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Molecular Structure and Conformational Composition of 2-Chloro-1-phenylethanone, $ClH_2C{-}C({=}O)Ph$, Obtained Using Gas-Phase Electron-Diffraction Data and Results from Theoretical Calculations

Kirsten Aarset*,[†] and Kolbjørn Hagen[‡]

Oslo University College, Faculty of Engineering, P.O. Box 4 St. Olavs plass N-0130 Oslo, Norway, and
Norwegian University of Science and Technology, NTNU, Department of Chemistry,
N-7491 Trondheim, Norway

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The structure and conformation of 2-chloro-1-phenylethanone, $ClH_2C{-}C({=}O)Ph$ (phenacyl chloride), have been determined by gas-phase electron diffraction (GED), augmented by results from ab initio molecular orbital calculations, employing the second-order Møller−Plesset (MP2) level of theory and the 6-311+G(d) basis set. The molecules may exist as a mixture of different conformers with the C−Cl bond either syn (torsion angle $\phi = 0°$) or gauche to the carbonyl bond. At 179 °C, the majority of the molecules (90 ± 11%) have the gauche conformation ($\phi = 112(3)°$). Torsion is also possible about the C−Ph single bond. Both experimental and theoretical data indicated, however, that the phenyl ring is coplanar or nearly coplanar with the carbonyl group. The results for the principal distances (r_g) and angles ($\angle_\alpha$) for the gauche conformer from a combined GED/ab initio study (with estimated 2σ uncertainties) are the following: $r(C{-}C)_{phenyl} = 1.394(2)$ (average value) Å, $r(C_{phenyl}{-}C_{carbonyl}) = 1.484(5)$ Å, $r(C_{carbonyl}{-}C_{alkyl}) = 1.513(5)$ Å, $r(C{-}Cl) = 1.790(5)$ Å, $r(C{=}O) = 1.218(6)$ Å, $r(C{-}H)_{phenyl} = 1.087(9)$ (average value) Å, $r(C{-}H)_{alkyl} = 1.090(9)$ Å (average value), $\angle C_{phenyl}{-}C{=}O = 119.5(9)°$, $\angle C_{phenyl}{-}C_{carbonyl}{-}C_{alkyl} = 119.2(10)°$, $\angle C{-}C{-}Cl = 109.8(12)°$, $\angle C_2{-}C_1{-}C_{carbonyl} = 122.8(15)°$, $\angle C{-}C_{alkyl}{-}H = 111.2°$ (ab initio value).

Introduction

In the past, we have studied molecules containing one or more carbonyl groups and attempted to find the factors that determine the conformation of such compounds. Among these are molecules with the general formulas $ClH_2C{-}C({=}O)X$, where X = H,[1] CH_3,[2] or Cl,[3] and $Cl_2HC{-}C({=}O)X$, where X = CH_3,[4] Cl,[5] or Ph.[6] Different conformers have been observed in these molecules where either C−Cl or C−H eclipses the carbonyl group. For some of the molecules, estimates of energy differences between conformers have also been determined, and results for bond distances and valence angles have been reported. A further aim was to study one particular member of this series of molecules, namely, that with only one chlorine atom and X = Ph. A study of 2-chloro-1-phenylethanone, $ClH_2C{-}C({=}O)Ph$ (phenacyl chloride), was therefore undertaken. Other molecules where a carbonyl group is attached to a phenyl ring have also been investigated earlier ($PhC({=}O)X$, with X = H,[7] Cl,[8] $C({=}O)H$,[9] $C({=}O)CH_3$,[9] or $C({=}O)Ph$[10]), and our results for 2-chloro-1-phenylethanone are compared with some of these earlier results.

