

Molecular Structure and Conformation of 1,1-Dichloro-2-propanone, $\text{CHCl}_2\text{-C(=O)-CH}_3$, as Determined by Gas-Phase Electron Diffraction and *ab Initio* Molecular Orbital Calculations

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The molecular structure and conformational composition of 1,1-dichloro-2-propanone (1,1-dichloroacetone) have been investigated by gas-phase electron diffraction at 60 °C. Results from *ab initio* molecular orbital calculations were used as constraints in the analysis. The experimental data are consistent with a model where the molecules exist predominantly with the hydrogen synperiplanar to the carbonyl group. Small amounts (up to 15%) of a second anticlinal form (C–Cl eclipsing C=O) cannot be ruled out. *Ab initio* calculations showed that both synperiplanar and anticlinal forms are stable conformers with the former conformer lower in energy by 2.25 kcal mol⁻¹ (MP2/6-311+G(d)). The geometrical parameters for the synperiplanar conformer (r_g and \angle_a) obtained from least squares analyses of the electron diffraction data, using results from the theoretical calculations to provide some constraints in the model used, are $r(\text{C-H})_{\text{av}} = 1.093(14)$ Å (average value), $r(\text{C=O}) = 1.196(6)$ Å, $r(\text{C}^1\text{-C}^2) = 1.524(4)$ Å, $r(\text{C}^2\text{-C}^3) = 1.496(4)$ Å, $r(\text{C}^1\text{-Cl})_{\text{av}} = 1.775(2)$ Å, $\angle\text{C}^3\text{C}^2\text{C}^1 = 115.2(5)^\circ$, $\angle\text{C}^1\text{C}^2\text{O} = 119.6(5)^\circ$, $\angle\text{C}^3\text{C}^2\text{O} = 125.2(5)^\circ$, $\angle\text{C}^2\text{C}^1\text{Cl}_{\text{av}} = 110.6(5)^\circ$, $\phi(\text{HC}^1\text{C}^2\text{O}) = 2(8)^\circ$, and $\phi(\text{HC}^3\text{C}^2\text{O}) = 25.6^\circ$ (*ab initio* value).

Introduction

We have been interested in the structure and conformational composition of molecules with a $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ bond for some time, and we have found that the conformational composition of molecules with the general formula $\text{XH}_2\text{C-C(=O)Y}$ depends on the nature of the substituents X and Y. For example, when X = Cl, the antiperiplanar form (the reference is between the C=O bond and the unique atom on the carbon atom. In chloroacetaldehyde, it is between the C=O bond and the C–Cl bond, whereas in dichloroacetaldehyde, it is between the C=O bond and the C–H bond) is favored for Y = H [chloroacetaldehyde]¹, the synperiplanar form is favored when Y = Cl or F [chloro- and fluoroacetyl chloride],^{2–5} and the anticlinal form is favored when Y = CH₃ [1-chloro-2-propanone].⁶

When chloro and dichloro compounds are compared, the conformational populations and the deduced stabilities are as follows: for chloroacetyl chloride² (X = Y = Cl), the synperiplanar form (C–Cl eclipsing the C=O bond) is 1.3 kcal mol⁻¹ lower in enthalpy than the anticlinal form (C–Cl anticlinal to the C=O bond). For dichloroacetyl chloride⁷ (Cl₂HC–C(=O)Cl), the amount of synperiplanar form present in the gas phase was found to be 72(6)% at 293 K, indicating that this form could perhaps be the low energy form. The population of the synperiplanar form was, however, found to be not sensitive to temperature variation, suggesting a small enthalpy difference and a positive entropy difference between the synperiplanar and anticlinal forms. A spectroscopy study,⁸ carried out on the same compound, concluded that the anticlinal conformer was 0.38(9) kcal/mol lower in enthalpy than the synperiplanar form (where C–H is eclipsing C=O). For

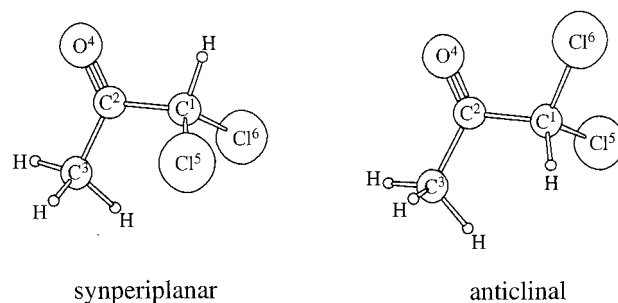


Figure 1. Molecular models of the synperiplanar and anticlinal conformers of 1,1-dichloroacetone with atom numbering.

