Conformational Structure of Gaseous 3-Chloropropanoyl Chloride by Electron Diffraction, Normal Coordinate Analysis, and ab Initio Molecular Orbital, and Density Functional Theory Calculations

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The molecular and conformational structures of 3-chloropropanoyl chloride ($CH_2Cl-CH_2-C(=O)Cl$) have been studied by using gas-phase electron diffraction (GED) data obtained at 22 °C (295 K) and ab initio molecular orbital (MO) and density functional theory (DFT) calculations up to the levels of MP4(SDQ) and B3LYP using larger basis sets. Normal coordinate calculations (NCA) taking into account nonlinear vibrational effects were also used in the analyses. The title compound may have up to four low-energy conformers in the gas phase, labeled according to the position of each of the two chlorine atoms in relation to the CCC propanoyl backbone, labeling the carbonyl chlorine torsion angle first: AA, AG, GG, and GA; where A is anti (ideal C−C−C−Cl torsion angle of approximately 180°) and G is gauche (ideal C−C−C−Cl torsion angle of approximately 60°). It has been judged from the experimental GED data and the theoretical calculations, as well as from previously published infrared (IR) studies on the molecule in both the liquid phase and in argon-trapped matrices at 10 K, that the gas phase consists of a mixture of at least three conformers: AA (most stable), AG, and GG, with the possibility of a smaller contribution ($<10\%$) from the higher-energy GA form. The GA conformer cannot be ruled out by the GED experimental data. Relevant structural parameter values obtained from the GED least-squares refinements, with calculated ab initio MO MP2/6-31+G(2d,p) values used as constraints, were as follows (AA values with estimated 2σ uncertainties): Bond lengths (r_{h1}): $r(C-C(=O)) = 1.505(4)$ Å, $r(C-CH_2Cl) = 1.520(4)$ Å, $r(C=O) = 1.197(4)$ Å, $r(C(=O)\text{-}Cl) = 1.789(3)$ Å, and $r(C-Cl) = 1.782(3)$ Å. Bond angles ($\angle_{h1}$): $\angle CCC = 111.5(11)°$, $\angle CCO = 127.0(5)°$, $\angle CC(O)Cl = 112.5(3)°$, and $\angle CCCl = 110.3(3)°$. Torsion angles ($\phi(C-C) = \phi(ClCCC)$): for AA, $\phi_1(C-C(O)) = \phi_2(C-CH_2Cl) = 180°$ (assumed for true C_s symmetry); for AG, $\phi_1(C-C(O)) = -140(5)°$, $\phi_2(C-CH_2Cl) = 76(13)°$; for GG, $\phi_1(C-C(O)) = 46(8)°$, $\phi_2(C-CH_2Cl) = 77(14)°$; for GA, $\phi_1(C-C(O)) = 67.9°$ (assumed), $\phi_2(C-CH_2Cl) = 177.8°$ (assumed). The non-AA conformers all have chiral C_1 symmetry with twice the statistical weight (multiplicity) of C_s. The MP2/6-31+G(2d,p) calculated composition (%) based on the zero-point energy (ZPE) corrected energy differences, and the statistical weights for conformers: AA/AG/GG/GA = 28/35/28/9 was assumed in the final GED refinement. The more recent literature concerning the title molecule, as well as for several related molecules, has been examined and a survey has been attempted in the present article. The new experimental results for 3-chloropropanoyl chloride are discussed and compared with the previously published findings.

I. Introduction

The more recent studies on the molecular structure and physical properties of fundamental organic species include the investigations on acetaldehyde[1] and its halogenated derivatives, like chloroacetaldehyde (2-chloroethanal),[2] chloroacetyl chloride (2-chloroethanoyl chloride),[3a] fluoroacetyl fluoride (2-fluoroethanoyl fluoride),[3b] bromoacetyl chloride (2-bromoethanoyl chloride),[4] and bromoacetyl bromide (2-bromoethanoyl bromide),[4] as well as the acid halides acetyl fluoride (ethanoyl fluoride),[5] acetyl chloride (ethanoyl chloride),[6] and acetyl bromide (ethanoyl bromide).[6] All of these molecules are represented by the general structural formula $YCH_2-C(=O)X$, where X and Y are either a hydrogen atom or a halogen substituent. For instance, to better illustrate the naming convention, chloroacetyl chloride[3a] is the compound with X = Y = Cl. These fundamental organic molecules have been investigated by using gas-phase electron diffraction (GED) and microwave (MW) data, confirming in all cases the existence of multiple conformers coexisting in the vapor phase, except for acetaldehyde[1] (X = Y = H) and the acetyl halides[5,6] (X = F, Cl, Br, Y = H). In acetaldehyde,[1] one of the hydrogens on the methyl group is eclipsing the carbonyl group (C=O), and this preferred eclipsing of the C=O bond is found to be an essential property in the conformational behavior of this class of molecules.[1−6] For instance, in chloroacetyl chloride,[3a] Steinnes et al. found a conformational mixture representing the chlorine on the methyl group (Y = Cl) in syn and gauche positions relative to the C=O bond, where syn was the lower-energy form. In most cases, this eclipsed position of the Y atom on the methyl group to the C=O bond represents the lower-energy conformer, and in most cases a gauche conformer is found to be the accompanying

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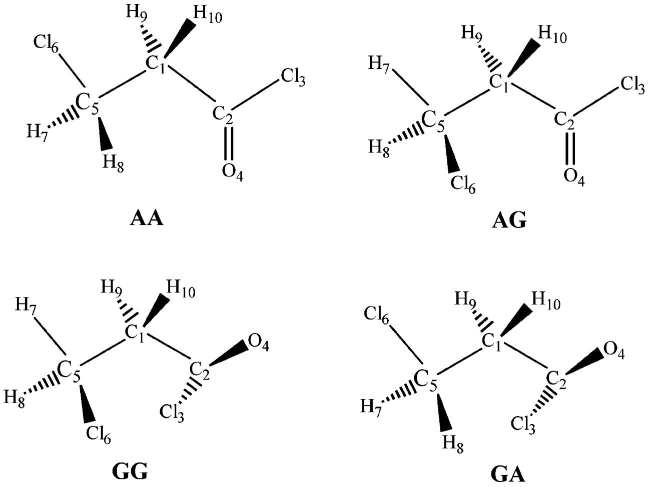

Figure 1. Stereochemical drawings of the four stable conformers of 3-chloropropanoyl chloride. The two-letter labels refer to the relative positions of the two chlorine atoms in the molecule (A = anti, G = gauche).

higher-energy form.[3−6] However, there are exceptions to this basic rule, where an anti form is the second form, and possibly also the lower-energy form, as in chloroacetaldehyde[2] (X = H, Y = Cl), where Dyngeseth et al. found the anti instead of the gauche form. In this molecule the anti form was in fact the lower-energy form compared to the syn conformer (94(7) % at 42 °C). Also in fluoroacetyl fluoride (X = Y = F), the anti form has been found to exist instead of the more usual gauche conformer.[3b]

