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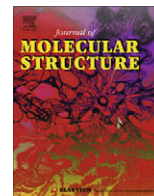**31** PUBLICATIONS **247** CITATIONS

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# Molecular structure and conformation of phenylacetyl chloride as obtained by gas-phase electron diffraction and theoretical calculations

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## ARTICLE INFO

## ABSTRACT

The structure and conformation of phenylacetyl chloride, $PhCH_2-(C=O)Cl$, has been determined by gas-phase electron diffraction (GED), using results from *ab initio* calculations (HF and MP2/6-311 + G(d,p)) to obtain restraints on some of the structural parameters. The molecules exist in the gas-phase (118 °C) as a mixture of two stable conformers; syn with $C=O$ eclipsing $C_{alkyl}-C_{phenyl}$ and gauche with $C=O$ eclipsing $C-H$. For both conformers the phenyl ring is about 90–120° out of the plane of the acetyl group. The experimentally observed conformational composition was 75(8)% gauche and 25(8)% syn (parenthesised values are $2\sigma$). Using theoretical values for the entropy difference between conformers, including the fact that there are two identical gauche forms, this composition corresponds to an enthalpy difference of $\Delta H°(gauche–syn) = -0.8(12) kJ mol^{-1}$. The results for the principal distances ($r_a$) and angles ($\angle_{h1}$) for the gauche conformer obtained from the combined GED/*ab initio* study ($2\sigma$ uncertainties) are: $r(C-H)_{phenyl} = 1.078(6)$ Å, $r(C-H)_{alkyl} = 1.089(12)$ Å, $r(C=O) = 1.180(6)$ Å, $r(C-C)_{phenyl} = 1.396(4)$ Å (average value), $r(C_{phenyl}-C_{alkyl}) = 1.509(16)$ Å, $r(C_{alkyl}-C_{carbonyl}) = 1.513(12)$ Å, $r(C-Cl) = 1.780$ (6) Å, $\angle C_{phenyl}-C_{alkyl}-C_{carbonyl} = 110.6(12)°$, $\angle C-C=O = 125.5(8)°$, $\angle C-C-Cl = 113.3(6)°$, $\angle C-C-H_{phenyl} = 119.9(2)°$ (average value), $\angle C_{phenyl}-C_{alkyl}-H = 110.8(2)°$ (average value), $\phi(C-C-C-C) = 118(4)°$, $\phi(C-C-C=O) = 95(2)°$.

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## 1. Introduction

We have earlier studied several acid halides with the general formula $XCH_2-(C=O)Y$ (X = Cl, Br, $CH_3$, Y = Cl, Br) [1–3] and observed a mixture of conformers where either C—X is eclipsing the C=O bond (syn conformer) or C—H eclipsing the C=O bond (gauche conformer). For all of these molecules the syn conformer has been found to be the most stable form. As an extension of these studies we were interested in studying a molecule where X is a phenyl group, and we have therefore investigated phenyl-acetyl chloride, $PhCH_2-(C=O)Cl$ (X = phenyl, Y = Cl), using gas-phase electron diffraction together with *ab initio* calculations. The phenyl group is a much larger substituent than those we have studied earlier and this could have an effect on both the conformational composition and on the value of the XCCO torsion angle in the gauche conformer. The relative conformational energies will determine if we can observe both conformers in the gas-phase, or if one conformer will dominate. The phenyl group can rotate around the C—$C_{phenyl}$ bond and it would be of

interest to see the value of this torsion angle as well. Earlier we have also published results for 2-chloro-1-phenylethanone where X = Cl and Y = phenyl [4].

## 2. Experimental

### 2.1. Gas-phase electron diffraction data collection

The sample of phenylacetyl chloride (99%+) was obtained from Aldrich Chemical Co and used without further purification. The diffraction experiments were made with the Oregon State University electron diffraction apparatus using an $r^3$ sector and Kodak Electron Image films. The nominal acceleration voltage was 60 kV and the average nozzle tip temperature was 118 °C. The voltage/distance calibration was done with $CO_2$ as reference. Experimental parameters, namely temperatures, nozzle-to-plate distances, weighting functions for creating weight matrix, correlation parameters, final scaling factors and electron wavelengths are listed in Table 1. Data reduction was performed using standard routines [5,6] employing published scattering factors [7]. Data analysis was carried out using the program "ed@ed" [8]. The experimental intensity curves are shown in Fig. 1.

