# Structure and Conformational Composition of Chloromethyl Chloroformate: An Electron-Diffraction and ab Initio Molecular Orbital Investigation

**Kolbjørn Hagen***

*Department of Chemistry, Norwegian University of Science and Technology, Rosenborg, N-7034 Trondheim, Norway*

**Victor Naumov**

*A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420088, Arbuzov str. 8, Kazan, Russia*

*Received: April 3, 1998; In Final Form: June 3, 1998*

Abstract: The structure and the conformational composition of chloromethyl chloroformate, ClC(=O)−O−$CH_2Cl$, has been studied by using gas-phase electron diffraction (GED), ab initio molecular orbital calculations, and earlier published vibrational spectroscopic data. The majority of the molecules [94(6)%] have a syn−gauche conformation where the $-CH_2Cl$ group is syn to the carbonyl bond [torsion angle $\phi(O{=}C_1{-}O_2{-}C_3) \approx 0°$] and $CH_2$−Cl is gauche to the $C_1$−O bond [torsion angle $\phi(Cl{-}C_3{-}O_2{-}C_1) = 83.5(19)°$]. The second conformer is a syn−anti form where the $CH_2Cl$ group is also syn to C=O but where $CH_2$−Cl is anti to $C_1$−O [$\phi(Cl{-}C_3{-}O_2{-}C_1) = 180°$]. Assuming the entropy difference between the two conformers obtained from ab initio calculations [MP2/6-31G(d)], this composition corresponds to an energy difference of $\Delta E° = 1.7(7)$ kcal mol$^{-1}$. The experimental bond distances ($r_g$) and bond angles ($\angle_\alpha$) of the major syn−gauche conformer, with estimated 2$\sigma$ uncertainties ($\sigma$ includes estimates of uncertainties in voltage/camera distance and of correlation in the experimental data) are: $r$(C−H) = 1.097(14) Å, $r$(C=O) = 1.193(2) Å, $r(C_1{-}O)$ = 1.348(3) Å, $r(C_3{-}O)$ = 1.416(4) Å, $r$(C−Cl) = 1.745(2) Å, $r(C_3{-}Cl)$ = 1.777(2) Å, ∠O−C=O = 126.8(3)°, ∠O−$C_1$−Cl = 108.9(3)°, ∠O−$C_3$−Cl = 111.4(5)°, ∠C−O−C = 117.8(7)°, ∠O−C−H = 108.3(17)°. A vibrational force field was evaluated by symmetrizing the quantum-mechanical [MP2/6-31G(d)] Cartesian force constants and scaling the results to fit the observed vibrational wavenumbers.

## Introduction

In simple carboxylic esters with the general formula XC(=O)−O−Y, most of the molecules studied have shown a syn conformation where O−Y eclipses the C=O bond. Some years ago a review about the conformation of such esters was published.[1] Since then several other investigations have been reported,[2−10] and in all of the studies where the conformation has been determined with certainty, the syn conformer has been found to be the low-energy form, and in most cases also the only one observed. If either X or Y is itself an unsymmetric group, there are possibilities for additional conformers in the molecules. One molecule with such an unsymmetrical Y-group is chloromethyl chloroformate, ClC(=O)−O−$CH_2Cl$ (Figure 1). Here the $CH_2Cl$ can be either syn or anti to the carbonyl group, and the $CH_2$−Cl can be either syn, gauche, or anti to C−O. In earlier studies of similar molecules, syn−gauche and/or syn−anti conformers have been observed but no syn−syn conformer has, to our knowledge, ever been found. The absence of a syn−syn form is probably due to the steric strain the molecule would experience in such a conformer. An early electron-diffraction investigation of chloromethyl chloroformate[11] reported a O=C−O−C torsion angle of about 90° and with the chlorine atom in the $-CH_2Cl$ group anti to the carboxyl carbon atom. Since no other similar molecules have been found with such a O=C−O−C torsion angle, the earlier result seems quite unlikely and a later vibrational spectroscopic investigation[12] did indeed conclude that chloromethyl chloroformate had a syn−gauche conformation where the $CH_2Cl$ group, as expected, was syn to C=O, and $CH_2$−Cl was gauche to C−O. No other conformers were observed.

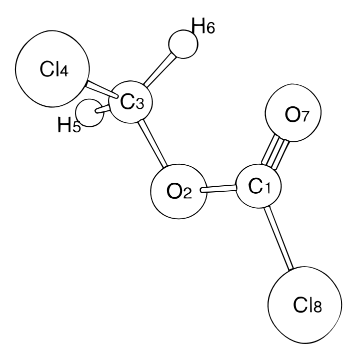


**Figure 1.** Diagram of the syn−gauche conformer of chloromethyl chloroformate with atom numbering.

To get a definitive answer about the conformation of the low-energy form of chloromethyl chloroformate and to find out if any other forms are present, we decided to do a new gas-phase electron diffraction study, this time assisted by ab initio molecular orbital calculations, and also assisted by the earlier published vibrational data. Results for both the geometry and the conformational composition of chloromethyl chloroformate are presented in this paper.

