Universität Bielefeld

Structural Chemistry of Hal-C$(NO_2)_3$: GED vs. XRD

UNEX Project

Yury V. Vishnevskiy
Skilizium-2013

Universität Bielefeld

$Cl\text{-}C(NO_2)_3$

Electron Diffraction Study of Gaseous $CH(NO_2)_3$ and $CCl(NO_2)_3$

By N. I. Sadova, N. I. Popik, L. V. Vilkov,* Ju. A. Pankrushev, and V. A. Shlyapochnikov
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r_a(Cl-C) = 1.712(4) Å

CCl_4: 1.767(2); CCl_3NO_2: 1.726(5); $CCl_2(NO_2)_2$: 1.757(8)

nature chemistry

ARTICLES

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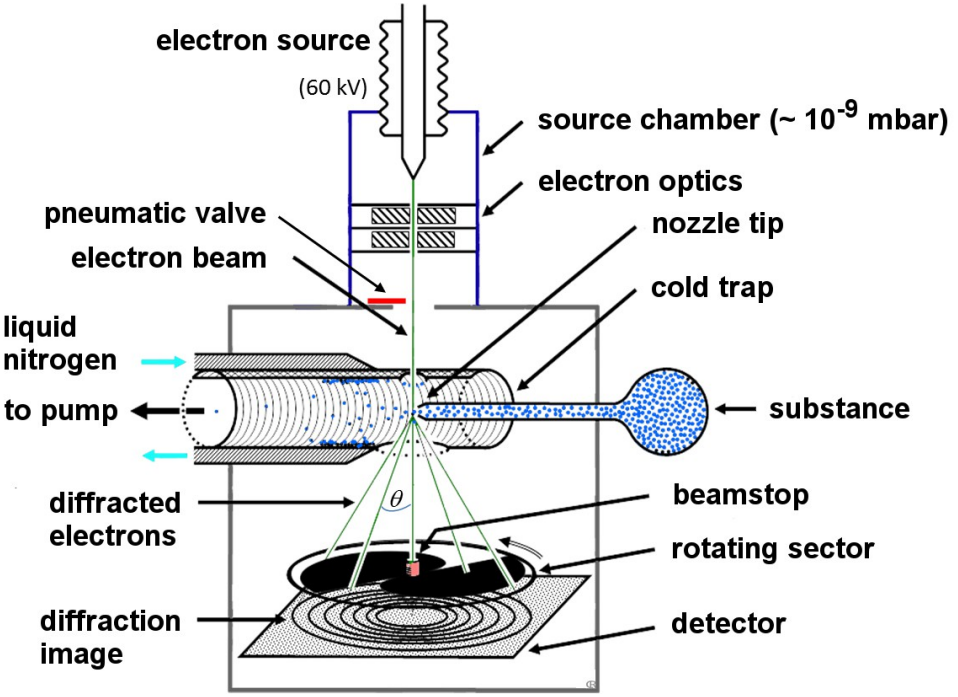
Chlorotrinitromethane and its exceptionally short carbon–chlorine bond

Michael Göbel[1], Boris H. Tchitchanov[1], Jane S. Murray[2,3], Peter Politzer[2,3]* and Thomas M. Klapötke[1,4]*

