Supplementary material for the article

"Gas-phase structure of 2,2,2 - TrichloroethylChloroformate studied by electron diffraction and quantum chemical calculations"

Diego M. Gil[1], MaríaE. Tuttolomondo[1], Sebastian Blomeyer[2], Christian G. Reuter[2], Norbert W. Mitzel[2] and Aída Ben Altabef[1,*,±]

[1] INQUINOA (CONICET-UNT), Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, San Lorenzo 456, T4000CAN. Tucumán. Argentina.

[2] Inorganic and Structural Chemistry, Centre for Molecular Materials CM_2, Faculty of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany.

Figure S1: Graphical representation of the two conformers of $Cl_3CCH_2OC(O)Cl$ with the corresponding direction of the dipole moment.

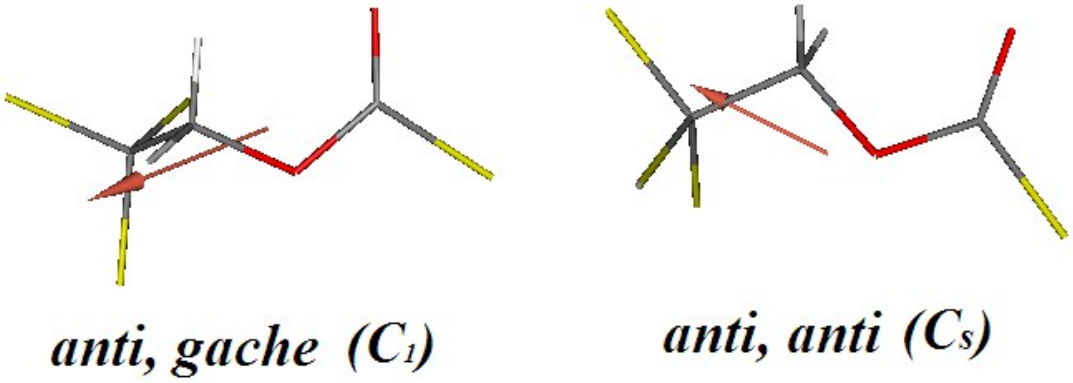

Figure S2: AIM plots for both conformers of $Cl_3CCH_2OC(O)Cl$. Red points indicate the bond critical points (BCP) for atomic interactions (on the atomic interactions lines, also called pond paths).

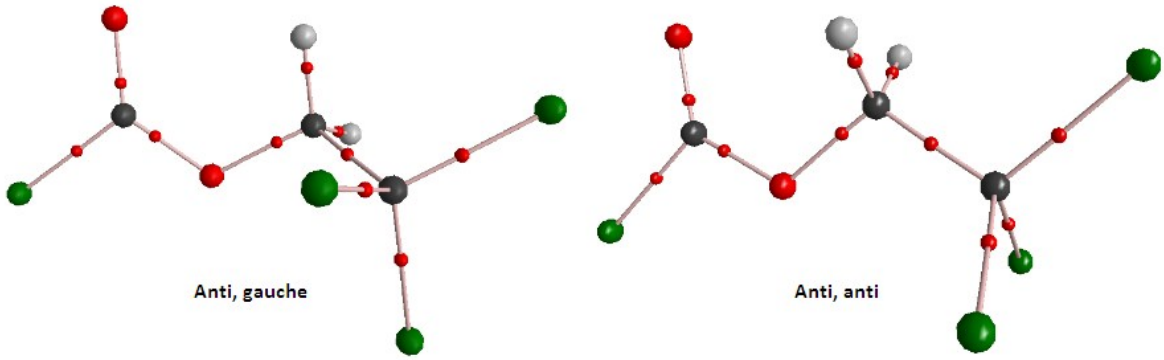

Figure S3: Theoretical (line) and experimental (dots) *s*M(*s*) curves as well as delta curve (below) from GED data refinement using the dynamic model.