S1089-5639(98)01744-7 CCC: $15.00 
Published on Web 08/11/1998

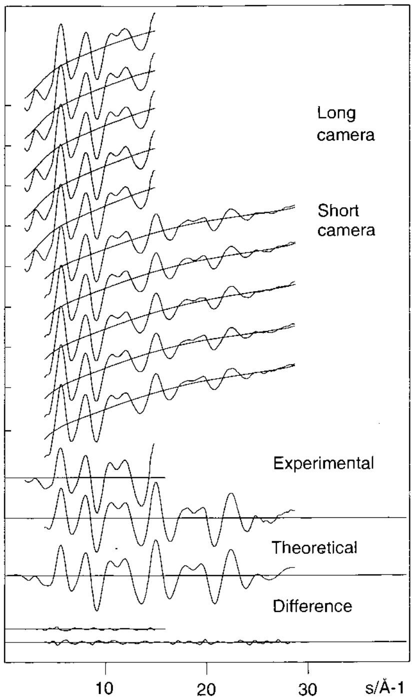


**Figure 2.** Intensity curves. Long camera and short camera curves are magnified 5 times relative to the backgrounds on which they are superimposed. Average curves are in the form $sI_m(s)$. The theoretical curve is calculated from the final model shown in Tables 1 and 4. Difference curves are experimental minus theoretical.

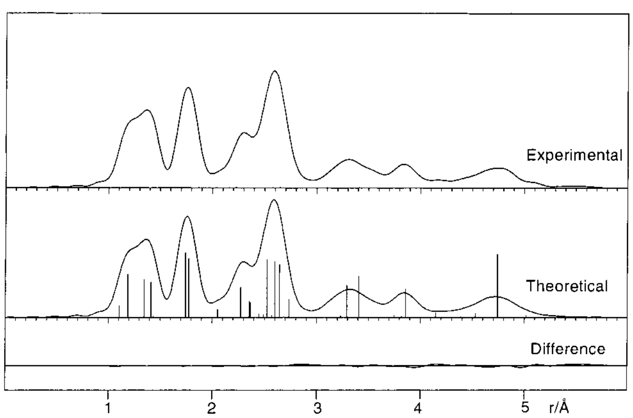


**Figure 3.** Radial distribution curves for chloromethyl chloroformate. The experimental curve is calculated from the average intensity curve with theoretical data for $\leq 1.75$ Å$^{-1}$ and with convergence factor B = 0.002 Å$^2$. Vertical bars indicate interatomic distances (see Table 4); the lengths of the bars are proportional to the weights of the terms.

## Experimental Section

Chloromethyl chloroformate was obtained from Fluka Chemical Co. The sample purity was checked by GC/MS and was found to be better than 98%. The electron-diffraction data were collected using the Balzers Eldigraph KDG-2 at the University of Oslo[13,14] on Kodak electron image plates with a nozzle-tip temperature of 298 K. The nozzle-to-plate distances were 498.71 and 248.81 mm for the long and the short camera experiments, respectively. The electron wavelength was $\lambda$ = 0.058625 Å. Five diffraction photographs from each of the two camera distances were used in the analysis. A voltage/distance calibration was made with benzene as reference.[15] Optical densities were measured by using an Agfa Arcus II commercial scanner[16] at the University of Oslo, and the data were reduced in the usual way.[17,18] The ranges of the data were $2.00 \leq s$ (Å$^{-1}$) $\leq 15.00$ and $4.00 \leq s$ (Å$^{-1}$) $\leq 29.00$ from the two camera distances and the data interval was $\Delta s = 0.25$ Å$^{-1}$. A calculated background[19] was subtracted from each plate to yield experimental intensity curves in the form $sI_m(s)$. The intensity curves with backgrounds are shown in Figure 2. An experimental radial distribution curve (RD) was calculated in the usual way from the average modified molecular intensity curve $I'(s) = sI_m(s)Z_OZ_{Cl}(A_OA_{Cl})^{-1}\exp(-0.002s^2)$, where $A = s^2F$ and $F$ is the absolute value of the complex electron scattering amplitudes, and by use of theoretical data for the unobserved or uncertain region, $s \leq 1.75$ Å$^{-1}$. This RD curve is shown in Figure 3. The scattering amplitudes and phases (used in subsequent calculations) were taken from tables.[20]

