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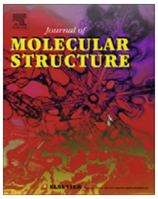

Molecular structure and conformational composition of methyl chloroacetate: An electron-diffraction and *ab initio* molecular orbital investigation

Kirsten Aarset [a],*, Kjell Gunnar Boldermo [b], Kolbjørn Hagen [b]

[a] *Oslo University College, Faculty of Engineering, P.O. Box 4, St. Olavs Plass, N-0130 Oslo, Norway*
[b] *Norwegian University of Science and Technology, NTNU, Department of Chemistry, N-7491 Trondheim, Norway*

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ABSTRACT

The molecular structure and conformational composition of methyl chloroacetate, $H_2ClC—C(=O)—O—CH_3$, have been determined by gas-phase electron-diffraction (GED), using results from *ab initio* molecular orbital calculations (HF, MP2 and MP3/6-311+G(d,p)) to obtain constraints on some of the structural parameters. The molecules exist in the gas-phase at 25 °C as a mixture of two stable conformers: syn with C—Cl eclipsing C=O and gauche with C—H approximately eclipsing C=O. In both of these conformers $O—CH_3$ is also eclipsing C=O. The experimentally observed conformational composition at 25 °C was 36(8)% syn and 64(8)% gauche (parenthesised values are 2σ), corresponding to a free energy difference between conformers of $\Delta G^{\circ}_{\text{exp}} = 1.4(9)$ kJ/mol. The corresponding theoretical values obtained for ΔG° are 1.1 kJ/mol (HF), 2.3 kJ/mol (MP2), and 2.4 kJ/mol (MP3). The results for the principal distances (r_{h1}) and angles ($\angle_{h1}$) for the major gauche conformer obtained from the combined GED/*ab initio* study (2σ uncertainties) are $r(\text{CO—CCl}) = 1.502(9)$ Å, $r(\text{C—H}) = 1.084(6)$ Å (average value), $r(\text{C—Cl}) = 1.782(4)$ Å, $r(\text{C=O}) = 1.213(4)$ Å, $r(\text{CO—O}) = 1.346(4)$ Å, $r(\text{CH}_3\text{—O}) = 1.468(10)$ Å, $\angle\text{C—C—Cl} = 110.0(6)°$, $\angle\text{C—C=O} = 124.7(6)°$, $\angle\text{C—C—O} = 108.3(10)°$, $\angle\text{C—O—C} = 115.9(8)°$, $\phi(\text{Cl—C—C=O}) = 111(2)°$, $\phi(\text{C—O—C=O}) = 3(3)°$.

1. Introduction

In the past we have studied molecules containing one or more carbonyl groups and attempted to find factors determining the conformation of such compounds. Among these are molecules with the general formula $ClH_2C—C(=O)R$, where R = H, CH_3, a phenyl group or a Cl atom [1–4]. In these compounds conformers where C—Cl and C=O have different positions relative to each other have been observed. In some of these compounds more than one conformer has been observed. In addition to the earlier studied compounds, we have now investigated methyl chloroacetate, $ClH_2C—C(=O)—O—CH_3$, where R = OCH_3, (Fig. 1) using GED and *ab initio* molecular orbital calculations. Our results are presented in the following.

2. Experimental

A commercial sample of methyl chloroacetate (99%) was obtained from Aldrich Chemical Co and used without further purification. The electron-diffraction experiments were performed using the Oregon State University apparatus with an r^3 sector and Kodak Electron Image plates. The nominal acceleration voltage was 60 kV and the nozzle-tip temperature was 25 °C. The voltage/distance calibration was done with CO_2 as a reference. Experimental parameters, namely temperatures, nozzle-to-plate distances, weighting functions for creating weight matrices, 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]. Experimental intensity and radial distribution (RD) curves, together with theoretical and difference curves for the final model of the molecules are presented in Figs. 2 and 3, respectively.

3. Structure analysis

3.1. Molecular orbital calculations

To determine the number of stable conformers, and also to get starting values for the parameters in the model used in the least-squares electron-diffraction refinements, *ab initio* molecular orbital calculations were performed using the Gaussian 98 [9] program with a 6-311+G(d,p) basis set and Hartree–Fock and Møller–Plesset (MP2 and MP3) level of theory. Four stable conformers were observed, but two of these conformers were higher in energy than the other two (approximately 40 kJ/mol higher). The high energy conformers have the $O—CH_3$ and the C=O bonds anti to each other. MP2 and MP3 calculations were performed only for the two low-energy conformers. These two conformers are depicted in Fig. 1.

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* Corresponding author. Tel.: +47 22453355.

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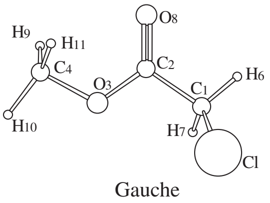
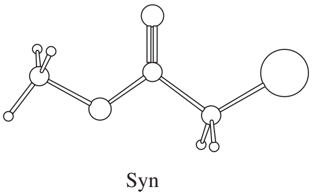

Fig. 1. Diagram showing the numbering scheme and the two conformers of methyl chloroacetate.

Table 1
Experimental parameters for methyl chloroacetate.