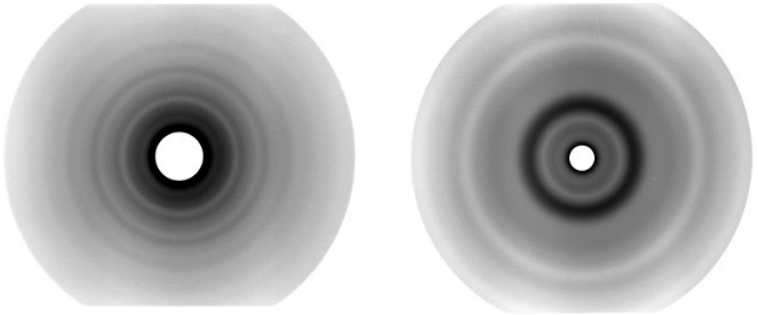
r_α(Cl-C) = 1.694(1) Å

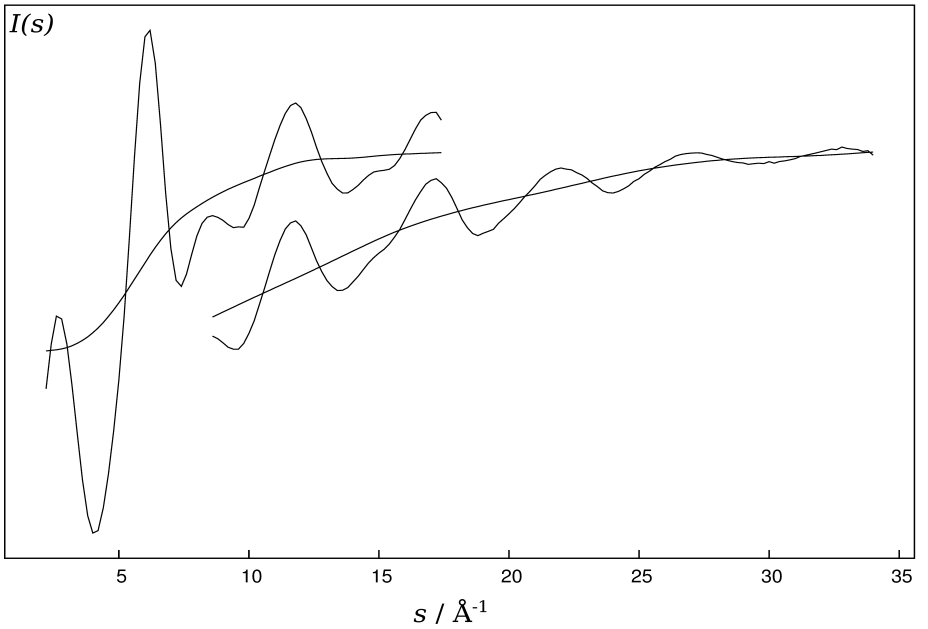
[1] M. Göbel, B. H. Tchitchanov, J. S. Murray, P. Politzer, T. M. Klapötke, *Nat. Chem.*, 1 (2009) 229.
[2] N. I. Sadova, N. I. Popik, L. V. Vilkov, A. Pankrushev, V. A. Shlyapochnikov, *J. Chem. Soc. Chem. Commun.*, 3 (1973) 708.
[3] S. Shibata, K. Iijima, R. Tani, I. Nakamura, *Reports of Faculty of Science, Shizuoka University*, 9 (1974) 33.
[4] R. E. Knudsen, C. F. George, J. Karle, *J. Chem. Phys.*, 44 (1966) 2334.
[5] N. I. Sadova, G. E. Slepnev, L. V. Vilkov, J. Struct. Chem., 18 (1977) 305.