**Table 1**
Experimental parameters for phenylacetyl chloride

| | | |
|---|---|---|
| Nozzle to plate distance/mm | 746.26 | 299.78 |
| Nozzle temperature/°C | 113 | 122 |
| Nominal electron wavelength/Å | 0.0489 | 0.0489 |
| Data interval/Å$^{-1}$ | 0.25 | 0.25 |
| No. of plates | 3 | 3 |
| $s_{min}$/Å$^{-1}$ | 2.5 | 10.5 |
| $s_{max}$/Å$^{-1}$ | 14.0 | 34.0 |
| $s_{w1}$/Å$^{-1}$ | 4.5 | 12.0 |
| $s_{w2}$/Å$^{-1}$ | 11.0 | 29.25 |
| Correlation parameter | 0.371 | 0.487 |
| Scale factor[a] | 1.182(19) | 0.841(34) |

[a] Values in parenthesis are estimated standard derivations.
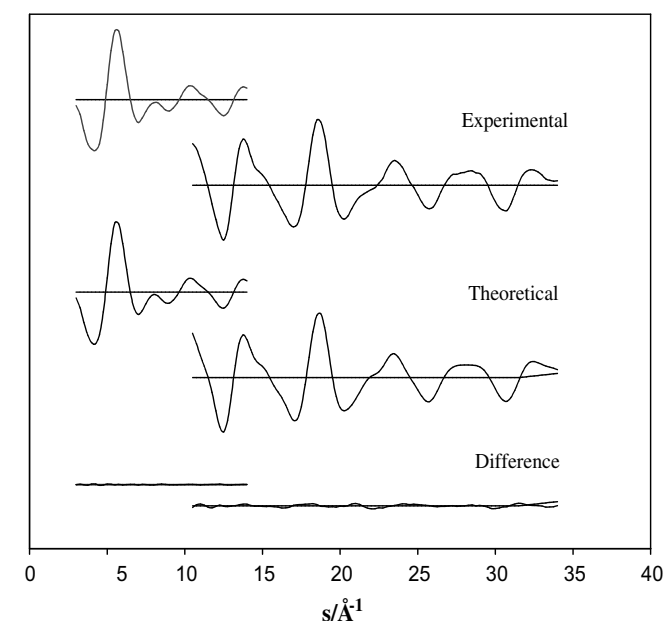


**Fig. 1.** Experimental intensity curves, $sI_m(s)$, from phenylacetyl chloride. The experimental curves are average molecular intensity data for two camera distances. The theoretical curve was calculated from the structural parameters given in Table 3. Difference curves are experimental minus theoretical.

## 3. Theoretical calculations

### 3.1. Molecular orbital calculations

*Ab initio* molecular orbital calculations at Hartree-Fock (HF) and second order Møller-Plesset (MP2) level of theory with the 6-311 + G(d,p) basis set, using the Gaussian98 program [9], indicated that phenylacetyl chloride exists as a mixture of two stable conformers. The important geometrical parameters obtained from the theoretical calculations are shown in Table 2. The conformers are denoted gauche with the C=O bond eclipsing the C—H bond and syn with the C=O bond eclipsing the C$_{alkyl}$—C$_{phenyl}$ bond. For both conformers the phenyl ring is out of the plane of the acetyl-chloride group by 90–120°. The restraints used in the least-squares refinements of the electron diffraction data for some of the structural parameters in the model described below, were obtained from the differences in bond lengths and angles between the MP2/6-311 + G(d,p) and the HF/6-311 + G(d,p) calculations.

### 3.2. Normal coordinate calculations

Vibrational quantities are an important part of the model used to analyse the experimental gas-phase electron diffraction data. *Ab initio* frequency calculations (HF/6-311 + G(d,p)) provided theo-

