MOLECULAR MECHANICS (MM3) STUDIES OF MONOCHLOROALKANES

JOONG-YOUN SHIM, NORMAN L. ALLINGER AND J. PHILLIP BOWEN*

Computational Center for Molecular Structure and Design, Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA

Monochloroalkanes were studied using molecular mechanics and parameters were developed and incorporated into MM3. The new force field reproduces well molecular structures, conformational energy differences and vibrational frequencies. The compounds studied were methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, neopentyl, cyclopentyl and cyclohexyl chloride, 4-*tert*-butyl-1-chlorocyclohexane and 1-chloroadamantane. The overall rms error for the averaged C—C and C—Cl bond lengths for the above set of compounds excluding *sec*-butyl chloride, neopentyl chloride and 1-chloroadamantane is 0·004 Å, and the rms error for the vibrational frequencies is 37 cm^{-1}. The moments of inertia (r_g) are approximately 1% greater than the microwave values (r_a^0). Thermodynamic quantities are also compared with those observed using various experimental methods.

1. INTRODUCTION

Alkyl halides represent an important class of organic compounds. They play important roles as key synthetic precursors for many types of compounds, primarily through functional group conversion via nucleophilic substitution.[1] The halogen atom influences the overall electrostatics and structural features, which in turn dictate the chemical reactivity of the system. The van der Waals radius of chlorine is 0·25 Å smaller than that of a methyl group, which leads to some spatial and electrostatic ambiguities in terms of confromational predictions. Discussion has focused extensively with respect to the *gauche–trans* energy difference of *n*-propyl chloride.[2] The stability of the *gauche* form here found by various experimental methods[2a,b,d,f,g] may be attributed to the attractive steric or van der Waals London dispersion forces between the methyl group and the chlorine.[3] However, other experimental results,[2a,c,d,h] as well as *ab initio* calculations,[4] lead to results that differ from those experimental studies. The MM3-calculated distances between the methyl group and the chlorine in *gauche*-propyl chloride are 3·28 Å for C—Cl and 2·936, 3·693 and 4·291 Å for H—Cl distances (Figure 1). For cyclohexyl chloride, where the chlorine substituent is axial, there are two *gauche* interactions, and the MM3-calculated distances

between the analogous methylene group and the chlorine are 3·277 Å for the C—Cl distance and 2·920 and 4·269 Å for the H—Cl distances (the torsional parameters for C—C—C—Cl were $V_1 = -0.50$, $V_2 = -0.68$, and $V_3 = 0.85$ kcal mol^{-1}, which are obtained after the *gauche* conformer-favored potential function determined by Durig *et al.*[2g] from Raman experiments).

With a geometry similar to that of *gauche-n*-propyl chloride, the axial conformer of cyclohexyl chloride might be expected to be more stable than the equatorial conformer. MM3 calculations on cyclohexyl chloride, using the C—C—C—Cl torsional parameters specifically determined to reproduce exactly the *gauche–trans* equilibrium for *n*-propyl chloride, would have the axial conformer 0·63 kcal mol (ΔG) more stable than the equatorial conformer (1 kcal = 4·184 kJ). However, this is contrary to extensive conformational studies[5,6] of cyclohexyl chloride, where the equatorial conformer is approximately 0·4–0·6 kcal mol^{-1} (ΔG) lower in energy than the axial conformer. Extensive molecular mechanics studies on chloride compounds[7] have been reported. Molecular structures, vibrational frequencies and thermodynamic properties of unsubstituted hydrocarbons have been well calculated with MM3.[8] Examination of the molecular structures, energy differences between stable conformations, energy barriers and vibrational frequencies have been carried

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* Author to whom correspondence should be addressed.

(a) *gauche* n-propyl chloride
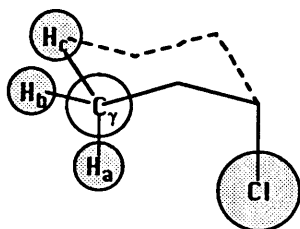
	MM3	RHF/6-31G*
ω(H$_c$-C$_\gamma$-C-C)	-57.3°	-57.9°
ω(C$_\gamma$-C-C-Cl)	-66.4°	-66.6°
r(C$_\gamma$-Cl)	3.289 Å	3.309 Å
r(H$_a$-Cl)	2.936 Å	2.952 Å
r(H$_b$-Cl)	4.291 Å	4.278 Å
r(H$_c$-Cl)	3.693 Å	3.704 Å

	MM3	RHF/6-31G*
ΔE° (*gauche - trans*)	-0.24 kcal/mol	0.37 kcal/mol
ΔH° (*gauche - trans*)	-0.16 kcal/mol	
ΔG° (*gauche - trans*)	-0.50 kcal/mol	

(b) axial cyclohexyl chloride
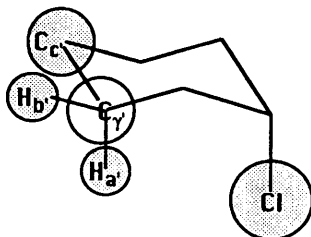
	MM3	RHF/6-31G*
ω(C$_c$-C$_\gamma$-C-C)	-53.9°	-53.2°
ω(C$_\gamma$-C-C-Cl)	-69.7°	-72.4°
r(C$_\gamma$-Cl)	3.277 Å	3.324 Å
r(H$_a$-Cl)	2.920 Å	2.975 Å
r(H$_b$-Cl)	4.269 Å	4.282 Å
r(H$_c$-Cl)	3.889 Å	3.937 Å

	MM3	RHF/6-31G*
ΔE° (axial - equatorial)	-0.76 kcal/mol	1.01 kcal/mol
ΔH° (axial - equatorial)	-0.61 kcal/mol	
ΔG° (axial - equatorial)	-0.47 kcal/mol	

Figure 1. Molecular structures for (a) *gauche-n*-propyl chloride and (b) axial cyclohexyl chloride obtained by the *ab initio* and the MM3 calculations based on the parameters which make the *gauche* form of *n*-propyl chloride more stable than the *trans* form

out. In each case the results are compared with experimental values. In this work, only monochlorides were considered with the objective of developing a suitable alkyl chloride force field.

METHODS

Molecular mechanics parameterization is an iterative process whereby a trial set of parameters are refined to reproduce the molecular geometry, thermodynamic, vibrational and other measurable quantities. Initial parameters were selected so as to reproduce the geometries and moments of inertia of alkyl chlorides, and they were subsequently refined to reproduce the fundamental vibrational frequencies. The parameters were then optimized to give the best fit for both molecular structures and vibrational frequencies. The force parameters required for calculations on alkyl chlorides were determined carefully by fitting to the experimental vibrational frequencies of the fundamental modes. The stretching force parameter (k_s) for the C—Cl bond, for example, was determined from the C—Cl stretching frequencies of various chlorides, and the value is slightly smaller than the MM2 value, which was taken from a spectroscopic force field.[9] The determination of the bending force parameters (k_b) for ∠(H—C—Cl) and ∠(C—C—Cl) are not straightforward owing to the high degree of mixing of several bending modes. The final parameters are approximately 90% as large as the force constants used by a spectroscopic force field[9] which is an extended valence force field containing some off-diagonal terms and transferable force constants. As seen in Table 1, from electron diffraction data (r_g), the typical values of the primary, secondary and tertiary C—Cl bond lengths are 1·796, 1·810 and 1·828 Å, respectively.

