</b> , 20, 1	l – 13	www.ch

ww.chemeurj.org

9

These are not the final page numbers! **77** 



Table 7. Details of the gas-phase electron diffraction experiment for 1 and 2.						
Parameter	1 FC	(NO <sub>2</sub> ) <sub>3</sub>	<b>2</b> B	rC(NO <sub>2</sub> ) <sub>3</sub>		
d <sub>nozzle-detector</sub> [mm]	250.0	500.0	250.0	500.0		
U <sub>acceleration</sub> [kV]	60	60	60	60		
I <sub>fast electrons</sub> [μA]	0.95	0.57	1.54	0.51		
$\lambda_{\text{electron}}^{[a]}$ [Å]	0.048901	0.048466	0.048647	0.048511		
T <sub>nozzle</sub> [K]	296	294	353	353		
p <sub>sample</sub> <sup>[b]</sup> [mbar]	2×10 <sup>-5</sup>	5×10 <sup>-5</sup>	2×10 <sup>-5</sup>	3×10 <sup>-5</sup>		
p <sub>residual gas</sub> [c] [mbar]	$5 \times 10^{-7}$	6×10 <sup>-7</sup>	$5 \times 10^{-7}$	7×10 <sup>-7</sup>		
t <sub>exposure</sub> [s]	10	8	4, 5, 6	5, 7, 9		
s range [Å <sup>-1</sup> ]	8.6-34.0	2.2-17.4	8.6-32.0	2.2–17.0		
inflection points <sup>[d]</sup>	5	3	6	5		

[a] Determined from  $C_6H_6$  diffraction patterns measured in the same experiment. [b] During the measurement. [c] Between measurements. [d] Number of inflection points on the background lines (see Figure S1 and S2 in the Supporting Information).

benzene diffraction patterns, recorded along with the substances under investigation.

**Gas-phase electron-diffraction structural analysis:** The structural analysis was performed with the UNEX program.<sup>[39]</sup> All refinements were done using two intensity curves simultaneously (see Figure S1 and S2 of Supporting Information), one from short and another from long camera distance, which were obtained by averaging independent intensity curves measured in the experiment. For the definition of independent geometrical parameters and their groups in least-squares refinements see Table 3. An additional dihedral angle  $\varphi$ (O4-C2-N3-O5) was used as an independent parameter to define the position of the atom O5 (Figure S5 in the Supporting

Information). The structures of  $FC(NO_2)_3$  (1) and  $BrC(NO_2)_3$  (2) were assumed to be of  $C_3$  symmetry. The differences between values of parameters in one group were kept fixed at the values taken from MP2/cc-pVTZ and MP2/SDB-ccpVTZ calculations. Mean square amplitudes were refined in groups (see Tables S1 and S2 in the Supporting Information). For this purpose the scale factors (one per group) were used as independent parameters. Thus, the ratios between different amplitudes in one group were fixed on the theoretical values, calculated from guadratic and cubic force fields by using the SHRINK program.[40] The final determined structural parameters are given in Table 3. Correlation coefficients are provided in the Supporting Information.

#### X-ray Crystallography

For compound 1 and 2 a Nonius Kappa CCD and for compound 3, an Oxford Xcalibur3 diffractometer with a CCD area detector were employed for data collection using  $Mo_{K\alpha}$  radiation ( $\lambda = 0.71073$  Å). The

Chem. Eur. J. 2014, 20, 1 – 13

www.chemeurj.org

10

structures were solved using direct (SHELXS97<sup>[41]</sup> methods or SIR2004<sup>[42]</sup>) and refined by fullmatrix least-squares on  $F^2$ (SHELXL).<sup>[41]</sup> All atoms were refined anisotropically. ORTEP plots are shown with thermal ellipsoids at the 50 (1, 3) or 30% (2) probability level, except for Figures 7 and 9. CCDC-917831 (1), CCDC-917832 (2), and CCDC-917833 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data\_request/cif. See Table 8 for the crystal and structure refinement data.

### Syntheses

**CAUTION!** All high nitrogen and oxygen containing compounds are potentially explosive energetic materials, although no hazards were observed during the preparation and handling of these compounds. Nevertheless, this necessitates additional meticulous safety precautions (earthed equipment, Kevlar gloves, Kevlar sleeves, face shield, leather coat, and ear plugs). In addition, especially fluorotrinitromethane shows significant degrees of toxicity. Particular care should be exercised in handling of this material and derivatives.