**TABLE 1: Experimental and Theoretical Values for Structural Parameters of the Syn−Gauche Conformer of Chloromethyl Chloroformate**[a]

| | experimental | | | theoretical[b] | | |
|---|---|---|---|---|---|---|
| | $r_\alpha$ | $r_g$ | $r_a$ | HF | MP2 | B3LYP |
| $\langle r(C-H)\rangle$[c] | 1.074 (14) | 1.097 | 1.092 | 1.073 | 1.087 | 1.087 |
| $r(C=O)$ | 1.183 (2) | 1.193 | 1.191 | 1.170 | 1.202 | 1.192 |
| $r(C_1-O)$ | 1.341 (3) | 1.348 | 1.347 | 1.321 | 1.354 | 1.348 |
| $r(C_3-O)$ | 1.408 (4) | 1.416 | 1.414 | 1.401 | 1.429 | 1.422 |
| $r(C_1-Cl)$ | 1.733 (2) | 1.745 | 1.743 | 1.732 | 1.742 | 1.766 |
| $r(C_3-Cl)$ | 1.761 (2) | 1.777 | 1.775 | 1.773 | 1.769 | 1.798 |
| $\angle O-C=O$ | 126.8 (3) | | | 126.7 | 127.0 | 127.5 |
| $\angle O-C_1-Cl$ | 108.9 (3) | | | 109.7 | 108.4 | 108.3 |
| $\angle C-O-C$ | 117.8 (7) | | | 117.3 | 114.0 | 115.6 |
| $\angle O-C_3-Cl$ | 111.4 (5) | | | 111.2 | 111.3 | 111.5 |
| $\langle\angle O-C-H\rangle$[c] | 108.3 (17) | | | 108.6 | 107.7 | 108.3 |
| $\phi(C_1-O_2-C_3-Cl)$ | 83.5 (19) | | | 85.6 | 83.1 | 87.2 |
| $\phi(C_3-O_2-C_1-Cl)$ | [181.7] | | | 181.9 | 181.7 | 181.5 |
| % gauche conformer | 94 (6) | | | 83 | 93 | 92 |
| $\Delta E$[d] | 1.7 (7) | | | 1.00 | 1.56 | 1.50 |

[a] Distances are given in angstroms; angles ($\angle_\alpha$) are given in degrees. Quantities in parentheses are estimated $2\sigma$ values and include estimates of uncertainty in voltage/nozzle heights and of correlation in the experimental data. [b] Distances are $r_e$. Basis set used was 6-31G(d). [c] Average value. [d] Theoretical energy differences between syn−gauche and syn−anti conformers, corrected for differences in zero-point energy.

**TABLE 2: Symmetry Coordinates and Observed and Calculated Wavenumbers for Chloromethyl Chloroformate**[a]

| | $\omega_{obs}$ | $\omega_{calcd}$ |
|---|---|---|
| $S_1 = \Delta r_{17}$ | 3060 | 3073 |
| $S_2 = \Delta r_{12}$ | 3000 | 2987 |
| $S_3 = \Delta r_{23}$ | 1805 | 1805 |
| $S_4 = \Delta r_{18}$ | 1448 | 1445 |
| $S_5 = \Delta r_{34}$ | 1344 | 1355 |
| $S_6 = \Delta r_{35}$ | 1264 | 1254 |
| $S_7 = \Delta r_{36}$ | 1117 | 1121 |
| $S_8 = {}^1/_{\sqrt{6}}\Delta(2\alpha_{712} - \alpha_{812} - \alpha_{718})$ | 1010 | 1012 |
| $S_9 = {}^1/_{\sqrt{2}}\Delta(\alpha_{812} - \alpha_{718})$ | 986 | 983 |
| $S_{10} = \Delta\alpha_{123}$ | 799 | 794 |
| $S_{11} = {}^1/_{\sqrt{6}}\Delta(\alpha_{234} + \alpha_{235} + \alpha_{236} - \alpha_{435} - \alpha_{436} + \alpha_{536})$ | 757 | 762 |
| $S_{12} = {}^1/_{\sqrt{6}}\Delta(2\alpha_{234} - \alpha_{235} - \alpha_{236})$ | 683 | 683 |
| $S_{13} = {}^1/_{\sqrt{2}}\Delta(\alpha_{235} - \alpha_{236})$ | 500 | 494 |
| $S_{14} = {}^1/_{\sqrt{6}}\Delta(2\alpha_{536} - \alpha_{436} - \alpha_{435})$ | 455 | 453 |
| $S_{15} = {}^1/_{\sqrt{2}}\Delta(\alpha_{435} - \alpha_{436})$ | 320 | 326 |
| $S_{16} = \Delta\gamma_{1782}$ | 278 | 284 |
| $S_{17} = {}^1/_2\Delta(\tau_{7123} + \tau_{8123})$ | | 90 |
| $S_{18} = {}^1/_3\Delta(\tau_{1234} + \tau_{1235} + \tau_{1236})$ | 80 | 76 |

[a] For atom numbering, see Figure 1.

