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Gas phase structures of trifluoroacetyl chloride, $CF_3C(O)Cl$, and chlorodifluoroacetyl chloride, $CF_2ClC(O)Cl$

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Abstract

The geometric structures of trifluoroacetyl chloride, $CF_3C(O)Cl$, and chlorodifluoroacetyl chloride, $CF_2ClC(O)Cl$ were determined by gas electron diffraction. The CF_3 group in $CF_3C(O)Cl$ adopts an eclipsed orientation relative to the C=O double bond. In the predominant conformer of $CF_2ClC(O)Cl$ (93(3)%) the two chlorine atoms are gauche to each other ($\Theta(ClCCCl) = 75.4(10)°$) with a small contribution of the trans form ($\Theta(ClCCCl) = 180°$). The experimental geometric parameters are compared to those obtained by ab initio calculations.

Keywords: Electron diffraction; Ab initio calculation; Conformational isomerism; Trifluoroacetyl chloride; Chlorodifluoroacetyl chloride

1. Introduction

The first synthesis of trifluoroacetyl chloride was reported almost 50 years ago [1]. Several spectroscopic studies were performed on this compound [2–4]. An early gas electron diffraction (GED) investigation [5] resulted in an extremely long $C(sp^2)$–$C(sp^3)$ bond in this compound (1.569(20) Å). Recently, the UV photolysis of matrix isolated $CF_3C(O)Cl$ was reported [6]. For chlorodifluoroacetyl chloride, $CF_2ClC(O)Cl$, two conformers can occur, depending on the torsional position of the CF_2Cl group, with the two chlorine atoms trans or gauche to each other (see Fig. 1). Recently, these conformational properties were studied by vibrational spectroscopy and ab initio methods [7]. Whereas the experiments result in an enthalpy

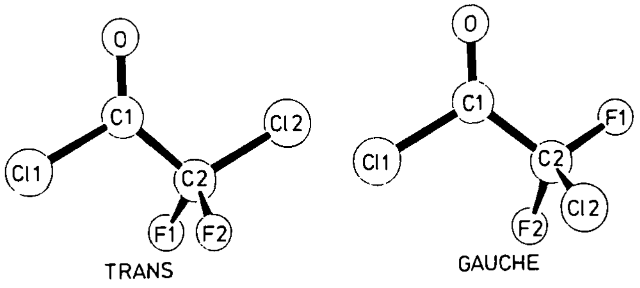

Fig. 1. Molecular models for trans and gauche conformers of $CF_2ClC(O)Cl$.

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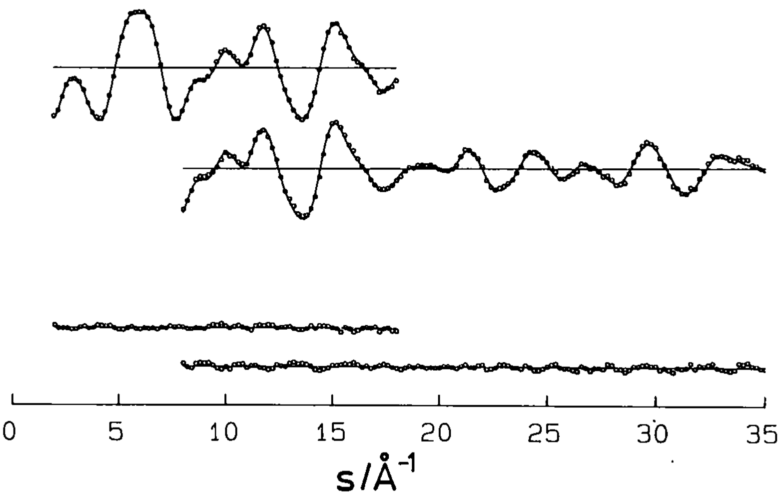

Fig. 2. Experimental (dots) and calculated (full line) molecular scattering intensities and differences for $CF_3C(O)Cl$.

difference $\Delta H° = H°(\text{trans}) - H°(\text{gauche})$ of 0.71(17) kcal mol^{-1}, the calculated energy difference ΔE is between −0.47 and +0.18 kcal mol^{-1}, depending on the computational approach. The relative contributions of the two conformers were not determined by these experiments.