A similar trend, showing typical values for the primary, secondary and tertiary C—F bond lengths of 1·39, 1·41 and 1·43 Å, respectively, was also observed from various microwave data (r_s) for monofluoroalkanes.[10] Therefore, it was decided to include an electronegativity correction parameter into MM3 for C—C bond(s) that are directly attached to chlorine to reproduce more or less systematically increased C—Cl bond lengths for primary, secondary and tertiary monochloroalkanes. It is also well known that the C—C or C—H bond length shortening adjacent to an electronegative substituent, such as fluorine or chlorine, is due to charge transfer to the electronegative substituent.[7i,11] The primary electronegativity correction parameters for the C—H and C—C bonds from the chlorine atom were also included in the MM3 parameter set as described previously for MM2.[12]

In order to determine the H—C—C—Cl torsional parameter, both the experimentally determined torsional vibrational frequencies and the rotational barriers of ethyl chloride, isopropyl chloride and *tert*-butyl chloride were used. Each compound has only one torsional parameter that contains chlorine, namely the H—C—C—Cl dihedral angle. Since MM3 utilizes the harmonic approximation for vibrational frequencies,[8] an H—C—C—Cl torsional parameter based exclusively on the experimental

Table 1. C—Cl bond length changes (in Å) according to the types of chloride in monochlorohydrocarbons[a]

Compound	Experiment		RHF/ 3–21G*	RHF/ 6–31G*	MP2/ 6–31G**	MM3
			Ab initio[b]			
Primary chlorides						
(Methyl chloride)	1·785[c,d]	Exp., r_g[e]	1·8058[d]	1·7845[d]	1·7744[d]	1·7885[d]
Ethyl chloride	1·802(3)[f]	ED, r_g	1·8182	1·7992	1·7863	1·7989
Propyl chloride	1·796(2)[g]	ED, r_g	1·8195[h]	1·8000[h]	1·7872[h]	1·8017[h]
n-Butyl chloride	1·796[i]	Exp., r_g[j]	1·8186[k]	1·7992[k]	1·7870[k]	1·8018[h]
Isobutyl chloride	1·791(3)[l]	ED, r_g	1·8333[m]	1·8181[m]	1·8002[m]	1·8038[h]
Average	1·796		1·822	1·804	1·790	1·802
Secondary chlorides						
Isopropyl chloride	1·812(1)[n]	ED, r_g	1·8309	1·8154	1·7987	1·8091
sec-Butylchloride	1·780(4)[d,o]	ED, r_g	1·8332[p]	1·8181[p]	1·7987[p]	1·8126[h]
Cyclopentyl chloride	1·810(4)[q]	ED, r_g	1·8246[h]	1·8085[h]	1·7947[h,r]	1·8110[h]
Cyclohexyl chloride	1·809(5)[s]	ED, r_g	1·8297[h]	1·8139[h]	1·7995[h,r]	1·8128[h]
Average	1·810		1·830	1·814	1·798	1·811
Tertiary chlorides						
tert-Butylchloride	1·828(5)[t]	ED, r_g	1·8426	1·8340	1·8125	1·8177
1-Chloroadamantane	1·792[d,u]	Exp., r_g[v]	1·8354[r]	1·8225[r]	1·8069	1·8181
Average	1·828		1·839	1·828	1·813	1·818

[a] Methyl chloride having no carbon attached to the chlorine is considered as a special case of the primary alkyl chloride.
[b] Gaussian 90 program, this work.
[c] Ref. 15.
[d] This value is not used in calculating the average.
[e] Converted from r_a structure of electron diffraction experiment [r(C—Cl) = 1·784(3)].
[f] Ref. 19.
[g] Ref. 2f.
[h] Boltzmann distribution averaged.
[i] Ref. 23.
[j] Converted from r_a structure of electron diffraction experiment [r(C—Cl) = 1·795(3)].
[k] The TT isomer.
[l] Ref. 26.
[m] The *gauche* isomer.
[n] Ref. 21.
[o] Ref. 24.
[p] The TG isomer.
[q] Ref. 33.
[r] Gaussian 92 program, this work.
[s] Ref. 6c.
[t] Ref 29c.
[u] Ref. 31.
[v] Converted from r_0 structure of microwave experiment [r(C—Cl) = 1·790(2)].

rotational barriers would give slightly higher torsional vibrational frequencies than those of the IR measurements. Thus, it was decided to reproduce preferentially the vibrational frequencies over the rotational energy barriers. The vibrational frequencies for ethyl chloride and isopropyl chloride, as well as the methyl rotational barriers for the aforementioned compounds, were used as the basis for MM3 parameterization (see below). The torsional parameter for the H—C—C—Cl torsional angle (type 5–1–1–12) has been set to 0·000, 0·000 and 0·520 kcal mol^{-1} for V_1, V_2 and V_3 terms, respectively.

In the next step, the MM3 torsional constants for the three-term Fourier function describing the

C—C—C—Cl torsional angle were determined. The smallest compound with this torsional angle is n-propyl chloride. Importantly, it is not easy to obtain unambiguous conformational energies and potential functions from the available experimental data. As a first approximation, the potential function for n-propyl chloride derived from the Raman spectrum by Durig *et al.*[2g] was used to determine the molecular mechanics torsional constants. Unfortunately, the selected values resulted in a very poor prediction of the conformations of cyclohexyl chloride, as described previously. After carefully scrutinizing Durig *et al.*'s data, although potentially accurate, the

assumed values for the F constants used to obtain the ΔH of each stable conformer are questionable. The other experimental measurements in the gas phase[2a–d,g] indicated that the equilibrium (ΔG) is very close to 0 kcal mol^{-1}, and that ΔH is also close to 0 kcal mol^{-1}. Also, the various levels of *ab initio* calculations indicate an energy preference of *trans* over *gauche*. In agreement with Tanaka *et al.*'s *ab initio* calculations,[4] our *ab initio* calculations give the *trans* conformer as the more stable (ΔE) by 0·21, 0·37, 0·34 and 0·39 kcal mol^{-1} using the RHF/ 3–21G*, RHF/6–31G*, RHF/6–31G** and MP2/ 6–31G** basis sets, respectively. Taking all of those results into account, the revised torsional parameter for C—C—C—Cl was used where $V_1 = -0.006$, $V_2 = -0.463$ and $V_3 = 1.145$ kcal mol^{-1}. With these torsional parameters, MM3 calculates the equatorial form of cyclohexyl chloride to be 0·33 kcal mol^{-1} (ΔE) more stable than the axial form, and the *trans* form of propyl chloride is calculated to be 0·14 kcal mol^{-1} (ΔE) more stable than the *gauche* form. The finally optimized parameters for mono-chloroalkanes are listed in Table 2.

Computational procedure

MM3(94) calculations including required conformational searches were carried out on a Silicon Graphics IRIS 4D/310GTX or 70GT workstation, and the fundamental vibrational modes were displayed by the VIBPLT program (included in the MM3 program package). The MM3 program is available to all users from the Technical Utilization Corporation, Inc., 325 Glen Village Court, Powell, OH 43065, or from Tripos Associates, 1699 South Hanley Road, St. Louis, MO 63144, and to academic users only from the QCPE, University of Indiana, Bloomington, IN 47405. The calculations described herein might be carried out with the MM3(94) and later versions of the program. After the conformational searches had been conducted, the relevant molecular structures were selected and, with the aid of the MEDIT program (included in the MM3 program package), the coordinate files were utilized to display and examine the corresponding 3D structures. Gaussian 90[13] or Gaussian 92 program,[14] either on an SGI IRIS 4D/310GTX or on an IBM RISC 6000 320 system, was used for our *ab initio* calculations. The

Table 2. MM3 parameters for alkyl chlorides

Stretching parameters

Bond type	k_s (mdyn Å^{-1})	l_0 (Å)	μ (D)
1–12	3·10	1·791	2·09

Bending parameters

Angle type	k_b (mdyn Å rad^{-2})	$\theta_0(^0)$[a]
1–1–12	0·80	106·200/106·400/108·000
5–1–12	0·75	105·660/106·300/107·050

Primary electronegativity correction parameters

Bond type	End of bond	Atom type	Correction to l_0 (Å)
1–1	1	12	−0·0085
1–5	1	12	−0·0075
1–12	1	1	0·0055

Torsional parameters

Angle type	V_1 (kcal mol^{-1})	V_2 (kcal mol^{-1})	V_3 (kcal mol^{-1})
1–1–1–12	−0·006	−0·463	1·145
5–1–1–12	0·000	0·000	0·520

[a] Angle type 1 (—CR$_2$—)/type 2 (—CRH—)/type 3(—CH$_2$—).

vibrational frequencies for the fundamental modes from the *ab initio* results were visually inspected with the VIBPLT program after transferring the Gaussian output to the necessary format.