dichloroacetyl fluoride,⁹ the synperiplanar form was found to be the most stable conformer. A total of 71(5)% of this form was present in the gas phase at 293 K. This result is in agreement with an earlier spectroscopy study.¹⁰

We were interested in studying the structure and conformational composition of 1,1-dichloro-2-propanone (1,1-dichloroacetone), $\text{Cl}_2\text{HC-C(=O)CH}_3$, and to compare the results for this molecule with those mentioned above. An IR and Raman spectroscopic study has been reported for 1,1-dichloroacetone.¹¹ In the solid state only the anticlinal form (see Figure 1) was observed. In the liquid state, both the anticlinal and the synperiplanar forms were found to be present. In the vapor phase, however, the synperiplanar form is, according to this study, the dominant form with the anticlinal form in low abundance.

Experimental Section

A commercial sample of 1,1-dichloro-2-propanone (98%) was obtained from Aldrich Chemical Co. and was used without further purification. Electron diffraction patterns were collected

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TABLE 1: Ab Initio (MP2/6-311+G(d)) Calculated Torsional Angles and Relative Energies for Conformers of $\text{XH}_2\text{C}-\text{C}(=\text{O})\text{Y}$ and $\text{X}_2\text{HC}-\text{C}(=\text{O})\text{Y}$ Molecules^a

torsion angle/ molecule	$\phi(\text{X}-\text{C}-\text{C}-\text{Y})$	$\phi(\text{H}-\text{C}-\text{C}-\text{Y})$	relative energies
$\text{ClH}_2\text{C}-\text{C}(=\text{O})\text{Cl}$	180.0	58.7	0.0
(X = Cl, Y = Cl)	66.7	185.6/-52.9	1.09
$\text{ClH}_2\text{C}-\text{C}(=\text{O})\text{CH}_3$	171.4	-67.8/49.5	1.29
(X = Cl, Y = CH_3)	39.2	160.5/-80.2	0.0
$\text{Cl}_2\text{HC}-\text{C}(=\text{O})\text{Cl}$	-62.5/62.5	180.0	0.64
(X = Cl, Y = Cl)	153.5/-83.8	33.0	0.0
$\text{Cl}_2\text{HC}-\text{C}(=\text{O})\text{CH}_3$	-71.5/51.9	171.1	0.0
(X = Cl, Y = CH_3)	154.8/-82.1	33.6	2.25

^a Torsion angles are in degrees, and energies are in kcal/mol.

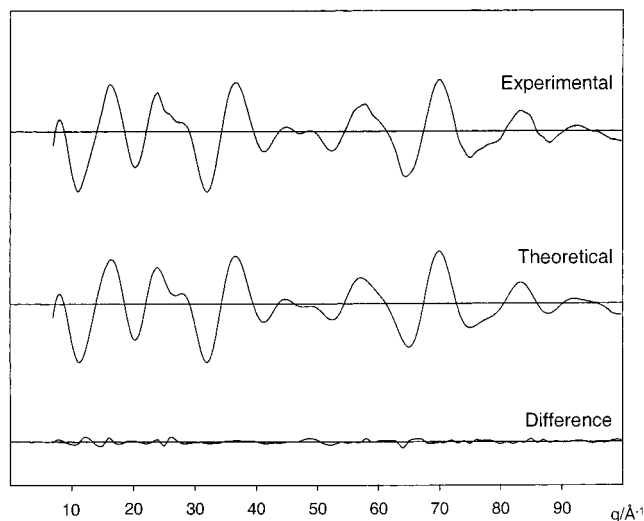


Figure 2. Intensity curves ($qI_m(q)$) for 1,1-dichloroacetone. The experimental curve is the average of the curves from eight (four long camera and four short camera) plates, and the theoretical curve was calculated from the structural parameters in Table 2. The difference curve is experimental minus theoretical curve.

