

# IR and computational studies of alkyl chloride conformations

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Received 12 July 1999; revised 5 December 1999; accepted 14 December 1999

**ABSTRACT:** ‘Natural bond orbitals’ population analysis calculations are used to explain the differences in infrared absorptions of alkyl chlorides conformers. Hydrogen *anti* to the C—Cl bond affords greater  $\sigma_{\text{C—H}} \rightarrow \sigma^*_{\text{C—Cl}}$  than does carbon *anti* to C—Cl,  $\sigma_{\text{C—C}} \rightarrow \sigma^*_{\text{C—Cl}}$ . Owing to the greater antibonding character in the former case, the C—Cl bond distance is generally larger, and the C—Cl infrared absorption of lower frequency. Attempts to quantify the use of intensities from infrared spectra to give the weight of the particular conformation of an alkyl chloride are reported. The difficulty is that the absorption coefficient  $\alpha$  (cf.  $A_A = \alpha_A C_A \ell$ ) is not known. The ratio  $\alpha_A/\alpha_B$  was approximated from intensities of infrared peaks of two conformations, A and B, as determined from various types of theoretical calculations. The ratio of absorbances  $A_A/A_B$  was determined from the spectra. Then,  $C_A/C_B$  was calculated and compared with the results from various types of pure calculation. In simple alkyl chlorides, this approach was modestly successful. Copyright © 2000 John Wiley & Sons, Ltd.

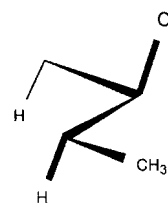
**KEYWORDS:** infrared; conformation; alkyl chlorides

## INTRODUCTION

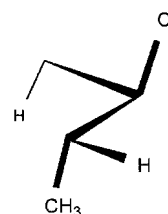
The human intellect is deeply rooted in personal experiences. This creates a problem in pursuit of understanding of the sciences, such as chemistry, as there is no direct experience with molecules, reaction mechanisms or, especially, quantum theory. One response has been to set up a series of models or representations as a framework to try to understand and predict chemical behavior. The line used as a representation for a covalent bond, and curved arrows, used in reaction mechanisms, are entrenched in textbooks, as higher representations cannot easily be displayed or comprehended.<sup>1,2</sup> The use of models or representations is both a blessing and a curse. Successful models afford some predictive power, but they tend to become icons, and assume greater significance than is deserved.

The present study returns to a simpler era of easily understood, if imperfect, representations. The study concerns the infrared spectra of alkyl chlorides. Unlike NMR, infrared spectroscopy is an ‘instantaneous’ technique in which peaks due to individual conformations of the molecule in question can be observed.<sup>3a</sup> (The arguments presented in the present paper have many analogies in the inorganic chemistry literature, e.g. Ref. 3b.) Extensive early work was devoted to the assignment of infrared peaks to individual conformations of various

molecules.<sup>4–9</sup> These studies correlated the C—X infrared absorption band with group(s) *anti* to C—X in the various possible conformations of the alkyl halide (cf. the list of compounds in Tables 2–4).<sup>3,4,10,11</sup> The notation used, e.g. S<sub>CH</sub>, signifies a secondary alkyl chloride in which both a carbon and a hydrogen are *anti* to the C—Cl bond, as in the diagram shown for 2-chlorobutane (**3**).<sup>4</sup> Although the categorization indicated in Table 1 is useful, computer graphics do not always indicate a strong coupling of the *anti* groups to the C—Cl vibration. The reasons for the



**3**: S<sub>HH</sub>



**3**: S<sub>CH</sub>

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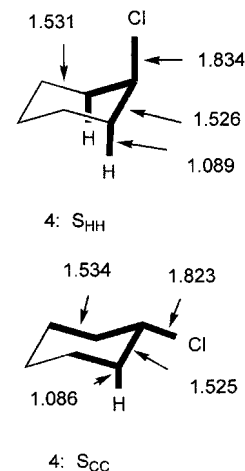
**Table 1.** Infrared frequencies for various alkyl chloride conformations

Conformation	Expected infrared frequency range (cm <sup>-1</sup> )
P <sub>H</sub>	648–657
P <sub>C</sub>	723–730
S <sub>HH</sub>	608–615
S <sub>CH</sub>	655–674
S <sub>CC</sub>	758
T <sub>HHH</sub>	560–581
T <sub>CHH</sub>	611–632

conformational correlations of Table 1 have received little attention in the literature.