**Table 2**
Results from the *ab initio* calculations for phenylacetyl chloride

| Parameter[a] | HF/6-311 + G(d,p) | | MP2/6-311 + G(d,p) | |
|---|---|---|---|---|
| | Syn | Gauche | Syn | Gauche |
| $r$(C—H)$_{phenyl,ave}$ | 1.076 | 1.075 | 1.088 | 1.088 |
| $r$(C—H)$_{alkyl,ave}$ | 1.084 | 1.082 | 1.096 | 1.094 |
| $r$(C=O) | 1.159 | 1.162 | 1.191 | 1.195 |
| $r$(C$_3$—C$_4$) | 1.388 | 1.390 | 1.402 | 1.404 |
| $r$(C$_4$—C$_5$) | 1.385 | 1.384 | 1.399 | 1.398 |
| $r$(C$_5$—C$_6$) | 1.385 | 1.387 | 1.400 | 1.401 |
| $r$(C$_6$—C$_7$) | 1.385 | 1.384 | 1.400 | 1.399 |
| $r$(C$_7$—C$_8$) | 1.385 | 1.386 | 1.399 | 1.400 |
| $r$(C$_3$—C$_8$) | 1.388 | 1.387 | 1.402 | 1.401 |
| $r$(C$_3$—C$_2$) | 1.509 | 1.518 | 1.503 | 1.514 |
| $r$(C$_2$—C$_1$) | 1.516 | 1.514 | 1.515 | 1.509 |
| $r$(C—Cl) | 1.795 | 1.785 | 1.803 | 1.791 |
| ∠C$_3$C$_4$C$_5$ | 120.6 | 120.5 | 120.5 | 120.3 |
| ∠C$_4$C$_5$C$_6$ | 120.1 | 120.1 | 120.0 | 120.1 |
| ∠C$_5$C$_6$C$_7$ | 119.7 | 119.7 | 119.8 | 119.8 |
| ∠C$_6$C$_7$C$_8$ | 120.1 | 120.1 | 120.0 | 120.1 |
| ∠C$_4$C$_3$C$_8$ | 118.9 | 119.0 | 119.2 | 119.4 |
| ∠C$_3$C$_8$C$_7$ | 120.6 | 120.5 | 120.5 | 120.3 |
| ∠C$_4$C$_3$C$_2$ | 120.5 | 120.0 | 120.4 | 119.6 |
| ∠C$_8$C$_3$C$_2$ | 120.5 | 121.0 | 120.4 | 121.0 |
| ∠C$_3$C$_2$C$_1$ | 113.7 | 111.9 | 112.2 | 108.9 |
| ∠CCO | 128.8 | 126.5 | 128.2 | 126.8 |
| ∠CCCl | 111.5 | 113.7 | 111.1 | 112.2 |
| ∠OCCl | 119.6 | 119.8 | 120.7 | 120.9 |
| ∠CCH$_{phenyl}$ | 119.9 | 119.9 | 119.9 | 119.9 |
| ∠C$_3$C$_2$H$_{ave}$ | 111.6 | 110.6 | 111.9 | 110.9 |
| ∠C$_2$C$_1$H$_{ave}$ | 106.9 | 107.4 | 107.3 | 108.4 |
| ∠HC$_1$H | 105.9 | 108.6 | 105.9 | 109.3 |
| $\phi$(C$_8$C$_3$C$_2$C$_1$) | 90 | 106 | 90 | 113 |
| $\phi$(CCCO) | 0 | 103 | 0 | 105 |
| $\phi$(CCCCl) | −180 | −77 | −180 | −73 |
| Energy | −841.48256929 | −841.48256007 | 842.88630280 | 842.88742827 |

[a] Distances are in Ångstrøm, angles are in degrees and energies are in Hartrees.

retical force fields for the molecular vibrations. To calculate the required vibrational parameters (amplitudes, curvelinear amplitude corrections and centrifugal distortion constants) from these force fields, the program SHRINK [10,11] was used. The force constants for the bonds were scaled by 0.9. The calculated vibrational quantities were used to convert the $r_a$ distances used in the electron diffraction model to the geometrically consistent $r_{h1}$ distances..
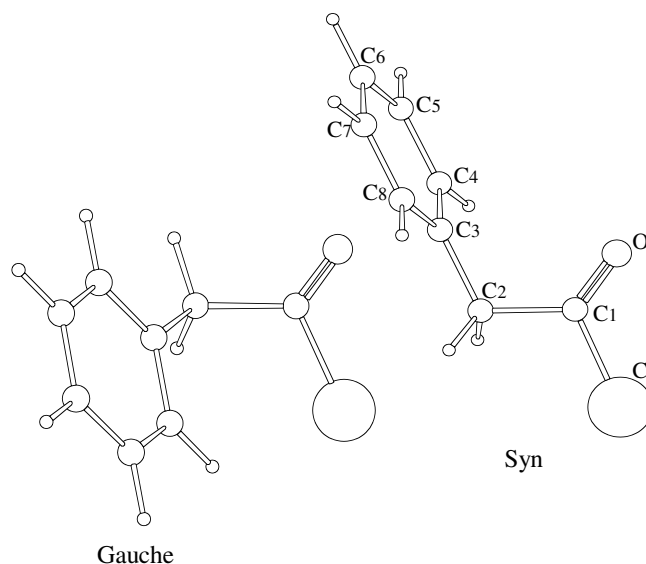