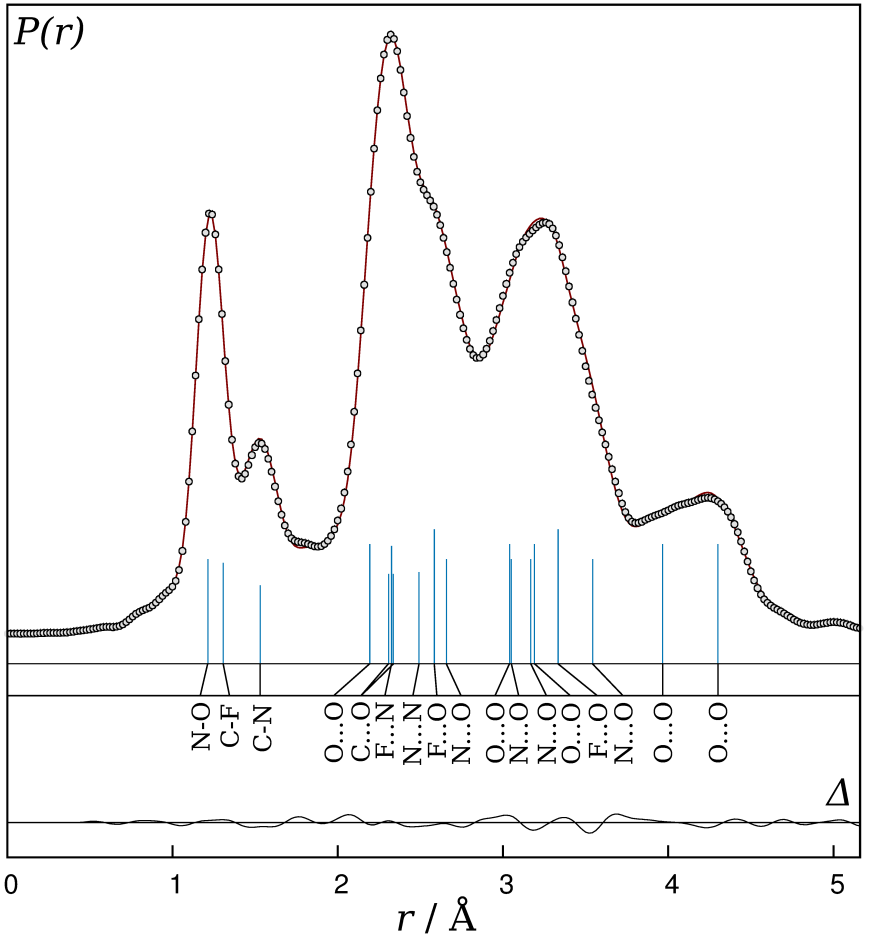
GED Instrument in Bielefeld

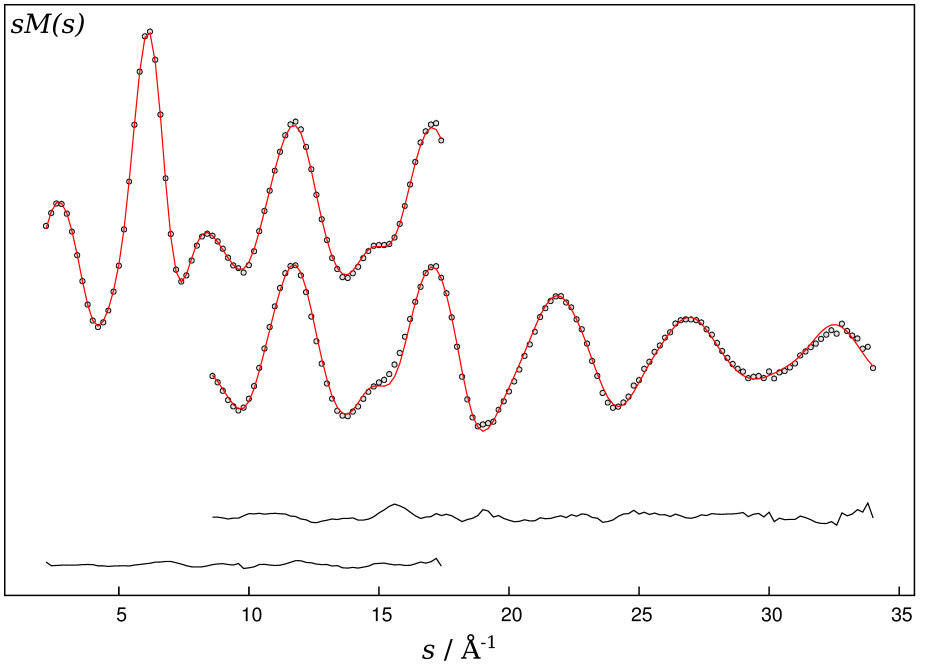


GED Investigation ($F\text{-}C(NO_2)_3$ example)