Progressively lower frequencies are found in the order primary > secondary > tertiary. The decrease in the C—Cl frequency parallels the increase in calculated bond distance.<sup>12,13</sup> RHF/6–31G\* calculations indicate a bond distance of 1.81 Å for the P<sub>H</sub> conformation of 1-chloropropane (**1**), 1.83 Å in the S<sub>HH</sub> conformation of chlorocyclohexane (**4**) and 1.84 Å for T<sub>HHH</sub> of 2-chloro-2-methylpropane. (These data are from RHF/6–31G\* calculations using Gaussian 94W, Revision D3).<sup>12</sup> The thesis of the present study is that progressively longer bonds in part arise from a cumulative admixture of antibonding character to the C—Cl bond, resulting in a lower degree of bonding, greater bond distances and lower IR frequencies.<sup>3b,13–15</sup> [In other respects, tertiary chlorides show differences in behavior. Although the infrared frequency for T<sub>CHH</sub> is greater than for T<sub>HHH</sub>, the calculated C—Cl bond distances are larger for T<sub>CHH</sub> (1.8389) than for T<sub>HHH</sub> (1.8368).]

In addition, conformers with hydrogen *anti* to the C—



Cl bond show lower IR frequencies than conformers with carbon *anti* to C—Cl, i.e. P<sub>C</sub> > P<sub>H</sub> and S<sub>CC</sub> > S<sub>CH</sub> > S<sub>HH</sub>.<sup>3–11</sup> The reason for these relationships has been clear from other studies for some time, although not explicitly discussed in the context of infrared spectra.<sup>13–15</sup> With hydrogens *anti* to chlorine, a greater C—Cl bond distance is often found, which reflects a lesser degree of bonding. Using a valence-bond model, one could say that there is a greater degree of hyperconjugation where hydrogen is *anti* to chlorine, leading to lesser C—Cl bonding and therefore to a greater bond distance.<sup>3b,13–15</sup>

In chlorocyclohexane (**4**) the ‘natural bond orbitals’ (NBO) population analysis originated by Weinhold and co-workers<sup>16</sup> [NBO Version 3.1, implementation in Gaussian 94]<sup>12</sup> clearly shows a significant second-order perturbation effect in which  $\sigma \rightarrow \sigma^*$  electronic interaction of the axial C—H bond with the antiparallel

**Table 2.** Frequencies, bond distances and NBO data for selected compounds

No.	Compound	Conformer	Infrared frequency (cm <sup>-1</sup> )	C—Cl bond distance (Å)	NBO: population of antibonding (C—Cl)* orbitals	NBO: energy $\sigma \rightarrow \sigma^*$ ( $\pi$ -interaction) (kcal mol <sup>-1</sup> )
<b>1</b>	1-Chloropropane	P <sub>H</sub>	650	1.812	0.0184	8.03
		P <sub>C</sub>	728	1.809	0.0134	4.82
<b>4</b>	Chlorocyclohexane	S <sub>HH</sub>	579	1.834	0.0356	7.95
		S <sub>CC</sub>	731	1.823	0.0263	5.10
<b>8</b>	3-Chloropropanenitrile	P <sub>H</sub>	669	1.817	0.0133	6.08
		P <sub>C</sub>	757	1.791	0.0104	3.50
<b>9</b>	2-Chloroethanol	P <sub>H</sub>	663	1.806	0.0174	7.62
		P <sub>OH</sub>	749	1.804	0.0094	3.32
<b>10</b>	1,2-Dichloroethane	P <sub>H</sub>	655 <sup>a</sup> , 675 <sup>b</sup>	1.796	0.0149	6.82
		P <sub>Cl</sub>	711 <sup>c</sup>	1.799	0.0171	4.79
<b>11</b>	1-Bromo-2-chloroethane	P <sub>H</sub>	666	1.794	0.0146	6.67
		P <sub>Br</sub>	726	1.802	0.0211	6.12
<b>12</b>	3-Chloroprop-1-ene	H ecl	737, 600	1.816	0.0244	9.24 ( $\pi$ )
		Cl ecl	727, 549	1.798	0.0140	6.75
<b>13</b>	1-Chloropropan-2-one	H ecl	728	1.793	0.0127	2.34 ( $\pi$ )
		Cl ecl	763	1.781	0.0087	3.47
<b>15</b>	(Chloromethyl)cyclopropane	P <sub>H</sub>	671?(vw)	1.798	0.0152	6.96
		P <sub>C</sub>	700	1.803	0.0218	5.95

<sup>a</sup> Symmetric stretch.

<sup>b</sup> Antisymmetric stretch.

<sup>c</sup> Antisymmetric stretch. The symmetric stretch, calculated to be 743 cm<sup>-1</sup>, has almost no intensity.