**Fig. 2.** Diagram showing the two conformers of phenylacetyl chloride and the atomic-numbering used.

### 3.3. Analysis of the structures

As stated earlier, theoretical calculations, using Hartree-Fock and Møller-Plesset level of theory, gave evidence for two stable conformers (syn and gauche). The two conformers are depicted in Fig. 2, which also shows the atom-numbering scheme. In the model used in the least-squares electron diffraction refinements, the structure of the gauche conformer was defined in terms of 23 independent geometrical parameters (see Table 3). The structure of the syn conformer was defined from the parameters in the gauche, by adding the differences between the parameters in the gauche and the syn conformer, obtained from the theoretical calculations (MP2/6-311 + G(d,p)). Some restraints were put on the $r_{h1}$ model, assuming that $\Delta r_{h1}$ is equal to $\Delta r_e$.

**Table 3**
Structural parameters obtained from electron diffraction (GED) refinements and theoretical calculations (MP2/6-311 + G(d,p)) for phenylacetyl chloride

| Parameter[a] | GED | | | Ab inito |
|---|---|---|---|---|
| Gauche | $r_{h1}/\angle_{h1}$ | Restraint[b] | | $r_e/\angle_e$ |
| *Independent parameters* | | | | |
| $r(C_3—C_4)$ | 1.400(2) | | | 1.404 |
| $r(C_3—C_4)—(C_4—C_5)$ | 0.006(2) | 0.001 | | 0.006 |
| $r(C_3—C_4)—(C_5—C_6)$ | 0.003(2) | 0.001 | | 0.003 |
| $r(C_3—C_4)—(C_6—C_7)$ | 0.005(4) | 0.002 | | 0.005 |
| $r(C_3—C_4)—(C_7—C_8)$ | 0.004(2) | 0.001 | | 0.004 |
| $r(C_3—C_4)—(C_3—C_8)$ | 0.003(2) | 0.001 | | 0.003 |
| $r(C_3—C_4)—(C_3—C_2)$ | −0.115(14) | 0.017 | | −0.110 |
| $r(C_3—C_4)—(C_2—C_1)$ | −0.111(18) | 0.019 | | −0.105 |
| $r(C=O)$ | 1.180(6) | | | 1.195 |
| $r(C—Cl)$ | 1.782(6) | | | 1.791 |
| $1/2 \cdot (r(C_{phenyl}—H) + r(C_2—H))$ | 1.088(8) | | | 1.091 |
| $r(C_2—H)—r(C_{phenyl}—H)$ | 0.011(10) | 0.006 | | 0.006 |
| $1/2 \cdot (\angle C_4C_3C_8 + \angle C_3C_4C_5)$ | 119.4(2) | | | 119.9 |
| $\angle C_4C_3C_8—\angle C_3C_4C_5$ | −1.1(10) | 0.6 | | −0.9 |
| $\angle C_3C_4C_5—\angle C_3C_8C_7$ | 0.0(2) | 0.1 | | 0.0 |
| $\angle C_4C_3C_2$ | 120.2(36) | | | 119.6 |
| $\angle C_3C_2C_1$ | 110.6(12) | | | 108.9 |
| $\angle CCO$ | 125.5(8) | | | 126.9 |
| $\angle CCCl$ | 113.3(6) | | | 112.2 |
| $\angle CCH_{phenyl,ave}$ | 119.9(2) | 0.1 | | 119.9 |
| $\angle C_3C_2H_{ave}$ | 110.8(2) | 0.2 | | 110.9 |
| $\phi(CCCC)$ | 118(4) | | | 113 |
| $\phi(CCCO)$ | 95(2) | | | 105 |
| $\alpha(\%)$ | 75(8) | | | |
| Syn | | | | |
| $\phi(CCCC)$ | 90 | | | 90 |
| $\phi(CCCO)$ | 0 | | | 0 |
| *Important distances and angles* | | | | |
| Gauche | $r_a/\angle_{h1}$ | $l_{exp}$ | | $l_{theo}$ |
| $r(C—H)_{phenyl}$ | 1.078(6) | 0.076 | | 0.077 |
| $r(C—H)_{alkyl}$ | 1.089(12) | 0.077 | | 0.077 |
| $r(C=O)$ | 1.180(6) | 0.032(14) | | 0.036 |
| $r(C—C)_{phenyl}$ | 1.396(4) | 0.050(4) | | 0.045 |
| $r(C_3—C_2)$ | 1.509(16) | 0.060(14) | | 0.052 |
| $r(C_2—C_1)$ | 1.513(12) | 0.059(14) | | 0.051 |
| $r(C—Cl)$ | 1.780(6) | 0.059(5) | | 0.057 |
| Syn | | | | |
| $r(C—H)_{phenyl}$ | 1.079(6) | 0.076 | | 0.077 |
| $r(C—H)_{alkyl}$ | 1.091(12) | 0.077 | | 0.077 |
| $r(C=O)$ | 1.176(6) | 0.032(14) | | 0.036 |
| $r(C—C)_{phenyl}$ | 1.395(4) | 0.050(4) | | 0.045 |
| $r(C_3—C_2)$ | 1.514(16) | 0.060(14) | | 0.052 |
| $r(C_2—C_1)$ | 1.502(12) | 0.059(14) | | 0.051 |
| $r(C—Cl)$ | 1.792(4) | 0.059(5) | | 0.057 |
| $\angle C_8C_3C_2$ | 120.8 | | | |
| $\angle C_3C_2C_1$ | 113.9 | | | |
| $\angle CCO$ | 126.9 | | | |
| $\angle CCCl$ | 112.1 | | | |