on 5×4 in. Kodak Electron Image plates using the Colgate apparatus. Nozzle-to-plate distances were 245 and 90 mm, and the nozzle temperature was 60 °C. An r^3 sector was used together with an electrically heated inlet, terminating in a nozzle made from a 28 Ga. hypodermic needle. The nominal accelerating voltage used was 40 keV, and the background pressure in the diffraction chamber was maintained at 1.0×10^{-5} Torr during exposures. Voltages were measured to five significant digits using a Fluka model 190 digital voltmeter across a calibrated precision resistor. Camera lengths were measured to a precision of 0.02 mm using a Klinger Optical precision cathetometer [see also Shen, Q.; Kapfer, C. A.; Boudjouk, P.; Hilderbrant, R. L. *J. Organomet. Chem.* **1979**, *169*, 147]. Exposure times for a 0.3 μA beam current were 50 s for the long distance plates and 150 s for the short distance plates. Benzene ($r_a = 1.397(4)$ Å)¹² was used for the final wavelength calibration, and the benzene data were collected immediately after each experiment under identical conditions as the sample. Four plates from each of the long and short camera distances were selected for data analysis. The data were corrected in the usual manner for emulsion saturation, plate flatness, and sector imperfections after which they are interpolated at integral values of q [$q = (40/\lambda) \sin(\theta/2)$] for analysis. The data were analyzed by using a least squares procedure outlined by Gundersen and Hedberg¹³ with tabulated values for scattering and phase shift factors.¹⁴

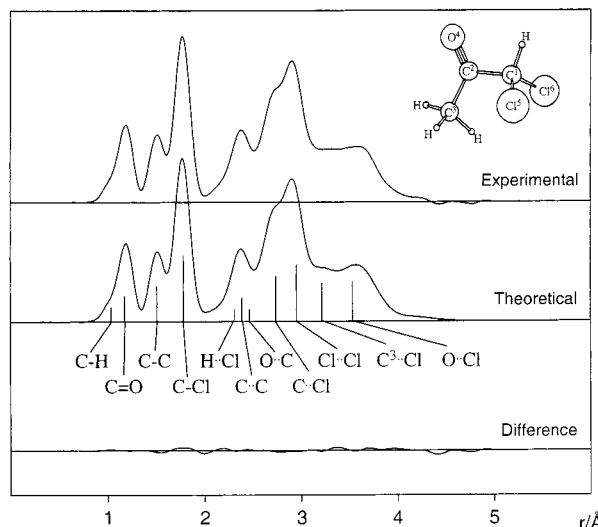


Figure 3. Radial distribution curves for 1,1-dichloroacetone. The experimental curve was calculated from the experimental intensity curve in Figure 2 with theoretical data in the inner unobservable part. The vertical bars indicate some of the most important interatomic distances, and the length of the bars are proportional to the distance weights.

TABLE 2: Parameter Values (r in Angstroms; \angle in Degrees; and l in Angstroms) for 1,1-Dichloroacetone

	GED		ab initio (MP2/6-311+G(d))	
	synperiplanar		synperiplanar	anticlinal
	$r_g/\angle\alpha$	l	$r_e/\angle\epsilon$	$r_e/\angle\epsilon$
$r(\text{C}-\text{H})_{\text{av}}$	1.093(14)	0.073(18)	1.091	1.092
$r(\text{C}=\text{O})$	1.196(6)	0.039(6)	1.216	1.211
$r(\text{C}-\text{C}^1)$	1.524(4) ^a	0.053(4)	1.533	1.542
$r(\text{C}-\text{C}^3)$	1.496(4) ^a	0.053(4)	1.506	1.508
$r(\text{C}-\text{Cl})$	1.776/1.773(2)	0.055(2)	1.776/1.772	1.784/1.756
$\angle\text{C}^1\text{C}^2\text{O}$	119.6(5) ^b		118.1	121.7
$\angle\text{C}^3\text{C}^2\text{O}$	125.2(5) ^b		123.7	124.0
$\angle\text{HCCl}$	107.8(6)		108.6	107.6
$\angle\text{C}^2\text{C}^1\text{Cl}_{\text{av}}$	110.6(5)		109.7	109.3
$\phi(\text{H}^4\text{C}^1\text{C}^2\text{O})$	2(8)		8.4	146.4
$\phi(\text{H}^8\text{C}^3\text{C}^2\text{O})$	[25.6] ^c		25.6	13.6
Dependent Parameters				
$\angle\text{C}^3\text{C}^2\text{C}^1$	115.2(5)	118.2	114.3	
$\text{O}\cdots\text{C}$	2.376(5)	0.063(5)	2.384	2.408
$\text{Cl}\cdots\text{C}^2$	2.713(8)	0.077(5)	2.708	2.704
$\text{Cl}\cdots\text{C}^3$	3.178(20)	0.19(5)	3.250	3.362
$\text{Cl}\cdots\text{Cl}$	2.913(6)	0.077(3)	2.940	2.939
$\text{O}\cdots\text{Cl}$	3.585(5)	[0.171] ^c	3.595	3.419

^a Distances not refined independently. ^b Angle values not refined independently. ^c Parameter value not refined.