**Table 3.** Comparison of calculation methods for frequency assignment (intensity)

No.	Compound	Observed frequency (cm <sup>-1</sup> )	MM3 calculated frequency (cm <sup>-1</sup> )	PM3 calculated frequency (cm <sup>-1</sup> ) (intensity)	RHF/6-31G* calculated frequency (cm <sup>-1</sup> ) (intensity)	B3LYP/6-31G* calculated frequency (cm <sup>-1</sup> ) (intensity)	
1	1-Chloropropane	P <sub>H<sub>3</sub></sub>	650	670	633 (9.2)	616 (41.4)	634 (27.8)
		P <sub>C<sub>3</sub></sub>	728	746	717 (12.5)	696 (64.4)	714 (45.7)
2	1-Chloro-2-methylpropane	P <sub>H<sub>3</sub></sub>	687	677	693 (12.2)	661 (37.4)	675 (32.8)
		P <sub>C<sub>3</sub></sub>	730	733	718 (12.4)	709 (56.3)	716 (45.5)
3	2-Chlorobutane	S <sub>HH<sub>3</sub></sub>	610	637	600 (10.8)	573 (46.6)	586 (32.0)
		S <sub>CH<sub>3</sub></sub>	670	693	676 (12.3)	634 (54.5)	652 (38.2)
		S <sub>HH</sub>	629	641	632 (9.0)	607 (21.3)	615 (23.6)
4	Chlorocyclohexane	S <sub>HH</sub>	559	579	563 (5.1)	540 (25.6)	542 (22.4)
		S <sub>CC<sub>3</sub></sub>	731	736	744 (13.9)	711 (46.7)	723 (44.9)
5	Chlorocyclobutane	S <sub>HH</sub>	620	635	—	601 (40.9)	600 (33.1)
		S <sub>CC</sub>	717, 529	702	—	697 (15.1), 506 (12.4)	726 (17.8), 522 (8.2)
6	2-Chloro-2-methylbutane	T <sub>HHH</sub>	560	585	580 (11.86)	534 (44.6)	533 (33.9)
		T <sub>CHH</sub>	618	624	641 (12.8)	590 (38.5)	603 (29.6)
7	1-Chloro-2-phenylethane	P <sub>H<sub>3</sub></sub>	656	673	655 (7.57)	639 (44.3)	—
		P <sub>C<sub>3</sub></sub>	717	742, 762, 769	720 (21.9)	710 (89.8)	—
8	3-Chloropropanenitrile	P <sub>H<sub>3</sub></sub>	669	673	640 (7.10)	640 (38.4)	658 (25.5)
		P <sub>C<sub>3</sub></sub>	757	763 (769)	742 (11.45)	733 (76.3)	750 (54.0)
9	2-Chloroethan-1-ol	P <sub>H<sub>3</sub></sub>	663	658	640 (11.1)	633 (56.7)	647 (39.1)
		P <sub>OH<sub>3</sub></sub>	749	756	734 (17.1)	725 (109.7)	751 (75.0)
10	1,2-Dichloroethane	P <sub>H<sub>3</sub></sub>	655, 675	648, 680	631 (s) (7.9), 648 (as) (6.0)	627 (34.3), 651 (44.0)	643 (24.3), 665 (31.3)
		P <sub>Cl<sub>3</sub></sub>	711	729	689 (as) (21.8)	685 (146.0)	697 (112.8)
11	1-Bromo-2-chloroethane	P <sub>H<sub>3</sub></sub>	666	658	623 (10.3), 639 (11.6)	640 (34.7)	655 (24.7)
		P <sub>Br<sub>3</sub></sub>	726	715, 727	691 (33.1)	710 (38.1)	716 (29.5)
13	1-Chloropropan-2-one	H <sub>ecl</sub>	728	762, 714	729 (7.69)	704 (34.4)	725 (35.6)
		Cl <sub>ecl</sub>	763	775, 754	742 (2.09)	ca. 740 (25.2) <sup>a</sup>	759 (32.8)

<sup>a</sup> Persistent imaginary frequency observed. These data are less accurate than others.

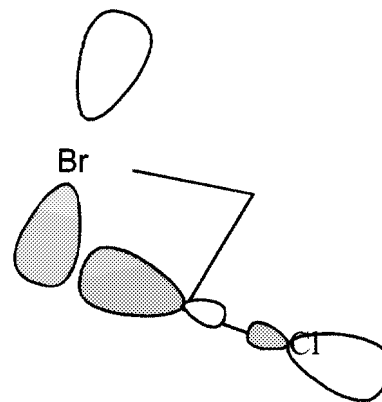
(C—Cl)\* antibonding orbital in the  $S_{HH}$  conformer is present.<sup>17</sup> In **4** ( $S_{CC}$ ), the C—C interaction with the equatorial (C—Cl)\* antibonding orbital also occurs, but to lesser extent (cf. Table 2). The reverse interaction,  $\sigma_{C-Cl} \rightarrow \sigma_{C-H}^*$ , is rather weak (ca 2. kcal compared with ca 7 kcal for the forward  $\sigma_{C-H} \rightarrow \sigma_{C-Cl}^*$  interaction), as expected owing to the electronegativity of chlorine.<sup>18</sup>

Table 2 lists frequency, bond distance and the NBO parameters for selected molecules. Compounds with electronegative atoms X *anti* to the C—Cl bond show high C—Cl frequencies and short bonds in part due to reduced interaction of the C—X bond with (C—Cl)\*, i.e.  $\sigma_{C-X} \rightarrow \sigma_{C-Cl}^*$ .<sup>17</sup> In general, this expectation is found for **8**, X = CN,<sup>19</sup> and for **9**, X = OH.<sup>20</sup> However, for **10**, X = Cl and **11**, X = Br,<sup>21</sup> the  $P_X$  frequencies are roughly similar to those for **1**, X = CH<sub>3</sub>.