Experimental Section

Gas-Phase Electron Diffraction. The sample of 2-chloro-1-phenylethanone was obtained from Fluka Chemie AG. The purity of the sample was reported to be better than 98%, and it was used without further purification. The diffraction experiments were made with the Oregon State apparatus using an r^3 sector and Kodak Electron Image plates. The nozzle temperature was 179 °C. The acceleration voltage was 60 kV (electron wavelength 0.048 71 Å), and nozzle-to-plate distances of 745.1 mm (long camera, LC) and 299.3 mm (middle camera, MC) were used. The voltage/distance calibration was done with CO_2 as the reference. The analytical procedures for the data reduction have been described elsewhere.[11−13] The data covering the ranges $2.50 \leq s/\text{Å}^{-1} \leq 14.75$ and $8.50 \leq s/\text{Å}^{-1} \leq 36.50$, with $\Delta s = 0.25$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin\theta$ and 2θ is the scattering angle), were processed as previously described.[13] The average experimental intensity curves are shown in Figure 1. Radial distribution (RD) curves (Figure 2) were calculated in the usual way by Fourier transformation of the functions $I'_m(s) = Z_O Z_{Cl}(A_O A_{Cl})^{-1} s I_m(s) \exp(-Bs^2)$, with $B = 0.0020$ Å^{-2} and where $A = s^2F$ and F is the absolute value of the complex scattering amplitudes. The scattering amplitudes and phases were taken from tables.[14]

Molecular Orbital Calculations. Ab initio molecular orbital calculations at the Hartree−Fock (HF) and second-order Møller−Plesset (MP2) levels of theory with the 6-311+G(d) basis set, using the Gaussian 98 program,[15] indicated that the molecules exist as a mixture of two stable conformers. These conformers are denoted syn (Cl−C−C=O torsion angle close to 0°, C−Cl eclipsing C=O) and gauche (Cl−C−C=O torsion angle ∼120°, C−H eclipsing C=O). For both conformers, the phenyl ring was calculated to be coplanar or nearly coplanar with the carbonyl group. Some of the geometrical parameters obtained from the theoretical calculations are shown in Table 1. The constraints used for some of the structural parameters in the

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[†] Oslo University College.

[‡] Norwegian University of Science and Technology.

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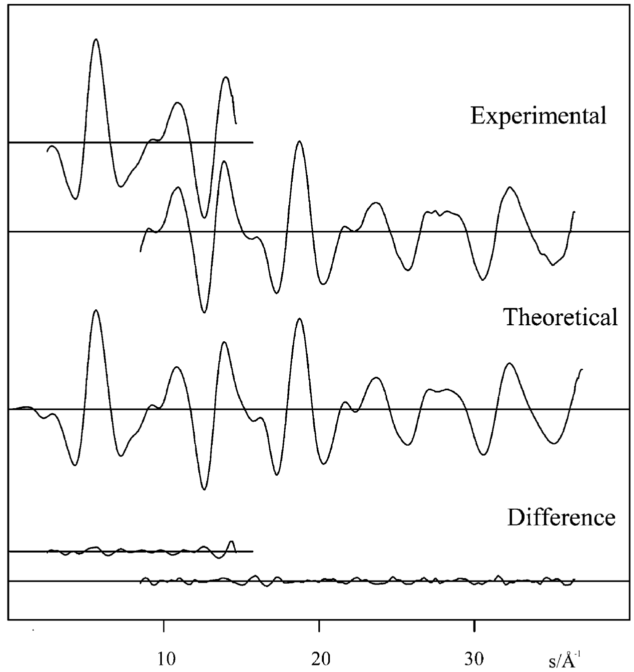


Figure 1. Average experimental intensity curves, $s^4I_t(s)$, for 2-chloro-1-phenylethanone (phenacyl chloride) shown together with a theoretical intensity curve calculated from the final model. The difference curves are experimental minus theoretical.

electron-diffraction model described below were obtained from these MP2/6-311+G(d) calculations.

Normal Coordinate Calculations. Vibrational quantities are an important part of the model used to analyze the experimental gas-phase electron-diffraction data. Ab initio frequency calculations (HF/6-311+G(d)) provided theoretical force fields for the molecular vibrations. To calculate the vibrational parameters (amplitudes, perpendicular corrections, and centrifugal distortions) from these force fields, the program SHRINK[16,17] was used. The calculated vibrational quantities were used to convert the r_a distances used in the electron-diffraction model to the geometrically consistent distances.