<b>Table 8.</b> Crystal and structure refinement data for $FC(NO_2)_3$ (1), $BrC(NO_2)_3$ (2), and $IC(NO_2)_3$ (3).						
	1 FC(NO <sub>2</sub> ) <sub>3</sub>	2 BrC(NO <sub>2</sub> ) <sub>3</sub>	<b>3</b> IC(NO <sub>2</sub> ) <sub>3</sub>			
chemical formula	CFN <sub>3</sub> O <sub>6</sub>	CBrN <sub>3</sub> O <sub>6</sub>	CIN <sub>3</sub> O <sub>6</sub>			
$F_{\rm w}$ [g mol <sup>-1</sup> ]	169.03	229.93	276.93			
crystal dimensions [mm]	0.30×0.30×0.23	0.30×0.30×0.21	0.37 ×0.19 ×0.03			
crystal description	colorless block	colorless block	pale-yellow block			
crystal system	monoclinic	monoclinic	monoclinic			
space group (No.)	Cc (9)	P2 <sub>1</sub> /c (14)	P2 <sub>1</sub> /c (14)			
a [Å]	5.4980(3)	9.9590(15)	9.6928(4)			
b [Å]	19.1919(11)	6.5930(8)	6.6961(2)			
c [Å]	5.4068(3)	10.5270(11)	10.6304(3)			
β [°]	104.505(3)	102.812(10)	93.782(3)			
V [Å <sup>3</sup> ]	552.33(5)	673.99(15)	688.45(4)			
Ζ	4	4	4			
$ ho_{ m calcd}~[ m gcm^{-3}]$	2.033	2.266	2.672			
$\mu$ [mm <sup>-1</sup> ]	0.229	6.092	4.645			
<i>T</i> [K]	100(2)	270(2)	173(2)			
F(000)	336	440	512			
heta range [°]	3.97-30.00	3.67-24.99	4.50-26.00			
index ranges	$-7 \leq h \leq 7$	$-11 \le h \le 11$	$-10 \le h \le 11$			
	$-26 \le k \le 26$	$0 \leq k \leq 7$	$-8 \leq k \leq 8$			
	$-7 \le l \le 7$	0 ≤ <i>l</i> ≤ 12	−13 <i>≤l</i> ≤12			
reflns measured	6048	11 022	3317			
reflns independent	807	1167	1325			
reflns unique	794	941	1103			
R1, wR2 (2 $\sigma$ data)	0.0350, 0.0902	0.0448, 0.1017	0.0306, 0.0769			
R1, wR2 (all data)	0.0355, 0.0908	0.0583, 0.1088	0.0363, 0.0788			
data/restraints/ parameters	807/100/2	1167/100/0	1325/100/0			
GOF on F <sup>2</sup>	1.095	1.073	0.970			
residual $ ho_{ extsf{min/max}}$ [e Å $^{-3}$ ]	-0.31/0.43	-0.56/0.66	-0.92/1.13			