Thus, 1,2-dichloroethane (**10**) represents an unusual case.<sup>4</sup> For the  $P_{Cl}$  conformer, the value of the frequency shown in Table 2 (711 cm<sup>-1</sup>) is for the antisymmetric coupled C—Cl stretch. This value seems low in view of the short C—Cl bond distance of 1.796 Å. The symmetric stretch, which has almost no intensity, indeed is predicted to occur at higher frequency, 743 cm<sup>-1</sup>. The NBO analysis for *anti* 1,2-dichloroethane (**10**) shows that there is a remarkable degree of  $\sigma_{C-Cl} \rightarrow \sigma_{C-Cl}^*$  interaction between the chlorines (energy 4.79 kcal). In addition, there is a through-space effect in which one chlorine lone pair interacts with the (C—Cl)\* of the other chlorine (energy 2.47 kcal).<sup>22</sup> This interaction is absent in the *gauche* conformer. The sum of the  $\sigma_{C-Cl} \rightarrow \sigma_{C-Cl}^*$  and the through-space lone pair  $\rightarrow \sigma_{C-Cl}^*$  interactions produces a more highly populated (C—Cl)\* state for the  $P_{Cl}$  than for the  $P_H$  conformer, and also a slightly longer C—Cl bond distance. The *anti*  $P_{Cl}$  C—Cl frequency, however, is higher than the *gauche*  $P_H$  frequency. These C—Cl frequencies are highly coupled, unlike many others in Table 2, and it is hard to evaluate the factors affecting frequency. An AIM bond orders calculation indicates that the *anti*  $P_{Cl}$  C—Cl bond order (1.031) is slightly higher than that of the *gauche*  $P_H$  (1.022).<sup>16</sup>

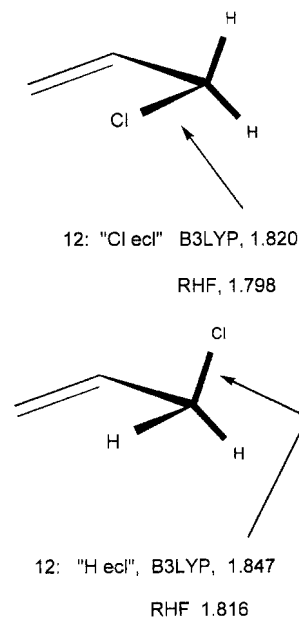
The long-range effect  $lp_{Br} \rightarrow \sigma_{Cl}^*$  is even greater (3.83 kcal) for the less closely held lone pair (lp) of 1-bromo-2-chloroethane (**11**). A crude representation is shown here. In view of this sizable ground-state interaction, the greater neighboring group assistance by bromine over chlorine in  $S_N1$  reactions is no surprise.

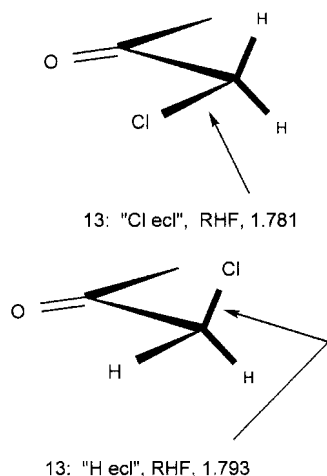
The cyclopropyl group accelerates carbocation reactions because its unusual high-energy ring bonds facilitate  $\sigma \rightarrow \pi$  interactions.<sup>23,24</sup> In (chloromethyl)cyclopropane (**15**) [and also in chlorocyclobutane (**5**)], a greater population of (C—Cl)\* in the  $P_C$  than in  $P_H$  conformer is evident (Table 2). Also, similar C—Cl bond lengths for  $P_C$  and for  $P_H$  conformers are found. For **15**, the C—Cl frequency for the  $P_C$  conformer (700 cm<sup>-1</sup>) is low compared with that of  $P_C$  for compounds **1**, **2**, **7** and **8**, which are usually well above 700 cm<sup>-1</sup> owing to less efficient  $\sigma \rightarrow \sigma^*$  interactions.



Replacement of one of the cyclopropyl carbons with oxygen giving chloromethyloxirane (epichlorohydrin)<sup>25</sup> (**16**) results in an increase in ir frequency to 724 cm<sup>-1</sup> for the  $P_C$  conformation. The  $P_O$  conformation is much higher in frequency (737 cm<sup>-1</sup>), if assignments are correct.