**Molecular Orbital Calculations.** Ab initio molecular orbital calculations of the syn−gauche and the syn−anti conformers of chloromethylchloroformate were done at different levels of theory using the GAUSSIAN 94 program.[21] These two minimum-energy conformers were fully optimized at the HF, MP2, and B3LYP level, using the 6-31G(d) basis set. The results for the geometry of the low-energy conformer (syn−

**TABLE 3: MP2/6-31G(d) Symmetry Force Constants and Refined Scale Factors for Chloromethyl Chloroformate**[a]

| $F_1$ | $F_2$ | $F_3$ | $F_4$ | $F_5$ | $F_6$ | $F_7$ | $F_8$ | $F_9$ | $F_{10}$ | $F_{11}$ | $F_{12}$ | $F_{13}$ | $F_{14}$ | $F_{15}$ | $F_{16}$ | $F_{17}$ | $F_{18}$ | | scale factors |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14.020 | | | | | | | | | | | | | | | | | | $F_1$ | 0.942 |
| 0.992 | 6.431 | | | | | | | | | | | | | | | | | $F_2$ | 0.917 |
| −0.179 | 0.461 | 5.136 | | | | | | | | | | | | | | | | $F_3$ | 0.917 |
| 0.792 | 0.642 | −0.090 | 3.680 | | | | | | | | | | | | | | | $F_4$ | 0.893 |
| 0.066 | −0.165 | 0.587 | 0.040 | 3.756 | | | | | | | | | | | | | | $F_5$ | 0.893 |
| −0.009 | −0.019 | 0.102 | 0.005 | 0.075 | 5.793 | | | | | | | | | | | | | $F_6$ | 0.875 |
| 0.021 | −0.075 | 0.109 | −0.001 | 0.071 | 0.020 | 5.727 | | | | | | | | | | | | $F_7$ | 0.875 |
| 0.351 | 0.300 | −0.136 | −0.528 | 0.005 | 0.000 | −0.042 | 1.324 | | | | | | | | | | | $F_8$ | 0.927 |
| −0.346 | 0.435 | 0.031 | 0.100 | 0.022 | 0.004 | 0.005 | −0.076 | 1.080 | | | | | | | | | | $F_9$ | 0.927 |
| −0.009 | 0.605 | 0.580 | 0.038 | −0.004 | 0.033 | −0.102 | 0.114 | 0.066 | 1.519 | | | | | | | | | $F_{10}$ | 1.106 |
| 0.050 | −0.087 | 0.611 | 0.017 | −0.177 | −0.016 | −0.017 | −0.009 | 0.019 | 0.060 | 0.880 | | | | | | | | $F_{11}$ | 0.891 |
| −0.005 | −0.047 | −0.079 | −0.009 | 0.325 | −0.017 | −0.007 | 0.009 | −0.009 | −0.023 | 0.128 | 1.110 | | | | | | | $F_{12}$ | 0.891 |
| −0.019 | 0.061 | 0.018 | 0.023 | 0.001 | 0.059 | −0.044 | −0.037 | 0.006 | −0.012 | −0.011 | −0.023 | 0.945 | | | | | | $F_{13}$ | 0.891 |
| −0.017 | 0.007 | 0.000 | 0.010 | −0.384 | 0.087 | 0.075 | 0.011 | −0.005 | −0.001 | 0.051 | −0.063 | 0.014 | 0.650 | | | | | $F_{14}$ | 0.891 |
| 0.012 | −0.016 | −0.007 | 0.000 | −0.010 | 0.021 | −0.031 | −0.012 | 0.001 | −0.035 | −0.018 | −0.035 | 0.129 | 0.002 | 0.835 | | | | $F_{15}$ | 0.891 |
| 0.004 | 0.014 | −0.014 | 0.002 | 0.009 | 0.002 | −0.001 | 0.010 | 0.001 | 0.007 | −0.005 | 0.020 | 0.003 | 0.000 | 0.004 | 0.685 | | | $F_{16}$ | 0.989 |
| −0.007 | −0.042 | 0.010 | 0.016 | 0.009 | 0.000 | 0.010 | −0.008 | −0.009 | −0.009 | 0.019 | 0.054 | −0.008 | 0.003 | −0.014 | 0.015 | 0.172 | | $F_{17}$ | 1.022 |
| −0.029 | −0.035 | −0.008 | 0.023 | 0.030 | −0.009 | 0.025 | −0.035 | −0.005 | −0.042 | 0.023 | 0.094 | −0.036 | −0.007 | −0.031 | −0.012 | 0.042 | 0.131 | $F_{18}$ | 1.022 |