The conformational aspects were further complicated when progressing to the literature for 2-propanone (acetone) and the propanoyl halide derivatives.[7−15] The propane-based acid halides, $CH_3-CH_2-C(=O)X$, with X = Cl (propanoyl chloride[11]), X = Br (propanoyl bromide[12]), and X = H (propanal[13]), have been shown by GED studies to prefer a syn methyl-to-oxygen arrangement with a second higher-energy gauche conformer also being stable in the vapor phase. In the gauche conformer, the $\phi(C-C-C=O)$ torsion angle is approximately 100−120° depending on the halogen atom present on the carbonyl group. The torsion angle was found lower for the propanoyl bromide ($\phi(C-C-C=O) = 101(9)°$)[12] than for the propanoyl chloride ($\phi(C-C-C=O) = 121(6)°$),[11] and it was also found correspondingly lower in the bromoacetyl-bromide [$\phi(Br-C-C=O) = 105°$ (calculated best fit)].[4] These results were all consistent with the larger bromine substituent on the carbonyl group of the molecules. The conformational properties of the α-halogenated propanones $XCH_2-C(=O)-CH_3$ and the disubstituted 1,3-dihalopropanones $XCH_2-C(=O)-CH_2X$ (X = F, Cl, Br and I) have been firmly investigated by Tormena et al.[7] in 2004 by using a concerted methodology based on density functional theory (DFT) calculations and experimental infrared (IR) spectroscopy, measuring the vibrational frequencies of the carbonyl (C=O) stretch for the conformers in four different solvents of varying polarities, and comparing these frequencies to the DFT-calculated values for proper vibrational assignment.

These studies, as well as other propanone investigations,[8−10] have shown a rather complex mixture of stable minimum-energy conformations. Four conformers of significance for the 1,3-dihalopropanones were observed, out of a total selection of six possible conformations, and these six conformational possibilities were all represented among the series of 1,3-difluoro-, 1,3-dichloro-, and 1,3-dibromopropanones.[7] We should, therefore, be expecting a four-conformer case also for the title compound, 3-chloropropanoyl chloride ($ClCH_2-CH_2-C(=O)Cl$); Figure 1, and this has previously been shown to be the case both from ab initio MO calculations at the HF and MP2 levels of theory[14] for this molecule, and also by FT-IR studies of the molecule in samples as a neat liquid at room temperature and isolated in argon matrices at 10 K.[15] However, in the latter work by Piétri et al.,[15] the characteristic conformer-specific frequencies for the four conformational possibilities AA, AG, GG, and GA (in these two-letter conformer labels, the references are always made to the chlorine to chlorine arrangement) were obtained from the calculated MP2 force field, and these values were compared to the sets of experimental frequencies obtained from the FT-IR spectra. It was observed that the specific frequencies corresponding to the higher-energy GA conformer could not be detected in the experimental spectra, and the other experimental absorption bands originally assigned to this conformer could also be argued to belong to one of the other three conformer possibilities.[15] Thus, it could be concluded, with a certain degree of reliability, that only the AA, AG, and GG conformers were present in the liquid state and in the cryogenic matrix for 3-chloropropanoyl chloride. In this regard, it would seem that the GA conformer of the molecule would be elusive in regards to experimental detection,[14,15] and that a theoretical value for its contribution to the gas-phase mixture must probably be enforced from higher-level ab initio MO and DFT calculations.

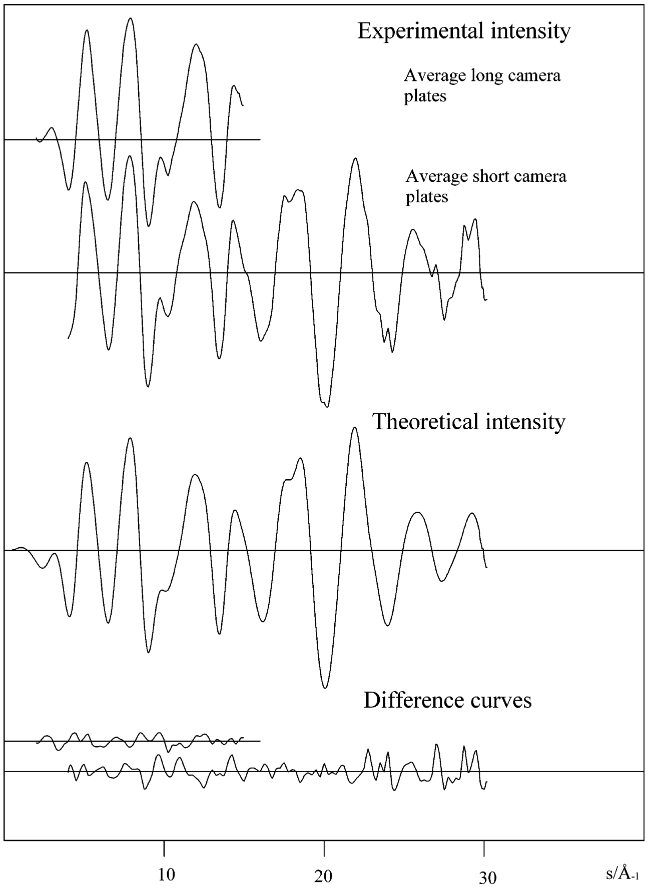

Figure 2. Molecular intensity curves ($sI_m(s)$) for 3-chloropropanoyl chloride. The experimental curves are the average molecular intensity data obtained from the plates from the two camera distances (long camera and short camera). The theoretical curve was calculated from the structural parameters given in Table 3. The difference curves result from subtracting the relevant part of the theoretical curve from each of the two experimental curves.

The present GED study is aided by extensive normal coordinate analysis (NCA) taking into account harmonic nonlinear effects and local centrifugal distortions in the molecule

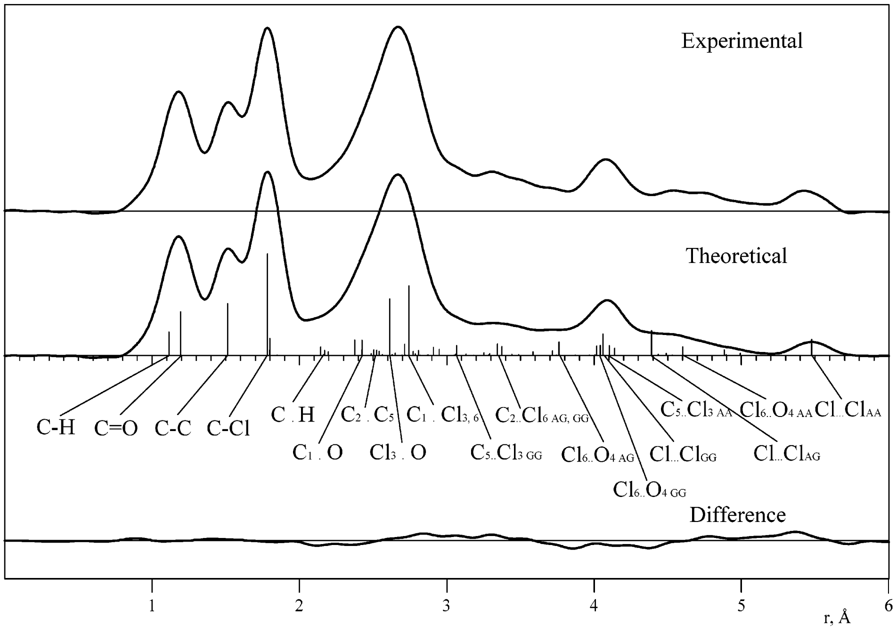

Figure 3. Radial distribution (RD) curves for 3-chloropropanoyl chloride. The experimental curve was calculated from the composite of the 2 sets of average experimental curves (6 LC + 6 SC) shown in Figure 2 with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 1.75$ and $B/\text{Å}^2 = 0.0020$. The difference curve is the experimental curve minus the theoretical curve. The vertical lines indicate the distribution of interatomic distances, they have lengths proportional to the distance weights.

using the SHRINK program system,[16−19] as well as ab initio MO and DFT calculations, giving suitable geometry parameters and quantum-mechanical (QM) force fields for all the conformers later utilized in the NCA. The calculations used the series of HF, MP2, MP4(SDQ), and DFT B3LYP methods in conjunction with the standard (Pople) higher-end 6-31+G(d,p) and 6-31+G(2d,p) electronic basis sets. The present work is also a natural progression from our previous paper on the hexachloropropanone molecule,[20] and the results of our study on the 3-chloropropanoyl chloride and their interpretation are thus the subject of this paper.