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Synthesis of fluorotrinitromethane (1): Potassium trinitromethanide (5.67 g, 30.0 mmol) was slowly added at  $0^{\circ}$ C into a colorless solution of Selectfluor (11.7 g, 33.0 mmol) in water (150 mL). After stirring for 12 h at ambient temperature, the reaction mixture turned colorless. Evaporation of the product out of the reaction mixture into a cooling trap yielded 4.27 g (84%) of 1 as a colorless oil. M.p. –45  $^{\circ}\text{C};~^{13}\text{C}\{^{1}\text{H}\}\,\text{NMR}$  (CDCl\_3):  $\delta\!=\!113.7\,\text{ppm}$  (doublet of septets,  ${}^{1}J_{C-F} = 333.4$ ,  ${}^{1}J_{C-14N} = 12.1$  Hz,  $C(NO_{2})_{3}$ );  ${}^{15}N$  NMR (CDCl<sub>3</sub>):  $\delta\!=\!-40.7$  (doublet,  $^2\!J_{\rm N\!-\!F}\!=\!14.2$  Hz, NO\_2) ppm;  $^{19}{\rm F}$  NMR (CDCl\_3):  $\delta\!=$ -87.3 ppm (septet,  ${}^{2}J_{F-14N}$  = 10.2 Hz); Raman:  $\tilde{\nu}$  = 1622 (16,  $\nu_{as}NO_{2}$ ), 1358 (30), 1298 (28, v<sub>s</sub>NO<sub>2</sub>), 1011 (8), 857 (100, vCN), 800 (6), 641 (2), 523 (9), 407 (22), 365 (66), 326 (12), 223 (8), 184 cm<sup>-1</sup> (19); IR:  $\tilde{\nu} = 1606$  (vs,  $\nu_{as}NO_2$ ), 1357 (w), 1288 (s,  $\nu_sNO_2$ ), 1012 (m), 856 (m,  $\nu$ CN), 794 cm<sup>-1</sup> (vs); MS (El+): m/z (%)=169 (1) [ $M^+$ ], 46 (100) [NO<sub>2</sub><sup>+</sup>]; elemental analysis calcd (%) for CFN<sub>3</sub>O<sub>6</sub> (169.03): C 7.11, N 24.86; found: C 7.27, N 24.95.

Synthesis of bromotrinitromethane (2): Bromine (13.9 g, 87.0 mmol) was added into an aqueous solution of trinitromethane (43.8 g in relation to 30% aqueous solution, 87.0 mmol in relation to pure trinitromethane) at ambient temperature. After stirring the orange reaction mixture for 30 min, the slightly yellow organic phase was extracted and the product crystallized at 0°C. The crystals of the crude product were filtered and washed with ice-cold water (3×10 mL). Warming the product to ambient temperature yielded 15.6 g (78%) of **2** as colorless oil. M.p.  $10^{\circ}$ C;  $^{13}$ C{ $^{1}$ H} NMR (CDCl<sub>3</sub>):  $\delta = 121.9 \text{ ppm}$  (septet,  ${}^{1}J_{C-14N} = 8.1 \text{ Hz}$ ,  $C(NO_{2})_{3}$ );  ${}^{15}N$  NMR (CDCl<sub>3</sub>):  $\delta = -34.8 \text{ ppm}$  (s, NO<sub>2</sub>); Raman:  $\tilde{\nu} = 1615$  (14,  $\nu_{as}NO_2$ ), 1346 (21), 1294 (8, v<sub>s</sub>NO<sub>2</sub>), 981 (3), 919 (11), 840 (88, vCN), 790 (4), 643 (2), 389 (21), 377 (24), 343 (100), 225 (22), 205 (12), 171 cm<sup>-1</sup> (26); IR:  $\tilde{\nu} = 1595$  (vs,  $\nu_{as}NO_2$ ), 1345 (m), 1277 (s,  $\nu_sNO_2$ ), 979 (m), 918 (w), 838 (s,  $\nu$ CN), 784 cm<sup>-1</sup> (vs); MS (El+): m/z (%) = 91 (8) [CBr<sup>+</sup>], 79 (3) [Br<sup>+</sup>], 46 (100) [NO<sub>2</sub><sup>+</sup>], 30 (66) [NO<sup>+</sup>]; elemental analysis calcd (%) for CBrN<sub>3</sub>O<sub>6</sub> (229.93): C 5.22, N 18.28; found: C 5.34, N 18.10.