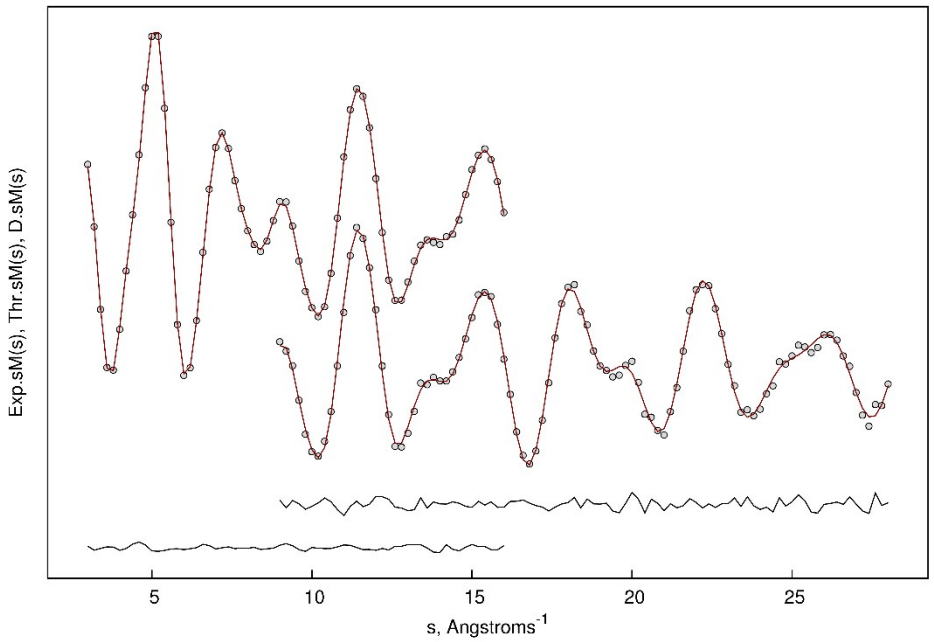

Figure S4: Theoretical (line) and experimental (dots)radial distributioncurves as well as delta curve (below) from GED data refinement using the *anti-gauche* model, only.

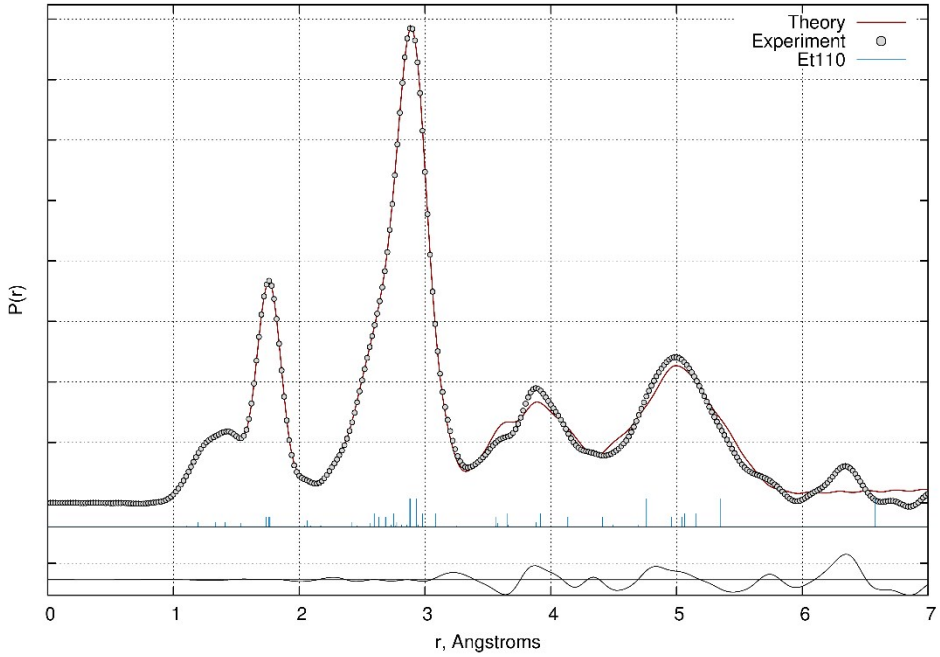

Figure S5: Theoretical (line) and experimental (dots) *s*M(*s*) curves as well as delta curve (below) from GED data refinement using the *anti-gauche* model, only.