[a] Stretches are given in aJ Å$^{-2}$; bends, in aJ rad$^{-2}$. Symmetry coordinates: see Table 2. Identical values were refined in groups.

gauche) and the energy differences between the syn−gauche and the syn−anti conformers are given in Table 1. Vibrational frequencies and Cartesian force fields, as well as zero-point energies (ZPE), were also calculated [MP2/6-31G(d)] for both the low-energy conformers. The geometry of the other two possible conformers, anti−anti and anti−gauche, were also fully optimized but only at the MP2/6-31G(d) level. These two forms were found to be stable conformers ($\phi_1 = 180°$, $\phi_2 = 180°$ and $\phi_1 = 190°$, $\phi_2 = 79°$), but both had much higher energy than the syn−gauche conformer, 7.43 and 5.46 kcal mol$^{-1}$, respectively. The syn−syn conformer was found to be a conformational maximum with an energy 10.28 kcal mol$^{-1}$ higher than the syn−gauche conformer (MP2).

**Normal Coordinate Calculations**. The ab initio Cartesian force fields were used in the program ASYM40[22] to obtain symmetry force fields. A set of scale constants for the nonredundant set of symmetry force constants was then refined to fit the observed vibrational wavenumbers for chloromethyl chloroformate, and the resulting scaled force fields were used to calculate vibrational amplitudes ($l$), perpendicular amplitude corrections ($K$), and centrifugal distortion constants ($\delta r$) used in the least-squares refinements described below. The symmetry coordinates used and the observed and calculated wavenumbers for the syn−gauche conformer are given in Table 2. In Table 3 the theoretical force field for this conformer is shown together with values for the refined scale constants.

**TABLE 4: Distances and Vibrational Amplitudes in the Gauche Conformer of Chloromethyl Chloroformate**[a]

| | $r_g$ | $l_{calcd}$ | $l_{exp}$ |
|---|---|---|---|
| C−H | 1.097 (14) | 0.077 | |
| C═O | 1.193 (2) | 0.038 | |
| $C_1$−O | 1.348 (3) | 0.047 | |
| $C_3$−O | 1.416 (4) | 0.050 | |
| $C_1$−Cl | 1.745 (2) | 0.050 | 0.053 (3)[b] |
| $C_3$−Cl | 1.777 (2) | 0.051 | 0.054 (3)[b] |
| $C_2$·H | 2.040 (22) | 0.103 | |
| O·O | 2.270 (4) | 0.052 | |
| $O_2$·$Cl_8$ | 2.524 (4) | 0.062 | |
| $O_7$·$Cl_8$ | 2.606 (6) | 0.058 | |
| C·C | 2.360 (9) | 0.064 | |
| $O_2$·$Cl_4$ | 2.638 (7) | 0.070 | |
| H·$Cl_4$ | 2.369 (26) | 0.107 | |
| $C_3$·$O_7$ | 2.735 (14) | 0.093 | |
| $C_3$·$Cl_8$ | 3.863 (7) | 0.066 | 0.082 (8) |
| $C_1$·$Cl_4$ | 3.299 (15) | 0.145 | 0.128 (15) |
| $O_7$·$Cl_4$ | 3.428 (29) | 0.244 | 0.205 (17) |
| Cl·Cl | 4.741 (11) | 0.169 | 0.159 (17) |
| $C_1$·$H_5$ | 3.217 (25) | 0.103 | |
| $O_7$·$H_5$ | 3.728 (26) | 0.119 | |
| $Cl_8$·$H_5$ | 4.513 (25) | 0.122 | |
| $C_1$·$H_6$ | 2.480 (37) | 0.146 | |
| $O_7$·$H_6$ | 2.450 (45) | 0.192 | |
| $Cl_8$·$H_6$ | 4.139 (35) | 0.143 | |

[a] Values are given in angstroms. Quantities in parentheses are estimated $2\sigma$ values and include estimates of uncertainty in voltage/nozzle heights and of correlation in the experimental data. [b] Refined as a group.