Synthesis of iodotrinitromethane (3): lodine monochloride (2.92 g, 18.0 mmol) was added into a yellow suspension of potassium trinitromethanide (3.40 g, 18.0 mmol) in dry carbon tetrachloride (40 mL) at ambient temperature. After stirring the reaction mixture for 1 h at 70°C, the dark-purple solution was filtered and washed with an ice-cold silver nitrate solution (40 mL, 20% aqueous solution). The organic phase was filtered to remove precipitated silver iodide and dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, the yellow solid was washed with ice-cold carbon tetrachloride (2×10 mL). Crystallization of the product from *n*-hexane yielded 1.0 g (20%) of **3** as pale-yellow crystals. M.p. 55 °C;  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta =$ 106.7 ppm (septet,  ${}^{1}J_{C-14N} = 6.4$  Hz,  $C(NO_{2})_{3}$ );  ${}^{15}N$  NMR (CDCl<sub>3</sub>):  $\delta =$ -30.8 ppm (s, NO<sub>2</sub>); Raman:  $\tilde{\nu} = 1616$  (5,  $\nu_{as}NO_2$ ), 1597 (35,  $\nu_{as}NO_2$ ), 1348 (37), 1298 (7, v<sub>s</sub>NO<sub>2</sub>), 1287 (5, v<sub>s</sub>NO<sub>2</sub>), 947 (5), 916 (14), 839 (97, vCN), 789 (5), 649 (5), 607 (2), 400 (31), 371 (39), 309 (100), 224 (31), 183 (61), 159 cm  $^{-1}$  (33); IR:  $\tilde{\nu}\!=\!1597$  (s,  $\nu_{\rm as}{\rm NO}_2$ ), 1583 (vs,  $\nu_{\rm as} {\rm NO}_2$ ), 1346 (m), 1290 (s,  $\nu_{\rm s} {\rm NO}_2$ ), 1278 (s,  $\nu_{\rm s} {\rm NO}_2$ ), 944 (m), 913 (m), 837 (s,  $\nu$ CN), 782 cm<sup>-1</sup> (vs); MS (EI+): m/z (%) = 277 (2)  $[M^+]$ , 231 (1) [*M*<sup>+</sup>-NO<sub>2</sub>], 139 (5) [CI<sup>+</sup>], 127 (100) [I<sup>+</sup>], 46 (39) [NO<sub>2</sub><sup>+</sup>], 30 (68) [NO<sup>+</sup>]; elemental analysis calcd (%) for CIN<sub>3</sub>O<sub>6</sub> (276.93): C 4.34, N 15.17; found: C 4.57, N 15.34.

### Acknowledgements

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Deutsche Forschungsgemeinschaft (DFG, core facility GED@BI), the Alexander von Humboldt Stiftung (stipend to Y.V.V.), the U.S. Army Research Labo-

ratory (ARL) under grant no. W911NF-09-2-0018, the Armament Research, Development and Engineering Center (ARDEC) under grant no. W911NF-12-1-0467, and the Office of Naval Research (ONR) under grant nos. ONR.N00014-10-1-0535 and ONR.N00014-12-1-0538 is gratefully acknowledged. The research students Sebastian Zech, M.Sc. and Andreas Ahlers, M.Sc. are thanked for their participation in this project.