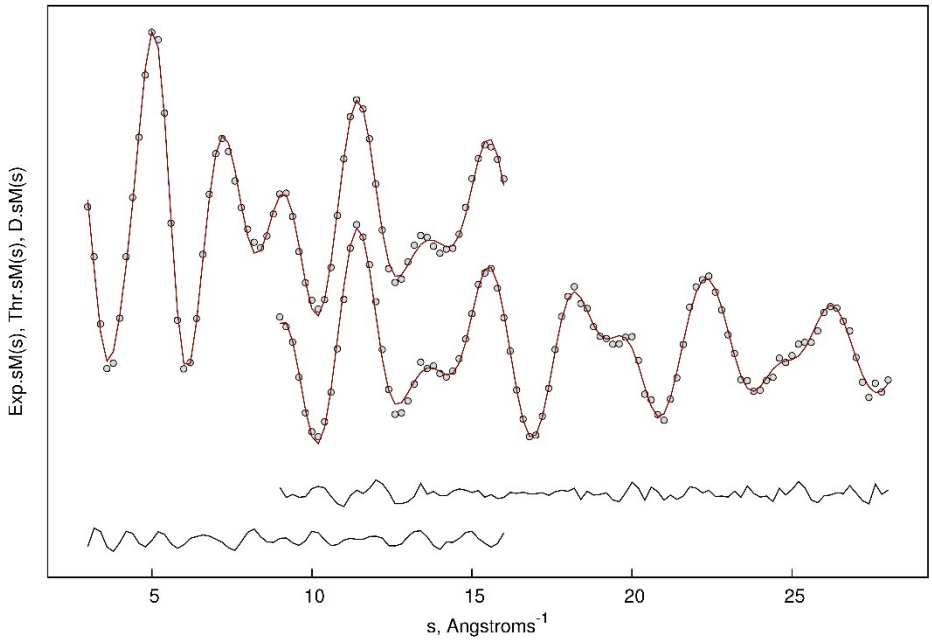

Figure S6: Theoretical (line) and experimental (dots) radial distributioncurves as well as delta curve (below) from GED data refinement using the *anti-anti* model, only.

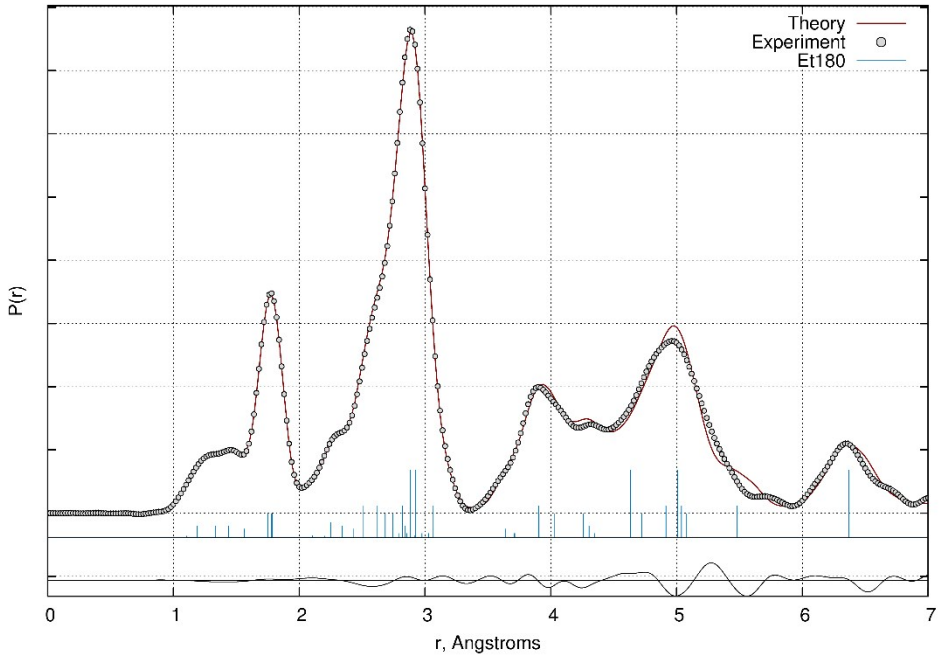

Figure S7: Theoretical (line) and experimental (dots) *s*M(*s*) curves as well as delta curve (below) from GED data refinement using the *anti-anti* model, only.