Analysis of the Structures. The theoretical calculations indicated that the molecules exist as mixtures of two different conformers both with the C═O bond nearly coplanar to the phenyl ring and with the C═O bond either syn or gauche to the C—Cl bond. The gauche conformer was found to be the predominant one. In the model adopted in the analysis of the electron-diffraction data, both conformers were included and the gauche conformer was defined by the following parameters: $^1/_2[r(\mathrm{C_{phenyl}}—\mathrm{C_{carbonyl}}) + r(\mathrm{C_{carbonyl}}—\mathrm{C_{alkyl}})]$, $r(\mathrm{C_{phenyl}}—\mathrm{C_{carbonyl}}) - \mathrm{r}(\mathrm{C_{carbonyl}}—\mathrm{C_{alkyl}})$, $r(\mathrm{C}—\mathrm{C})_{\mathrm{phenyl}}$, $r(\mathrm{C}{=}\mathrm{O})$, $^1/_2[r(\mathrm{C}—\mathrm{H})_{\mathrm{phenyl}} + r(\mathrm{C}—\mathrm{H})_{\mathrm{alkyl}}]$, $r(\mathrm{C}—\mathrm{H})_{\mathrm{phenyl}} - r(\mathrm{C}—\mathrm{H})_{\mathrm{alkyl}}$, $r(\mathrm{C}—\mathrm{Cl})$, $\angle\mathrm{C_{phenyl}}—\mathrm{C}{=}\mathrm{O}$, $\angle\mathrm{C_{phenyl}}—\mathrm{C_{carbonyl}}—\mathrm{C}$, $\angle\mathrm{C}—\mathrm{C_{alkyl}}—\mathrm{H}$, $\angle\mathrm{C}—\mathrm{C}—\mathrm{Cl}$, $\angle\mathrm{C_2}—\mathrm{C_1}—\mathrm{C_{carbonyl}}$, $\phi(\mathrm{C_2CCO})$, and $\phi(\mathrm{OCCCl})$. In the phenyl ring, all C—C bonds were assumed equal and the valence angles in the ring were all assumed to be 120°. The theoretical calculations showed these assumptions to be reasonable. The molecule is depicted in Figure 3, where the two conformers are shown. The atom numbering scheme is also shown.

In the gas-phase electron diffraction (GED) model, the structure of the syn conformer was defined from the parameters in the gauche conformer by constraining all parameters, except the torsion angles, to the differences observed in the (MP2/6-311+G(d)) theoretical calculations.

The electron-diffraction refinements were carried out by the least-squares method,[18] adjusting a theoretical $sI_m(s)$ curve simultaneously to the two average intensity curves (one from each camera distance) using a unit weight matrix. The geometries were defined on the basis of geometrically consistent parameters. These were converted to the r_a type required by the scattering intensity formula by using calculated values of centrifugal distortions (δr), perpendicular amplitude corrections (K), and root-mean-square amplitudes of vibration (l).

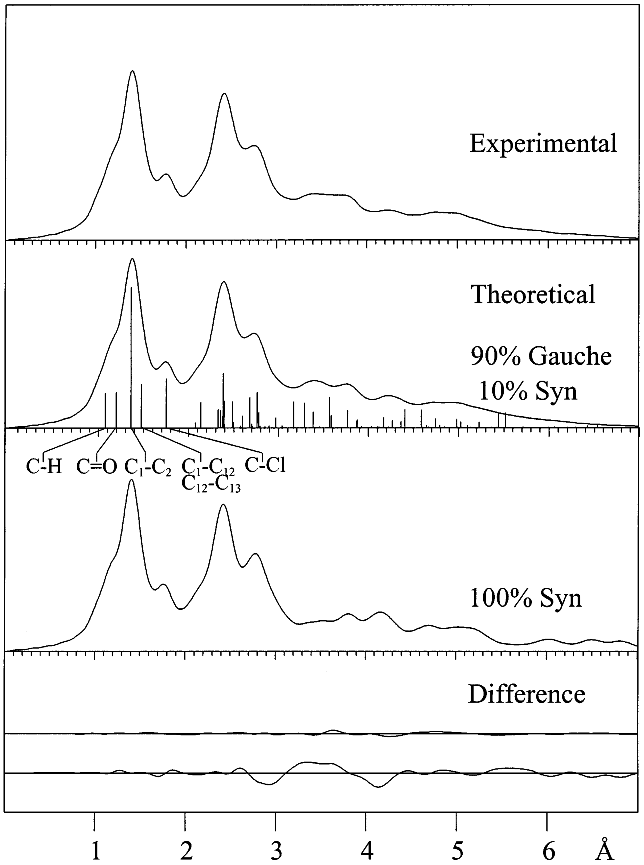


Figure 2. Radial distribution curves for 2-chloro-1-phenylethanone. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 2.25$ and $B/\text{Å}^2 = 0.002$. The difference curves are experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights.