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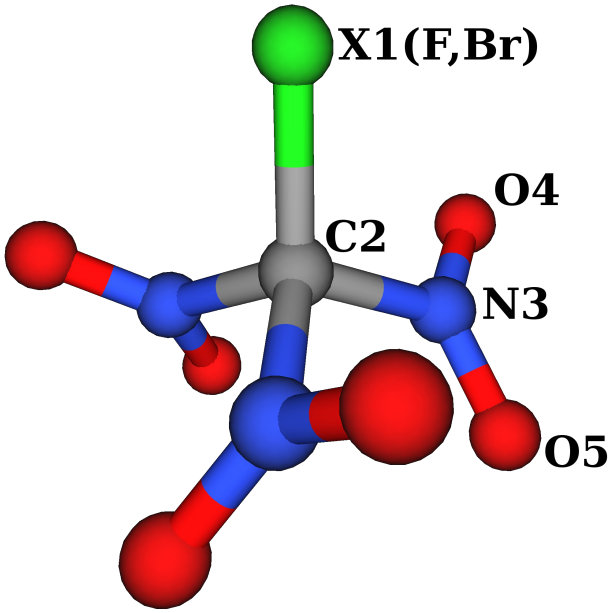
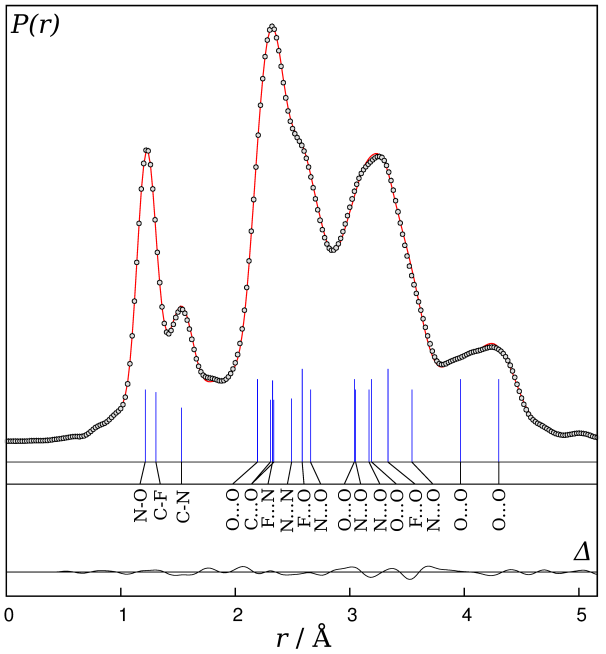
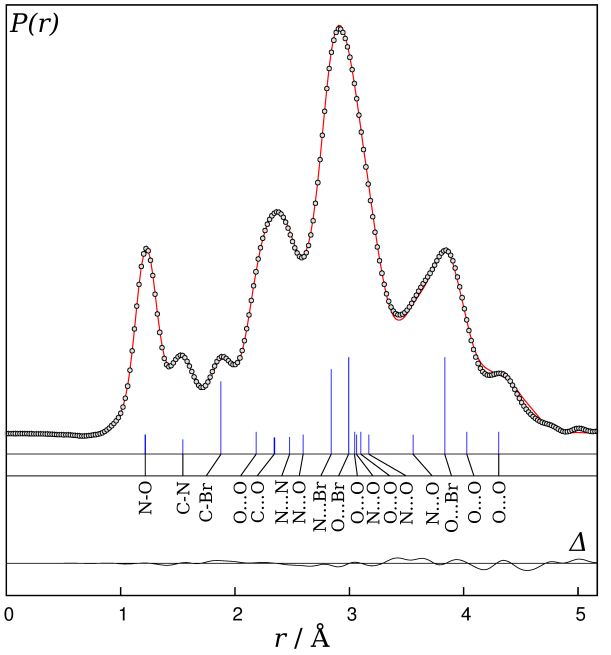
F-, Cl-, Br-, I-, At-C(NO_2)$_3$