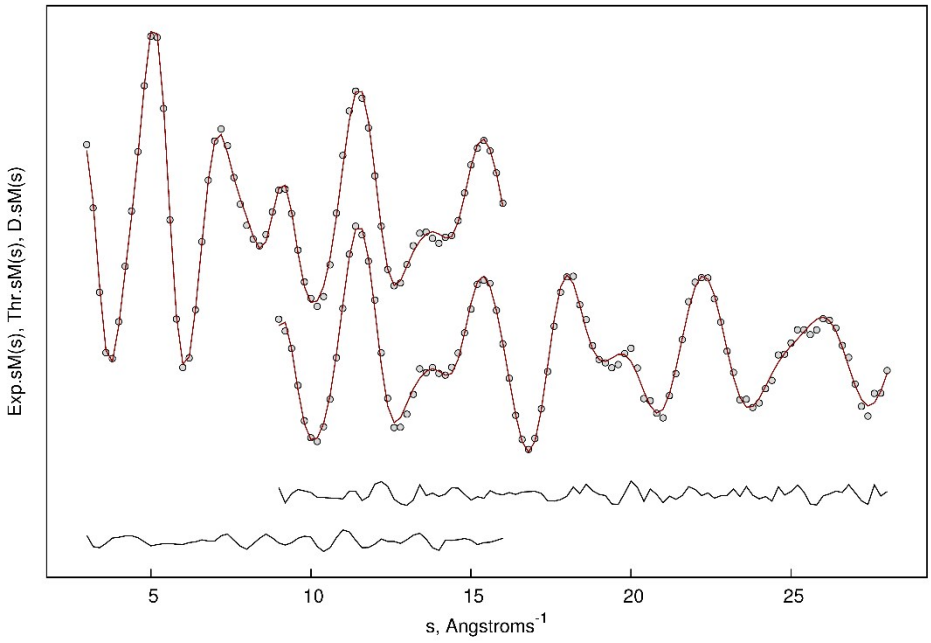

Figure S8: Simulated Raman spectra for both conformers of $Cl_3CCH_2OC(O)Cl$ and the spectrum in liquid phase.