II. Experimental Section

Gas Electron Diffraction (GED) Experiment. The sample of 3-chloropropanoyl chloride was used as received (purity >98%) from Aldrich Chemical Co. Electron-diffraction patterns were recorded with the Oslo Balzers gas-phase electron diffraction apparatus on Kodak Electron Image Plates with an average nozzle-tip temperature of 22 °C (295 K). The nominal accelerating voltage was 42 kV and the average electron wavelength was $\lambda = 0.058690$ Å. The nozzle-to-plate distances were 498.72 mm for the long camera (LC) and 248.53 mm for the short camera (SC), while the sector-to-plate distance was 4.24 mm. Six diffraction photographs from both the LC and the SC distances were used in the final analysis. Each plate was traced for its total intensity using a Joyce-Loebl double-beam microdensitometer, and several of the plates were also traced twice, and the data were reduced and averaged in the usual way.[21−23] The ranges of data are $2.00 \leq s/\text{Å}^{-1} \leq 15.00$ and $4.00 \leq s/\text{Å}^{-1} \leq 30.25$, for the LC and the SC distance experiments, respectively. The data interval is $\Delta s = 0.25$ Å^{-1}.

A calculated background[24] was subtracted from the data for each plate to yield experimental intensity curves in the form $sI_m(s)$. The average curves from each of the two camera distances are shown in Figure 2, together with the final theoretical intensity curve and corresponding difference curves. In Figure 3 is shown the final experimental radial distribution (RD) curve calculated in the usual way from the modified molecular intensity curves of the type $I'(s) = sI_m(s)Z_{Cl}Z_{Cl}(A_{Cl}A_{Cl})^{-1}\exp(-0.0020s^2)$, where $A = s^2F$ and F is the absolute value of the complex electron scattering amplitudes. In Figures 4 and 5 are shown additional RD curves calculated for the purpose of conformational analysis, as will be discussed later. Theoretical intensity data were added to the experimental intensity data for the unavailable region ($s \leq 1.75$ Å^{-1}) before the Fourier transform to the RD curve was made. The scattering amplitudes and phases were taken from tables in ref 25.

III. Structure Analysis

III.1. Ab Initio MO and DFT Calculations. Ab initio MO and DFT calculations were made for each conformer of 3-chloropropanoyl chloride at the HF/6-31+G(d,p), MP2(*fc*)/6-31+G(2d,p), MP4(SDQ)/6-31+G(2d,p), and DFT B3LYP/6-31+G(2d,p) levels of theory using GAUSSIAN 98.[26] Since it was impossible to determine completely the structure of each conformer with GED alone, the results for the fully optimized geometries were incorporated into the refined model as constant geometrical differences based on the MP2/6-31+G(2d,p) calculations. These differences provide a way of linking the four conformers AA, AG, GG, and GA together, in particular, the differences between structural parameters. There were no imaginary frequencies calculated for the four conformers through the use of frequency calculations in GAUSSIAN 98, supporting their existence as true minimum-energy conformations. The augmenting of GED analysis with ab initio MO and DFT results is well established,[27−29] and the results from the theoretical calculations are listed in Table 1 for the obtained general parameter values, and in Table 2 for all the torsion angles and the relative energies (ΔE; kcal mol^{-1}), with corresponding Boltzmann-type estimates of conformational compositions at 22 °C (295 K). Zero-point energies (ZPE) and vibrational/rotational entropies were also estimated for the optimized geometries using the thermochemical results for each type of calculation from the corresponding frequency calculations. The exception was

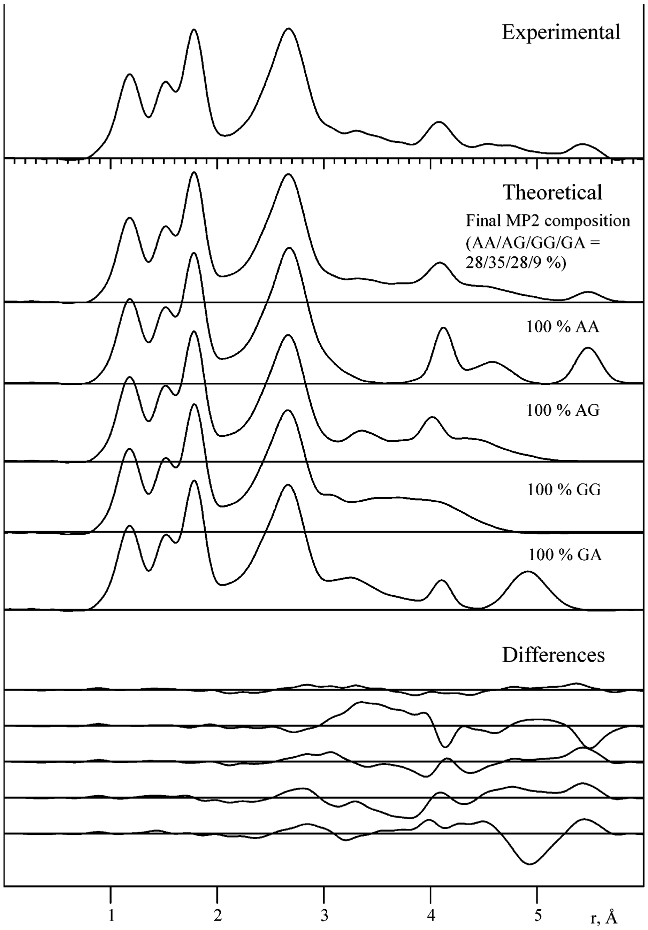

Figure 4. Radial distribution (RD) curves for 3-chloropropanoyl chloride. Theoretical RD curves from the final refined model assuming 100% of each conformer AA, AG, GG, and GA are shown, along with the RD curve corresponding to the final (MP2-constrained) composition.

that the MP4(SDQ) energies were corrected using the ZPE values obtained from the MP2/6-31+G(2d,p) thermal calculations.