It was possible to refine simultaneously most of the important structural parameters, the amplitudes associated with the bonded distances (except C—H), and the conformational composition. Structure parameters that could not be refined were constrained at the ab initio values (MP2/6-311+G(d)); see Table 2.

Results from the final refinements are given in Table 2. A theoretical intensity curve calculated for the final model is shown in Figure 1, together with experimental and difference curves. Figure 2 contains the corresponding RD curves, and the correlation matrix for the refined parameters is given in Table 3.

Discussion

Of the two possible conformers (syn and gauche position of the C—Cl bond relative to the C═O bond), the theoretical calculations found the gauche conformer to be more stable. It was found to be 3.7 kJ mol^{-1} (HF/6-311+G/(d)) or 5.6 (MP2/6-311+G(d)) kJ mol^{-1} lower in energy than the syn conformer. Least-squares refinements carried out on the electron-diffraction data showed that a model consisting mainly of the gauche

TABLE 1: Results from the ab initio Calculations for 2-Chloro-1-phenylethanone

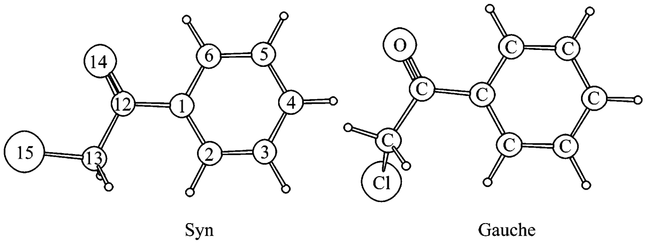
	MP2/6-311+G(d)		HF/6-311+G(d)	
parameter[a]	gauche	syn	gauche	syn
$r(C{=}O)$	1.223	1.218	1.188	1.183
$r(C{-}Cl)$	1.787	1.767	1.794	1.773
$r(C_{phenyl}{-}C_{carbonyl})$	1.494	1.499	1.496	1.503
$r(C_{carbonyl}{-}C_{alkyl})$	1.523	1.527	1.525	1.524
$r(C{-}H)_{phenyl,av}$	1.087	1.087	1.074	1.074
$r(C{-}H)_{alkyl,av}$	1.090	1.092	1.077	1.080
$r(C_1{-}C_2)$	1.406	1.406	1.390	1.391
$r(C_2{-}C_3)$	1.398	1.399	1.386	1.386
$r(C_3{-}C_4)$	1.400	1.399	1.384	1.384
$r(C_4{-}C_5)$	1.402	1.402	1.388	1.388
$r(C_5{-}C_6)$	1.396	1.396	1.381	1.381
$r(C_1{-}C_6)$	1.406	1.406	1.393	1.393
$\angle C_2C_1C_6$	119.6	119.5	119.2	119.1
$\angle C_4C_5C_6$	120.1	120.2	119.9	120.0
$\angle C_1C_2C_3$	120.0	120.1	120.4	120.5
$\angle C_1C_6C_5$	120.2	120.2	120.4	120.5
$\angle C_2C_3C_4$	120.2	120.2	120.0	119.9
$\angle C_3C_4C_5$	119.9	119.8	120.1	120.0
$\angle C_6C_1C_{carbonyl}$	118.0	117.6	117.8	117.7
$\angle C_2C_1C_{carbonyl}$	122.3	122.8	122.9	123.2
$\angle C_{phenyl}C_{carbonyl}C_{alkyl}$	119.1	116.1	120.1	116.6
$\angle C_{phenyl}C_{carbonyl}O$	121.7	121.4	121.6	121.3
$\angle C_{alkyl}C_{carbonyl}O$	119.2	122.5	118.2	122.1
$\angle CCCl$	108.1	109.5	108.1	109.9
$\Phi(C_2CCO)$	−10.2	15.5	−2.6	0.0
$\Phi(OCCCl)$	114.1	−2.9	108.4	0.0
energy (hartree/mol)	−842.872 386 676	−842.870 257 017	−841.475 230 343	−841.473 809 243
ΔE (kJ/mol)	0.00	5.59	0.00	3.73

[a] The distances are in angstroms, and the angles are in degrees.