RESULTS AND DISCUSSION

Molecular structure

The molecular structures of the alkyl chlorides are reproduced adequately with MM3 using the force field determined in this study. The molecular structures of alkyl chlorides derived from our calculations along with those determined from various experimental methods are presented in Tables 3–15. The calculated C—Cl bond lengths are seen to be a few thousandths of an angstrom longer than desired, but this was necessary to fit the moments of inertia. The moments of inertia were determined directly from microwave experiments and, therefore, provide a fundamental index of the correct geometry. From electron diffraction methods, the C—Cl bond lengths (r_g) are within the range 1·791–1·802 (average 1·796), 1·809–1·812 (average 1·810) and 1·828 Å for the primary, secondary and tertiary alkyl chlorides, respectively (Table 1). From *ab initio* methods at the RHF/6–31G* level, the C—Cl bond lengths (r_e) are within the range 1·799–1·818 (average 1·804), 1·809–1·818 (average 1·814) and 1·823–1·834 (average 1·828 Å) for the primary, secondary and tertiary alkyl chlorides, respectively. MM3 has C—Cl bond lengths (comparable to r_g) within the range 1·799–1·804 (average 1·802), 1·809–1·813 (average 1·811) and 1·818 Å for the primary, secondary and tertiary alkyl chlorides, respectively. RHF/3–21G* C—Cl bond lengths (r_e) are slightly longer and MP2/ 6–31G** level *ab initio* C—Cl bond lengths are slightly shorter than values from electron diffraction experiments (r_g). The primary, secondary and tertiary C—Cl bond lengths seem correctly calculated by molecular mechanics. MM3 calculates well the typical $\angle$(C—C—Cl) values of 111 and 109° for the primary and secondary monochloroalkanes, as reported.[7i] The unusually larger $\angle$(C—C—Cl) (112°) is observed when there is steric hindrance at the γ-position to the chlorine. For example, the TG form of *n*-butyl chloride or the *gauche* form of isobutyl chloride has a γ-methyl group with a *gauche* interaction. This makes the $\angle$(C—C—Cl) larger to relieve the steric hindrance. As expected, a smaller $\angle$(C—C—Cl) value (108°) is observed in isopropyl chloride and *tert*-butyl chloride, and may be due to the electronegativity effect of C—Cl.

Methyl chloride

For the molecular structure of methyl chloride, experimental data are available from electron diffraction (r_g),[15] microwave (r_0),[16,17] or IR/Raman (r_e)[18] studies.

The MM3 results for the C—Cl bond length differ from the electron diffraction value by 0·004 Å.[15] The MM3-calculated values for $\angle$(H—C—H) and $\angle$(H—C—Cl) are also very close to those obtained from either experimental or *ab initio* results (Table 3).

Ethyl chloride

The calculated molecular structure for ethyl chloride compared with the electron diffraction results[19] give an rms difference of 0·004 Å for the C—C and C—Cl bond lengths. The C—C bond length is slightly shorter (0·005 Å) than that of the electron diffraction experiment (r_g) but longer than those obtained from a recent microwave experiment (r_s).[20] This finding suggests that our C—C bond length is within a reasonable range. The reason for the smaller $\angle$(H—C—H) in the CH$_3$ group is due to the large $\angle$(C$_\alpha$—C$_\beta$—H) of the CH$_3$ group from our calculation, compared to the experimental value.[19,20] The molecular structure of ethyl chloride is given in Table 4.

n-Propyl chloride

The MM3 structure of propyl chloride was compared with the data from an electron diffraction experiment.[2f] The rms difference for the C—C and C—Cl bond lengths is 0·006 Å. The molecular geometries from our calculations are in reasonable agreement with both quantum calculations[4] and experiment,[2f] and are presented in Table 5.

Isopropyl chloride

Among available electron diffraction[21] and microwave[22] experimental data for isopropyl chloride, the former are used for comparison purposes as presented in Table 6. The overall molecular structure is fitted well to give a 0·002 Å rms difference for the averaged C—C and C—Cl bond length.

n-Butyl chloride

The molecular structure of *n*-butyl chloride from the MM3 Boltzmann distribution was compared with the structure from a recent electron diffraction study,[23] and is listed in Table 7. Another electron diffraction investigation[24a] showed a C—Cl bond length (1·780 Å) that is too short when compared with other primary alkyl chlorides (1·796 Å). The MM3-calculated geometry is close to the experimental structure[23] with an rms difference for the C—C and C—Cl bond lengths of 0·005 Å.

Isobutyl chloride

For isobutyl chloride, microwave[25] and electron diffraction data[26,27] have been found in the literature.

Table 3. Molecular structure (bond lengths in Å and angles in degrees) of methyl chloride

$$C_\alpha—Cl$$

Parameter	Exp.,r_g [a,b]	MW/IR,r_0 [c]	IR/R,r_e [d]	Ab initio [e]	MM3	MM3 − Exp.,r_g [b]
r(C—H)	1·12	1·090(2)	1·0854(5)	1·0779	1·1050	−0·02
r(C—Cl)	1·785	1·7854(10)	1·7760(3)	1·7845	1·7885	0·004
∠(H—C—H)	110(2)	110·75(25)	110·35(5)	110·4663	110·042	0
∠(H—C—Cl)	—	—	—	108·4852	108·894	—

[a] Converted from the r_a structure of the ED experiment [r(C—Cl) = 1.784 and r(C—H) = 1.11(1)].
[b] Ref. 15.
[c] Refs 16 and 17.
[d] Ref. 18.
[e] Gaussian 90 program, RHF/6–31G* basis set, this work.

Table 4. Molecular structure (bond lengths in Å and angles in degrees) of ethyl chloride

$$C_\beta—C_\alpha—Cl$$

Parameter	ED/MW,r_g [a]	MW,r_s [b]	Ab initio [c]	MM3	MM3 − ED/MW,r_g [a]
r(C—C)	1·528(4)	1·520(1)	1·5170	1·5228	−0·005
r(C$_\alpha$—Cl)	1·802(3)	1·789(1)	1·7992	1·7989	−0·003
r(C$_\alpha$—H)(CH$_2$)	—	1·089(1)	1·0789	1·1059	—
r(C$_\beta$—H)$_{av}$(CH$_3$)	1·103(4)	1·092	1·0842	1·1102	0·007
″(C$_\beta$—C$_\alpha$—Cl)	110·7(3)	111(7)	111·499	110·873	0·17
″(H—C$_\alpha$—Cl)	—	106·55(5)	106·22	107·240	—
∠(H—C$_\alpha$—C$_\beta$)(CH$_2$)	—	111·60(5)	111·815	111·516	—
∠(C$_\alpha$—C$_\beta$—H)(CH$_3$)$_{av}$	110·6(30)	110·01	109·830	111·578	0·98
∠(H—Cα—H)(CH$_2$)	109·2	109·80(5)	108·46	108·251	−0·95
∠(H—C$_\beta$—H)(CH$_3$)$_{av}$	110·0(16)	108·88	108·48	107·284	−2·72
Rms (bond length)					0·004

[a] Ref. 19.
[b] Ref. 20.
[c] Gaussian 90 program, RHF/6–31G* basis set, this work.

The MM3 C—Cl bond length of 1·804 Å is similar to that from electron diffraction given by Pauli et al.[27] (1·804 Å). A more recent electron diffraction study by Schei and Hilderbrandt[26] found the C—Cl bond distance to be shorter (1·791 Å). The rms difference between MM3 and the electron diffraction results by Schei and Hilderbrandt[26] for the C—C and C—Cl bond lengths is 0·007 Å. The molecular structure of isobutyl chloride is given in Table 8.

sec-Butyl chloride

For sec-butyl chloride, only relatively old electron diffraction data published by Ukaji and Bonham[24] or Yamaha et al.[28] were available for comparison. Both of these investigations showed shorter C—Cl bond lengths than MM3, and they are close to C—Cl bond length of the primary alkyl chloride. The ∠(C—C—Cl) by Ukaji and Bonham[24] is about 4° larger than MM3 calculations. The C—C and C—Cl bond length rms

difference from Ukaji and Bonham[24] is as large as 0·017 Å, owing to the a 0·033 Å difference in C—Cl bond length (Table 9).

tert-Butyl chloride

Intensive experimental work[29] has been done on the molecular structure of tert-butyl chloride. The structures determined by various methods are given in Table 10. The molecular mechanics structure is compared with the data from electron diffraction by Hilderbrandt and Wieser,[29c] and shows a 0·005 Å rms difference for the C—C and C—Cl bond lengths. Our calculated C—Cl bond length is 0·010 Å shorter. Even the microwave C—Cl bond length (r_0) measured by Braun et al.[29d] is longer than the molecular mechanics bond lengths. In other tertiary chlorides where the non-bonded interactions between chlorine and the β-methyl group are absent owing to the restricted geometry around chlorine, our calculated C—Cl bond lengths look good