III.2. Normal Coordinate Analysis (NCA). Ab initio MO force fields for 3-chloropropanoyl chloride calculated at the MP2/6-31+G(2d,p) level of theory were transformed from Cartesian coordinates to nonredundant internal coordinates by using SHRINK[16−19] for taking into account nonlinear (curvilinear) effects, giving also the corresponding transformed unscaled quantum-mechanical (QM) MP2 force field. The unscaled QM MP2 force fields were subsequently used to calculate shrinkage corrections through the perpendicular amplitude corrections (K) and rotational and local centrifugal distortion constants (δr), as well as the longitudinal root-mean-square (rms) amplitudes of vibration (l) employed in the GED least-squares analysis. The SHRINK program was also used to calculate the potential energy distribution (PED) for each of the four conformers AA, AG, GG, and GA of 3-chloropropanoyl chloride. The resulting 24 vibrational modes and their corresponding wavenumber frequencies (ϖ_i) were sorted according to the potential energy distribution to pair the modes described in the nonredundant internal coordinates contributing more significantly to a particular vibrational wavenumber. For the AA conformer of true C_s symmetry, the vibrational normal modes were divided as 15 A′ and 9 A″ among the eligible irreducible representations, and this symmetry benefit was properly reproduced by the SHRINK NCA calculations. The final least-squares outcome of the GED refinement procedure, using the QM MP2-based sets of shrinkage corrections from the SHRINK program, gave molecular conformational structures for 3-chloropropanoyl chloride described as the r_{h1} type geometry; cf. Tables 3 and 4.

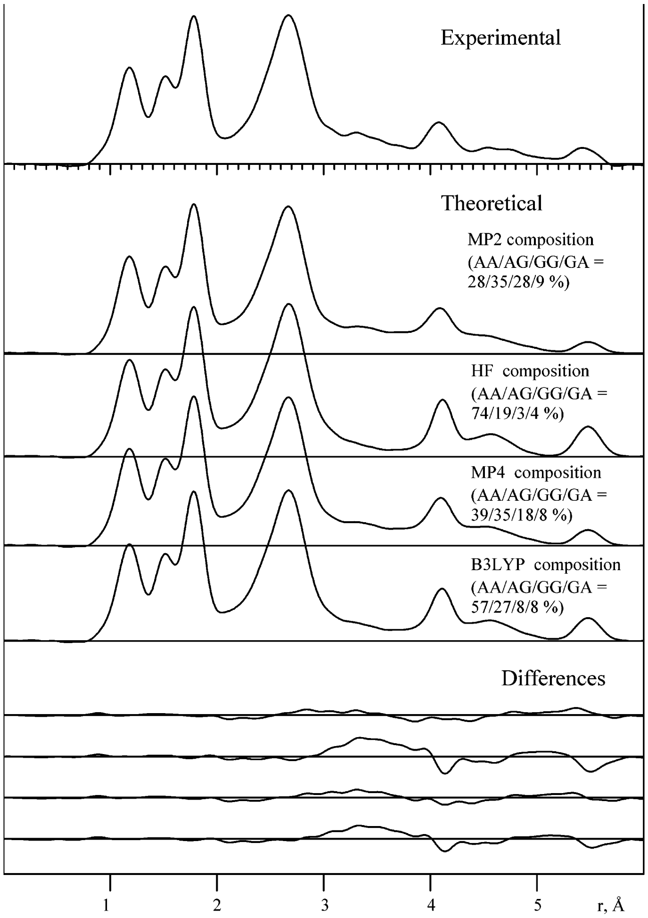

Figure 5. Radial distribution (RD) curves for 3-chloropropanoyl chloride. Theoretical RD curves are shown as being the result of the conformational compositions as predicted by each of the ab initio MO and DFT methods used in this work (MP2, HF, MP4(SDQ) and DFT B3LYP). All other parameters were fixed to the optimally refined values assembled in Table 3.

III.3 Gas Electron Diffraction Refinements. *The GED Molecular Parameters.* Since the AA conformer was predicted to be the lower energy form, it was used as the refinement vehicle for the GED analysis. The AG, GG, and GA conformers were each linked to the AA conformer by a set of molecular parameter differences held at values assumed from the MP2/6-31+G(2d,p) theoretical calculations. The 12 independent molecular parameters which were fit to the experimental data were (the '⟨ ⟩' symbols denote average value parameters): $r\langle(\mathrm{C{-}C})\rangle$, $\mathrm{r}\langle(\mathrm{C{-}Cl})\rangle$, $r(\mathrm{C{=}O})$, $\mathrm{r}\langle(\mathrm{C{-}H})\rangle$, $\angle\mathrm{CCC}$, $\angle\langle(\mathrm{CCCl})\rangle$, $\angle\mathrm{CCO}$, and $\angle\langle(CCH)\rangle$ (not refined), as well as the torsional angle parameters for AG and GG: $\phi_1(\mathrm{C{-}C{-}C{-}Cl_3})$ and $\phi_2(\mathrm{C{-}C{-}C{-}Cl_6})$ for each of the two conformers. The torsion angles for the AA conformer were 180° for each parameter as a consequence of C_s symmetry. The torsion angles for the lower-abundant GA conformer were constrained to the MP2 values. The vibrational properties of each conformer were specified by 45 amplitude parameters, each one corresponding to an interatomic distance in the molecule, giving a final model with 180 weighted distances. The amplitudes were refined together in groups depending on the interatomic distances. Many of the amplitude groups could be successfully refined, but those that could not be refined were held at values calculated with the SHRINK program.[16−19] In the final refinements, seven inde-

TABLE 1: Selected ab Initio MO and DFT-Calculated Parameter Values for the AA and AG Conformers of 3-Chloropropanoyl Chloride[a]

	method/basis set							
	HF/6-31+G(d,p)		MP2/6-31+G(2d,p)[b]		MP4(SDQ)/6-31+G(2d,p)		DFT B3LYP/6-31+G(2d,p)	
parameters[c]	AA	AG	AA	AG	AA	AG	AA	AG
$r(C_1{-}C_2)$	1.5088	1.5115	1.5065	1.5091	1.5124	1.5151	1.5086	1.5115
$r(C_1{-}C_5)$	1.5206	1.5187	1.5207	1.5180	1.5247	1.5220	1.5244	1.5214
$r(C_2{-}Cl_3)$	1.7719	1.7736	1.8066	1.8085	1.8045	1.8072	1.8201	1.8223
$r(C_5{-}Cl_6)$	1.7910	1.7913	1.7999	1.7998	1.8059	1.8066	1.8107	1.8131
$r(C{=}O)$	1.1701	1.1682	1.1939	1.1918	1.1900	1.1878	1.1845	1.1826
$\angle C_2C_1C_5$	111.0	113.0	110.8	112.1	110.9	112.4	111.6	113.5
$\angle C_1C_2Cl_3$	113.1	112.9	111.7	111.6	112.1	111.9	111.9	111.7
$\angle C_1C_5Cl_6$	109.9	111.7	109.5	110.6	109.6	110.9	109.8	111.6
$\angle C_1C_2O_4$	126.5	126.7	127.2	127.3	126.9	127.1	127.6	127.8
$\angle Cl_3C_2O_4$	120.4	120.4	121.0	121.1	121.0	121.0	120.5	120.5
$\angle C_1C_5H_7$	111.7	110.0	111.7	110.6	111.8	110.5	111.9	110.5
$\angle C_1C_5H_8$	111.7	111.7	111.7	111.7	111.8	111.8	111.9	111.9
$\phi_1(Cl_3CCC)$	180.0	−167.8	180.0	−168.2	180.0	−168.5	180.0	−170.0
$\phi_2(Cl_6CCC)$	180.0	75.2	180.0	70.8	180.0	71.7	180.0	75.4
symmetry	C_s	C_1	C_s	C_1	C_s	C_1	C_s	C_1

[a] Notice the difference in basis set used for the HF calculation compared to the electron-correlated methods; the 6-31+G(d,p) basis set contained 142 basis functions for this molecule, and the 6-31+G(2d,p) basis set contained 178 basis functions, with 2 sets of d-functions (6D type) for the non-hydrogen atoms. For the sake of minimizing the use of space, only the more important AA and AG conformer parameters have been assembled in this table. [b] In the GED least-squares refinement procedure, the MP2 calculations were actively used in constraining the difference in parameter values between the four conformers (AA, AG, GG, GA); cf. Table 3. The corresponding MP2 force fields were used to calculate shrinkage corrections for the GED analysis employing the SHRINK program system.[16−19] [c] Distances (r) are in angstroms (Å); bond and torsion angles ($\angle$, ϕ) are in degrees.