**Keywords:** electron diffraction · halogens · NMR spectroscopy · quantum chemistry · X-ray diffraction

- [1] L. Birckenbach, K. Huttner, W. Stein, Ber. Dtsch. Chem. Ges. B 1929, 62B, 2065-2075.
- [2] a) L. Schischkoff, Justus Liebigs Ann. Chem. 1857, 103, 364-366; b) A.
   Hantzsch, A. Rinckenberger, Ber. Dtsch. Chem. Ges. 1899, 32, 628-641.
- [3] a) L. Schischkoff, Justus Liebigs Ann. Chem. 1857, 101, 213–217; b) C. O. Parker, W. D. Emmons, H. A. Rolewicz, K. S. McCallum, Tetrahedron 1962, 17, 79–87.
- [4] a) V. I. Pepkin, Y. N. Matyushin, G. K. Khisamutdinov, V. I. Slovetskii, A. A. Fainzil'berg, *Khim. Fiz.* **1993**, *12*, 1399–1403; b) G. K. Khisamutdinov, V. I. Slovetsky, Y. M. Golub, S. A. Shevelev, A. A. Fainzil'berg, *Russ. Chem. Bull.* **1997**, *46*, 324–327.
- [5] W. Will, Ber. Dtsch. Chem. Ges. 1914, 47, 961-965.
- [6] A. K. Macbeth, D. D. Pratt, J. Chem. Soc. Trans. 1921, 119, 354-358.
- [7] a) V. Grakauskas, K. Baum, J. Org. Chem. 1968, 33, 3080–3082; b) L. T. Eremenko, A. A. Borisenko, S. I. Petrov, V. F. Andronov, Russ. Chem. Bull. 1968, 17, 423–424; c) M. D. Coburn, C. B. Storm, D. W. Moore, T. G. Archibald, Magn. Reson. Chem. 1990, 28, 16–20.
- [8] a) V. A. Shlyapochnikov, A. A. Fainzil'berg, S. S. Novikov, *Russ. Chem. Bull.* 1962, *11*, 478–479; b) V. A. Shlyapochnikov, D. V. Levchenkov, A. B. Kharitonkin, *Russ. Chem. Bull.* 2001, *50*, 1173–1180.
- [9] a) S. G. Vulfson, A. P. Timosheva, A. N. Vereshchagin, B. A. Arbuzov, V. A. Shlyapochnikov, *J. Mol. Struct.* **1977**, *40*, 225–231; b) D. V. Levchenkov, A. B. Kharitonkin, V. A. Shlyapochnikov, *Russ. Chem. Bull.* **2001**, *50*, 385–389.
- [10] a) N. I. Sadova, N. I. Popik, L. V. Vilkov, Y. A. Pankrushev, V. A. Shlyapochnikov, J. Chem. Soc. Chem. Commun. 1973, 708–709; b) N. I. Sadova, N. I. Popik, L. V. Vilkov, Y. A. Pankrushev, V. A. Shlyapochnikov, J. Struct. Chem. 1975, 15, 593–595; c) N. I. Sadova, N. I. Popik, L. V. Vilkov, J. Struct. Chem. 1976, 17, 257–262.
- [11] N. I. Golovina, L. O. Atovmyan, J. Struct. Chem. 1967, 8, 230-233.
- [12] M. Göbel, B. H. Tchitchanov, J. S. Murray, P. Politzer, T. M. Klapötke, Nat. Chem. 2009, 1, 229–235.
- [13] a) T. M. Klapötke, B. Krumm, R. Moll, S. F. Rest, Z. Anorg. Allg. Chem. 2011, 637, 2103–2110; b) T. M. Klapötke, B. Krumm, R. Moll, Chem. Eur. J. 2013, 19, 12113–12123; c) T. M. Klapötke, B. Krumm, R. Moll, A. Penger, S. M. Sproll, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, Z. Naturforsch. 2013, 68b, 719–731; d) T. M. Klapötke, B. Krumm, R. Moll, S. F. Rest, W. Schnick, M. Seibald, J. Fluorine Chem. 2013, 156, 253–261; e) Q. J. Axthammer, T. M. Klapötke, B. Krumm, R. Moll, S. F. Rest, Z. Anorg. Allg. Chem. 2014, 640, 76–83.
- [14] a) G. Socrates, Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 3edrd edWiley, Chichester, 2004; b) T. M. Klapötke, B. Krumm, R. Moll, S. F. Rest, M. Suceska, Z. Naturforsch. 2014, 69b, 8–16.
- [15] M. J. Kamlet, R. E. Oesterling, H. G. Adolph, J. Chem. Soc. 1965, 5838– 5849.
- [16] J. P. Foster, F. Weinhold, J. Am. Chem. Soc. 1980, 102, 7211-7218.
- [17] R. F. W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, 1990.
- [18] M. A. Blanco, A. M. Pendas, E. Francisco, J. Chem. Theory Comput. 2005, 1, 1096–1109.
- [19] a) F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. 2 1987, S1–S19; b) A. F. Holleman, E. Wiberg, N. Wiberg, Lehrbuch der Anorganischen Chemie, 102ednd ed-Walter de Gruyter, Berlin, 2008.
- [20] a) S. K. Bhattacharjee, H. L. Ammon, Acta Crystallogr. 1982, B38, 2503– 2505; b) Y. Oyumi, T. B. Brill, A. L. Rheingold, J. Phys. Chem. 1985, 89,

Chem. Eur. J. **2014**, 20, 1–13

www.chemeurj.org

eurj.org

11

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77** 





4824-4828; c) H. Schödel, R. Dienelt, H. Bock, Acta Cryst. **1994**, C50, 1790-1792.