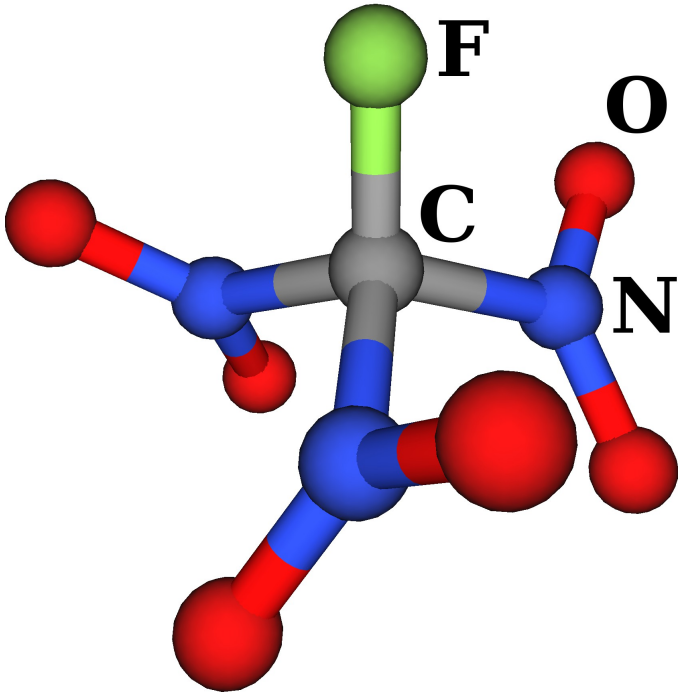


	C–F	C–Cl	C–Br	C–I	C–At
r_a(GED), Å	1.307(4)	1.712(4)	1.876(2)	(2.089)	(2.199)
r_α(XRD), Å	1.297(3)	1.694(1)	1.853(5)	2.097(4)	?

MP2/def2-TZVP

[1] N. I. Sadova, N. I. Popik, L. V. Vilkov, A. Pankrushev, V. A. Shlyapochnikov, *J. Chem. Soc. Chem. Commun.*, 3 (1973) 708.

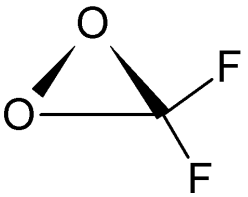
$F\text{-}C(NO_2)_3$



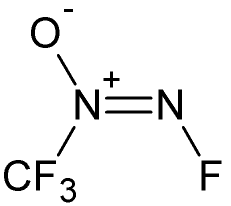
CF_4 MW: r_e(C-F) = 1.315(2) Å

$F\text{-}C(NO_2)_3$ GED: r_e(C-F) = 1.300(4) Å

$CClF_2NO$ GED: r_α(C-F) = 1.310(2) Å (g)



MW: r_0(C-F) = 1.316(2) Å

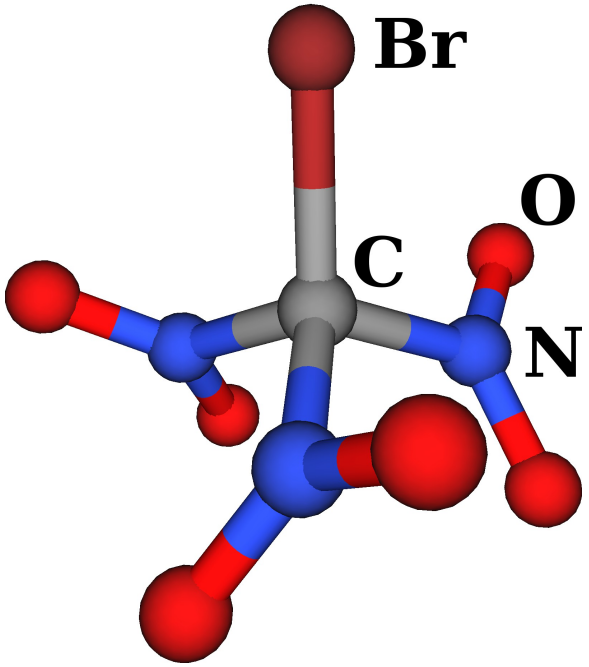


GED: r_a(C-F) = 1.312(3) Å

	C–F	C–Cl	C–Br	C–I	C–At
r_a(GED), Å	**1.307(4)**	1.712(4)	1.876(2)	(2.089)	(2.199)
r_α(XRD), Å	**1.297(3)**	1.694(1)	1.853(5)	2.097(4)	?