In the present paper we report GED results for the structures of $CF_3C(O)Cl$ and $CF_2ClC(O)Cl$ and for the conformational properties of the latter compound. Furthermore, ab initio calculations were performed for $CF_3C(O)Cl$ at the HF/3-21G* and HF/6-31G* levels, using the GAUSSIAN 90 program system [8]. Analogous calculations for $CF_2ClC(O)Cl$ have been reported previously by Durig et al. [7].

2. Experimental

$CF_3C(O)Cl$ was synthesized by reaction of trifluoroacetic acid with pentachlorophosphorane according to Ref. [1]. The compound was purified by trap-to-trap distillation and the purity was checked by IR spectroscopy.

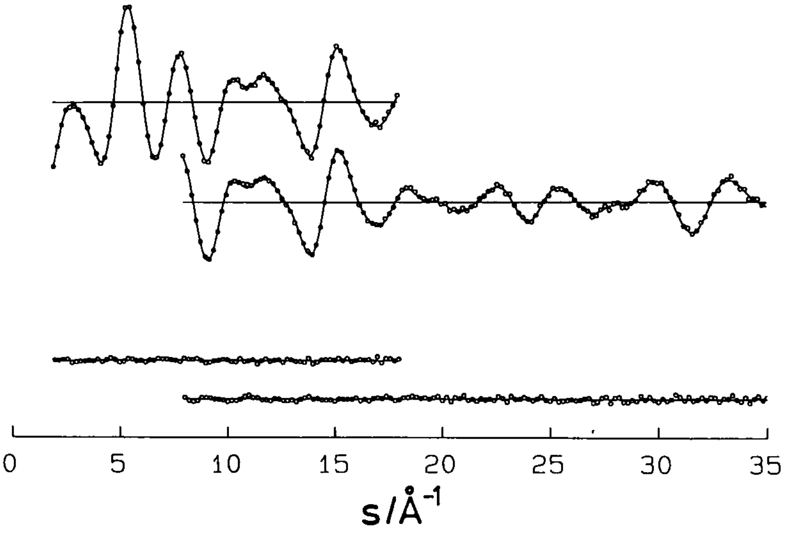

Fig. 3. Experimental (dots) and calculated (full line) molecular scattering intensities and differences for $CF_2ClC(O)Cl$.

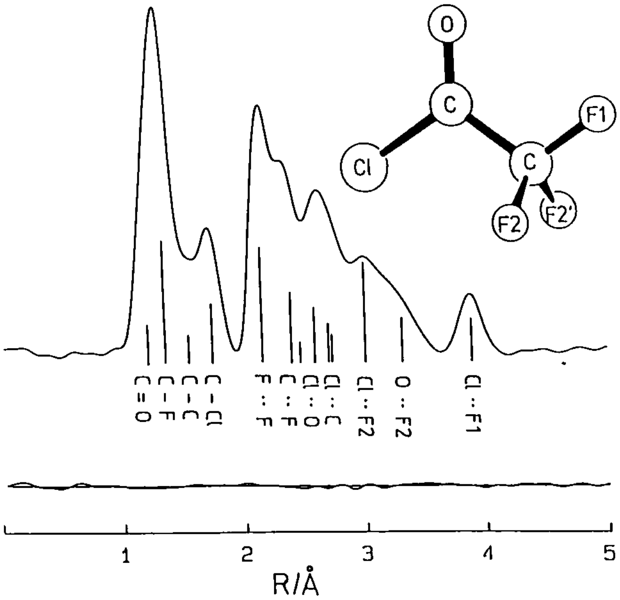

Fig. 4. Experimental radial distribution curve, difference curve and molecular model for $CF_3C(O)Cl$. Interatomic distances are indicated by vertical bars.