Theoretical Calculations

Ab initio molecular orbital calculations were carried out using the Gaussian 94 program,¹⁵ for the synperiplanar [$\phi(\text{HC}^1\text{C}^2\text{O}) \approx 0^\circ$, $\phi(\text{HC}^3\text{C}^2\text{O}) \approx 0^\circ$] and anticlinal [$\phi(\text{HC}^1\text{C}^2\text{O}) \approx 120^\circ$ and $\phi(\text{HC}^3\text{C}^2\text{O}) \approx 0^\circ$] conformers. Optimized geometries were obtained for both forms. The synperiplanar form was found to be 2.07 kcal/mol (HF/6-31G(d)) and 1.82 kcal/mol (MP2/6-31G(d)) lower in energy than the anticlinal form. To check the basis set dependence of this energy difference, MP2 calculations were also made using the 6-311+G(d) basis set. Here the energy difference was found to be 2.25 kcal/mol. Values of zero-point energies and the entropies of both forms were calculated together with vibrational frequencies and Cartesian force constants. The absence of imaginary frequencies confirmed that these two forms are true minima on the potential energy surface. Theoretical force fields were then scaled to the experimental vibrational

TABLE 3: Correlation Matrix for the Parameters of 1,1-Dichloroacetone^a

	σ_{LS}	r_1	r_2	r_3	\angle_4	r_5	\angle_6	\angle_7	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	ϕ
1. $r(C^1-C^2)$	0.0013	100															
2. $r(C=O)$	0.0018	-2	100														
3. $r(C-H)$	0.0047	-20	21	100													
4. $\angle CCCI$	0.1507	-7	17	2	100												
5. $r(C-Cl)$	0.0007	-6	19	11	-19	100											
6. $\angle C^1CO$	0.1559	-24	-53	-7	-25	-18	100										
7. $\angle HCCI$	0.2091	-1	-16	0	-97	28	26	100									
8. $l(C-C)$	0.0014	-3	39	4	9	14	-20	-9	100								
9. $l(C=O)$	0.0020	-21	-44	33	-11	-4	32	12	-13	100							
10. $l(O\cdots C)$	0.0017	-4	-12	3	-9	2	7	12	-13	12	100						
11. $l(C-H)$	0.0058	-5	-71	2	-14	-13	43	13	-29	70	11	100					
12. $l(C-Cl)$	0.0007	-7	-27	7	-8	-9	16	8	-42	25	10	27	100				
13. $l(CIC^2)$	0.0015	7	17	-2	29	5	-25	-34	13	-10	-15	-12	-10	100			
14. $l(Cl\cdots C^3)$	0.0181	12	14	-5	36	-1	-35	-31	6	-13	-6	-13	-6	6	100		
15. $l(Cl\cdots Cl)$	0.0011	-12	-2	3	-38	3	14	37	-2	5	2	2	6	10	-27	100	
16. ϕ	2.5033	-13	-9	8	-46	2	26	44	-4	12	10	10	4	-20	-77	43	100

^a Distances are in angstroms and valence angles in degrees. σ_{LS} is the standard deviations from the least squares refinements.

frequencies earlier determined, using the program ASYM40,¹⁶ and the resulting force fields were used to obtain values for vibrational amplitudes (l) and perpendicular amplitude corrections (K). Using five scale constants ranging from 0.84 to 0.97, the experimental frequencies were fitted to within an average deviation of ± 10 cm⁻¹.

The conformational composition of 1,1-dichloroacetone can be estimated from the theoretical electronic energy difference, the calculated entropy difference, and the zero-point energy differences between the synperiplanar and the anticlinal forms. At the HF/6-31G(d) level of theory, the calculated value for ΔH° (corrected for differences in ZPE) is 1.98 kcal/mol. The ΔS° value (including the $R \ln 2$ factor) is 1.43 cal/mol K. The conformational composition predicted from these values is 9% anticlinal and 91% synperiplanar for a nozzle temperature of 60 °C. At the MP2/6-31G(d) level, the corresponding ΔH° and ΔS° values are 1.72 kcal/mol and 1.42 cal/mol K, respectively, resulting in a conformational composition of 13% anticlinal and 87% synperiplanar conformers. Using MP2/6-311+G(d) calculations, the obtained values are 2.15 kcal/mol and 1.58 cal/mol K, with a predicted conformer composition of 8% anticlinal and 92% synperiplanar as a result.