[a] Distances are in Ångstrøm and angles are in degrees. Parenthesized values are 2σ.
[b] Obtained from the differences between the MP2/6-311 + G(d,p) and the HF/6-311+G(d,p) calculations.
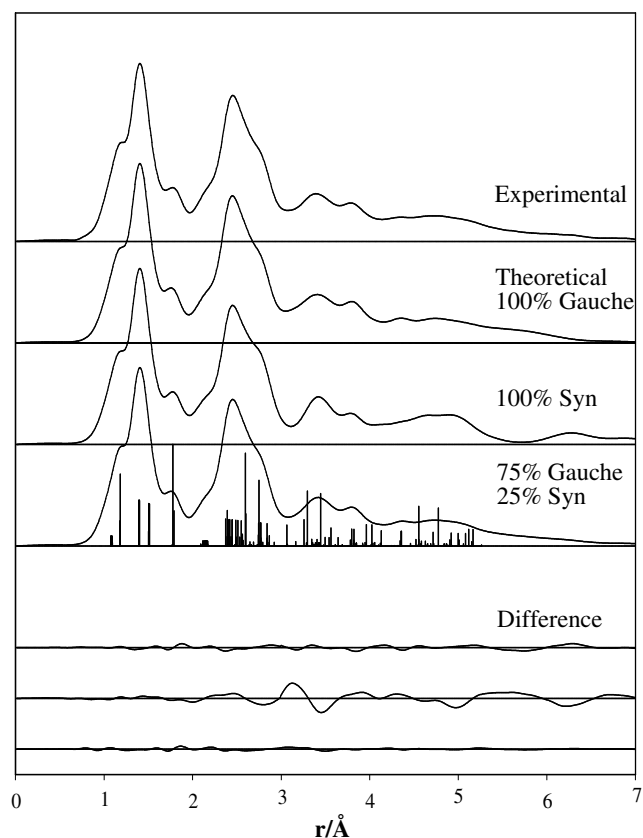


**Fig. 3.** Radial distribution curves for phenylacetyl chloride. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 < s/\text{Å}^{-1} < 2.50$ and $B/\text{Å}^2 = 0.002$. Difference curves are experimental minus theoretical. The vertical lines indicate interatomic distances and have lengths proportional to the distance weights.

In the model employed all $C—H_{phenyl}$ distances were assumed to be equal. The same assumption was also used for all $C—H_{alkyl}$ distances, for the $CCH_{phenyl}$ angles and for the $CCH_{alkyl}$ angles. Flexible restraints were used for some of the other parameters during the refinements, using the SARACEN method [12–14]. Of the independent parameters 12 were unrestrained in the refinements. The results from the electron diffraction refinements are given in Table 3. Intensity curves calculated for the final models are shown in Fig. 1, together with experimental and difference curves. The corresponding RD-curves are given in Fig. 3 and the correlation matrix in Table 4.