## Structure Analysis

The structure of each of the two conformers of chloromethyl chloroformate can be described by six distance and five bond-angle parameters. In addition two torsion angles for the two C−O single bonds are needed to describe the structure. The parameters chosen for each conformer were $r$(C−H), $r$(C═O), $\langle r(\mathrm{C{-}O})\rangle = {}^1/_2[r(\mathrm{C_1{-}O}) + r(\mathrm{C_3{-}O})]$, $\Delta r(\mathrm{C{-}O}) = r(\mathrm{C_3{-}O}) - r(\mathrm{C_1{-}O})$, $\langle r(\mathrm{C{-}Cl})\rangle = {}^1/_2[r(\mathrm{C_1{-}Cl}) + r(\mathrm{C_3{-}Cl})]$, $\Delta r(\mathrm{C{-}Cl}) = r(\mathrm{C_3{-}Cl}) - r(\mathrm{C_1{-}Cl})$, ∠O−C═O, ∠O−$C_1$−Cl, ∠O−$C_3$−Cl, ∠O−C−H, $\phi(\mathrm{O{=}C_1{-}O_2{-}C_3})$, and $\phi(\mathrm{Cl{-}C_3{-}O_2{-}C_1})$. Average values were used for the C−H distances and the O−C−H angles. Not all parameters could be determined independently, and the results from the ab initio calculations were used to establish constraints in the model. The difference between the two types of C−Cl bonds in the molecule, $\Delta r$(C−Cl), was kept constant at the theoretical MP2 value. In addition the differences between corresponding parameters in the two conformers were kept constant at the ab initio (MP2) values. There were also amplitude parameters constructed by grouping individual amplitudes together; the makeup of these is seen in the table of the final results. From the experimental RD curve and from results for related molecules, as well as results from theoretical calculations, trial values for bond distances and bond angles could be obtained. Refinements of the structure, based on the electron diffraction data, were done by the method of least squares,[23] adjusting a theoretical $sI_m(s)$ curve simultaneously to the 10 experimental data sets (one from each of the photographic plates) by using a unit weight matrix. Not all the vibrational amplitudes could be refined simultaneously with the geometrical parameters, and these were kept constant at the values calculated by ASYM40. The O═C−O−C torsion angle in the syn−gauche conformer was close to 0°. This parameter

**TABLE 5: Correlation Matrix (×100) for Parameters of Chloromethyl Chloroformate**

| | | $\sigma_{LS}{}^a \times 100$ | $r_1$ | $r_2$ | $r_3$ | $r_4$ | $r_5$ | $\angle_6$ | $\angle_7$ | $\angle_8$ | $\angle_9$ | $\angle_{10}$ | $\angle_{11}$ | $l_{12}$ | $l_{13}$ | $l_{14}$ | $l_{15}$ | $l_{16}$ | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $\langle r(C-H)\rangle$ | 0.49 | 100 | | | | | | | | | | | | | | | | |
| 2 | $r(C=O)$ | 0.06 | 11 | 100 | | | | | | | | | | | | | | | |
| 3 | $\langle rC-O)\rangle$ | 0.06 | −3 | 10 | 100 | | | | | | | | | | | | | | |
| 4 | $\Delta r(C-O)$ | 0.19 | −30 | −28 | 30 | 100 | | | | | | | | | | | | | |
| 5 | $\langle r(C-Cl)\rangle$ | 0.05 | 1 | 6 | 1 | −18 | 100 | | | | | | | | | | | | |
| 6 | $\angle O-C=O$ | 10.5 | −11 | −25 | 5 | 48 | 3 | 100 | | | | | | | | | | | |
| 7 | $\angle O_2-C_1-Cl_8$ | 9.1 | 15 | −12 | −24 | 18 | −42 | −1 | 100 | | | | | | | | | | |
| 8 | $\angle C-O-C$ | 24.7 | −27 | 17 | −13 | −18 | 14 | −31 | 2 | 100 | | | | | | | | | |
| 9 | $\angle O_2-C_3-Cl_4$ | 16.5 | 10 | −27 | −34 | −4 | −24 | 38 | 50 | −17 | 100 | | | | | | | | |
| 10 | $\angle O_2-C3-H$ | 124.3 | −25 | 19 | 19 | −3 | 37 | 8 | −47 | 47 | −40 | 100 | | | | | | | |
| 11 | $\phi$ | 68.4 | −12 | 7 | −12 | −22 | 28 | 8 | −2 | 47 | 39 | 27 | 100 | | | | | | |
| 12 | $l(C-Cl)$ | 0.06 | −42 | 1 | 21 | 45 | 8 | 27 | −24 | 21 | −7 | 39 | 18 | 100 | | | | | |
| 13 | $l(C_3\cdot Cl_8)$ | 0.27 | −9 | 12 | 2 | −15 | 30 | −1 | −20 | 20 | 7 | 26 | 36 | 18 | 100 | | | | |
| 14 | $l(C_1\cdot Cl_4)$ | 0.51 | −2 | 2 | 1 | −2 | 12 | 17 | −13 | 10 | 17 | 18 | 53 | 18 | 10 | 100 | | | |
| 15 | $l(O_7\cdot Cl_4)$ | 1.31 | −3 | −14 | 11 | 35 | −40 | 3 | 31 | 3 | −14 | −13 | −57 | 2 | −29 | −46 | 100 | | |
| 16 | $l(Cl\cdot Cl)$ | 0.56 | 0 | −19 | 5 | 40 | −49 | 16 | 29 | −8 | −12 | −15 | −44 | 1 | −40 | −16 | 57 | 100 | |
| 17 | % gauche | 2.15 | −4 | 24 | −3 | −44 | 61 | −16 | −41 | 12 | 9 | 28 | 53 | 6 | 49 | 21 | −68 | −82 | 100 |

[a] $\sigma_{LS}$ is the standard deviation from least squares.