Nozzle-to-plate distance (mm)	300.01	747.35
Nozzle temperature (°C)	25	25
Nominal electron wavelength (Å)	0.0498	0.0498
Data interval ($Å^{-1}$)	0.25	0.25
No. of plates	4	3
s_{min} ($Å^{-1}$)	2.0	9.0
s_{max} ($Å^{-1}$)	15.0	27.0
s_{w1} ($Å^{-1}$)	4.0	11.0
s_{w2} ($Å^{-1}$)	13.0	23.2
Correlation parameter	−0.0454	0.4749
Scale factor[a]	1.290(15)	0.808(30)

[a] Values in parentheses are the estimated standard derivations.

The results for important geometrical parameters from the *ab initio* calculations are given in Table 2.

3.2. Normal coordinate analysis

Vibrational quantities are an important part of the model used to analyse the experimental data. *Ab initio* frequency calculations (HF/6-311+G(d,p)) provided theoretical force fields for the molecular vibrations. To calculate the required vibrational parameters (amplitudes, perpendicular amplitude corrections and centrifugal distortions) from these force fields, the program SHRINK [10,11] was used. The force constants for 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 [11].

3.3. Analysis of the gas-phase electron-diffraction data

Only the two low-energy forms of methyl chloroacetate (Fig. 1) observed in the theoretical calculations were included in the model used in the analysis of the experimental electron-diffraction data. These two forms have the O—CH_3 bond eclipsing the carbonyl bond. In one of the low-energy conformers the C—Cl bond is eclipsing the C═O bond (syn conformer), while in the other form the C—H bond is approximately eclipsing the C═O bond, and C—Cl and C═O are therefore gauche to each other (gauche conformer).

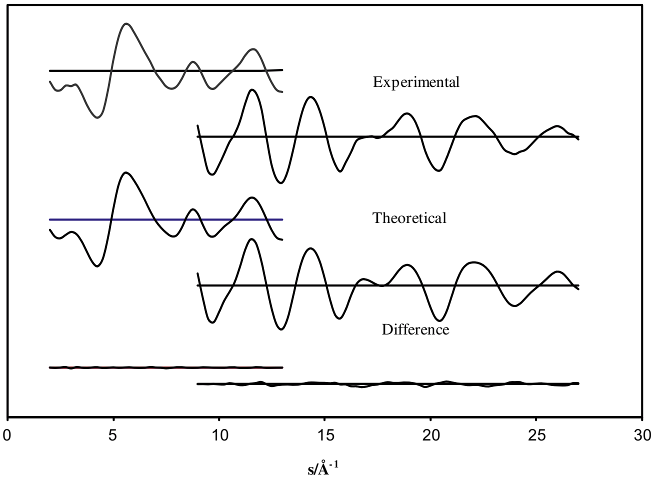

Fig. 2. Experimental intensity curves, $s^4I_t(s)$, for methyl chloroacetate, together with theoretical curve calculated from the final model and difference curves. Difference curves are experimental minus theoretical.

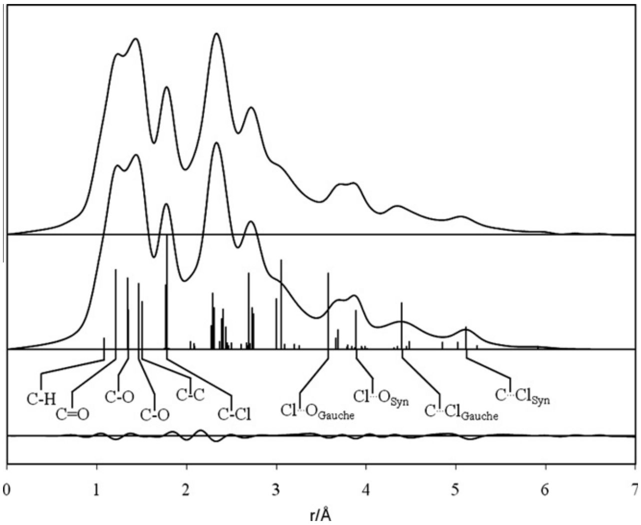

Fig. 3. Radial distribution curves for methyl chloroacetate. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leqslant s/Å^{-1} \leqslant 2.00$ and $B/Å^2 = 0.002$. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights.

The parameters used to define the model for the gauche conformer are given in Table 2. The structure of the syn conformer was defined by applying calculated differences between related parameters for the gauche and the syn conformers obtained in the *ab initio* calculations (MP3/6-311+G(d,p)).

In the model used the C—H_{methyl} bonds were assumed to be equal. The same assumption was also used for the C—C—H_{methyl} angles. The least-squares refinements were performed using the program ed@ed [8]. Values for the independent parameters are given in Table 2 and the important interatomic distance values are given in Table 3.

Intensity curves calculated for the final model are shown in Fig. 2, together with experimental and difference curves. Fig. 3 contain the corresponding RD-curves, and the correlation matrix for the refined parameters is given in Table 4.

4. Discussion

In Table 2 parameter values obtained for methyl chloroacetate (GED, r_{h1}-values) are shown together with theoretical values from the MP3/6-311+G(d,p) calculations. Most experimental parameter values are as expected. r(C═O) is calculated shorter than the experimental value, but this has been observed in many of these molecules. The O—CH_3 bond distance is found to be surprisingly long, both compared with calculated values and with experimental values observed in related molecules [12,13]. We have no good explanation for this.

A good fit between the experimental and the theoretical intensity and RD-curves was obtained using a model with only the two low-energy conformers found in the *ab initio* calculations. This is not surprising since the other two conformers, where O—CH_3 is anti to C═O, were found to be more than 40 kJ/mol higher in energy. The two conformers found experimentally both have the methoxy group syn to the carbonyl group, in one conformer the