Table 5. Molecular structure (bond lengths in Å and angles in degrees) of *n*-propyl chloride

$$C_\gamma\!-\!C_\beta\!-\!C_\alpha\!-\!Cl$$

Parameter	ED/MW, $r_g^{a,b}$		Ab initio[c,d]		MM3[e]		MM3 − ED/MW, r_g^b	
	trans	*gauche*	*trans*	*gauche*	*trans*	*gauche*	*trans*	*gauche*
$r(C\!-\!C)_{av}$	1·525(2)		1·523	1·522	1·5289		0·004	
$r(C_\alpha\!-\!Cl)$	1·796(2)		1·897	1·900	1·8017		0·008	
$r(C\!-\!H)_{av}$	1·113(3)		1·083	1·083	1·1106		−0·002	
$\angle(C_\alpha\!-\!C_\beta\!-\!C_\gamma)$	111·3(13)	113·9(5)	111·0	113·9	112·076	113·730	0·8	−0·2
$\angle(C_\beta\!-\!C_\alpha\!-\!Cl)$	111·3(7)	112·2(6)	110·1	110·7	110·991	111·957	−0·3	−0·2
$\angle(H\!-\!C_\alpha\!-\!Cl)$	—	—	106·3[f]	106·2[f]	107·106	107·021[g]	—	—
$\angle(C_\beta\!-\!C_\gamma\!-\!H)_{av}$	111·6	111·6	110·7	110·6	111·498	111·613	−0·1	0·0
$\angle(C_\alpha\!-\!C_\beta\!-\!H)$	109·8	109·1	109·2	108·0	109·780	109·237[g]	0·0	0·1
$\angle(C_\beta\!-\!C_\alpha\!-\!H)$	112·4	112·4	113·2	113·2	111·588	111·362	−0·8	−1·0
$\angle(H\!-\!C\!-\!H)_{av}$	—	—	107·9[f]	107·9[f]	107·444	107·165	—	—
$\angle(C_\gamma\!-\!C_\beta\!-\!C_\alpha\!-\!Cl)$	180·0	63·9(12)	180·0	65·7	180·0	66·4	0·0	2·5
Rms (bond length)								0·006

[a] The ratio of the *trans* to *gauche* is 38 : 62 at room temperature.
[b] Ref. 2f.
[c] Ref. 4.
[d] RHF/4–31G basis set.
[e] Boltzmann distribution averaged. The ratio of the *trans* to *gauche* is 39 : 61 at 25 °C.
[f] Gaussian 90 program, RHF/6–31G* basis set, this work. [g] Averaged.

Table 6. Molecular structure (bond lengths in Å and angles in degrees) of isopropyl chloride
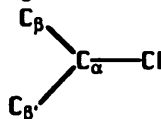
Parameter	ED, r_g^a	MW, r_s^b	Ab initio[c]	MM3	MM3 − ED, r_g^a
$r(C_\alpha\!-\!C_\beta)$	1·527(1)	1·520(7)	1·5203	1·5259	−0·001
$r(C_\alpha\!-\!Cl)$	1·812(1)	1·800(7)	1·8154	1·8091	−0·003
$r(C_\beta\!-\!H)_{av}$	1·104(4)	1·093	1·0837	1·1101	0·006
$\angle(C_\beta\!-\!C_\alpha\!-\!C_{\beta'})$	112·7(4)	112·88((113)	113·268	112·381	−0·3
$\angle(C_\beta\!-\!C_\alpha\!-\!Cl)$	109·0	109·33(73)	109·322	108·569	−0·4
$\angle(H\!-\!C_\alpha\!-\!Cl)$	106·1	105·55(98)	104·30	105·765	−0·3
$\angle(C_\beta\!-\!C_\alpha\!-\!H)(CH)$	109·8(20)	109·72(80)	110·121	110·648	0·8
$\angle(C_\alpha\!-\!C_\beta\!-\!H)_{av}(CH_3)$	110·4	110·06	110·468	111·671	1·3
$\angle(H\!-\!C_\beta\!-\!H)_{av}(CH_3)$	108·5(8)	108·84	108·45	107·183	−1·3
$\angle(Cl\!-\!C_\alpha\!-\!C_\beta\!-\!H_g)^d$	—	62·4(11)	57·7	59·5	—
$\angle(Cl\!-\!C_\alpha\!-\!C_\beta\!-\!H_t)^d$	—	−57·4(13)	63·1	61·2	—
$\angle(Cl\!-\!C_\alpha\!-\!C_\beta\!-\!H_i)^d$	—	−178·4(38)	−177·4	−179·0	—
Rms (bond length)					0·002

[a] Ref. 21.
[b] Ref. 22a.
[c] Gaussian 90 program, RHF/6–31G* basis set, this work.
[d] H_g is *trans* to the other methyl group, H_t is *trans* to chlorine and H_i is in between chlorine and the other methyl group (see Ref. 20a).

compared with the experimental results. For example, the C—Cl bond lengths of 4-chloronortricyclene (1·763 Å)[30] and 1-chloroadamantane (1·790 Å)[31] from microwave methods are approximately 0·02 Å shorter than the MM3 value, which is preferentially fitted to electron diffraction data, where the electron diffraction bond length, r_g, is 0·01–0·02 Å longer than microwave bond length, r_s. Our calculated C—Cl bond lengths for 4-chloronortricyclene and 1-chloroadamantane are 1·791 and 1·818 Å, respectively.

Table 7. Molecular structure (bond lengths in Å and angles in degrees) of n-butyl chloride

$$C_\delta\text{—}C_\gamma\text{—}C_\beta\text{—}C_\alpha\text{—}Cl$$

Parameter	Exp., r_g [a-c]	ED, r_g [d,e]	MM3 [f]	MM3 − Exp., r_a [c]
$r(C\text{—}C)_{av}$	1·537	1·533(3)	1·5319	−0·005
$r(C_\alpha\text{—}Cl)$	1·796	1·780(4)	1·8018	0·006
$r(C\text{—}H)_{av}$	1·121	1·110(5)	1·1115	−0·010
$\angle(C\text{—}C\text{—}C)_{av}$	112·1(8)	112·1(9)	113·102	1·0
$\angle(C_\beta\text{—}C_\alpha\text{—}Cl)$	110·8(6)	110·8(10)	111·546	0·7
$\angle(C\text{—}C\text{—}H)_{av}$	110·6(10)	110·6(20)	110·125	−0·5
$\angle(H\text{—}C_\alpha\text{—}Cl)$	—	—	107·016	—
$\angle(H\text{—}C\text{—}H)_{av}$	109·5	—	107·169	−2·3
Rms (bond length)				0·005

[a] The TG : TT : GG : GT : GG' ratio is 50 : 25 : 15 : 5 : 5 at 18 °C.
[b] Converted from the r_a structure of the electron diffraction experiment [$r(C\text{—}C)_{av} = 1\cdot535(4)$, $r(C\text{—}Cl) = 1\cdot795(3)$ and $r(C\text{—}H)_{av} = 1.115(10)$].
[c] Ref. 23.
[d] Ref. 24a.
[e] Ref. 24b (the TG : TT : GG : GT : GG' ratio is 37 : 11 : 17 : 11 : 24 at 22 °C).
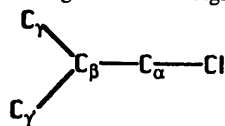[f] Boltzmann distribution averaged. The TG : TT : GG : GT : GG' ratio is 43 : 29 : 12 : 15 : 1 at 25 °C.

Table 8. Molecular structure (bond lengths in Å and angles in degrees) of isobutyl chloride