**TABLE 6: Geometrical Parameters in Molecules with the General Formula $XC(=O)-O-CH_2Y$[a]**

| | X = Cl, Y = Cl | X = Cl, Y = H | X = F, Y = H | X = H, Y = F | X = H, Y = $CH_3$ | X = $CH_3$, Y = H |
|---|---|---|---|---|---|---|
| $r(C=O)$ | 1.193 (2) | 1.191 (4) | [1.182] | 1.194 (15, 3)[b] | 1.213 (3) | 1.209 (6) |
| $r(C-X)$ | 1.745 (2) | 1.755 (4) | [1.330] | 1.100 (3, 10) | 1.108 (5) | 1.496 (7) |
| $r(CX-O)$ | 1.348 (3) | 1.327 (6) | 1.326 (19) | 1.355 (20, 3) | 1.354 (4) | 1.360 (7) |
| $r(O-CH_2Y)$ | 1.416 (4) | 1.445 (7) | 1.448 (25) | 1.404 (3, 20) | 1.466 (3) | 1.442 (7) |
| $r(C-Y)$ | 1.777 (2) | 1.098 (24) | 1.086 (7) | 1.369 (10, 12) | 1.493 (5) | 1.109 (3) |
| $\angle O-C=O$ | 126.8 (3) | 128.1 (6) | 129.2 (19) | 125.8 (3, 10) | 124.4 (1) | 123.0 (9) |
| $\angle O-C-X$ | 108.9 (3) | 108.7 (4) | 107.2 (19) | 108.5 (15, 3) | 108.4 (1) | 111.4 (9) |
| $\angle C-O-C$ | 117.8 (7) | 114.4 (17) | 114.0 (8) | 115.8 (3, 5) | 117.8 (1) | 116.4 (9) |
| $\angle O-C-Y$ | 111.4 (5) | | 109.4 (9) | 109.6 (3, 10) | 109.7 (1) | 109.1 (9) |
| $\phi(O=C-O-C)$ | [1.6] | 0.0 | 0.0 | 1.5 (10, 5) | 0.0 | 0.0 |
| $\phi(C-O-C-Y)$ | 83.5 (19) | 60.0 | 60.0 | 83.9 (10, 8) | 81.7 (4) | 58.1 (9) |
| method | ED, $r_g$ | ED, $r_g{}^c$ | MV, $r_0$ | MV, $r_0$ | ED, $r_g$ | ED, $r_g$ |
| ref | this work | 2 | 4 | 6 | 5 | 7 |

[a] Distances ($r$) are given in angstroms, angles ($\angle$) are given in degrees. Values in parentheses are estimated uncertainties and may have different definitions in the different publications. [b] Reported uncertainty estimates are not symmetrical. [c] Calculated from the $r_a$ distances given in the paper.

could not be well determined from the GED data and it was kept at the ab initio value. In the final refinement 11 geometrical parameters, five amplitude parameters and the conformational composition were refined simultaneously. The results for the geometrical parameters are shown in Table 1, and the interatomic distances and the vibrational amplitudes are shown in Table 4. Table 5 is the correlation matrix for the refined parameters. Intensity curves for the final model are shown in Figure 2 and the corresponding radial distribution curves are shown in Figure 3.

## Discussion

As expected, our investigation showed that both the two low-energy conformers of chloromethyl chloroformate have the $CH_2Cl$ group syn to the carbonyl bond. The old ED investigation[11] is therefore clearly not correct. The syn−gauche conformer was found to have the lowest energy. This is in agreement with the result reported in the earlier vibrational investigation.[12] The amount of syn−anti form present in our experiment was, unfortunately, low enough to make the value of the experimental energy difference quite uncertain. Our value of 1.7(7) kcal mol$^{-1}$ is larger than all three calculated values (1.00, 1.56, and 1.50 kcal mol$^{-1}$ after correction for differences in ZPE), but all three are within error limits of the experimental value. The ab initio calculations indicated that the anti−anti and anti−gauche conformers are also stable forms, but as they are so much higher in energy, we could find no experimental evidence for them.