Theoretical calculations were also made for different conformers of molecules similar to 1,1-dichloroacetone. Some of the results from these calculations are summarized in Table 1.

Electron Diffraction Analysis

A model with the C¹-H bond synperiplanar to the C=O bond was tested first. In this analysis, the geometrical parameters chosen to define the model were $r(C-H)_{av}$, $r(C=O)$, $r(C^1-C^2)$, $r(C^2-C^3)$, $r(C-Cl)_{av}$, $\angle C^1C^2O$, $\angle C^1C^2C^3$, $\angle C^2C^1Cl$, $\angle HCCI$, and torsion angles $\phi(HCCO)$ for the CHCl₂ and the CH₃ groups. It was not possible to refine all of the bond distances and valence angles simultaneously. The difference between the two carbon-carbon bonds, $r(C^1-C^2) - r(C^2-C^3)$, was kept constant at the MP2/6-311+G(d) value. All C-H bonds are assumed identical; the difference between the two C-Cl bonds was also assumed from theoretical values, and C₃ symmetry was assumed for the methyl group. The amplitudes of vibrations and perpendicular amplitude corrections were, as mentioned above, calculated using ASYM40 and the scaled ab initio force field for the synperiplanar conformer. This single conformer model fits the experimental electron-diffraction data very well ($R = 7.83\%$). The intensity and radial distribution curves corresponding to this model are shown in Figures 2 and 3, respectively. The results from the final least squares

refinement, using this single conformer model, are summarized in Table 2 where also the corresponding parameter values from the ab initio calculations are shown.

From the results of the theoretical energy calculations, the presence of a small amount of an anticlinal form is judged to be not unlikely. A two conformer model, with the presence of both the synperiplanar and the anticlinal forms, was therefore tested. In this model, the calculated geometrical differences between the two forms were included as fixed constraints. Some of the differences between parameters within each conformer were also included as fixed constraints. For example, in the anticlinal form, the C-Cl bond eclipsing the C=O bond is calculated to be longer than the other C-Cl bond by 0.028 Å, and the C¹C²O and C³C²O valence angles have a difference of 2.3°. Refinements using this second model fit the data ($R = 7.83\%$) as well as the one conformer model. The composition parameter was refined to a value of 2% with an associated uncertainty of 12% (2σ). No significant changes in the geometrical parameters were observed between these two models. The intensity and radial distribution curves from this second model are indistinguishable from those showed in Figures 2 and 3. The correlation matrix for the final refinement is given in Table 3.

Discussions

Our work has shown that almost all of the 1,1-dichloroacetone molecules at 293 K have a conformation where the C-H bond is eclipsing the carbonyl bond (synperiplanar form). The same conclusion was also reported in the earlier spectroscopic study¹¹ for the gas phase of this compound. These results are in agreement with our ab initio calculations where the energy differences between conformers was found to be 2.25 kcal/mol. Our result for the conformation of 1,1-dichloroacetone may be compared with the results of ED investigations on 1,1-dichloroacetyl chloride, HCl₂C-C(=O)Cl, and 1,1-dichloroacetyl fluoride, HCl₂C-C(=O)F, molecules where the CH₃ group in 1,1-dichloroacetone is replaced by a halogen atom. For 1,1-dichloroacetyl chloride, the old GED study⁷ concluded that both possible conformers (synperiplanar and anticlinal) had about equal enthalpy, but there are other results in this study that indicated that the synperiplanar form had the lowest enthalpy. The spectroscopy study⁸ of 1,1-dichloroacetyl chloride, however, concluded that the anticlinal conformer (C-H anticlinal to C=O) has the lowest enthalpy in the gas phase. We have carried out ab initio calculations for this molecule at the same level as for 1,1-dichloroacetone (MP2/6-311+G(d)) and