In 3-chloroprop-1-ene (allyl chloride) (**12**), the simple conformational designations such as given in Table 1 are not possible. Instead, designations such as 'H ecl' or 'Cl ecl' are used (indicating that hydrogen or chlorine is eclipsed with the unsaturated group, as shown in the structure presented (the nomenclature of conformations of haloalkenes in the literature is not uniform;<sup>26</sup> Ref. 26b summarizes previous findings and clarifies the situation).<sup>27</sup> Interaction of the relatively high-energy  $\pi$  system with (C—Cl)\* should be fairly efficient.<sup>17</sup> Indeed, **12** shows a very high interaction energy (9.2 kcal) and a greater bond distance for the C—Cl bond in the 'H ecl' conformer where the  $\pi \rightarrow \sigma^*$  interaction exists. The 'Cl ecl' form shows only a weaker  $\sigma_{C-H} \rightarrow \sigma_{C-Cl}^*$  interaction. Multiple coupled IR frequencies exist for each conformation, hence comparison of IR frequencies is difficult. The diagram also shows the difference between





RHF and B3LYP/6-31G\* results. The density function calculations give uniformly longer calculated bond distances, but the trends of the data are similar.

In 1-chloropropan-2-one (chloroacetone) (**13**),<sup>28</sup> the electronegative oxygen should inhibit the  $\pi \rightarrow \sigma^*$  electronic interaction. An exceptionally short C—Cl bond exists in both conformations, and the IR C—Cl frequency is high, i.e. 763 and 728  $\text{cm}^{-1}$  for the most directly applicable modes.<sup>29</sup>

An attempted correlation of C—Cl bond distance and C—C bond distance with the C—Cl IR frequency for the compounds of Table 3 using neural nets disclosed a correlation coefficient of only 0.94 (NeuroShell2, 1993 version, from Ward Systems Group, Frederick, MD, USA was used). The change in bond distance (e.g. for axial vs equatorial chlorocyclohexanes **4**,  $\Delta l = 0.011$  Å) and the difference in ir frequency for C—Cl in **4** ( $\Delta \nu = 152$   $\text{cm}^{-1}$ ) lie in a similar energy domain (bond distance,  $\Delta E = 50$  cal and frequency,  $\Delta E = 72$  cal).<sup>30,31</sup> Calculations at a higher level of theory are probably required for a better correlation. Other effects may serve to impede a close correlation. For example, chlorine lone-pair back-donation to the neighboring (C—C)\* or (C—H)\* bonds occurs. Thus the bond distance and ir frequency result from a complex interplay of different effects.

## ATTEMPTED QUANTITATIVE ANALYSIS OF CONFORMER POPULATIONS

Prior to 1985, few attempts to gain quantitative conformer populations from IR spectra had appeared in the literature.<sup>4</sup> Recently, extensive work by Durig and co-workers has correlated experimental determinations of conformer populations with the results of theoretical calculations.<sup>32</sup>

Table 3 shows that calculated infrared frequencies, at various levels of theory, are in reasonable agreement with observed frequencies. For example, in 1-chloro-2,2-dimethylpropane, the observed  $P_c$  C—Cl stretching

frequency is 720  $\text{cm}^{-1}$ , and the calculated values are 767 (MM3), 725 (PM3) and 732  $\text{cm}^{-1}$  (RHF/6-31G\*).<sup>33</sup> The exception is AM1 calculations (data too poor to report). The question remains of whether calculated band intensities are also accurate.

One might ask whether calculations alone could not provide the energy differences, and from these, the weights of each conformation. Allinger and co-workers showed that a special version of molecular mechanics had excellent predictive capabilities for each C—Cl frequency and, presumably, the energy of the conformer.<sup>34,35</sup> However, with programs currently available (to us), 1-chloro-2-phenylethane (**7**) was calculated to have the following ratios of *gauche* ( $P_H$ ) to *anti* ( $P_c$ ) conformations: 57:43 (for MM3), 23:77 (PM3) and 8:92 (*ab initio* RHF/6-31G\*). Although this case shows rather extreme variations, an experimental check upon theoretical predictions is useful. 1-Chlorocyclobutane (**5**) is another case in which calculations disagree widely (Table 4).<sup>36,37</sup>

One of the most useful methods for the application of IR spectroscopy for determination of conformer populations came from Park et al.<sup>38</sup> and also Abraham and Bretschneider.<sup>39</sup> The intensity of an IR absorption due to a particular conformer A is given by the classical equation  $A_A = \alpha_A C_A \ell$ , where  $A_A$  is the absorbance of conformer A,  $\alpha_A$  is the absorption coefficient, and  $C_A$  is the concentration of conformer A. Similar expressions can be written for conformer B, etc. The difficulty is that absorbances cannot be directly related to the desired concentration as the absorption coefficients  $\alpha$  generally are not known.<sup>36</sup>