- [21] a) A. Bondi, J. Phys. Chem. **1964**, 68, 441–451; b) M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. **2009**, A113, 5806–5812.
- [22] R. W. Taft in Steric Effects in Organic Chemistry (Ed.: M. S. Newman), John Wiley & Sons, New York, 1956.
- [23] J. Hine, W. C. Bailey Jr., J. Org. Chem. 1961, 26, 2098-2099.
- [24] A. Brändström, J. Chem. Soc. Perkin Trans. 2 1999, 1855-1857.
- [25] a) T. Clark, M. Hennemann, J. S. Murray, P. Politzer, J. Mol. Model. 2007, 13, 291–296; b) P. Politzer, P. Lane, M. C. Concha, Y. Ma, J. S. Murray, J. Mol. Model. 2007, 13, 305–311; c) P. Politzer, J. S. Murray, M. C. Concha, J. Mol. Model. 2007, 13, 643–650; d) P. Politzer, J. S. Murray, P. Lane, Int. J. Quantum Chem. 2007, 107, 3046–3052; e) J. S. Murray, P. Lane, P. Politzer, J. Mol. Model. 2009, 15, 723–729.
- [26] a) P. Auffinger, F. A. Hays, E. Westhof, P. S. Ho, *Proc. Natl. Acad. Sci. USA* 2004, 101, 16789–16794; b) H.-G. Stammler, Y. V. Vishnevskiy, C. Sicking, N. W. Mitzel, *CrystEngComm* 2013, 15, 3536–3546.
- [27] P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, Acc. Chem. Res. 2005, 38, 386-395.
- [28] J. S. Murray, M. C. Concha, P. Lane, P. Hobza, P. Politzer, J. Mol. Model. 2008, 14, 699–704.
- [29] C. Møller, M. S. Plesset, Phys. Rev. 1934, 46, 618-622.
- [30] A. A. Granovsky, Firefly, Version 7.1.G.
- [31] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, J. Comput. Chem. 1993, 14, 1347–1363.
- [32] Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Rob, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Och-

terski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT (USA), **2004**.

- [33] M. N. Glukhovtsev, A. Pross, M. P. McGrath, L. Radom, J. Chem. Phys. 1995, 103, 1878-1885.
- [34] a) D. Feller, J. Comput. Chem. 1996, 17, 1571–1586; b) K. L. Schuchardt,
   B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, J. Chem. Inf. Model. 2007, 47, 1045–1052.
- [35] T. A. Keith, AlMAll, Version 14.04.17, TK Gristmill Software, Overland Park KS (USA), 2014.
- [36] R. J. F. Berger, M. Hoffmann, S. A. Hayes, N. W. Mitzel, Z. Naturforsch. 2009, 64b, 1259–1268.
- [37] Y. V. Vishnevskiy, J. Mol. Struct. 2007, 833, 30-41.
- [38] Y. V. Vishnevskiy, J. Mol. Struct. 2007, 871, 24-32.
- [39] Y. V. Vishnevskiy, UNEX, Version 1.5.7.
- [40] a) V. A. Sipachev, J. Mol. Struct. 1985, 22, 143–151; b) V. A. Sipachev, Struct. Chem. 2000, 11, 167–172; c) V. A. Sipachev, J. Mol. Struct. 2001, 567–568, 67–72; d) V. A. Sipachev, J. Mol. Struct. 2004, 693, 235–240.
- [41] a) G. M. Sheldrick, SHELX-97, University of Göttingen, Göttingen (Germany), 1997; b) G. M. Sheldrick, Acta Crystallogr. 2008, A64, 112-122.
- [42] a) M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *SIR2004*, Institute of Crystallography, Bari (Italy), **2004**; b) M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2005**, *38*, 381–388.

Received: April 14, 2014 Published online on ■■ ■, 2014

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



# **FULL PAPER**

**Twisted theory**: A comprehensive spectroscopic and structural study of the halogenotrinitromethanes is presented. The structures were determined by X-ray diffraction and electron diffraction. Intramolecular N···O and Hal···O interactions, both competitors in terms of the orientation of the nitro groups by rotation about the C–N bonds, lead to a propeller-type twisting of these groups favoring the mentioned interactions (see figure).



### Halogenotrinitromethanes

T. M. Klapötke,\* B. Krumm, R. Moll, S. F. Rest, Y. V. Vishnevskiy, C. Reuter, H.-G. Stammler, N. W. Mitzel\*



Halogenotrinitromethanes: A Combined Study in the Crystalline and Gaseous Phase and Using Quantum Chemical Methods