$$C_\gamma \diagdown \atop C_\gamma \diagup {C_\beta\text{—}C_\alpha\text{—}Cl}$$
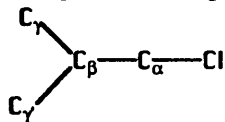
Parameter	ED/MW, r_g [a,b]		MW, r_0 [c]	MM3 [d]		MM3 − ED/MW, r_g [b]	
	gauche	trans	gauche	gauche	trans	gauche	trans
$r(C\text{—}C)_{av}$	1·532(2)		1·532	1·5348		0·003	
$r(C_\alpha\text{—}Cl)$	1·791(3)		1·77(6)	1·8038		0·013	
$r(C\text{—}H)_{av}$	1·111(4)		1·094 [e]	1·1114		0·000	
$\angle(C_\alpha\text{—}C_\beta\text{—}C_\gamma)$	109·3(7)	111·8	110·8	109·681	111·984	0·4	0·2
$\angle(C_\alpha\text{—}C_\beta\text{—}C_{\gamma'})$	114·3	111·8	110·8	111·819	111·984	−2·5	0·2
$\angle(C_\gamma\text{—}C_\beta\text{—}C_{\gamma'})$	109·0(7)	109·0(7)	110·8	109·500	110·712	0·5	1·7
$\angle(C_\beta\text{—}C_\alpha\text{—}Cl)$	111·1(7)	114·0(9)	112(1)	112·209	113·513	1·1	−0·5
$\angle(H\text{—}C_\alpha\text{—}Cl)_{av}$	105·9(25)		—	106·823	107·743	0·9	1·8
$\angle(C_\beta\text{—}C_\alpha\text{—}H)_{av}(CH_2Cl)$	112·5		—	111·434	111·069	−1·1	−1·4
$\angle(C_\gamma\text{—}C_\beta\text{—}H)_{av}(CH)$	109·5		108·13	108·417	107·365	−1·1	−2·1
$\angle(C_\beta\text{—}C_\gamma\text{—}H)_{av}(CH_3)$	113·1(12)		111	111·736	111·702	−1·4	−1·4
$\angle(H\text{—}C_\alpha\text{—}H)(CH_2Cl)$	—	—	—	107·839	107·376	—	—
$\angle(H\text{—}C_\gamma\text{—}H)_{av}(CH_3)$	—	—	—	107·243	107·150	—	—
$\angle(Cl\text{—}C\text{—}C\text{—}H)$	—	—	50(1)	−54·8	180·0	—	—
$\angle(Cl\text{—}C\text{—}C\text{—}C)$	68(3)	60	—	65·4	62·5	−2·6	2·5
	−172(3)	−60	—	−172·9	−62·5	−0·9	−2·5
Rms (bond length)						0·007	

[a] The ratio of gauche to trans is 62 : 38 at 28 °C. For the gauche isomer, the Cl is trans to one of terminal CH_3 group.
[b] Ref. 26.
[c] Ref. 25.
[d] Boltzmann distribution averaged. The ratio of gauche to trans is 73 : 27 at 25 °C.
[e] $r(C_\alpha\text{—}H)$ is excluded.

Table 8. Molecular structure (bond lengths in Å and angles in degrees) of isobutyl chloride

$$C_\gamma \diagdown C_\beta - C_\alpha - Cl \diagup C_{\gamma'}$$

| Parameter	ED/MW, $r_g^{a,b}$ gauche	ED/MW, $r_g^{a,b}$ trans	MW, r_0^e gauche	MM3^d gauche	MM3^d trans	MM3 − ED/MW, r_g^b gauche	MM3 − ED/MW, r_g^b trans
r(C—C)$_{av}$	1·532(2)		1·532	1·5348		0·003	
r(C$_\alpha$—Cl)	1·791(3)		1·77(6)	1·8038		0·013	
r(C—H)$_{av}$	1·111(4)		1·094^e	1·1114		0·000	
∠(C$_\alpha$—C$_\beta$—C$_\gamma$)	109·3(7)	111·8	110·8	109·681	111·984	0·4	0·2
∠(C$_\alpha$—C$_\beta$—C$_{\gamma'}$)	114·3	111·8	110·8	111·819	111·984	−2·5	0·2
∠(C$_\gamma$—C$_\beta$—C$_{\gamma'}$)	109·0(7)	109·0(7)	110·8	109·500	110·712	0·5	1·7
∠(C$_\beta$—C$_\alpha$—Cl)	111·1(7)	114·0(9)	112(1)	112·209	113·513	1·1	−0·5
∠(H—C$_\alpha$—Cl)$_{av}$	105·9(25)		—	106·823	107·743	0·9	1·8
∠(C$_\beta$—C$_\alpha$—H)$_{av}$(CH$_2$Cl)	112·5		—	111·434	111·069	−1·1	−1·4
∠(C$_\gamma$—C$_\beta$—H)$_{av}$(CH)	109·5		108·13	108·417	107·365	−1·1	−2·1
∠(C$_\beta$—C$_\gamma$—H)$_{av}$(CH$_3$)	113·1(12)		111	111·736	111·702	−1·4	−1·4
∠(H—C$_\alpha$—H)(CH$_2$Cl)	—	—	—	107·839	107·376	—	—
∠(H—C$_\gamma$—H)$_{av}$(CH$_3$)	—	—	—	107·243	107·150	—	—
∠(Cl—C—C—H)	—	—	50(1)	−54·8	180·0	—	—
∠(Cl—C—C—C)	68(3)	60	—	65·4	62·5	−2·6	2·5
	−172(3)	−60		−172·9	−62·5	−0·9	−2·5
Rms (bond length)						0·007	

^{a} The ratio of gauche to trans is 62:38 at 28 °C. For the gauche isomer, the Cl is trans to one of terminal CH$_3$ group (see Figure 4).
^{b} Ref.26.
^{c} Ref. 25.
^{d} Boltzmann distribution averaged. The ratio of gauche to trans is 73:27 at 25 °C.
^{e} r(C$_\alpha$—H) is excluded.

Table 9. Molecular structure (bond lengths in Å and angles in degrees) of sec-butyl chloride

$$C_\gamma - C_\beta \diagdown C_\alpha - Cl \diagup C_{\beta'}$$
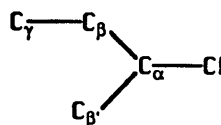
| Parameter	ED, $r_g^{a,b}$	ED^c	Ab initio^d	MM3^e	MM3 − ED, r_g^b
r(C—C)$_{av}$	1·533(3)	1·54(1)	1·5245	1·5302	−0·003
r(C$_\alpha$—Cl)	1·780(4)	1·79(1·5)	1·8181	1·8126	0·033
r(C—H)$_{av}$	1·109(5)	—	1·0848	1·1111	0·002
∠(C—C—C)$_{av}$	111·4(10)	111(1·5)	111·896	113·422	2·0
∠(C—C—Cl)$_{av}$	112·4(12)	109·5	110·363	108·679	−3·7
∠(H—C$_\alpha$—Cl)	—	—	104·25	105·619	—
∠(C—C—H)$_{av}$	110·6(20)	109·5	110·654	110·599	0·0
∠(H—C—H)$_{av}$	—	—	107·76	107·044	—
Rms (bond length)					(0·017)

^{a} The TG:GG' : GT ratio is 48:27:25 at room temperature (Ref. 24b)
^{d} Data of the TG form. Gaussian 90 program, RHF/6–31G* basis set, this work.
^{e} Boltzmann distribution averaged. The TG:GG' :GT ratio is 62:15:23 at 25 °C.
^{b} Ref. 24.
^{c} Ref. 28.

Table 10. Molecular structure (bond lengths in Å and angles in degrees) of *tert*-butyl chloride
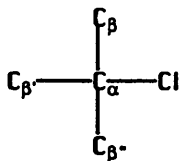
Parameter	ED,r_g[a]	MW,r_0[b]	*Ab initio*[c]	MM3	MM3 – ED,r_g[a]
$r(C_\alpha—C_\beta)$	1·528(2)	1·528(2)	1·5249	1·5289	0·001
$r(C_\alpha—Cl)$	1·828(5)	1·828(5)	1·8340	1·8177	−0·010
$r(C_\beta—H)_{av}$	1·102(7)	1·097(23)	1·0842	1·1099	0·008
$\angle(C_\beta—C_\alpha—C_{\beta'})$	111·6(2)	111·73(170)	111·48	111·033	−0·6
$\angle(C_\beta—C_\alpha—Cl)$	107·3(3)	—	107·376	107·860	0·6
$\angle(C_\alpha—c_\beta—H)_{av}$	110·8(9)	—	110·502	111·762	1·0
$\angle(H—C_\beta—)_{av}$	108·1(12)	109·45(3)	108·42	107·086	−1·0
Rms (bond length)					0·005

[a] Ref. 29c.
[b] Ref. 29d.
[c] Gaussian 90 program, RHF/6–31G* basis set, this work.

Neopentyl chloride

Hastings and Bauer[32] reported electron diffraction data for 1-chloro-2,2-dimethylpropane (neopentyl chloride) in 1950. The averaged C—C bond length obtained from their study was 0·02 Å longer than the MM3 value. The rms difference for C—C and C—Cl bond lengths is 0·04 Å. The MM3 values, however, are considered adequate, since the errors reported in the experimental values are large (Table 11).