The usual response to the lack of knowledge of absorption coefficients is to conduct temperature studies.<sup>10,11,32,38,39</sup> From the absorbances taken at various temperatures, the enthalpy can be calculated from the relationship  $\ln(A_A/A_B) = -\Delta H^\circ/RT + C$ . Variable low-temperature studies of ir conformation have been successful,<sup>26,32</sup> but with the high-temperature equipment available to us, leakage of the cells was severe at the higher temperature ranges. These variable-temperature techniques also assume that neither  $\alpha_A/\alpha_B$  nor  $\Delta H^\circ$  itself is temperature dependent. The dielectric constant ( $DK$ ) of the medium increases as temperature drops.<sup>35,38,39</sup> Frequency calculations show that the peak intensities are sensitive to dielectric constant of the medium, particularly for bifunctional molecules in which the conformers have different dipole moments.<sup>39</sup> The largest change in peak intensities occurs between medium and low dielectric constant solvents. For 1,2-dichloroethane (**10**), the calculated ratio of the  $P_H/P_{Cl}$  peak intensities is 0.236 at a  $DK$  of 30, and 0.235 for a  $DK$  of 10 and 0.227 at a  $DK$  of 2. For **13**, the calculated ratio of peak intensities is 1.373 at a  $DK$  of 30 and 1.339 at a  $DK$  of 8. For molecules with more than one polar functional group,  $\Delta H^\circ$  is well known to vary with the dielectric constant of the medium.<sup>35,38,39</sup>

A technique was investigated involving both calcu-

Table 4. Mole fractions of conformations

No.	Compound	Conformer A/B	Absorbance ratio, A:B (intensity ratio, A:B) <sup>a</sup>	Observed mole fraction, $X_A$ B3LYP <sup>b</sup> (PM3) <sup>b</sup>	Calculated $X_A$		
					PM3	MM3	RHF/6-31G* B3LYP/6-31G*
1	1-Chloropropane	P <sub>H</sub> /P <sub>C</sub>	0.536 (0.608)	0.47 (0.42)	0.38	0.43	0.30
2	1-Chloro-2-methylpropane	P <sub>H</sub> /P <sub>C</sub>	0.645 (0.718)	0.47 (0.36)	0.28	0.27	0.33 <sup>c</sup>
3	2-Chlorobutane	S <sub>HH</sub> /S <sub>CH</sub>	1.74 (0.839)	0.67 (0.72)	0.71	0.58	0.67
		S <sub>HH</sub> /S <sub>HH'</sub>	7.22 (1.20)	0.84 (0.86)	0.80	0.79	0.83
4	Chlorocyclohexane	S <sub>HH</sub> /S <sub>CC</sub>	0.192 (0.368)	0.30 (0.34)	0.27	0.35	0.15 <sup>b</sup>
5	Chlorocyclobutane	S <sub>HH</sub> /S <sub>CC</sub>	0.051 (1.86)	0.03, 0.03 (—)	0.68	—	0.05
6	2-Chloro-2-methylbutane	T <sub>HHH</sub> /T <sub>CHH</sub>	4.80 (1.15)	0.81 (0.83)	0.70	0.56	0.60
7	1-Chloro-2-phenylethane	P <sub>H</sub> /P <sub>C</sub>	0.204 (0.337)	0.41 <sup>e</sup> (0.38)	0.46	0.22	0.09
8	3-Chloropropanenitrile	P <sub>H</sub> /P <sub>C</sub>	0.80 (0.473)	0.63 (0.50)	0.53 <sup>c</sup>	0.26	0.48
9	2-Chloroethan-1-ol	P <sub>H</sub> /P <sub>OH</sub>	0.953 (0.533)	0.64 (0.49)	0.52	0.87	0.54
10	1,2-Dichloroethane	P <sub>H</sub> /P <sub>Cl</sub>	0.132 0.116 (0.278), (0.207)	0.32, 0.36 (0.27), (0.30)	0.19	0.26	0.21
11	1-Bromo-2-chloroethane	P <sub>H</sub> /P <sub>Br</sub>	0.135 (0.839)	0.14 (0.17)	0.16	0.24	0.14

<sup>a</sup> Intensities are taken from B3LYP/6-31G\* calculations, except as noted.

<sup>b</sup> Calculation made using intensity ratios from B3LYP calculations or (in parentheses) from PM3 calculations.

<sup>c</sup> Zero-point energy correction not made.