$CF_2ClC(O)Cl$ was obtained by the reaction between dry $CF_2ClC(O)OH$ and PCl_5 and it was subsequently purified several times by fractional condensation at reduced pressure.

The GED intensities were recorded with a Balzers KD-G2 Gasdiffractograph [9] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample reservoirs were cooled to −85°C ($CF_3C(O)Cl$) or −50°C ($CF_2ClC(O)Cl$) and the inlet system and nozzle were maintained at room temperature. The photographic plates (Kodak Electron Image) were analyzed with a modified ELSCAN-2500 microdensitometer [10] and the usual procedures for data reduction and structure refinement were applied [11]. The averaged molecular scattering intensities in the s-ranges 2–18 and 8–35 $Å^{-1}$ are shown in Figs. 2 and 3.

3. GED analyses

Radial distribution functions (RDF) were calculated by Fourier transform of the molecular intensities using an artificial damping function $\exp(-\gamma s^2)$, ($\gamma = 0.0019$ $Å^2$). Preliminary structural models, which were derived from the RDFs, were refined by least squares fit of the molecular intensities. A diagonal weight matrix was applied to the intensities and known scattering amplitudes and phases were used [12].

3.1. $CF_3C(O)Cl$

Analysis of the RDF (Fig. 4) demonstrates that the CF_3 group eclipses the carbonyl C=O bond. Thus, C_s symmetry was assumed in the least

Table 1
Geometric parameters of $CF_3C(O)Cl$

Parameter	GED[a]		HF/3-21G*	HF/6-31G*
C=O	1.186(4)	(p_1)	1.185	1.164
C-C	1.533(6)	(p_2)	1.519	1.537
C-F	1.329(2)	(p_3)	1.340	1.310
C-Cl	1.742(4)	(p_4)	1.735	1.741
C-C=O	126.2(8)	(p_5)	123.4	122.8
C-C-Cl	110.9(5)	(p_6)	111.9	113.5
Cl-C=O	123.1(7)		124.7	123.7
F-C-F	108.7(2)	(p_7)	108.8	109.0

[a] r_a distances in angstrom and $\angle_\alpha$ in degree. Error limits are 3σ values.

Table 2
Interatomic distances and vibrational amplitudes for $CF_3C(O)Cl$[a]

Bond	Distances	Amplitudes		Bond	Distances	Amplitudes	
C=O	1.19	0.038(6)	(a_1)	Cl···O	2.59	0.077(8)	(a_6)
C–F	1.33	0.048(2)	(a_2)	Cl···C	2.70		
C–C	1.53	0.050[b]		O···F1	2.71	0.100[b]	
C–Cl	1.74	0.057(5)	(a_3)	Cl···F2	3.00	0.154(12)	(a_7)
F···F	2.16	0.055(2)	(a_4)	O···F2	3.30	0.141(19)	(a_8)
C···F	2.35	0.054(5)	(a_5)	Cl···F1	3.89	0.078(8)	(a_9)
C···O	2.43						

[a] Values in angstrom, error limits are 3σ values. For atom numbering see Fig. 4.
[b] Not refined.

squares refinement. The CF_3 group was constrained to C_{3v} symmetry with a possible tilt angle between the C_3 axis and the C–C bond direction. In the least squares analysis, this angle converged toward a small value (<1°) and the error limit was larger than this value. Therefore, it was set to zero in further refinements. This assumption is in agreement with the ab initio calculations, which predict a tilt angle of less than 1°. Vibrational amplitudes for closely spaced interatomic distances were refined in groups. With these assumptions seven geometric parameters p_i and nine vibrational amplitudes a_k were refined simultaneously in the final least squares analysis.