TABLE 4: Geometry Parameters Determined for 1,1-Dichloroacetone and Some Related Molecules^a

	chloroacetone ClH ₂ C–C(=O)–CH ₃	1,1-dichloroacetone Cl ₂ HC–C(=O)–CH ₃	hexachloroacetone Cl ₃ C–C(=O)–CCl ₃	dichloroacetyl chloride Cl ₂ HC–C(=O)–Cl	dichloroacetyl fluoride Cl ₂ HC–C(=O)–F
<i>r</i> (C=O)	1.216(3)	1.196(6)	1.202(11)	1.189(3)	1.190(4)
<i>r</i> (C ² –C ¹)	1.537(18)	1.524(4) ^b	1.590(10)	1.535(8)	1.534(8)
<i>r</i> (C ² –C ³)	1.507(16)	1.496(4) ^b	1.590(10)		
<i>r</i> (C–Cl)	1.787(3)	1.776/1.773(2) ^c	1.764/1.775/1.777(3) ^c	1.771(4)	1.768(2)
∠C ¹ C ² O	121.5(16)	119.6(5)	118.2(5)	123.3(13)	126.4(12)
∠C ³ C ² O	119.0(9)	125.2(5)	118.2(5)		
ref	6	this work	17	7	9

^a Distances (*r*_g) are in angstroms, and angles (∠_α) are in degrees. Values in parentheses are 2σ. ^b Differences between C–C distances kept constant at the ab initio values. ^c Differences between C–Cl distances kept constant at the ab initio value.

found the synperiplanar conformer to be 0.64 kcal/mol lower in energy than the anticlinal conformer. This value is much lower than the corresponding value found for 1,1-dichloroacetone (2.25 kcal/mol), but it certainly is in much better agreement with the old ED work⁷ than with the later spectroscopy results.⁸

For 1,1-dichloroacetyl fluoride, the synperiplanar conformer was also found to be the most stable form. Here, the ED investigation,⁹ the spectroscopy study,¹⁰ and the ab initio calculations all were in agreement. A high level calculation⁹ (CCSD(T)/TZP//MP2/6-31+G** + 0.89ZPE(HF/6-31+G**)) gave the synperiplanar conformer as 0.79 kcal/mol lower in energy than the anticlinal conformer. To make direct comparisons between the chloride and fluoride molecules, calculations of relative energies of the synperiplanar and anticlinal conformers of 1,1-dichloroacetyl fluoride at the MP2/6-311+G(d) level were carried out. The synperiplanar conformer was found to be 0.63 kcal/mol more stable than the anticlinal form, a value almost identical to the value calculated for 1,1-dichloroacetyl chloride. This is a strong indication that the conformational composition of the two 1,1-dichloroacetyl halides are quite similar. The spectroscopy investigation of 1,1-dichloroacetyl chloride therefore probably should be redone.

The calculated anticlinal/synperiplanar energy difference in 1,1-dichloroacetone (2.25 kcal/mol) is much larger than that in dichloroacetyl chloride (0.64 kcal/mol). There are two Cl⋯Me anticlinal interactions in the synperiplanar form of dichloroacetone and only one such interaction in the anticlinal form. In dichloroacetyl chloride there are two Cl⋯Cl anticlinal interactions in the synperiplanar form and only one such interaction in the anticlinal form. It appears that the Cl⋯Cl anticlinal interaction is less favorable than the Cl⋯Me anticlinal interaction. As a result, the anticlinal/synperiplanar energy difference in dichloroacetyl chloride is reduced compared to that in 1,1-dichloroacetone. This same effect can also be seen when comparing the results for chloroacetone and chloroacetyl chloride. In chloroacetone, the conformer with Me and Cl anticlinal to each other is the low energy form,⁶ and in chloroacetyl chloride, the conformer with Cl and Cl anticlinal to each other is the high energy form². Theoretical calculations (MP2/6-311+G(d)) are in agreement with the experimental results for these molecules. In chloroacetone, the conformer with Me and Cl anticlinal to each other is calculated to be 1.29 kcal/mol lower in energy, and in chloroacetyl chloride, the conformer with Cl and Cl anticlinal to each other is 1.09 kcal/mol higher in energy. The sizes of a methyl group and a chlorine atom are almost the same. This difference in conformational behavior is therefore clearly not a result of differences in steric strain and is probably due to differences in dipole–dipole interactions. The conformational composition of 1,1-dichloroacetone is consistent with the results observed in similar molecules.

In Table 4, results for bond distances and valence angles found in 1,1-dichloroacetone are compared with results observed in some related molecules. Most of the parameter values for 1,1-dichloroacetone are as expected. The much longer C–C bonds in hexachloroacetone¹⁷ compared with the other two acetones are probably due to larger steric repulsion in the hexasubstituted molecule.

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