Cyclopentyl chloride

The molecular structure for cyclopentyl chloride is known from electron diffraction[33] and microwave[34] experiments. (Interestingly, while cyclopentane is a free pseudo rotor, the chloride consists of a mixture of just two conformations, both of which have an envelope conformation with C_s symmetry. They differ in the position of the chlorine, axial and equatorial, with the latter being more stable. MM3 similarly finds these two stable conformations.) Our calculated averaged C—C bond lengths are close to the averaged C—C bond length from electron diffraction data.[33] The rms difference for the C—C and C—Cl bond lengths is 0·001 Å, compared with the electron diffraction data by Hilderbrandt and Shen.[33] The MM3 molecular geometry was also compared with the recent microwave data by Groner *et al.*[35] representing different structural parameters for stable axial and equatorial isomers. Interestingly, our calculations predict the shortest C—C bond lengths for the $C_\alpha—C_\beta$ bonds, which are closest to the electronegative chlorine atom. Microwave data,[35] however, show that the shortest bond length in axial isomer is the $C_\gamma—C_{\gamma'}$, and the $C_\beta—C_\gamma$ bond length is

shortest in the equatorial isomer. The accuracy of the molecular structures from the above microwave study is questionable, since they were derived from the rotational constants of very few isotopic species. The molecular structures of cyclopentyl chloride are given in Table 12.

Cyclohexyl chloride

The calculated molecular structure of cyclohexyl chloride is in close agreement with that determined by the electron diffraction method,[6c] and the rms difference for the C—C and C—Cl bond lengths is 0·003 Å. Our calculated angles are also in agreement with electron diffraction[6c] and microwave[6c,36] data. The molecular structures of cyclohexyl chloride are presented in Table 13.

4-tert-Butyl-1-cyclohexyl chloride

The molecular structures from electron diffraction studies by Dallinga and Toneman[37] are presented along with MM3 structures in Table 14. Comparing our calculated bond lengths with the electron diffraction data, the rms differences for the C—C and C—Cl bond lengths are 0·003 Å and 0·006 Å for the *cis* and *trans* isomers, respectively. The comparison of bond angles gives agreement that is relatively poor, but apparently to within the accuracy of the experiment.

1-Chloroadamantane

For larger systems such as 1-chloroadamantane, our calculated structure appears to be rather different from the microwave structure.[31] However, since we calcu-late the moments of inertia of this molecule correctly, we
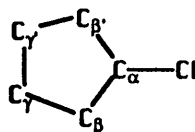
Table 11. Molecular structure (bond lengths in Å and angles in degrees) of neopentyl chloride (1-chloro-2,2-dimethylpropane)

$$C_\gamma - C_\beta - C_\alpha - Cl$$
with C_γ above and $C_{\gamma'}$ below C_β
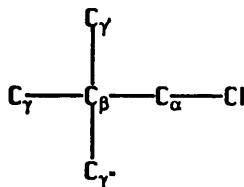
Parameter	ED[a]	*Ab initio*[b]	MM3	MM3 − ED[a]
$r(C—C)_{av}$	1·56	1·5355	1·5391	−0·02
$r(C_\alpha—Cl)$	1·74(3)	1·8029	1·8053	0·07
$r(C—H)_{av}$	1·09$_{assumed}$	1·0843	1·1113	0·02
$\angle(C_\beta—C_\alpha—Cl)$	111(2)	114·808	113·880	2·9
$\angle(C_\alpha—C_\beta—C_{\gamma'},C_{\gamma'})$	111(2)	111·025	110·994	0·0
$\angle(C_\alpha—C_\beta—C_\gamma)$	—	105·909	108·165	—
$\angle(C_{\gamma'}—C_\beta—C_{\gamma'})_{av}$	108(2)	111·010	108·867	0·9
$\angle(C—C—H)_{av}$	—	111·007	111·674	—
$\angle(H—C—H)$	109·5$_{assumed}$	107·863	107·081	−2·4
$\angle(C_\gamma—C_\beta—C_\alpha—Cl)$	—	−179·9	180·0	—
$\angle(C_{\gamma'}—C_\beta—C_\alpha—Cl)$	—	−61·4	−61·2	—
$\angle(C_{\gamma'}—C_\beta—C_\alpha—Cl)$	—	61·6	61·2	—
Rms (bond length)				(0·04)

[a] Ref. 32.
[b] Gaussian 90 program, RHF/6–31G* basis set, this work.

Table 12. Molecular structure (bond lengths in Å and angles in degrees) of cyclopentyl chloride

$$C_\alpha - Cl$$
cyclopentane ring with $C_\gamma, C_{\beta'}, C_{\gamma'}, C_\beta, C_\alpha$

Parameter	ED,r_g[a-c]	MW[b,d] Axial	MW[b,d] Equatorial	MM3[b] Axial	MM3[b] Equatorial	MM3[e]	MM3[e] − ED,r_g[c]
$r(C—C)_{av}$	1·542(1)	1·543	1·539	1·5410	1·5398	1·5407	−0·001
$r(C_\alpha—Cl)$	1·810(4)	1·792(22)	1·777(13)	1·8130	1·8045	1·8110	0·001
$r(C—H)_{av}$	1·096(4)	1·096	1·096	1·1113	1·1115	1·1113	0·015
$\angle(C—C—C)_{av}$	—	104·4	104·3	104·898	104·379	104·778	—
$\angle(C_\beta—C_\alpha—Cl)$	—	110·9(14)	113·4(9)	109·561	112·210	110·170	—
$\angle(H—C_\alpha—Cl)$	111·9(16)	102·2(6)	102·2(10)	107·141	106·791	107·061	−4·8
$\angle(C—C—H)_{av}$	—	111·5	111·2	111·267	111·043	111·215	—
$\angle(H—C—H)_{av}$	101·4(34)	107·9	107·9	107·630	108·092	107·736	6·3
Rms (bond length)							0·001

[a] The axial:equatorial conformers ratio is 64 : 36 at 22 °C
[b] Both the axial and the equatorial isomers have C_s symmetry.
[c] Ref. 33.
[d] Ref. 35.
[e] Boltzmann distribution averaged. The axial:equatorial conformers ratio is 77 : 23 at 25 °C.

Table 13. Molecular structure (bond lengths in Å and angles in degrees) of cyclohexyl chloride
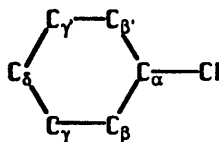
Parameter	ED,$r_g^{a,b}$	MW,r_0^c equatorial	MM3		MM3^d	MM3 − ED,r_g^b
			Equatorial	Axial		
r(C—C)$_{av}$	1·530(2)	1·53	1·5326	1·5334	1·5329	0·003
r(C$_\alpha$—Cl)	1·809(5)	1·793(11)	1·8120	1·8142	1·8128	0·004
r(C—H)$_{av}$	1·112(5)	—	1·1128	1·1128	1·1128	0·001
$\angle$(C$_\alpha$—C$_\beta$—C$_\gamma$)	111·8(4)	111·22(26)	110·813	112·932	111·597	−0·2
$\angle$(C$_\beta$—C$_\gamma$—C$_\delta$)	110·4(4)	111·22(26)	111·219	111·266	111·236	0·8
$\angle$(C$_\gamma$—C$_\delta$—C$_{\gamma'}$)	111·3(4)	111·22(26)	111·281	111·223	111·260	0·0
$\angle$(C$_\beta$—C$_\alpha$—C$_{\beta'}$)	111·3(4)	111·22(26)	111·291	111·446	111·348	0·1
$\angle$(C$_\beta$—C$_\alpha$—Cl)	109·3(4)	—	109·228	109·651	109·385	0·1
$\angle$(H—C$_\alpha$—Cl)	—	105·28(19)	105·648	105·019	105·415	—
$\angle$(H—C—C)$_{av}$	109·9(6)	—	109·801	109·677	109·755	−0·1
$\angle$(H—C—H)$_{av}$	—	107·71(26)	106·802	106·949	106·856	—
$\angle$(C$_\alpha$—C$_\beta$—C$_\gamma$—C$_\delta$)	55·5(7)	—	55·6	53·9	55·0	−0·5
$\angle$(C$_\beta$—C$_\gamma$—C$_\delta$—C$_{\gamma'}$)	−54·4(11)	—	−54·8	−55·1	−54·9	−0·5
$\angle$(C$_\gamma$—C$_\delta$—C$_{\gamma'}$—C$_{\beta'}$)	54·4(11)	—	54·8	55·1	54·9	−0·4
$\angle$(C$_\gamma$—C$_\beta$—C$_\alpha$—C$_{\beta'}$)	−57·0(7)	—	−56·8	−51·9	−55·0	2·0
Rms (bond length)						0·004

[a] The equatorial:axial ratio is 70 : 30 at room temperature.
[b] Ref. 6c.
[c] Ref. 36.
[d] Boltzmann distribution averaged. The equatorial:axial ratio is 63 : 37 at 25 °C.