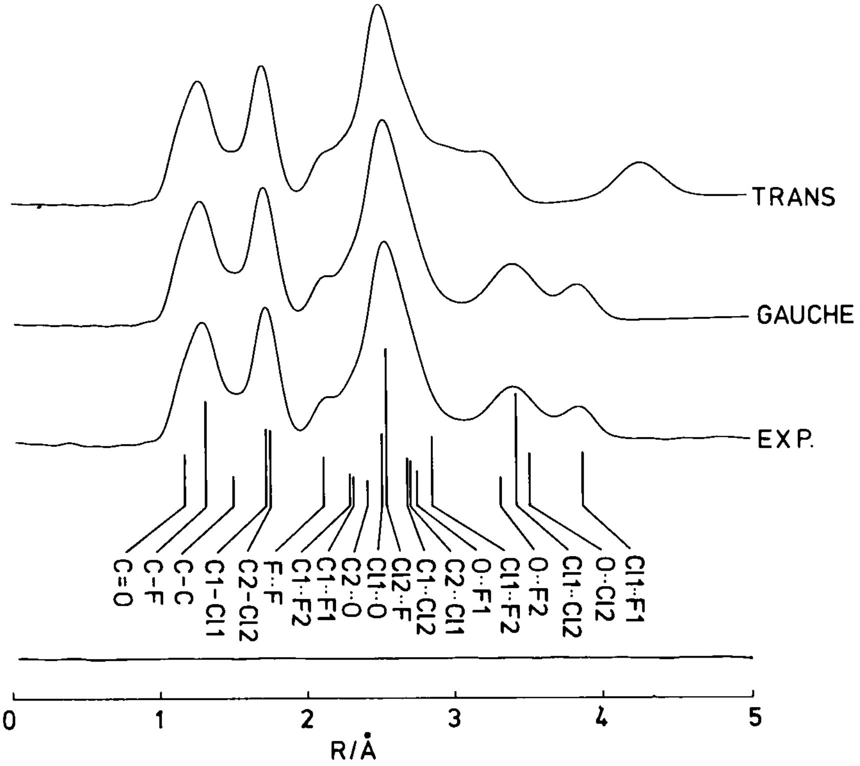

Fig. 5. Calculated radial distribution function for trans and gauche forms, experimental curve and difference curve for $CF_2ClC(O)Cl$. Interatomic distances of the gauche form are indicated by vertical bars.

Only one correlation coefficient between these parameters possessed a value larger than |0.7|: $a_7/a_8 = 0.72$. The results are listed in Table 1 (geometric parameters) and Table 2 (vibrational amplitudes), from which further constraints are evident.

3.2. $CF_2ClC(O)Cl$

Comparison of calculated RDFs for the trans and gauche conformers with the experimental curve (Fig. 5) clearly shows that the gauche form is the dominant conformer in the gas phase. In the first step, the molecular intensities were fitted with a gauche model only. The two closely spaced C–Cl bond distances and the similar C–C–Cl and C–C–F angles can not be determined accurately in a GED analysis. Therefore, mean values were refined for these parameters and the differences ΔCCl = (C2–Cl2) – (C1–Cl1), ΔCCCl = (C2–C1–Cl1) – (C1–C2–Cl2) and ΔCCF = (C–C–F1) – (C–C–F2) were constrained to the result of the MP2/6-31G* calculation [7]. Estimated uncertainties for these differences are given in square brackets in Table 3 and are taken into account in the error limits for the geometric parameters. The two C–F bond lengths and ClCF bond angles in the CF_2Cl group were set equal. The predicted ab initio differences for the C–F distances are only 0.001 Å (HF/3-21G*), 0.006 Å (HF/6-31G*) and 0.004 Å (MP2/6-31G*) [7]. Differences between the ClCF angles (Cl2–C2–F1 and Cl2–C2–F2) can not be taken from these ab initio calculations, since the number of angles around the C2 atom given in Table 3 of Ref. [7] is incomplete. Calculations at the HF/3-21G* level, which were performed by us, predict a difference of only 0.3° for the ClCF angles. Assumptions for vibrational amplitudes are evident from Table 4. Nine geometric parameters p_i and eleven vibrational amplitudes a_k were refined simultaneously. The following correlation coefficients are larger than |0.7|: $p_2/p_7 = -0.71$, $p_2/p_8 = -0.70$, $p_5/p_7 = -0.83$,