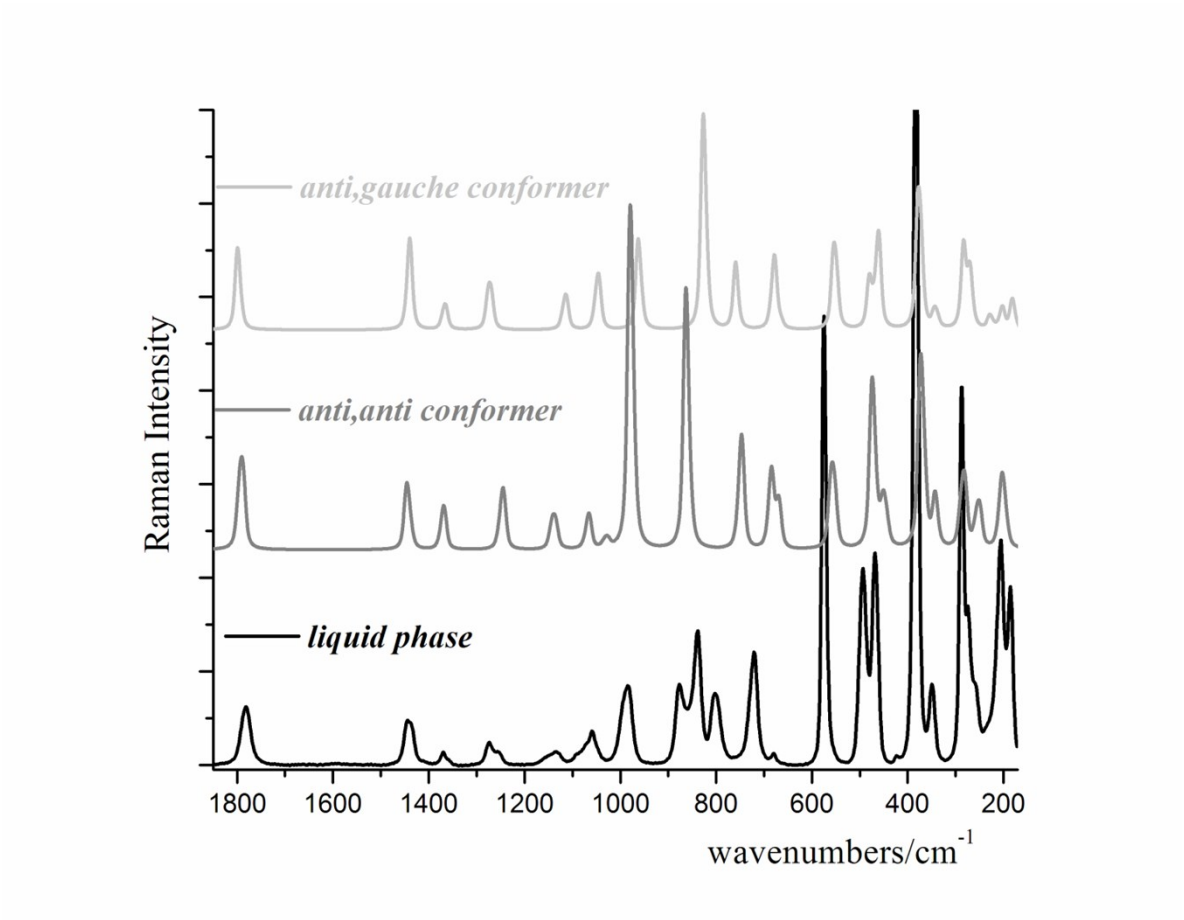

Table S1: Detailed conditions of the GED experiments.

	data set 1	data set 2
nozzle-to-plate distance (mm)	500	250
electron beam current (nA)	1000	1000
electron wavelength (Å)	0.048799	0.048636
exposure time (s)	10–15	10–20
background pressure (mbar)	3×10^{-7}	3×10^{-7}
residual gas pressure[a] (mbar)	1×10^{-6}	1×10^{-6}

[a] During recording.

Table S2: Optimized structural parameters (bond lengths, angles and selected dihedral angles) for both conformers of $Cl_3CCH_2OC(O)Cl$ calculated at PBEPBE and MP2 methods with 6-311G(3df,2pd) basis sets as well as experimental ones obtained from gas electron diffraction data.

Parameter [a]	C_1conformer			C_s conformer			Experimental [b]
	PBEPBE	MP2		PBEPBE	MP2		
	6-311G(3df,2pd)		6-311G(d,p)	6-311G(3df,2pd)		6-311G(d,p)	
C(4)-H mean	1.097	1.087	1.090	1.098	1.089	1.091	$1.090(15)^{5.0}$
C(1)-Cl(8)	1.760	1.734	1.742	1.761	1.735	1.742	$1.744(2)_a$
C(1)=O(2)	1.194	1.189	1.191	1.196	1.192	1.194	$1.184(8)^{5.0}$
C(1)-O(3)	1.349	1.341	1.345	1.342	1.334	1.338	$1.327(9)^{5.0}$
O(3)-C(4)	1.438	1.422	1.425	1.442	1.427	1.428	$1.422(10)^{5.0}$
C(4)-C(5)	1.531	1.524	1.523	1.526	1.519	1.518	$1.535(10)^{5.0}$
C(5)-Cl mean	1.786	1.763	1.770	1.785	1.763	1.770	$1.772(2)_a$
O(2)=C(1)-Cl(8)	124.1	124.3	124.2	124.4	124.5	124.5	$124.9(17)^{0.5}$
O(2)=C(1)-O(3)	128.3	127.8	127.9	127.4	126.8	126.8	126.2(9)
Cl(8)-C(1)-O(3)	107.6	107.9	107.9	108.2	108.6	108.7	$108.9(14)^{0.5}$
C(1)-O(3)-C(4)	115.6	115.3	115.2	113.2	112.7	112.5	$110.6(23)^{0.5}$
O(3)-C(4)-C(5)	110.2	109.3	110.1	107.9	106.9	107.5	$105.1(10)^{0.5}$
Cl-C(5)-Cl	109.7	109.8	110.3	109.7	109.9	110.3	$109.2(9)^{0.5}$
Cl(8)-C(1)-O(3)-C(4)	178.9	176.3	177.2	179.9	179.9	180.0	$179.1(24)^{0.5}$
C(1)-O(3)-C(4)-C(5)	116.3	107.5	109.9	179.9	179.9	180.0	Fixed to 180.0

[a] Bond lengths in Å, angles in degrees. See Figure 2a and 2b for numbering of atoms.