Table 14. Molecular structure (bond lengths in Å and angles in degrees) of 4-*tert*-butyl-1-chlorocyclohexane
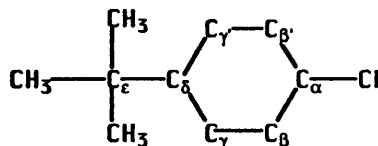
Parameter	Ex,r_g^{a-c}		MM3		MM3 − Exp.,r_g^c	
	cis	trans	cis	trans	cis	trans
r(C—C)$_{av}$	1·545	1·542	1·5417	1·5412	−0·003	−0·001
r(C$_\alpha$—Cl)	1·818	1·830	1·8140	1·8116	−0·004	−0·018
r(C—H)$_{av}$	1·115	1·112	1·1122	1·1125	−0·003	0·001
$\angle$(C—C—C)(ring)	111	111	111·593	110·833	1	0
$\angle$(C—C$_\delta$—C$_\varepsilon$)$_{av}$	112(2)	115(1)	113·349	113·363	1	−2
$\angle$(C$_\delta$—C$_\varepsilon$—C)$_{av}$(CH$_3$)	108(1)	107(1)	110·941	110·937	3	4
$\angle$(C$_\beta$—C$_\alpha$—Cl)	—	—	109·773	109·376	—	—
$\angle$(H—C$_\alpha$—Cl)	—	—	105·116	105·732	—	—
$\angle$(H—C—H)$_{av}$	—	—	106·693	106·872	—	—
$\angle$(H—C—C)$_{av}$	—	—	110·040	110·132	—	—
Rms (bond length)					0·003	0·006

[a] For the *cis* form, the chlorine is axial and the *tert*-butyl group is equatorial. For the *trans* form, both the chlorine and *tert*-butyl group are equatorial.
[b] Converted from the r_a structure of the ED experiment [r(C—C)$_{av}$ = 1·543, r(C—Cl) = 1·817 and r(C—H)$_{av}$ = 1·109].
[c] Ref. 37.

believe that the MM3 structure is accurate. (Many assumed values are used in the solution of microwave structures.) For this reason, the rms difference for the C—C and C—Cl bond lengths of 1-chloroadamantane (0·009 Å) is not used for calculating the overall rms error. The molecular structure of 1-chloroadamantane is given in Table 15.

Vibrational frequencies

Our calculated vibrational spectra are in fair agreement with experiment. Eight alkyl halide compounds, methyl chloride, ethyl chloride, *trans* and *gauche* forms of *n*-propyl chloride, isopropyl chloride, *trans* and *gauche* forms of isobutyl chloride, *tert*-butyl chloride, neopentyl chloride, and cyclopentyl chloride were used for comparing our calculated fundamental vibrational frequencies with the experimental values. The rms error is $37 \, \text{cm}^{-1}$, which is only slightly higher than the $35 \, \text{cm}^{-1}$ value that was obtained by MM3 calculations on hydrocarbons. The MM3 C—Cl vibrational frequency difference from experiment, averaged over seven compounds excluding cyclopentyl chloride, is $18 \, \text{cm}^{-1}$. (Since no complete IR assignment for axial and equatorial isomers of cyclopentyl chloride has been made, there was no way to compare the MM3 calculated C—Cl vibrational frequencies for the individual conformations.) Shipman *et al.*[38] observed the liquid IR spectra of 36 alkyl chlorides, and they were able to determine a characteristic frequency range for the various structural types of alkyl chlorides. The characteristic C—Cl stretching ranges were 648–730, 608–758 and 560–632 cm^{-1} for primary, secondary and tertiary chlorides, respectively. Our calculated C—Cl vibrational frequencies listed above were in the ranges 671–762, 591–747, and 601–998 cm^{-1} for primary, secondary and tertiary

chlorides, respectively. Our calculated values fit well the ranges Shipman *et al.* determined.

Correlation of the C—Cl stretching vibrational frequencies with the molecular structures was attempted with our force field. It is clearly shown that the torsion angle ω(C—C—C—Cl) is approximately proportional to the C—Cl stretching frequency, as shown in Table 16 and Figure 2, which means a long-range coupling with the C—C vibration occurs. The C—Cl stretching frequency increases as the torsion angle ω(C—C—C—Cl) approaches 180°, where the C—Cl and C—C stretching modes
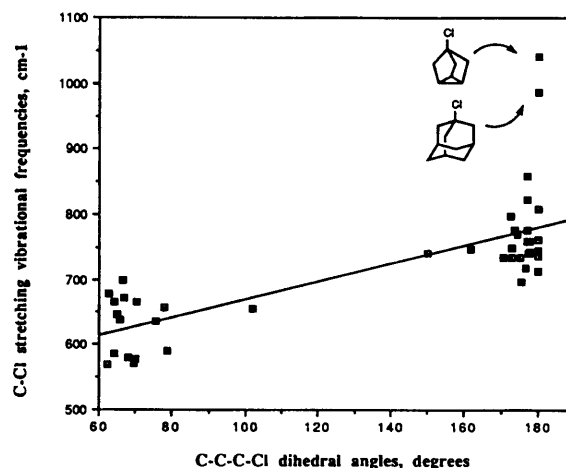
Figure 2. Correlation between the C—Cl stretching frequencies (in cm^{-1}) and C—C—C—Cl torsional angles (in degrees) for monochloroalkanes by MM3. In the case of many torsion angles for one compound, only the one with the largest absolute value was used

Table 15. Molecular structure (bond lengths in Å and angles in degrees) of 1-chloroadamantane

Parameter	Exp.,r_g[a,b]	*Ab initio*[c]	MM3	MM3 – Exp.,r_g[b]
r(C—C)$_{av}$	1.543	1.5362	1.5375	−0.006
r(C$_\alpha$—Cl)	1.792	1.8225	1.8181	0.026
r(C—H)$_{av}$	1.094	1.0864	1.1132	0.020
Rms (bond length)				(0.009)

[a] Converted from the r_0 structure of the MW experiment [r(C—C)$_{av}$ = 1·541(1), r(C—Cl) = 1·790(2) and r(C—H)$_{av}$ = 1·09$_{assumed}$].
[b] Ref. 31.
[c] Gaussian 90 program, RHF/6–31G* basis set, this work.

Table 16. C—Cl stretching vibrational frequencies for monochloroalkanes with the values of C—C—C—Cl torsional angels by MM3
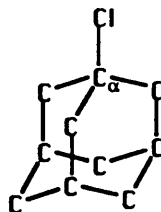
Compound	Form	ω(C—C—C—Cl) (°)	ν(C—Cl) (cm^{-1})
n-Propyl chloride	trans	180·0	744
	gauche	66·4	699
n-Butyl chloride	TG	66·8	671
	TT	180·0	740
	GT	177·6	741
	GG	64·2	665
	GG'	78·1	658
Isobutyl chloride	gauche	65·4, −172·9	735
	trans	62·5, −62·5	679
sec-Butyl chloride	TG	−65·8	639
	GT	175·7	698
	GG'	−65·0	646
Neopentyl chloride		180, −61·2, 61·2	762
2-Chloro-2-methylbutane	gauche	64·1	586
	trans	180	808(630)[a]
2-Chloro-2,3-dimethylbutane	trans	62·4, −62·4	569
	gauche	173·5, −63·3	777
2-Chloro-3,3-dimethylbutane		177·9, −61·7, 60·1	743
2-Chloro-2,3,3-trimethylbutane		180·0, −60·5, 60·5	737
3-Chloro-2,2,3-trimethylpentane		177·8, 58·4, −62·6, −63·6	742(573)[a]
3-Chloro-2,2,3,4,4-pentamethylpentane		165·0, 47·2, −72·8	771
		51·9, −67·4, 174·3	
3-Chloro-2,2,3,5,5-pentamethylhexane		175·1, −65·0, 55·9, −72·5	735(596)[a]
Cyclopentyl chloride	Equatorial	161·9, −161·9	747
	Axial	78·5, −78·5	591
Cyclohexyl chloride	Equatorial	177·5, −177·5	742
	Axial	69·7, −69·7	578
1-Chloro-1-methylcyclohexane	Equatorial	172·4, −172·4	797(659)[a]
	Axial	67·9, −67·9	580
trans-1-Chloro-3-methylcyclohexane,	Equatorial	177·0, −176·8	777
	Axial	70·2, −69·2	666(585)[a]
1-Chloro−2,2-dimethylcyclohexane	Equatorial	178·8, −177·9, 64·5, −56·8	760
	Axial	170·7, −68·6, 69·7, 53·2	734
1-Chloro−3,3-dimethylcyclohexane	Equatorial	177·0, −176·7	760
	Axial	73·9, −75·8	636(593)[a]
1-Chloro-4,4-dimethylcyclohexane	Equatorial	177·1, −177·1	859(759)[a]
	Axial	70·0, −70·0	578
1-Chloro-4-tert-butylcyclohexane	trans	177·2, —177·2	823
	cis	69·6, −69·6	571(676)[a]
2-Bicyclo[2.2.2]octyl-2-chloropropane		63·9, −57·3, —176·7	719
4-Chloronortricyclene		180·0, 180·0, −180·0	1041
3-Chloro-bicyclo[3.1.0]hexane,	trans	150·0, −150·0	742(902)[a]
	cis	101·9, −101·9	656
1-Adamantyl chloride		180·0, 180·0, −180·0	987
2-(1-Adamantyl)-2-chloropropane		180·0, −180·0, 60·5, −60·5	714
2-(1-Adamantyl)-2-chloro-3,3-Dimethylbutane		51·2, 173·0, −68·3, 750(772)[a]	
		−75·1, 162·1, 44·7	
2-(1-Norbornyl)-2-chloropropane		62·5, −62·5, 180	746(696)[a]