<sup>d</sup> Inaccurate. Minimization oscillated.

lated and experimental data, and the results are shown in Table 4. In this approach, absorbances  $A_A$  and  $A_B$  for C—Cl are taken from the spectrum (peak areas are determined by the Grams/32 curve-fitting program Grams/32e Spectral Notebook, Version 4.84, Level 1, Galactic Industries, Salem, NH, USA). Ratios of absorption coefficients  $\alpha_A/\alpha_B$  are approximated by ratios of peak intensities provided by B3LYP/6–31G\* frequency calculations at the *DK* of the bulk liquid. For larger molecules, intensity ratios are taken from calculations at the RHF/6–31G\* or PM3 levels.<sup>40</sup> In the latter case, *DK* cannot be varied, and a ‘gas-phase’ *DK* is implicitly used.<sup>35</sup> The ratio of the concentrations of conformers is calculated from the relationship  $C_A/C_B = (A_A/A_B)(\alpha_B/\alpha_A)$ . These concentration ratio values are converted to mole fractions ( $X_A$ ) and these can then be compared with the values derived from various calculations. If peak heights are used, instead of peak areas very poor agreement of calculated and experimental data is found<sup>41</sup>. [In another approach to the evaluation of  $\alpha_A/\alpha_B$  ratios, the spectra of **8** and **10** were determined in a series of solvents covering a range of *DK*. Using our own data and data from Bermani *et al.*,<sup>41d</sup> a plot of  $RT\ln(A_G/A_T)$  vs  $(\epsilon - 1)/(2\epsilon + 1)$  should provide an *x*-intercept that is  $\Delta E_v + RT\ln(\alpha_G/\alpha_T)$ .<sup>31</sup> This technique so far has failed to yield good data.]

The conformational analysis of chlorocyclohexane (**4**) is perhaps the best understood of any molecule of this study. The ‘observed–calculated’ mole fraction  $X_A$  for **4**, i.e. 0.30, is similar to some values from pure calculation 0.27 (MM3) and 0.35 (PM3), and to the literature experimental value, 0.29.<sup>42</sup> The energies from *ab initio* calculations provide  $X_A$  values that are too low (ca 0.17). The ratio  $\alpha_A/\alpha_B$  approximated from *ab initio* intensities, 0.37, is considerably higher than values given by Slazer *et al.*, i.e. 0.12–0.15.<sup>41a</sup> This ratio seems unusually small (cf. Table 4).

Simple alkyl chlorides,<sup>9</sup> e.g. **1–4**, but not the tertiary chloride **6**, showed fair agreement between ‘observed–calculated’ and (pure) calculated mole fractions of conformers,  $X_A$ . Generally, the mole fractions determined using PM3 peak intensity ratios seem to give better agreement with pure calculations than intensity ratios from B3LYP/6–31G\* calculations. Similarly, studies of bifunctional molecules **8–11** were modestly successful. However, the PM3 data were not accurate since the correct *DK* could not be used.

For unsaturated compounds, i.e. 3-chloroprop-1-ene (allyl chloride) (**12**), Sourisseau and co-workers suggest that the ‘H ecl’ and ‘Cl ecl’ peaks are superposed<sup>43a</sup>. Som and Kastha<sup>42b</sup> also report superposition of peaks from different conformers. A prominent peak is seen at  $737\text{ cm}^{-1}$ , close to the prediction of *ab initio* calculations for ‘H ecl,’ but nothing is seen near  $700\text{ cm}^{-1}$ , where several programs predict ‘Cl ecl’ to show a strong absorbance. Grams/32 deconvolution suggests that an absorption at  $727\text{ cm}^{-1}$  is indeed hiding under the more

intense  $737\text{ cm}^{-1}$  peak. However,  $X_A$  (‘H ecl’) is determined to be 0.73. The pure calculated values range from 0.79 (MM3) to 0.92 (*ab initio*). Using the  $600\text{ cm}^{-1}$  (‘H ecl’) and  $549\text{ cm}^{-1}$  (‘Cl ecl’) as suggested by McLachlan and Nyquist,<sup>44</sup> an  $X_A$  (‘H ecl’) of 0.54 is found. Hence, the agreement between various data forms is not satisfactory.

Regarding the C=C absorption(s) of **12**, calculations predict a very weak intensity of the ‘H ecl’ conformer, only about one tenth that of ‘Cl ecl.’ The observed spectrum shows just one C=C absorption, probably due to the less prevalent conformer, ‘Cl ecl.’

For 1-chloropropan-2-one (**13**), the results from evaluation of the C—Cl stretch vs the carbonyl stretch also were not in agreement. The observed C—Cl absorptions at  $728$  and  $759\text{ cm}^{-1}$  agree with B3LYP/6–31G\* predictions of  $725\text{ cm}^{-1}$  (‘H ecl’) and  $763\text{ cm}^{-1}$  (‘Cl ecl’). The ‘observed–calculated’  $X_A$  (‘H ecl’) of 0.18 was also in fair agreement with the predictions of B3LYP calculations, 0.23. The carbonyl region showed two peaks at  $1724$  and  $1746\text{ cm}^{-1}$  compared with B3LYP predictions (using the recommended scaling factor)<sup>12,45</sup> of  $1730$  and  $1747\text{ cm}^{-1}$  for ‘H ecl’ and ‘Cl ecl,’ respectively. However, the ‘observed–calculated’  $X_A$  of 0.53 from carbonyl intensities was in poor agreement with data from C—Cl intensities and from calculation.<sup>46</sup> In our hands, the C—Cl frequencies seem to provide conformer populations in best agreement with calculation.