## 4. Discussion

The two stable conformers of phenylacetyl chloride (gauche and syn) were predicted by the HF calculations to have nearly equal energies, while the MP2 calculations predicted the gauche conformer to be 3.0 kJ mol$^{-1}$ lower in energy than the syn form. From the experimental data a conformational composition of 75(8)% gauche and 25(8)% syn was determined. This composition corresponds to a free energy difference of $\Delta G°$(gauche–syn) = −3.6 ($\sigma$ = 0.6) kJ mol$^{-1}$. Using a theoretical value for the entropy difference between the two conformers from the HF/6-311 + G(d,p) calculations ($\Delta S°$ = 1.21 J mol$^{-1}$ K$^{-1}$), and including the fact that there are two equivalent gauche forms, this conformational composition corresponds to an experimental enthalpy difference of $\Delta H°$(gauche–syn) = −0.8 ($\sigma$ = 0.6) kJ mol$^{-1}$. The HF energy values correspond at 118 °C to a composition of 70% gauche and 30% syn, which is in fair agreement with the experimental results.

**Table 4**
Correlation matrix for phenylacetyl chloride

|  | Parameter | $p_1$ | $p_7$ | $p_8$ | $p_9$ | $p_{10}$ | $p_{12}$ | $p_{16}$ | $p_{17}$ | $p_{18}$ | $p_{19}$ | $p_{21}$ | $u_1$ | $u_3$ | $u_{16}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $p_1$ | $r(C_3{-}C_4)$ | 100 | 62 | 68 |  |  | −65 |  |  |  |  |  | 61 | 80 |  |
| $p_7$ | $r(C_3{-}C_4){-}(C_2{-}C_1)$ |  | 100 |  |  |  | −51 |  |  |  |  |  |  | 51 |  |
| $p_8$ | $r(C{=}O)$ |  |  | 100 |  |  | −52 | 52 | 59 |  |  |  | 66 | 62 |  |
| $p_9$ | $1/2 \cdot (r(C_{phenyl}{-}H) + r(C_2{-}H))$ |  |  |  | 100 | −52 |  |  |  |  |  |  |  |  |  |
| $p_{10}$ | $r(C_2{-}H){-}r(C_{phenyl}{-}H)$ |  |  |  |  | 100 |  | −52 |  |  |  |  |  |  | 51 |
| $p_{12}$ | $1/2 \cdot (\angle C_4C_3 C_8 + \angle C_3C_4 C_5)$ |  |  |  |  |  | 100 | −58 | −69 |  | 55 |  |  | −64 |  |
| $p_{16}$ | $\angle C_3C_2C_1$ |  |  |  |  |  |  | 100 | 58 |  |  |  |  |  |  |
| $p_{17}$ | $\phi(CCCC)$ |  |  |  |  |  |  |  | 100 |  | −74 |  |  |  |  |
| $p_{18}$ | $\phi(CCCO)$ |  |  |  |  |  |  |  |  | 100 |  | −94 |  |  |  |
| $p_{19}$ | $\angle CCH_{phenyl,ave}$ |  |  |  |  |  |  |  |  |  | 100 | 55 |  |  |  |
| $p_{21}$ | $r(C{-}Cl)$ |  |  |  |  |  |  |  |  |  |  | 100 |  |  |  |
| $u_1$ | $l(C_3{-}C_4)$ |  |  |  |  |  |  |  |  |  |  |  | 100 | 70 |  |
| $u_3$ | $l(C_3{-}C_2)$ |  |  |  |  |  |  |  |  |  |  |  |  | 100 |  |
| $u_{16}$ | $l(C{=}O)$ |  |  |  |  |  |  |  |  |  |  |  |  |  | 100 |

Only correlation factors larger then 50 are shown.

**Table 5**
Parameters from GED for the gauche conformer of $CH_2X{-}COCl$, X = Ph, Cl, Br and $CH_3$

| Parameter[a] | X = Ph | X = Cl | X = CH$_3$ | X = Br |
|---|---|---|---|---|
| $r(C{=}O)$ | 1.180(6) | 1.800(5) | 1.191(7) | 1.188(9) |
| $r(C_{alkyl}{-}C_{carbonyl})$ | 1.509(16) | 1.514(9) | 1.516(18) | 1.519(18) |
| $r(C{-}Cl)$ | 1.780(6) | 1.774(27) | 1.798(7) | 1.789(11) |
| $\angle XC_{alkyl}C_{carbonyl}$ | 110.6(12) | 112.9(13) | 112.7(11) | 111.0(15) |
| $\angle CCO$ | 125.5(8) | 126.7(13) | 126.8(9) | 127.6(13) |
| $\angle CCCl$ | 113.3(6) | 110.8(11) | 112.9(5) | 111.3(11) |
| $\phi(XCCO)$ | 95(2) | 120(10) | 128(14) | 110[b] |
| $\alpha(\%)$ | 75(8) | 33(9) | 35(13) | 53(8) |
| References | This work | 1 | 2 | 3 |