Table 3
Geometric parameters of $CF_2ClC(O)Cl$

Parameter	GED[a]		MP2/6-31G*[b]
C=O	1.179(4)	(p_1)	1.199
C–C	1.519(8)	(p_2)	1.540
$(C–F)_{mean}$	1.325(3)	(p_3)	1.344
$(C–Cl)_{mean}$	1.746(2)	(p_4)	1.753
Δ(CCl) = (C2–Cl2) – (C1–Cl1)	0.020[10]		0.020
C1–Cl1	1.736(6)		1.748
C2–Cl2	1.756(6)		1.758
C2–C1=O	128.0(18)	(p_5)	122.4
$(C–C–Cl)_{mean}$	111.1(4)	(p_6)	111.5
Δ(CCCl) = (C2–C1–Cl1) – (C1–C2–Cl2)	3.6[10]		3.6
C2–C1–Cl1	112.9(7)		113.3
C1–C2–Cl2	109.3(7)		109.7
Cl1–C1=O	119.2(17)		124.3
$(C–C–F)_{mean}$	109.2(6)	(p_7)	109.4
Δ(CCF) = (C–C–F1) – (C–C–F2)	2.4[10]		2.4
C–C–F1	110.4(8)		110.6
C–C–F2	108.0(8)		108.2
$(Cl2–C2–F)_{mean}$	110.9(7)	(p_8)	[c]
F–C–F	107.1(14)		108.4
Θ(ClCCCl)	75.4(10)	(p_9)	79.3

[a] r_a distances in angstrom and $\angle_\alpha$ angles in degree. Error limits are 3σ values and include possible systematic errors (see text). For atom numbering see Fig. 1.

[b] From Ref. [7].

[c] This value is missing from Ref. [7]. The result of our HF/3-21G* calculation is 109.4° (see text).

Table 4
Interatomic distances and vibrational amplitudes for $CF_2ClC(O)Cl$[a]

Bond	Distances	Amplitudes		Bond	Distances	Amplitudes	
C=O	1.18	0.030(6)	(a_1)	C1···Cl2	2.68	0.069(7)	(a_7)
C–F	1.33	0.044(3)	(a_2	C2···Cl1	2.72		
C–C	1.52	0.050[b]		O···F1	2.75	0.100[b]	
C1–Cl1	1.74	0.046(2)	(a_3)	Cl1···F2	2.85	0.20(5)	(a_8)
C2–Cl2	1.76			O···F2	3.34	0.29(6)	(a_9)
F···F	2.13	0.054(6)	(a_4)	O···Cl2	3.52		
C1···F2	2.31	0.056(10)	(a_5)	Cl1···Cl2	3.42	0.133(9)	(a_{10})
C1···F1	2.34			Cl1···F1	3.87	0.082(8)	(a_{11})
C2···O	2.43						
Cl1···O	2.53	0.065(3)	(a_6)				
Cl2···F	2.55						

[a] Values in angstrom, error limits are 3σ values. For atom numbering see Fig. 1.
[b] Not refined.

$p_5/p_8 = -0.93$, $p_7/p_8 = -0.94$, $p_7/a_8 = -0.81$, $p_8/a_8 = 0.80$ and $a_8/a_7 = 0.70$.

In the second step, least squares refinements were performed for mixtures of trans and gauche conformers. The differences in geometric parameters of the two forms were set to the MP2 values. The fit of the experimental intensities slightly improved for a 7% trans contribution, with an estimated uncertainty of ±3%. From this conformational composition we obtain $\Delta G^\circ = 1.1(3)$ kcal mol^{-1}. The results of the final refinement are listed in Table 3 (geometric parameters) and Table 4 (vibrational amplitudes).