TABLE 2: Theoretical Data for Conformational Torsion Angles, Relative Energies, and Composition at 22 °C (295 K) for 3-Chloropropanoyl Chloride from all the ab Initio MO and DFT Calculations[a]

	AA conformer	AG conformer	GG conformer	GA conformer
		HF/6-31+G(d,p)		
ΔZPE (kcal mol^{-1})[b]	0.0	0.0415	0.1109	0.1132
ΔE_o (kcal mol^{-1})[c]	0.0	1.18	2.27	2.09
$\phi_1(Cl_3CCC)$	180.0	−167.8	57.0	71.3
$\phi_2(Cl_6CCC)$	180.0	75.2	63.1	178.4
composition (%)	73.3	19.5	3.1	4.1
		MP2(*fc*)/6-31+G(2d,p)		
ΔZPE (kcal mol^{-1})	0.0	0.0489	0.1801	0.1663
ΔE_o (kcal mol^{-1})	0.0	0.28	0.41	1.08
$\phi_1(Cl_3CCC)$	180.0	−168.2	59.6	67.9
$\phi_2(Cl_6CCC)$	180.0	70.8	59.4	177.8
composition (%)	28.1	35.1	27.8	9.0
		MP4(SDQ)/6-31+G(2d,p)		
ΔZPE (kcal mol^{-1})[d]	[0.0]	[0.0489]	[0.1801]	[0.1663]
ΔE_o (kcal mol^{-1})	0.0	0.47	0.85	1.30
$\phi_1(Cl_3CCC)$	180.0	−168.5	58.9	67.2
$\phi_2(Cl_6CCC)$	180.0	71.7	60.4	177.9
composition (%)	38.7	34.7	18.1	8.5
		DFT B3LYP/6-31+G(2d,p)		
ΔZPE (kcal mol^{-1})	0.0	0.0195	0.1261	0.1437
ΔE_o (kcal mol^{-1})	0.0	0.83	1.58	1.53
$\phi_1(Cl_3C_2C_1C_5)$	180.0	−170.0	58.0	68.0
$\phi_2(Cl_6C_5C_1C_2)$	180.0	75.4	64.3	178.6
composition (%)	56.5	27.4	7.7	8.4

[a] The uncorrected absolute electronic energy values for the AA conformer from the different methods were (hartrees): $E_{AA}(HF) = -1109.777583$; $E_{AA}(MP2) = -1110.725444$; $E_{AA}[MP4(SDQ)] = -1110.773375$; $E_{AA}(DFT\ B3LYP) = -1112.377023$. The ϕ_1 and ϕ_2 parameters are the conventional torsion angles for rotation about $C_2{-}C_1$ and $C_1{-}C_5$, respectively, with respect to the two chlorine atoms. The conformer composition values were obtained for $T = 295$ K (22 °C) by using simple Boltzmann statistics to obtain the mole fractions followed by multiplication by 100. [b] Calculated differences in the zero point energies (ZPE) between the conformers. For the HF calculations, the ZPE differences were scaled by the recommended factor of 0.8929,[31] and the scaled values are listed in the table. [c] Relative conformer energies corrected by the respective ZPE differences (kcal mol^{-1}). [d] The MP4(SDQ) conformer energies were corrected using the corresponding MP2 ZPE energy values; noted here by using brackets enclosing the values.

pendent geometrical parameters, as described above, two torsion parameters ϕ_1 and ϕ_2 for each of the AG and GG conformers, as well as seven amplitudes were refined simultaneously. The results are given in Table 3. Table 4 lists some of the more important experimental nonbonded interatomic distances together with theoretical ones for the AA conformer taken from the MP2/6-31+G(2d,p) calculations. The correlation matrix for the refined parameters is shown in Table 5. Theoretical RD curves from the final refined model assuming 100% of each conformer are shown in Figure 4, along with the RD curve for

TABLE 3: Parameters Used to Define the Structure and the Values Obtained from the Combined GED/MP2 Least-Squares Refinements of 3-Chloropropanoyl Chloride Using Curvilinear "Shrinkage" Vibrational Corrections (r_{h1})[a]

:	AA conformer		AG conformer		GG conformer		GA conformer		MP2/6-31+G(2d,p), AA conformer	
parameter	r_{h1}, $\angle_{h1}$	l_{exp}	r_{h1}, $\angle_{h1}$	l_{exp}	r_{h1}, $\angle_{h1}$	l_{exp}	r_{h1}, $\angle_{h1}$	l_{exp}	r_e, $\angle_e$	l_{theo}
$r(\langle C{-}C\rangle)$	1.513(4)	0.054(4)	1.513(4)	0.054(4)	1.515(4)	0.054(3)	1.517(4)	0.054(4)	1.5136	0.050
$\Delta(C{-}C_2)^b$	[−0.0071]		-		-		-		−0.0071	
$\Delta(C{-}C_5)$	[+0.0071]		-		-		-		+0.0071	
$r(\langle C{-}Cl\rangle)$	1.786(3)	0.056(4)	1.787(3)	0.057(4)	1.791(3)	0.057(4)	1.790(3)	0.057(4)	1.8033	0.054
$\Delta(C{-}Cl_3)^c$	[+0.0033]		-		-		-		+0.0033	
$\Delta(C{-}Cl_6)$	[−0.0033]		-		-		-		−0.0033	
$r(C{=}O)$	1.197(4)	0.049(6)	1.195(4)	0.049(6)	1.193(4)	0.049(6)	1.195(4)	0.049(6)	1.1939	0.037
$r(\langle C{-}H\rangle)$	1.118(13)	[0.076]	1.119(13)	[0.076]	1.118(13)	[0.076]	1.118(13)	[0.076]	1.0897	0.076
$\angle CCC$	111.5(11)		112.8(11)		113.7(11)		111.3(11)		110.8	
$\angle(\langle CCCl\rangle)$	111.3(3)		111.8(3)		112.0(3)		111.4(3)		110.6	
$\Delta(CCCl_3)^d$	[+1.1359]		-		-		-		+1.1359	
$\Delta(CCCl_6)$	[−1.1359]		-		-		-		−1.1359	
$\angle CCO$	127.0(5)		127.1(5)		127.3(5)		127.3(5)		127.2	
$\angle(\langle CCH\rangle)$	[110.5]		[110.0]		[109.4]		[109.9]		110.5	
$\phi_1(C_1{-}C_2)^e$	[180.0]		−140(5)		46(8)		[67.9]		180.0	
$\phi_2(C_1{-}C_5)$	[180.0]		76(13)		77(14)		[177.8]		180.0	
Selected Dependent Parameters:										
$r(C_2{-}C_1)$	1.505(4)	0.054(4)	1.508(4)	0.054(4)	1.508(4)	0.054(4)	1.508(4)	0.054(4)	1.5065	0.050
$r(C_1{-}C_5)$	1.520(4)	0.054(4)	1.517(4)	0.054(4)	1.521(4)	0.054(4)	1.527(4)	0.055(4)	1.5207	0.050
$r(C_2{-}Cl_3)$	1.789(3)	0.059(4)	1.791(3)	0.059(4)	1.800(3)	0.061(4)	1.798(3)	0.060(4)	1.8066	0.056
$r(C_5{-}Cl_6)$	1.782(3)	0.053(4)	1.782(3)	0.054(4)	1.782(3)	0.054(4)	1.781(3)	0.054(4)	1.7999	0.051
$\angle CCCl_3$	112.5(3)		112.3(3)		112.6(3)		112.6(3)		111.7	
$\angle CCCl_6$	110.3(3)		111.3(3)		111.3(3)		110.2(3)		109.5	
$100\alpha^f$	[28.1]		[35.1]		[27.8]		[9.0]		28.1	