[1] S. Brodersen, *J. Mol. Spectr.*, 145 (1991) 331.
[2] B. A. Smart, P. T. Brain, H. E. Robertson, D. W. H. Rankin, *Inorg. Chem.*, 37 (1998) 2687.
[3] H. Burger, P. Weinrath, G. A. Arguello, H. Willner, J. Demaison, *J. Mol. Spectr.*, 171 (1995) 589.
[4] C. Leibold, J. Foropoulos, H. M. Marsden, J. M. Shreeve, H. Oberhammer, *Inorg. Chem.*, 41 (2002) 6125.

$Br\text{-}C(NO_2)_3$



CBr_4 GED: r_a(C-Br) = 1.940(2) Å

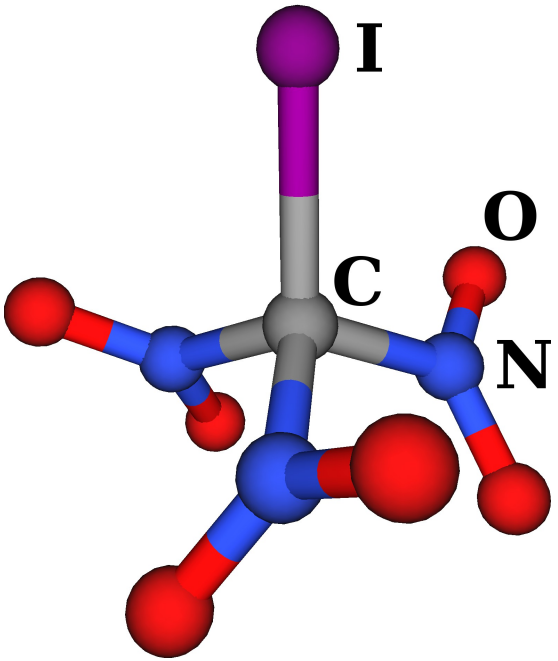
$Br\text{-}C(NO_2)_3$ GED: r_a(C-Br) = 1.885(9) Å

$Br\text{-}C(SiMe_3)_3$ GED: r_a(C-Br) = 1.911(35) Å

	C–F	C–Cl	**C–Br**	C–I	C–At
r_a(GED), Å	1.307(4)	1.712(4)	**1.876(2)**	(2.089)	(2.199)
r_α(XRD), Å	1.297(3)	1.694(1)	**1.853(5)**	2.097(4)	?

[1] H. Thomassen, K. Hedberg, *J. Mol. Struct.*, 240 (1990) 151.
[2] N. I. Sadova, N. I. Popik, L. V. Vilkov, *J. Struct.Chem.*, 17 (1976) 257.
[3] P. T. Brain, M. Mehta, D. W. H. Rankin, H. E. Robertson, C. Eaborn, J. D. Smith, A. D. Webb, *J. Chem. Soc. Dalton Trans.*, 3 (1995) 349.