conformer (90(11)%) and with a small amount of the syn conformer gave the best fit to the electron-diffraction data. Thus, this conformational mixture was used to calculate the structural parameters in Table 2 and the theoretical intensities and RD curves shown in Figures 1 and 2, respectively. A model with the gauche conformer alone gave only a slightly poorer fit to the experimental data. It is therefore difficult from the electron-diffraction analysis alone to say with absolute certainty that a syn conformer is present in the gas phase at the temperature of the experiment. The experimental result for the conformational composition corresponds to a free energy difference of $\Delta G°_{exp} = 8.3$ kJ mol^{-1}. The theoretical value from the MP2/6-311+G-(d) calculations is $\Delta G°_{theo} = 7.5$ kJ mol^{-1}, corresponding to a theoretical conformational mixture of 88% gauche and 12% syn. Using the theoretical value for the entropy difference, including the fact that there are two equivalent gauche forms, an experimental energy difference of $\Delta E°_{exp} = 6.4$ kJ mol^{-1} can be obtained. This value is in good agreement with the MP2/6-311+G(d) value of $\Delta E°_{theo} = 5.6$ kJ mol^{-1}.

In Table 4, the structure and the conformation of molecules with the general formula $ClH_2C{-}C({=}O)X$ (X = H[1], CH_3[2], Cl[3], or Ph) are compared. For all molecules, except for X = Cl, the predominant conformer is the one with the C−X and C=O bonds pointing away from each other in a gauche or anti position. For X = Cl, however, we have larger amounts of a conformer where the C−X and C=O bonds are syn to each other. We may assume that the potential for torsion about the $H_2ClC{-}C({=}O)X$ single bond may be determined mainly by two forces, steric repulsion and electrostatic interaction. If X = H, CH_3, or Ph, there is one large dipole on each of the two central carbon atoms ($C_{alkyl}{-}Cl$ and $C_{carbonyl}{=}O$). The molecule will have the lowest energy when these dipoles are pointing away from each other. This will give an anti or a gauche conformation. The steric repulsion will increase, however, when X is approaching the Cl atom. This repulsion is probably larger for X = Ph than for X = CH_3 or X = H. The ClCCO torsional angle is therefore expected to decrease in the order X = H, CH_3, and Ph, and this finding is born out experimentally (see Table 4). The torsion angle is close to 180° in chloroacetaldehyde[1] (X = H), 138(7)° in chloroacetone[2] (X = CH_3), and 112-(3)° in phenacyl chloride (X = Ph). For X = Cl ($ClH_2C{-}C({=}O)Cl$), the predominant conformer was found to be the one with C=O syn to C−X. However, in this molecule, there are two dipoles on one of the carbon atoms ($C_{carbonyl}{-}Cl$ and $C_{carbonyl}{=}O$) and the dipole−dipole interactions are therefore similar in both the syn and the anti conformers. Since the steric repulsion between Cl and O probably is smaller than the repulsion between Cl and Cl, the major conformer is expected to be syn (C=O syn to C−Cl). This is also observed experimentally.

In addition to the different possible positions of C=O relative to C−Cl, the molecule may also have different positions for the C=O bond relative to the phenyl group. In earlier studies of similar molecules,[7−10] it was found that C=O normally is coplanar or nearly coplanar with the phenyl group, possibly because of the effect of conjugation between the phenyl ring and the carbonyl group in a planar conformation. Both MP2 and HF calculations also indicated that the C=O bond is nearly coplanar with the phenyl group. When attempting to refine the CCCO torsional angle for the gauche conformer, a value of −2°



Syn Gauche

Figure 3. Diagrams showing the numbering scheme and conformers of 2-chloro-1-phenylethanone.

TABLE 2: Structural Parameters Obtained from Electron-Diffraction Refinements and from Theoretical Calculations for the Gauche Conformer of 2-Chloro-1-phenylethanone