[a] Distances (r) and rms vibrational amplitudes (l) are in angstroms (Å); bond and torsion angles ($\angle$, ϕ) are in degrees. The "$\langle\ \rangle$" denotes average parameter values. The values in parentheses represent 2σ. [b] $\Delta(C{-}C_2) = r(C_1{-}C_2) - r(\langle C{-}C\rangle)$, $\Delta(C{-}C_5) = r(C_1{-}C_5) - r(\langle C{-}C\rangle)$. [c] $\Delta(C{-}Cl_3) = r(C_2{-}Cl_3) - r(\langle C{-}Cl\rangle)$, $\Delta(C{-}Cl_6) = r(C_5{-}Cl_6) - r(\langle C{-}Cl\rangle)$. [d] $\Delta(CCCl_3) = \angle CCCl_3 - \angle(\langle CCCl\rangle)$, $\Delta(CCCl_6) = \angle CCCl_6 - \angle(\langle CCCl\rangle)$. [e] $\phi_1(C_1{-}C_2) = \phi_1(Cl_3C_2C_1C_5)$; $\phi_2(C_1{-}C_5) = \phi_2(Cl_6C_5C_1C_2)$. [f] The gas-phase composition of the conformers as assumed in the GED refinements (based on the ZPE-corrected MP2/6-31+G(2d,p) energy values). The final average "goodness of fit" factor $R = [\Sigma w_i\Delta_i^2/\Sigma w_i(s_iI_m^{exp}(s))^2]^{1/2} = 0.2228$, where $\Delta_i = s_iI_m^{exp}(s) - s_iI_m^{calc}(s)$.

TABLE 4: Selected Nonbonded Distances and Rms Vibrational Amplitudes as Obtained from the GED/MP2 Least-Squares Refinements of 3-Chloropropanoyl Chloride for All the Conformers, together with the Calculated MP2 Values for the AA Conformer Using Curvilinear Vibrational Corrections in Obtaining the Amplitudes[a]

:	AA conformer		AG conformer		GG conformer		GA conformer		MP2/6-31+G(2d,p), AA conformer	
parameter	r_{h1}	l_{exp}	r_{h1}	l_{exp}	r_{h1}	l_{exp}	r_{h1}	l_{exp}	r_e	l_{theo}
Torsion Independent										
$Cl_3{\cdot}O_4$	2.609(7)	0.066(11)	2.610(7)	0.067(11)	2.611(7)	0.067(11)	2.610(7)	0.067(11)	2.629	0.060
$C_1{\cdot}Cl_3$	2.743(6)	0.076(11)	2.744(6)	0.076(11)	2.757(6)	0.076(11)	2.755(6)	0.076(11)	2.748	0.069
$C_1{\cdot}Cl_6$	2.712(6)	0.079(11)	2.728(6)	0.078(11)	2.732(6)	0.079(11)	2.718(6)	0.079(11)	2.716	0.073
$C_2{\cdot}C_5$	2.500(15)	0.078(11)	2.519(15)	0.076(11)	2.537(15)	0.080(11)	2.506(15)	0.092(11)	2.492	0.072
$C_1{\cdot}O_4$	2.422(7)	0.065(11)	2.424(7)	0.065(11)	2.424(7)	0.065(11)	2.426(7)	0.065(11)	2.423	0.059
$C_1{\cdot}H_7$	2.193(11)		2.177(11)		2.175(11)		2.199(11)		2.172	0.105
$C_1{\cdot}H_8$	2.193(11)		2.191(11)		2.195(11)		2.197(11)		2.172	0.105
Torsion Dependent										
$C_5{\cdot\cdot}Cl_3$	4.117(11)	0.047(20)	3.991(32)	0.053(20)	3.067(83)	0.108(21)	3.253(21)	0.158(21)	4.121	0.073
$C_2{\cdot\cdot}Cl_6$	4.082(11)	0.045(20)	3.333(16)	0.121(21)	3.364(158)	0.127(21)	4.087(11)	0.049(20)	4.086	0.071
$C_5{\cdot\cdot}O_4$	2.820(23)	0.118(12)	2.961(35)	0.113(12)	3.571(42)	0.132(12)	3.423(15)	0.197(13)	2.809	0.112
$H_7{\cdots}O_4$	2.807(29)		3.963(83)		4.506(31)		3.859(22)		2.806	0.248
$H_8{\cdots}O_4$	2.807(29)		2.657(121)		3.846(114)		3.383(23)		2.806	0.248
$Cl_6{\cdots}O_4$	4.583(21)	0.143(86)	3.773(232)	0.254(86)	4.033(205)	0.297(87)	4.958(11)	0.180(86)	4.588	0.109
$H_7{\cdots}Cl_3$	4.461(18)		4.861(44)		3.993(147)		2.873(11)		4.459	0.173
$H_8{\cdots}Cl_3$	4.461(18)		4.402(90)		2.518(155)		3.667(25)		4.459	0.173
$Cl_3{\cdots}Cl_6$	5.447(12)	0.097(23)	4.356(163)	0.256(25)	4.042(260)	0.291(26)	4.868(21)	0.154(24)	5.453	0.102

[a] Interatomic distances (r) and rms vibrational amplitudes (l) are in angstroms (Å). The values in parentheses represent 2σ.

the final (MP2-constrained) composition. In Figure 5, we have calculated theoretical RD curves for 3-chloropropanoyl chloride as being the result of the conformational compositions as predicted by each of the ab initio MO and DFT methods used in this work (MP2, HF, MP4(SDQ), and B3LYP; respectively), with the composition values being noted on the figure for readability. In these calculations all the remaining parameters were held constrained at the already optimized GED values, as assembled in Table 3, thus making the obtained RD-curves directly comparable.