[a] Distances are in Ångstrøm and angles in degrees. Parenthesized values are $2\sigma$.
[b] Parameter value estimated.

The MP2-energy values for the two forms correspond to a mixture of 85% gauche and 15% syn.

The experimental value for $\Delta H°$ in phenylacetyl chloride is quite different from the values observed for chloroacetyl chloride, $CH_2Cl{-}C({=}O)Cl$, where the conformer with C−Cl syn to C=O was found to be the most stable form ($\Delta H° = 6(2)$ kJ mol$^{-1}$) [1]. It is also different from the values observed in bromoacetyl chloride, $CH_2Br{-}C({=}O)Cl$ ($\Delta H° = 4.2(4)$ kJ mol$^{-1}$) [3,15] and in propionyl chloride, $CH_3CH_2{-}C({=}O)Cl$, ($\Delta H° = 5.4(17)$ kJ mol$^{-1}$) [2]. The larger size of the phenyl group compared with Cl, $CH_3$ and Br is probably responsible for this difference. Cl and $CH_3$ have about the same size, but they have very different electronegativities. Despite this difference in eletronegativity, chloroacetyl chloride and propionyl chloride have similar energy difference between conformers. Steric effects must therefore be more important than dipole–dipole interactions in determining the conformational composition. It should be noted that in bromoacetyl chloride 53(8)% of the molecules are in the gauche conformation at 70 °C. This composition is between the composition observed in choloracetyl chloride (33(9)% gauche at 110 °C) and in phenylacetyl chloride (75(8)% gauche at 118 °C).

In the syn conformer of phenylacetyl chloride the phenyl ring is perpendicular to the acetyl chloride group ($\phi(CCCC) = 90°$), giving this conformer $C_s$ symmetry. In the gauche form the phenyl group is twisted somewhat towards the chlorine atom ($\phi(CCCC) = 118(4)°$). This is close to the MP2-value of 113° for this torsion angle. The CCCO torsion angle in the gauche form was found experimentally to be 95(2)°. This is somewhat smaller than the MP2-value of 105°.

The results from the ab initio calculations for the geometry of phenylacetyl chloride are presented in Table 2. As expected the C=O bond distance was calculated longer by MP2 ($r_e = 1.195$ Å,

gauche) than by HF ($r_e = 1.162$ Å, gauche). Experimentally the length of this distance was found to be between the two theoretical values ($r_{h1} = 1.180(6)$ Å). The same relationship was also observed for the C−C distances in the phenyl ring. In the gauche conformer the $C_{phenyl}C_{alkyl}C_{carbonyl}$ angle differ by 3° between HF and MP2 calculations (111.9° and 108.9°, respectively). The experimental value (110.6°) is about half way between the two theoretical values.

As we can see from Table 2, $CH_2COCl$ has deformed the benzene ring to some extent. The valence angles at C3 and C6 are smaller than 120°, the rest of the angles in the benzene ring are larger than 120°. Domenicano and coworkers [16] have published a study of benzene ring deformations and related them to group electronegativities for the substituents. Using their formulae and our geometry for phenylacetyl chloride, the HF-results for the gauche conformer corresponds to a group electronegativity for $CH_2COCl$ of 2.75 (Pauling units) while the MP2-results corresponds to 2.89 (Pauling units).

In Table 5 some of the parameter values for phenylacetyl chloride are compared with corresponding values observed in chloroacetyl chloride, bromoacetyl chloride and propionyl chloride. The values for important bond lengths and valence angles in these four molecules are quite similar, most are equal within error limits. However, the X−C−C=O torsion angle for the gauche conformer is quite different in phenylacetyl chloride (95(2)°) compared with chloroacetyl chloride and propionyl chloride (120(10)° and 128(14)°, respectively), probably again due to the larger phenyl ring compared with the smaller Cl or $CH_3$.

### Acknowledgements

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