parameter[a]	electron diffraction $r_{h1}/\angle_{h1}$	ab initio[b] $r_e/\angle_e$
$^1/_2[r(C_{phenyl}-C_{carbonyl}) + r(C_{carbonyl}-C_{alkyl})]$	1.498 (5)	1.508
$r(C_{phenyl}-C_{carbonyl}) - r(C_{carbonyl}-C_{alkyl})$	[−0.029]	−0.029
$r(C-C)_{phenyl,av}$	1.394 (2)	1.401
$r(C=O)$	1.218 (6)	1.223
$^1/_2[r(C-H)_{phenyl,av} + r(C-H)_{alkyl,av}]$	1.089 (9)	1.088
$r(C-H)_{phenyl,av} - r(C-H)_{alkyl,av}$	[−0.003]	−0.003
$r(C-Cl)$	1.790 (5)	1.787
$\angle C_{phenyl}CO$	119.5 (9)	121.7
$\angle C_{phenyl}C_{carbonyl}C$	119.2 (10)	119.1
$\angle CCH_{alkyl,av}$	[111.2]	111.2
$\angle CCCl$	109.8 (12)	108.1
$\angle C_2C_1C_{carbonyl}$	122.8 (15)	122.3
$\Phi(C_2CCO)_{gauche}$	[−10.2]	−10.2
$\Phi(OCCCl)_{gauche}$	112 (3)	114.1
$\Phi(C_2CCO)_{syn}$	[15.5]	15.5
$\Delta E°$ (kJ/mol)	[−2.9]	−2.9
α_{gauche}	0.90 (11)	0.88
$\Delta E°$ (kJ/mol)	6.7	5.6
$\Delta G°$ (kJ/mol)	8.3	7.5

parameter[a]	r_{h1}	$l_{refined}$	r_e	$l_{calculated}$
$r(C-C)_{phenyl,av}$	1.394 (2)	0.046 (4)	1.401	0.045
$r(C_{phenyl}-C_{carbonyl})$	1.484 (5)	0.051 (10)	1.494	0.050
$r(C_{carbonyl}-C_{alkyl})$	1.513 (5)	0.053 (10)	1.523	0.051
$r(C-Cl)$	1.790 (5)	0.053 (4)	1.787	0.053
$r(C=O)$	1.218 (6)	0.033 (4)	1.223	0.036
$r(C-H)_{phenyl,av}$	1.087 (9)		1.087	0.074
$r(C-H)_{alkyl,av}$	1.090 (9)		1.090	0.074
$r(C_1\cdots O)$	2.338 (14)			0.058
$r(C_{alkyl}\cdots O)$	2.385 (17)			0.061
$r(C_1\cdots C_3)_{av}$	2.414 (3)			0.055
$r(C_6\cdots C_{carbonyl})$	2.456 (21)			0.066
$r(C_2\cdots C_{carbonyl})$	2.527 (18)			0.066
$r(C_1\cdots C_{alkyl})$	2.586 (20)			0.070
$r(C_{carbonyl}\cdots Cl)$	2.708 (23)			0.092
$r(C_1\cdots C_4)_{av}$	2.787 (4)			0.062
$r(C_6\cdots O)$	2.733 (38)			0.099
$r(C_2\cdots C_{alkyl})$	2.991 (35)			0.109
$r(C_2\cdots Cl)$	3.206 (80)			0.232
$r(C_1\cdots Cl)$	3.313 (39)			0.179
$r(C_2\cdots O)$	3.606 (16)			0.068
$r(O\cdots Cl)$	3.579 (44)			0.190
$r(C_3\cdots C_{carbonyl})$	3.795 (13)			0.067
$r(C_5\cdots C_{carbonyl})$	3.748 (15)			0.067
$r(C_6\cdots C_{alkyl})$	3.831 (23)			0.076
$r(C_5\cdots O)$	4.124 (38)			0.101
$r(C_4\cdots C_{carbonyl})$	4.270 (7)			0.070
$r(C_3\cdots C_{alkyl})$	4.381 (36)			0.113
$r(C_3\cdots Cl)$	4.470 (89)			0.274
$r(C_6\cdots Cl)$	4.624 (35)			0.266
$r(C_3\cdots O)$	4.748 (15)			0.074
$r(C_4\cdots O)$	4.954 (26)			0.089
$r(C_5\cdots C_{alkyl})$	4.993 (22)			0.081
$r(C_4\cdots C_{alkyl})$	5.214 (27)			0.099
$r(C_4\cdots Cl)$	5.512 (72)			0.298
$r(C_5\cdots Cl)$	5.575 (49)			0.306

[a] The distances (r) and amplitudes (l) are in angstroms, and the angles ($\angle$) are in degrees. The values in parentheses are 2σ and include estimates of uncertainties in voltage/nozzle height and of correlation in experimental data. The values in square brackets were kept constant at the calculated values. [b] The MP2 level of theory and 6-311+G(d) basis set were used.