4. Discussion

Table 5 compares skeletal geometric parameters of some carbonyl chlorides XC(O)Cl. This comparison shows that the C=O double bonds and the C–Cl single bonds are affected in the same direction by the electronegativity of X. The general trend of the C=O bonds is a slight shortening with increasing electronegativity of X, whereas the C–Cl bonds shorten markedly from 1.798(2) Å in $CH_3C(O)Cl$ to 1.725(2) Å in FC(O)Cl. The former bond is the longest C(sp^2)–Cl bond known for gas phase structures. The C–Cl bonds in $CF_3C(O)Cl$ (1.742(4) Å) and $CF_2ClC(O)Cl$ (1.736(6) Å) are intermediate and equal to those in ClC(O)Cl. This is in agreement with electronegativities of the CF_3 and CF_2Cl groups, which are close to that of chlorine. The lengthening of the C–C bond from 1.506(3) Å in $CH_3C(O)Cl$ to 1.533(6) Å in $CF_3C(O)Cl$ can be rationalized by electrostatic repulsion between the positive partial charges of the carbonyl- and CF_3-carbon atoms ($F_3C^{\delta+}$–$C^{\delta+}$(O)Cl). The intermediate C–C distance in $CF_2ClC(O)Cl$ (1.519(8) Å) is in agreement with this bonding model.

The CF_3 group in $CF_3C(O)Cl$ eclipses the C=O

Table 5
Skeletal parameters of some carbonyl chlorides, XC(O)Cl

XC(O)Cl	C=O	C–Cl	C–C	O=C–Cl	X–C–Cl
HC(O)Cl[a]	1.185(3)	1.772(2)	—	123.1(2)	110.4(5)
$CH_3C(O)Cl$[b]	1.187(3)	1.798(2)	1.506(3)	121.2(5)	111.6(6)
$CF_3C(O)Cl$[c]	1.186(4)	1.742(4)	1.533(6)	123.1(10)	110.9(5)
$CF_2ClC(O)Cl$[c]	1.179(4)	1.736(6)	1.519(8)	119.2(17)	112.8(7)
FC(O)Cl[d]	1.173(2)	1.725(2)	—	127.5(3)	108.8(4)
ClC(O)Cl[e]	1.1789(12)	1.7423(6)	—	124.08(4)	111.85(5)

[a] r_z structure [15]. [b] r_z (ED + MW) [16]. [c] r_a and $\angle_\alpha$ (this work). [d] r_z structure (ED + MW) [17]. [e] r_z structure (ED + MW) [18].

double bond. Such an orientation of the CF_3 group has also been observed in the case of $CF_3C(O)F$ [13]. Recent gas phase studies of $CF_3C(O)SX$ compounds with X = H, CH_3 and Cl [14], however, result in orientations of the CF_3 groups which are intermediate between staggered and eclipsed.

The predominant conformer of $CF_2ClC(O)Cl$ possesses a gauche structure (Θ(ClCCCl) = 75.4(10)°). The C–F bond deviates from the exactly eclipsed orientation with Φ(OCCF1) of 17.7(13)°. The trans conformation, where the C2–Cl2 bond eclipses the C=O bond, is higher in energy. From the GED analysis we obtained $\Delta G^\circ = 1.1(3)$ kcal mol^{-1}, which agrees within the experimental uncertainties with the ΔH° value derived from spectroscopic data by Durig et al. [7] ($\Delta H^\circ = 0.71(17)$ kcal mol^{-1}). Both experimental values demonstrate a clear preference for the gauche conformer, whereas ab initio calculations predict either the predominance of the trans form ($\Delta E = -0.47$ kcal mol^{-1}, HF/3-21G*) or only a slight preference for the gauche structure ($\Delta E = 0.09$ from HF/6-31G* and $\Delta E = 0.18$ kcal mol^{-1} from MP2/6-31G*).

Acknowledgments

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