$I\text{-}C(NO_2)_3$



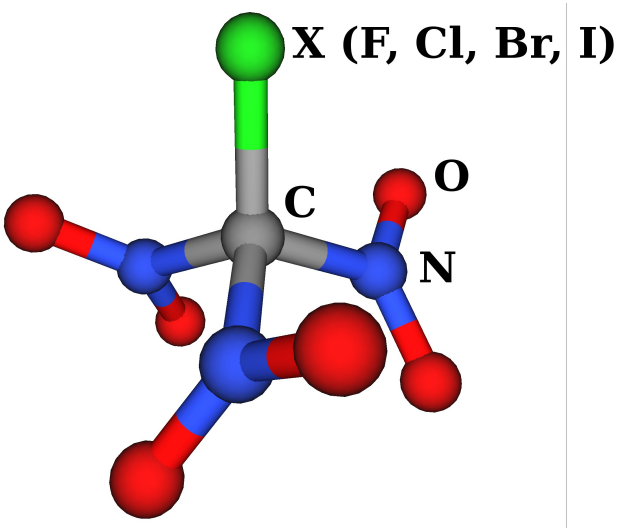
CI_4 GED: r_g(C-I) = 2.157(10) Å

$I\text{-}CF_3$ GED: r_a(C-I) = 2.138(5) Å

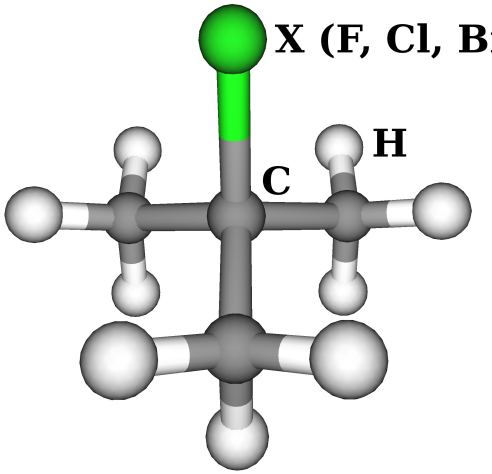
	C–F	C–Cl	C–Br	**C–I**	C–At
r_a(GED), Å	1.307(4)	1.712(4)	1.876(2)	**(2.089)**	(2.199)
r_α(XRD), Å	1.297(3)	1.694(1)	1.853(5)	**2.097(4)**	?

[1] M. Hargittai, G. Schultz, P. Schwerdtfeger, M. Seth, *Struct. Chem.*, 12 (2001) 377.
[2] V. Typke, M. Dakkouri, H. Oberhammer, *J. Mol. Struct.*, 44 (1978) 85.

Hal-C Shortening: AIM Charges



VS.



Halogen charges:

	Hal-C(NO_2)$_3$	Hal-C(CH_3)$_3$
F	-0.66	-0.69
Cl	-0.03	-0.30
Br	0.10	-0.20
I	0.25	-0.07

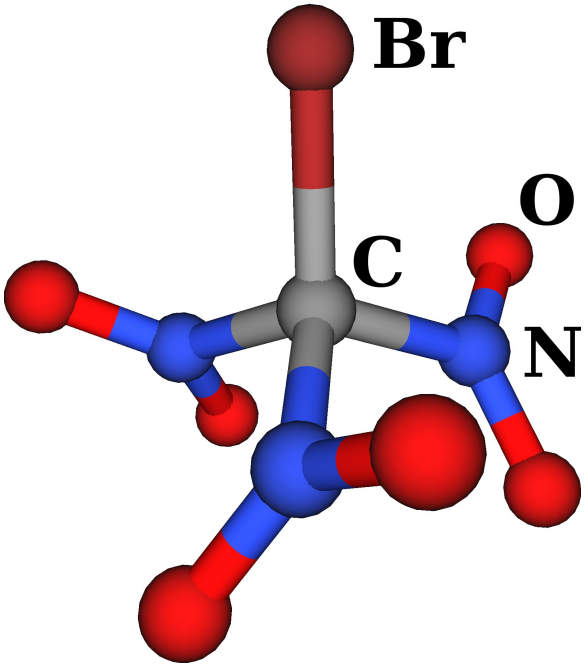
Carbon charges:

	Hal-C(NO_2)$_3$	Hal-C(CH_3)$_3$
F	1.42	0.59
Cl	0.75	0.15
Br	0.63	0.05
I	0.52	-0.06

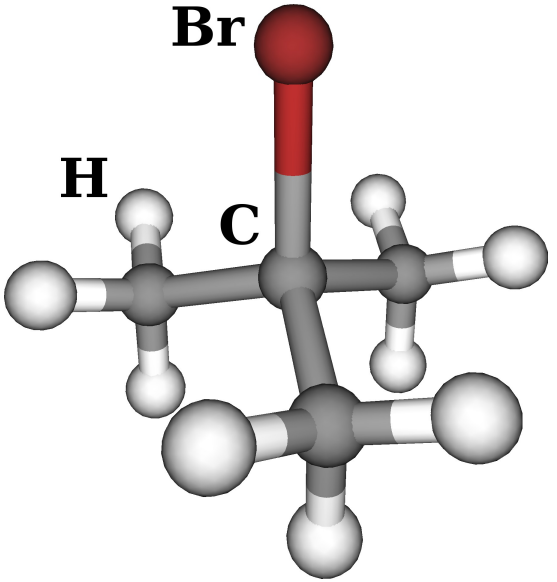
NBO changes show similar behaviour.