## EXPERIMENTAL

Alkyl chlorides were prepared from alcohols by standard procedures,<sup>47</sup> but most often were purchased. These were purified by distillation to the point that no extraneous absorptions were observed by <sup>13</sup>C NMR. Spectra were taken on an Analect RFX-65 instrument and later on a Nicolet Impact 410 Omni system. The spectra were taken neat, using recently polished sodium chloride cells. Occasionally, KBr cells were used. In later work, spectra were taken directly in the absorption mode, but early data in the transmittance mode were converted to absorbance by the Grams/32 program. The Grams/32 program was used to obtain absorbance peak areas using the Gaussian–Lorentzian option. Repeat determinations were in reasonable, but not perfect, agreement. Peak areas determined from programs associated with the FT-IR instrument were not accurate. Evaluation of observed peak areas, even with sophisticated programs such as Grams/32, is not always straightforward. Of the four curve-fitting methods in the Grams/32 program, Gaussian–Lorentzian (the default, which was used), pure Lorentzian, Voight and log-normal, agreement with one another was not particularly good. However, a check on the Grams/32 data in three cases, using the old ‘cut-and-weight’ method, were in good agreement.

Energy and frequency calculations were done on a

Pentium PC using the Gaussian94, Revision D3, program, for quantum calculations and on a VAX for MM3 data.<sup>16,35,48</sup> Frequency calculations were performed at the same basis set as the original, and no imaginary frequencies were found. Repeat calculations using new coordinates gave similar data, but not precisely the same, particularly for intensities. In the case of RHF/6-31G\* calculations, the frequencies were scaled by 0.8927 as recommended,<sup>48</sup> and these data are reported in Table 3. In general, this scaling factor appeared to be too extreme, as the RHF/6-31G\* calculated frequencies were generally lower than the observed values (Table 3). For B3LYP/6-31G\* calculations, the recommended scaling factor of 0.961 yielded data that were uniformly too low in frequency for the C—Cl stretch, although this scaling factor is good for carbonyl. If anything, the scaling factor should be ca 1.01 for the chlorides of this study, but since this was so close to unity no scaling factor was applied for C—Cl. No scaling was used for the zero-point energy corrections to the B3LYP energies, as the differential ZPE correction generally was very small. PM3 calculations were performed using HyperChem. In view of the concern about the reliability of the minimizations using HyperChem, a check on these data using PM3 under Gaussian 94 was performed and found to be in good agreement. Unfortunately, the option of Gaussian 94 to allow single-point PM3 calculations at varying dielectric constants did not work (the calculation merely reported the original 'gas-phase' data). For *ab initio* calculations on monofunctional compounds, a uniform *DK* of 6 was used, which is close to the *DK* for most alkyl chlorides. For monofunctional molecules, the dependence upon *DK* was small. For bifunctional compounds, the literature dielectric constant, taken near room temperature, was used. For bifunctional molecules, the intensities, in particular, were dielectric constant sensitive, although the ratio was much less so. Solvent effect calculations were performed using the SCIPCM approximation of the cavity in the dielectric medium.<sup>12</sup> The NBO calculations were performed using SCF densities.

Since MM3 was not fully parameterized for some of the compounds in question, the following parameters were taken from the most closely similar cases: 2-chloroethylbenzene, torsional parameter for atom types 12-1-1-50,  $V_1$  0.0,  $V_2$  -0.250,  $V_3$  0.550; for chlorocyclobutane, torsional parameters for atom types 12-56-56-56 in later stages of the study,  $V_1$  0.0,  $V_2$  -0.25,  $V_3$  1.1; for atom types 5-56-56-12,  $V_1$  0.0,  $V_2$  0.0,  $V_3$  0.406; stretching parameter for 12-56,  $K_s$  3.26;  $L_0$  1.81; bending parameters, 12-56-56,  $K_b$  0.25,  $\theta$ , 112.9, 5-56-12,  $K_b$  0.65,  $\theta$ , 111. For (chloromethyl)cyclopropane, torsional parameters for atom types 12-1-22-22,  $V_1$  0.0,  $V_2$  -0.25,  $V_3$  0.55; for 12-1-22-5,  $V_1$  0,  $V_2$  0.0,  $V_3$  0.406; bending parameter for 12-1-22,  $K_b$  0.65,  $\theta$  108.2. For **8**, an oscillation was encountered in the MM3 minimization, and the energy data are inaccurate.

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