(0° is coplanar) was obtained, with a large uncertainty of 32°. In the final least-squares refinement of the electron-diffraction data, the CCCO torsional angle was therefore kept constant at the ab initio (MP2/6-311+G(d)) value.

In Table 2, the electron-diffraction results are presented together with the MP2/6-311+G(d) results. In general, the values are in reasonable agreement. As can be seen from Table 1, only small differences in parameter values are observed when the level of theory is changed from HF to MP2. One exception is the C═O bond length. The C═O bond is calculated to be longer by the MP2 level of theory compared with the HF results. The experimental value for the C═O bond is in better agreement with the MP2 result. If higher levels of theory are used, we normally find a shorter value for C═O using MP3 compared with MP2, while the MP4 level of theory gives a larger value again. Calculations made for chloroacetaldehyde gave C═O values of 1.179 Å (HF), 1.213 Å (MP2), 1.199 Å (MP3), and 1.218 Å (MP4).

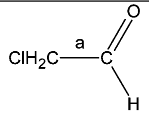
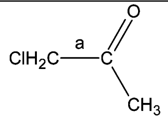
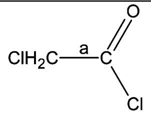
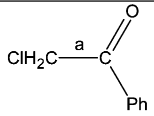
Some bond distances and valence angles for previously studied phenyl compounds with carbonyl groups are reported in Table 4, where results from this study and from theoretical calculations are also shown. As expected, the C−C distances

TABLE 3: Correlation Matrix (×100) for Parameters Refined in the Final Least-Squares Refinements for 2-Chloro-1-phenylethanone

		σ_{LS} [a]	r_1	r_2	r_3	r_4	r_5	$\angle_6$	$\angle_7$	$\angle_8$	Φ_9	$\angle_{10}$	l_{11}	l_{12}	l_{13}	l_{14}	α
1	$^1/_2[r(C_{phenyl}{-}C_{carbonyl}) + r(C_{carbonyl}{-}C_{alkyl})]$	0.0017	100	22	30	24	−10	−7	34	9	−22	−16	−29	22	11	−25	15
2	$r(C{-}C)_{phenyl,av}$	0.0004		100	−15	−4	−14	26	34	1	−15	9	27	4	45	43	9
3	$r(C{=}O)$	0.0019			100	66	3	4	20	9	4	−1	−78	5	14	−69	−8
4	$^1/_2[r(C{-}H)_{phenyl,av} + r(C{-}H)_{alkyl,av}]$	0.0032				100	1	18	3	9	0	−2	−64	6	20	−56	9
5	$r(C{-}Cl)$	0.0017					100	−11	7	−20	12	25	1	−15	−8	−4	−41
6	$\angle C_{phenyl}CO$	0.3473						100	−9	−27	21	−6	−18	−7	17	−8	21
7	$\angle CCCl$	0.4272							100	−32	−30	−34	6	13	16	8	−20
8	$\angle C_{phenyl}C_{carbonyl}C$	0.4995								100	−18	21	−19	6	2	−14	31
9	$\Phi(C_2CCO)_{gauche}$	1.2309									100	27	−6	−17	−4	−7	−26
10	$\angle C_{phenyl}C_{phenyl}C_{carbonyl}$	0.5238										100	14	−18	5	13	−59
11	$l(C{-}C)_{phenyl}$	0.0013										0	100	−2	−11	92	−20
12	$l(C{-}Cl)$	0.0014												100	−5	0	21
13	$l(C{=}O)$	0.0014													100	4	3
14	$l(C_{phenyl}{-}C_{carbonyl})$	0.0036														100	−12
15	α	0.0386															100

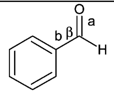
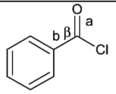
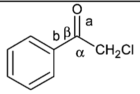
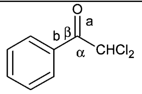
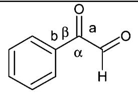
[a] Standard deviations from least-squares refinements. The distances (*r*) and amplitudes (*l*) are in angstroms, and the angles (∠) are in degrees.