Table 6 offers a comparison of the structures of some molecules with the general formula $RC(=O)-O-CH_2R'$. For the three compounds where R′ is not hydrogen, syn−gauche conformers were found in each case. With R′ = Cl this is the major form; with R′ = F it was the only form found;[6] while with R′ = $CH_3$ it was the minor form (39%).[5] The R′−C−C−O torsion angle is surprisingly close in all three molecules, 83.5(19)°, 83.9(10)°, and 81.7(4)°. Our value of 83.5° is also in good agreement with the ab initio values we have calculated.

Most of the parameter values in Table 6 are as expected. The O−C=O angle is larger and the C=O bond is shorter when R = halogen. The same effect is also found when acid halides are compared with aldehydes or ketones. Another parameter that shows some variation is the C−O−C bond angle. This angle seems to be larger whenever R′ is not a hydrogen atom and we have a syn−gauche conformer present.

Most of the parameters determined experimentally for the syn−gauche conformer of chloromethyl chloroformate are in agreement with the ab initio values. In general the HF calculations seem to underestimate the bond distances while the MP2 and DFT calculations probably overestimate them slightly. This is a trend seen quite often, but the differences are not very large. The agreement with the calculated bond angles and torsion angles is quite good.

## Conclusion

Chloromethyl chloroformate has been found to exist as a mixture of two conformers, both of which have the $CH_2Cl$ group syn to the carbonyl group. This is in agreement with earlier results for other carboxylic esters. The low-energy form has $CH_2$−Cl gauche to O−C [torsion angle = 83.5(19)°], the second form has $CH_2$−Cl anti to O−C, and the experimental energy difference is $\Delta E = 1.7(7)$ kcal mol$^{-1}$.

**Acknowledgment.** We are very grateful to Snefrid Gundersen and Hans Vidar Volden, University of Oslo, for help with the collection of the experimental data. This work has received support from The Research Council of Norway (Program for Supercomputing) through grants of computing time.

## References and Notes

(1) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1.
(2) Shen, Q. *Acta Chem. Scand.* **1978**, *A32*, 245.
(3) Durig, J. R.; Griffin, M. G. *J. Mol. Struct.* **1977**, *64*, 252.
(4) Groner, P.; Tolley, C. L.; Durig, J. R. *J. Mol. Struct.* **1990**, *223*, 471.
(5) Peng, Z.; Shlykov, S.; Van Alsenoy, C.; Geise, H. J.; Van der Veken, B. *J. Phys. Chem.* **1995**, *99*, 10201.
(6) Lopata, A. D.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2204.
(7) Pyckhout, W.; Van Alsenoy, C.; Geise, H. J. *J. Mol. Struct.* **1986**, *144*, 265.
(8) True, N. S.; Bohn, R. *J. Mol. Struct.* **1978**, *50*, 205.
(9) Daeyaert, F.; Desseyn, H. O.; Van der Veken, B. J. *Spectrochim. Acta* **1988**, *44A*, 1165.
(10) Charles, S. W.; Jones, G. I. L.; Owen, N. L.; West, L. A. *J. Mol. Struct.* **1976**, *32*, 111.
(11) Kashima, M. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 79.
(12) Daeyaert, F.; Van der Veken, B. J. *J. Mol. Struct.* **1989**, *198*, 239.
(13) Zeil, W.; Haase, L. *Z. Instrumentenkd.* **1966**, *74*, 84.
(14) Bastiansen, O.; Graber, G.; Wegmann, L. *Balzers High Vacuum Rep.* **1969**, *25*, 1.
(15) Gundersen, S.; Strand, T. G.; Volden, H. V. *J. Mol. Struct*. **1995**, *346*, 121.
(16) Gundersen, S., Strand, T. G. *J. Appl. Crystallogr*. **1996**, *29*, 638.
(17) Hagen, K.; Hedberg, K. *J. Am. Chem. Soc*. **1973**, *95*, 1003.
(18) Andersen, B.; Seip, H. M.; Strand, T. G.; Stølevik, R. *Acta Chem. Scand*. **1969**, *23*, 3224.
(19) Gundersen, G.; Hedberg, K. *J. Chem. Phys*. **1969**, *51*, 2500.
(20) Hedberg, L. *Abstracts of Papers*, 5th Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March 1974, p 37.
(21) Ross, A. W.; Fink, M.; Hilderbrandt, R. *International Tables of Crystallography*, Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. 4, p 245.
(22) GAUSSIAN 94, Revision D.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
(23) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc*. **1993**, *160*, 117. (ASYM20). The later ASYM40 version was presented in Hedberg, L. *Abstracts*, 15th Austin Symposium on Molecular Structure, Austin, TX, March 1994.