MP2(full)/SDB-cc-pVTZ

Hal-C Shortening: NBO



VS.



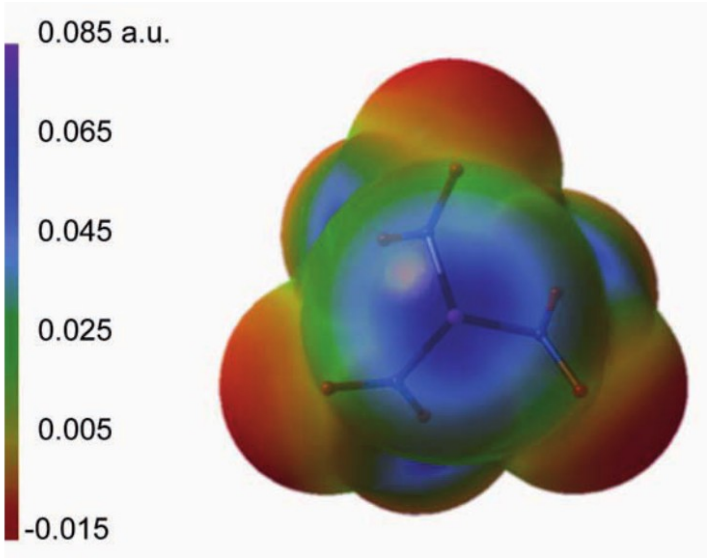
σ(Br-C):

$0.68(sp^{6.7})_{Br} + 0.73(sp^{2.8})_{C}$

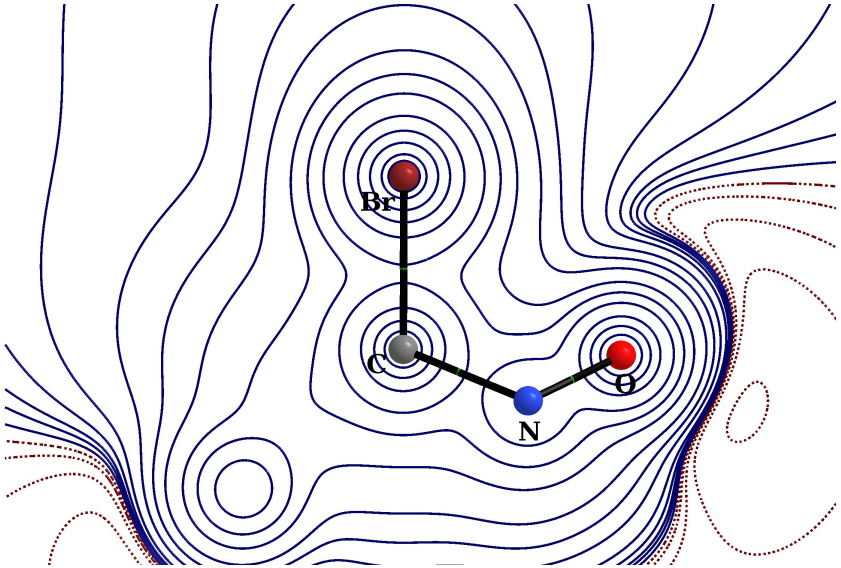
$0.73(sp^{6.1})_{Br} + 0.68(sp^{5.7})_{C}$

MP2(full)/SDB-cc-pVTZ

Hal-C Shortening: ESP



vs.



Br-C(NO_2)$_3$: ρ=0.001 a.u.

Br-C(NO_2)$_3$: ESP Profile

Repulsive interaction between Hal and O (also supported by NBO).

MP2(full)/SDB-cc-pVTZ

[1] M. Göbel, B. H. Tchitchanov, J. S. Murray, P. Politzer, T. M. Klapötke, *Nat. Chem.*, 1 (2009) 229.

Summary

1) Hal-C$(NO_2)_3$ have indeed very short Hal-C bonds!
2) MP2/(SDB-)cc-pVTZ and MP2/def2-TZVP are quite accurate.
3) NBO and AIM are useful theoretical instruments here.
4) The electronegativity concept explains Hal-C shortening.