TABLE 4: Parameter Values Obtained for 2-Chloro-1-phenylethanone and Related Molecules with the General Formula $ClH_2C{-}C({=}O)X$, where X = H, CH_3, or Cl[d]

Parameter [a]	 2-Chloro-1-ethanone (Chloroacetaldehyde)			 1-Chloro-2-propanone (Chloroacetone)			 Chloroacetylchloride			 2-chloro-1-phenylethanone		
	ED (r_a)	HF	MP2	ED(r_a)	HF	MP2	ED(r_a)	HF	MP2	ED(r_a)	HF	MP2
r(C=O)	1.206(3)	1.179	1.213	1.215(3)	1.186	1.219	1.182(4)	1.162	1.195	1.219(6)	1.188	1.223
r(C-C)(a)	1.521(5)	1.514	1.516	1.535(18)	1.524	1.525	1.521(9)	1.514	1.515	1.515(5)	1.496	1.494
r(C-Cl)	1.782(4)	1.786	1.779	1.785(3)	1.791	1.783	1.782(18)	1.778	1.775	1.790(5)	1.794	1.787
∠CCCl	110.4(3)	111.0	110.5	113.7(9)	113.7	113.2	112.9(17)	111.1	110.5	109.8(12)	108.1	108.1
∠CCO	123.3(6)	122.1	122.5	121.5(16)	118.2	118.6	126.9(9)	124.6	125.0	119.5(9)	118.2	119.2
ΦCLCCO[b]	180			138(7)			116.4(77)			112 (3)		
%Conformer[c]	94(7)			95(8)			23(7)			90(11)		
References	1			2			3			This Work		

[a] The distances are in angstroms, and the angles are in degrees. For molecules with several conformers, the parameters are given for the most stable one. [b] ΦClCCO is defined as 0 when C═O eclipses C—Cl. [c] % of the conformer given by the ΦClCCO angle. [d] The theoretical calculations were performed using the 6-311+G(d) basis set.

TABLE 5: Parameter Values Obtained for 2-Chloro-1-phenylethanone and Related Molecules with the General Formula $PhC({=}O)X$, where X = H, Cl, $CHCl_2$, or $C({=}O)H$[c]

Parameter [a]	 Benzaldehyde		 Benzoyl chloride			 2-Chloro-1-phenylethanone			 2,2-Dichloro-1-phenylethanone			 Phenylglyoxal		
	ED (r_g)	HF	MW (r_s)	HF	MP2	ED (r_g)	HF	MP2	ED (r_a)	HF	MP2	ED (r_g)	HF	MP2
r(C=O)(a)	1.212 (3)	1.185	1.210[b]	1.166	1.198	1.220 (6)	1.188	1.223	1.206 (3)	1.186	1.222	1.228 (3)	1.189	1.227
$r(C\text{-}C)_{phenyl,ave}$	1.397 (3)	1.387	1.399[b]	1.397	1.401	1.395 (2)	1.397	1.401	1.403 (2)	1.387	1.407	1.400 (2)	1.388	1.402
r(C-C)(b)	1.479 (4)	1.484	1.452 (6)	1.487	1.487	1.486 (5)	1.496	1.494	1.494 (6)	1.495	1.491	1.487 (9)	1.489	1.485
r(C-Cl)			1.807(2)	1.784	1.792	1.792 (5)	1.794	1.787	1.778(3)	1.777	1.776			
∠CCCl				116.3	115.1	109.8 (12)	108.1	108.1	112.2 (2)	112.2	111.3			
∠CCC(α)						119.2 (11)	120.1	119.1	120.7 (5)	121.9	121.6	120.3 (5)	123.1	121.7
∠CCO(β)	123.6 (4)	124.8	123.19(35)	125.4	125.4	119.5 (9)	118.2	119.2	120.1 (7)	122.9	122.1		122.8	123.0
Reference	7		8			This work			6			9		

[a] The distances are in angstroms, and the angles are in degrees. For molecules with several conformers, the parameters are taken from the most stable one. [b] Assumed. [c] The theoretical calculations were performed using the 6-311+G(d) basis set.

in the phenyl ring are quite similar for these compounds, independent of the groups attached to the ring. There are larger differences observed in the C═O bond. In Ph—C(═O)—CH$_2$-Cl (this study), $r_g(C{=}O) = 1.220(6)$ Å, and in Ph—C(═O)—CHCl$_2$,[6] $r_g(C{=}O) = 1.207(6)$. Results from the ab initio calculations, however, indicated that these distances should be nearly equal. We have no good explanation for this difference observed between the experimental and theoretical results.

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