Refinements and Shrinkage Corrections. Least-squares refinements[30] of the molecular parameters were made by adjusting a theoretical $sI_m(s)$ curve simultaneously to the 12 experimental intensity curves, one from each of the photographic plates taken

TABLE 5: Correlation Matrix (×100) for the GED/MP2 Least-Squares Refined Parameters of 3-Chloropropanoyl Chloride

	σ_{LS}[a]	r_1	r_2	r_3	r_4	$\angle_5$	$\angle_6$	$\angle_7$	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	l_{17}	l_{18}
$r\langle C-C\rangle$	0.118	100																	
$r\langle C-Cl\rangle$	0.064	−4	100																
$rC{=}O$	0.137	−5	−5	100															
$r\langle C-H\rangle$	0.469	−6	4	−29	100														
$\angle CCC$	37.3	−33	−1	−4	13	100													
$\angle\langle CCCl\rangle$	12.2	−39	−23	13	−3	22	100												
$\angle CCO$	16.7	5	30	9	−8	−24	−25	100											
$\phi(C_1C_2)_{AG}$	177.6	1	0	−3	−1	−19	−22	22	100										
$\phi(C_1C_5)_{AG}$	463.1	5	1	−5	−2	11	−6	−7	41	100									
$\phi(C_1C_2)_{GG}$	298.1	−9	−1	1	4	4	12	16	−15	−57	100								
$\phi(C_1C_5)_{GG}$	490.5	0	1	3	2	−23	−3	4	−42	−82	32	100							
$l(C{=}O)$	0.187	−21	4	0	50	13	2	−14	−9	−11	7	9	100						
$l(C-Cl_3)$	0.096	−14	0	19	−1	3	1	−18	−13	−14	4	12	41	100					
$l(C-C_2)$	0.127	−9	0	20	−15	−2	14	6	2	−6	8	1	8	−3	100				
$l(Cl_3{\cdot}O)$	0.381	−3	0	19	−6	12	−41	−42	−4	9	−32	−1	25	40	−1	100			
$l(C_5{\cdot\cdot}Cl)$	0.720	−2	0	−2	−2	−13	−14	16	73	38	−16	−38	−5	−4	3	−2	100		
$l(Cl_6{\cdot\cdot}O)$	3.034	−1	0	0	0	1	1	5	32	31	9	−46	−1	0	2	−6	25	100	
$l(Cl{\cdot\cdot}Cl)$	0.805	−1	−1	3	−1	−1	2	−4	−7	−10	3	8	7	11	2	7	−6	6	100

[a] Standard deviations (× 100) from least-squares refinement. Distances (*r*) and amplitudes (*l*) are in angstroms; angles (∠, *ϕ*) are in degrees.

at the two camera distances LC and SC, using a unit weight matrix. The structures were converted to the r_{h1} type geometry using values for the rotational and local centrifugal distortion constants (δr), perpendicular amplitude corrections (K_T), and rms amplitudes of longitudinal vibration (l) calculated at the temperature of the GED experiment at 22 °C (295 K), using nonlinear corrections in the coordinate transformations employed in the NCA with the SHRINK program described primarily by Sipachev,[16−18] as previously discussed.

IV. Results and Discussion

In the present work, the final GED least-squares refinements were based on the MP2-calculated conformational composition for 3-chloropropanoyl chloride. Attempts at refining the gaseous mixture with four contributing conformers (AA, AG, GG, GA) were performed, but the results were deemed too unreliable. Instead, we have calculated a series of RD-curves for the molecule, presented in Figure 4 (100% curves) and Figure 5 (composition curves). From Figure 4, the AA contributions to the RD-curve were best visible at 4.10 Å, which were the two different torsion-dependent carbon to chlorine nonbonding interactions, and at the longer distance 5.45 Å, which was the unique chlorine to chlorine interaction. Since this latter contribution was only present in the AA conformer, it was used to help making an approximate evaluation of the conformational composition based on the variations presented in Figure 5. As could be seen, the only difference between the MP2 curve and the MP4 curve was the change from 28% contribution of both AA and GG (MP2) to 39% AA and only 18% GG (MP4), thus giving a “flow” of about 10% from the GG conformer to the AA conformer, in going from the MP2 to the MP4 results, while the AG conformer remained constant at 35% contribution; cf. Figure 5. However, closely inspecting the MP4 curve, the amount of the AA conformer of 39% was still somewhat high, while the 28% figure in the MP2 curve for the same conformer was probably somewhat low. Thus, from the inspection of the curves in Figure 5, we could conclude with some degree of certainty that an approximate 30−35% contribution was a reasonable estimate for AA in the experimental gaseous mixture at 22 °C (295 K). Early GED refinements performed by Muren[32] gave indeed an experimental conformational composition for 3-chloropropanoyl chloride as 39(19) % AA and 42(40) % AG, which was in good accordance with the present argument. However, also these results were unreliable in concluding about the contribution of the more elusive GG and GA conformers. Especially the GG conformer, based on the visible inspection of peaks representing the two torsion-dependent C •• Cl distances at 3.1−3.4 Å, was judged to contribute at least approximately 20−25% to the gaseous mixture at this temperature; cf. Figure 5, which was much higher than the estimates of Muren.[32]

The direct eclipsing of the C═O bond seems to be a fundamental property of these propanone and propanoyl halide systems,[1−15] and only in special cases, like in the DFT calculations for 1,3-difluoropropanone and 1,3-dichloropropanone reported by Tormena et al.,[7] was an anti arrangement of the C−X bond relative to the carbonyl C═O bond found to be a stable conformation on the potential energy surface (PES; X = F, Cl), as in the reported syn−anti conformer of these two molecules.[7] In the case of the 1,3-dihalopropanones studied by Tormena et al., up to four different conformers for each molecule were observed, although in the liquid state the compositions were highly dependent on the solvent polarity. There was a clear preferance for the higher dipole molecular structures in the more polar solvents, like acetonitrile, $CH_3{-}CN$. For the molecule 1,3-dichloropropanone, a full gas-phase electron diffraction study has been reported[8a] in 2002. The experimental GED results lead to the conclusion that only two conformers were present in the gas composition at 92 °C (365 K). The more abundant conformer gauche−gauche of C_2 symmetry was in accordance with the IR results,[7] while the second form observed by GED[8a] was claimed to be the syn−gauche conformer. In the IR study,[7] the second more important conformer of 1,3-dichloropropanone was taken to be the syn−anti instead, based on the DFT calculations using a larger basis set for the presumed vapor state. While previous studies have indeed revealed the chlorine atom being able to hold an anti position in relation to the carbonyl oxygen bond, like in the chloroacetaldehyde,[2] the DFT results for 1,3-dichloropropanone[7] were most probably in error, based on the recent GED results[8a] using high-quality data, as well as previous molecular-mechanics (MM) calculations.[8b]

IR and Raman vibrational studies on 1,1-dichloropropanone ($Cl_2HC{-}C({=}O){-}CH_3$) was reported by Durig et al. in 1990,[9] as well as the GED/ab initio MO study on this 2-conformer-case molecule by Hagen et al. in 2002.[10] The molecules were found to exist in the vapor state as a mixture of the more abundant (85−100%) syn, where there was an unique C−H lying in the C−C═O plane, and the higher-energy gauche form,