[b] Values for conformer of C_s symmetry, standard deviations given as $3\sigma_{LS}$, superscript numbers indicate the regularization coefficient, subscript letters state if parameters were refined in groups with fixed differences in between. The O(2)=C(1)–O(3) angle was not refined explicitly results from O(2)=C(1)–Cl(8), Cl(8)–C(1)–O(3) and the assumed planarity of the Cl(8)–C(1)–O(2)–O(3) moiety.

Table S3: Relative abundances (MP2/6-311G(d,p), 328 K) for pseudoconformers used in the dynamic model for structure refinement of gas-phase electron diffraction data.

Φ (pseudoconformer) / °	rel. abundance[a] / %
100	12.14 (2)
110	18.10 (2)
120	14.63 (2)
130	10.53 (2)
140	8.64 (2)
150	8.54 (2)
160	9.74 (2)
170	11.49 (2)
180	6.18 (1)

Table S4: The calculated thermodynamic and molecular parameters (298.15 K) for both conformations of $Cl_3CCH_2OC(O)Cl$ calculated at B3LYP/6-311++G(d,p) level.

Parameter	**C_1 conformer**	**$C_s$conformer**
Thermal Energy (kcal mol^{-1})		
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	37.426	37.412
Total	39.204	39.189
Heat capacity (cal mol^{-1}K^{-1})		
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	26.207	26.242
Total	32.169	32.203
Entropy (cal mol^{-1}K^{-1})		
Translational	41.928	41.928
Rotational	31.379	31.523
Vibrational	29.708	30.293
Total	103.015	103.743
Dipole moment (Debye)		
μ_x	–1.0746	1.0464
μ_y	0.2817	0.2789
μ_z	–1.3582	–0.0004
Total	1.7546	1.1118
Rotational constants (GHz)		
A	1.47537	1.43175
B	0.45918	0.42809
C	0.42998	0.41123
Rotational temperature (K)		
A	0.07081	0.06871
B	0.02204	0.02055
C	0.02064	0.01974
Thermal properties (Hartree/particle)		
Zero-point (ZP) correction	0.052699	0.052618
Thermal correction to energy	0.062475	0.062452
Thermal correction to enthalpy	0.063419	0.063397
Thermal correction to Gibbs free energy	0.014473	0.014105
Sum of electronic and ZP energies	–2106.885133	–2106.885409
Sum of electronic and thermal energies	–2106.875357	–2106.875575
Sum of electronic and thermal enthalpies	–2106.874413	–2106.874630
Sum of electronic and thermal free energies	–2106.923358	–2106.923922

Table S5: C–O, C-C and C=O bond lengths (Å), electron occupancy and energy (kJ·mol^{-1}) of the natural bond orbitals for $Cl_3CCH_2OC(O)Cl$.[a]

	***anti-gauche* (C_1)**	***anti-anti* (C_s)**
***d*(C(4)–O(3))**	1.437	1.439
Occupancy σ C–O	1.98079	1.97991
Energy	-0.88590	-0.88107
Occupancy σ* C–O	0.03832	0.03853
Energy	0.20020	0.19495
***d*(C(4)–C(5))**	1.531	1.527
Occupancy σ C–C	1.98863	1.98882
Energy	-0.74432	-0.74932
Occupancy σ* C–C	0.05563	0.05149
Energy	0.26401	0.26900
***d*(C(1)=O(2))**	1.187	1.189
Occupancy σ C=O	1.99786	1.99743
Energy	-1.18324	-1.18148
Occupancy σ* C=O	0.02937	0.02890
Energy	0.58802	0.58460

[a] Calculated at B3LYP/6-311++G(d,p) level.

Table S6: The charge distribution calculated by the Mulliken method using DFT/B3LYP/6-311++G(d,p) for C_1 and C_s conformers of $Cl_3CCH_2OC(O)Cl$.

Atoms [a]	Atomic charges (Mulliken)	
	C_1 conformer	C_s conformer
C(1)	0.75868	0.75579
O(2)	-0.54270	-0.54404
O(3)	-0.55163	-0.54713
C(4)	-0.08703	-0.08622
C(5)	-0.18376	-0.17993
H(6)	0.23756	0.22466
H(7)	0.22189	0.22465
Cl(8)	-0.00724	-0.00776
Cl(9)	0.05240	0.05650
Cl(10)	0.04597	0.04696
Cl(11)	0.05585	0.05652

[a] See Fig. 2 for atoms numbering scheme.