TABLE 6: Comparison of Selected Parameter Values for Six Related Halogenated Propanones and Propanoyl Halides from GED Studies[a]

	propanoyl chloride	propanoyl bromide	3-chloropropanoyl chloride	1,3-dichloropropanone	1,1-dichloropropanone	hexachloropropanone
formula	$CH_3CH_2C(=O)Cl$	$CH_3CH_2C(=O)Br$	$ClCH_2CH_2C(=O)Cl$	$ClCH_2C(=O)CH_2Cl$	$Cl_2CHC(=O)CH_3$	$Cl_3CC(=O)CCl_3$
type/symmetry	r_g/C_s (syn)[b,c]	r_g/C_s (syn)[b]	r_{h1}/C_s (AA)	r_g/C_2 (ac-ac)	r_g/C_1 (syn)	r_g/C_2
	X = Cl	X = Br	X = Cl	X = Cl	X = Cl	X = Cl
$r(C=O)$	1.186(3)	1.183(5)	1.197(4)	1.210(2)	1.196(6)	1.202(11)
$r(C-X)$	1.798(3)	1.981(5)	1.789(3)/1.782(3)	1.789(1)	1.775(2) (av)	1.772(3)
$r(C-C(O))$	1.523(10)	1.524(9)	1.505(4)	1.526(3)	1.524(4) ($-CHCl_2$)	1.590(10)
$r(C-C)$	1.527(10)	1.526(11)	1.520(4)	-	1.496(4) ($-CH_3$)	-
∠CCC	112.5(5)	111.8(9)	111.5(11)	[118.0]	115.2(5)	123.5(11)
∠CCO	127.0(4)	126.6(6)	127.0(5)	121.0(4)	119.6(5)/125.2(5)	118.2(5)
∠CCX	112.2(3)	112.5(4)	111.3(3) (av)	110.2(4)	110.6(5) (av)	109.5(3)
more stable conformer	synperiplanar $\phi(CCCO) = 0°$	synperiplanar $\phi(CCCO) = 0°$	AA $\phi_1 = \phi_2 = 180°$ [d]	anticlinal−anticlinal $\phi_1 = \phi_2 = 116°$ [e]	synperiplanar $\phi(HCCO) = 2(8)°$	C_2 conformer $\phi_1 = \phi_2 = 32(1)°$ [f]
ref.	11, 12	12	present work	8a	10	20

[a] Distances (r) are in angstroms; angles (∠, ϕ) are in degrees. [b] The r_g values are converted from the reported weighted average r_a values and vibrational amplitudes at 293 K. [c] Values based on the set reported in Table 4 of ref 12. [d] $\phi_1 = \phi(Cl_3C-C-C)$; $\phi_2 = \phi(Cl_6C-C-C)$. [e] $\phi_1 = \phi_2 = \phi(Cl-C-C=O)$. [f] $\phi_1 = \phi_2 = \phi(Cl-C-C=O)$.

with one of the two C−Cl bonds ideally lying in the C−C═O plane. The ϕ(H−C−C═O) torsion angle was approximately 146° in the gauche form, and was found higher in energy by 2.25 kcal mol^{-1} compared to the syn conformer, according to the MP2 calculations, which was in agreement with the IR study.[9] In comparison, as can be seen in Table 2, the AA conformer of 3-chloropropanoyl chloride was calculated to be lower in energy than the AG, GG, and GA conformers from all the methods employed in this work. The energy differences were found larger from the HF and the DFT B3LYP calculations than from the more unanimous MP2 and MP4(SDQ) calculations. The latter two methods gave AA the lower energy by values ranging from 0.3 to 1.3 kcal mol^{-1}, with the GA conformer having the highest energy in both calculations; cf. Table 2. A sound chemical reasoning for the relative energies and the conformational preferences of 3-chloropropanoyl chloride was best attempted by looking at the behavior of the somewhat similar systems 1,3-dichloropropanone[8a] and the 1,1-dichloropropanone,[9,10] as well as comparing the nonbonding Cl··Cl and C··Cl distances with the values obtained from tables of the ideal van der Waals atomic radius,[33] primarily basing the discussion on standard electronic and steric factors. Given that eclipsing of the carbonyl group is regarded a fundamental property, the molecular conformers in question[8−10] have a choice of eclipsing the C═O bond with either a chlorine or a hydrogen atom. In the 1,3-dichloropropanone, the gauche−gauche was found to be more abundant form,[8a] giving a clear preference for the hydrogen atom lying in the plane of the C═O bond, which was clearly supported by the findings in 1,1-dichloropropanone.[9,10] Presumably, this is mostly a consequence of C═O···H−C hydrogen bonding. In 3-chloropropanoyl chloride, we thus find conformers having these characteristics (AA, AG, GG, and GA), where also the whole $-CH_2Cl$ chloromethyl group could be regarded as eclipsing the C═O bond in the AA and AG forms. The sum of the values for the van der Waals radius for the carbon and chlorine atoms was 3.66 Å,[33] slightly longer than the GED distances obtained for the gauche interactions for this atomic pair found in the GG conformer (3.1−3.4 Å), presumably making this interaction slightly repulsive in this conformer, while being shorter than the corresponding interactions in the AA conformer (ca. 4.1 Å in AA; cf. Table 4). Taking twice the chlorine van der Waals distance gave a value of 3.62 Å, a value shorter than any chlorine··chlorine interaction found in the four conformers. This should make this important nonbonded interaction for the most part attractive in nature for all the conformers, but possibly favoring the GG form, where this interaction was determined to be 4.042 Å from the GED refinements (the lowest of all conformers), thus counteracting the seemingly unfavorable carbon···chlorine distances. Together, these and other factors would contribute to the relative energies for the conformers, while also making the multiconformational mixture of gaseous 3-chloropropanoyl chloride quite difficult to assess from the experimental GED data we have used in this work.

In Table 6, we have assembled the GED structural results for 1,1-dichloropropanone,[10] 1,3-dichloropropanone,[8a] our previous work on the hexachloropropanone,[20] as well as results for propanoyl chloride[11] and propanoyl bromide,[12] together with 3-chloropropanoyl chloride in the present work. The parameter values for 3-chloropropanoyl chloride were in good accordance with expected values based on comparisons with these other related halogenated propanoyl halides and propanones, both in the r(C−C) and r(C═O) bond distances, and in the ∠CCC and ∠CCO bond angles. The somewhat puzzling point to consider regarding structural parameter values for the present molecule, was the relative length of the two C−Cl bond distances in 3-chloropropanoyl chloride. As can be seen from Table 1 and Table 3, the MP2 and the DFT B3LYP calculations gave the methyl CH_2-Cl a shorter bond distance value than the corresponding carbonyl C(═O)−Cl bond, in contrast to the results from the HF and, in part, the MP4(SDQ) calculations; cf. Table 1. These internal discrepancies between the different methods could be resolved by investigating the potential energy distribution (PED) for the AA conformer of the molecule from the NCA calculations to discover the normal mode vibrational frequencies, the corresponding diagonal internal coordinate force constants, as well as employing arguments based on the IR intensities and Raman activities for the two structurally different C−Cl bond distances, which were all consistent with the results obtained by Badawi et al.[14] for the AA 3-chloropropanoyl chloride. According to all these data, the methyl CH_2-Cl bond distance value should indeed be found reasonably shorter than the carbonyl C(═O)−Cl bond, as the former could be assigned a higher vibrational frequency based on reasonable IR-intensity and Raman activity considerations.[14] Badawi et al. found scaled representative HF values of 662 and 435 cm^{-1} being assigned to the methyl CH_2-Cl and carbonyl C(═O)−Cl bond distances, respectively,[14] compared to the corresponding unscaled MP2 values of 693 and 445 cm^{-1}, using the PED contribution table obtained from our NCA computations using SHRINK.[16−19]

In conclusion, the present work has given reasonable arguments and results for the experimental and theoretical structure and the conformational composition of 3-chloropropanoyl chloride, using GED and higher level ab initio MO and DFT methods, as well as a survey of the recent results from the scientific literature regarding the fundamental organic species represented by the propanoyl halides and halogenated propanones discussed in this work.

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Supporting Information Available: Text giving SHRINK data files for the four possible low-energy conformers of 3-chloropropanoyl chloride. This material is available free of charge via the Internet at http://pubs.acs.org.

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