[a] For the C—Cl frequency, the value in parentheses may be considered as another possibility.

that are coupled occur and the bonds are near the plane (if one is present). Good examples appear to be the higher C—Cl frequency of the trans form [ω(C—C—C—Cl) = 180·0°] of propyl chloride relative to that of the gauche form [ω(C—C—C— Cl) = 66·4°] (744 and 699 cm^{-1}, respectively) and the higher C—Cl frequency of the gauche form [ω(C—C—C—Cl) = 172·9°] of isobutyl chloride relative to that of the trans form [ω(C—C—C—Cl) = 62·5°]) (735 and 679 cm^{-1}, respectively). Extraordinarily high C—Cl stretching

vibrational frequencies due to the highly efficient coupling were calculated for 1-chloroadamantane (987 cm^{-1}) and 4-chloronorticyclene (1041 cm^{-1}), with a coupling of C—Cl stretching to three C—C stretching and a shift of about three times that in the mono coupled case. Our calculated C—Cl stretching frequency for 1-chloroadamantane is close to the experimental value (958 cm^{-1}) reported recently from liquid-phase Raman spectroscopy.[39] Frequently this coupling is interfered with by the restricted geometry (2-bicyclo[2.2.2]octyl-2-chloropropane, 719 cm^{-1}) or by other substituents attached to the C—C—C—Cl skeleton (e.g. 2-chloro-2,3,3-tri-methylbutane, 737 cm^{-1}). From the C—Cl stretching frequencies and molecular geometries of a variety of alkyl chlorides as depicted in Table 16, it seems that even though there is generally a characteristic range for C—Cl stretching according to the alkyl chloride type, the long-range coupling to the C—Cl bond and other environmental effects may significantly affect the values of these frequencies.

Moments of inertia and dipole moments

The moments of inertia of alkyl chlorides are reported in Table 17. The molecular mechanics moments of inertia (r_g) are in good agreement with the experimentally determined microwave data, and usually about 0.5–1% higher (as is appropriate for r_g) except in a few cases, i.e. ethyl, n-propyl and isobutyl chloride. Some of the errors in the moments of inertia could certainly be improved by introducing a torsion–bend interaction energy term, but this has not been included in MM3.

The alkyl chlorides considered here are all mono-chlorinated saturated hydrocarbons. Because it is assumed that the C—C and C—H bonds have no bond dipoles, the total dipole moment of a particular molecule is simply determined by the bond moment of the C—Cl bond alone. Even the polarization of C_α—C_β bonds is disregarded in our dipole moment calculations. The value used in MM3(94) for the bond moment of C—Cl is 2.09 D. The MM3 values reproduce the

Table 17. Rotational constants (MHz) and moments of inertia (in u Å^2)[a] of alkyl halides[b]

	Methyl chloride			
Parameter	MW/IR[c]	IR/Raman[d]	MM3 (r_g)	% (MM3 − MW/IR[c])
A	154423·11	156051·11		
B	13292·799	13292·877		
C	13292·799	13292·877		
I_a	3·27	3·24	3·3051	1·07
I_b	38·030	38·03	38·3401	0·82
I_c	38·030	38·03	38·3401	0·82

	Ethyl chloride		
	MW[e]	MM3 (r_g)	% (MM3 − MW[e])
A	31337·449(26)		
B	5493·716(4)		
C	4962·292(5)		
I_a	16·132	16·3899	1·60
I_b	92·020	92·6948	0·73
I_c	101·874	102·6114	0·72

	n-Propyl chloride					
	ED/MW[f]		MM3 (r_g)		% (MM3 − ED/MW[f])	
	trans	gauche	trans	gauche	trans	gauche
A	25830·68(18)	11824·41(5)				
B	2379·11(2)	3317·82(5)				
C	2271·02(2)	2851·79(5)				
I_a	19·58	42·75	19·8850	42·8506	1·56	0·24
I_b	212·49	152·37	214·6851	155·1552	1·03	1·83
I_c	222·60	177·27	224·8696	179·7175	1·02	1·38

Table 17. *Continued*

Isopropyl chloride

	MW[g]	MM3 (r_g)	% (MM3 − MW[g])
A	8068·09(5)		
B	4570·82(2)		
C	3207·57(2)		
I_a	62·66	63·4196	1·21
I_b	110·60	110·8508	0·23
I_c	157·61	157·8653	0·16

Isobutyl chloride

	MW[h,i]	MM3[i]	(r_g)% (MM3 − MW[h])
A	7527·05(100)		
B	2146·21(2)		
C	1793·59(2)		
I_a	67·16	67·4119	0·38
I_b	235·55	239·5415	1·69
I_c	281·85	285·1916	1·19

tert-Butyl chloride

	MW[j]	MM3 (r_g)	% (MM3 − MW[j])
A	4518·703		
B	3017·852		
C	3017·852		
I_a	111·875	112·4402	0·51
I_b	167·514	168·7861	0·76
I_c	167·514	168·7861	0·76

Cyclopentyl chloride

	MW[k]		MM3 (r_g)		% (MM3 − MW[k])	
	Axial	Equatorial	Axial	Equatorial	Axial	Equatorial
A	4547·659(7)	6424·51(14)				
B	2290·193(3)	1832·304(6)				
C	2073·357(4)	1523·163(5)				
I_a	111·163	78·69	111·4338	78·9981	0·24	0·39
I_b	220·737	275·899	222·4575	277·8124	0·78	0·69
I_c	243·822	331·896	245·7154	333·3474	0·78	0·44

Cyclohexyl chloride

	MW[l]		MM (r_g)		% (MM3 − MW[l])	
	Axial	Equatorial	Axial	Equatorial	Axial	Equatorial
A	3217·786(5)	4292·09(9)				
B	1760·564(4)	1396·982(5)				
C	1508·617(4)	1127·346(4)				
I_a	157·105	117·78	158·1672	118·9209	0·68	0·97
I_b	287·142	361·874	288·8399	363·5765	0·59	0·47
I_c	335·100	448·425	336·9573	450·4553	0·55	0·45

Table 17. *Continued*

4-Chloronortricyclene		
	MW[m]	MM3 (r_g)	% (MM3 – MW[m])
A	—		
B	140·46(1)		
C	140·46(1)		
I_a	—	132·9024	—
I_b	359·44	363·6746	
I_c	359·44	363·0663	

1-Chloroadamantane		
	MW[n]	MM3 (r_g)	% (MM3 – MW[n])
A	—		
B	836·432(10)		
C	836·432(10)		
I_a	—	300·8535	—
I_b	604·390	607·6746	0·54
I_c	604·390	607·6746	0·54

[a] The conversion factor from rotational constant to moment of inertia is $5·05531 \times 10^5$.
[b] The percentage difference was calculated from the difference of moment of inertia [MM3 (r_g) value – MW value] divided by MW value.
[c] Ref. 17.
[d] Ref. 18.
[e] Ref. 20.
[f] Ref. 2f.
[g] Ref. 22b.
[h] Ref. 25.
[i] Data for the *gauche* form.
[j] Ref. 29d.
[k] Ref. 35.
[l] Ref. 6c.
[m] Ref. 30.
[n] Ref. 31.

experimental values with an rms difference of 0·13 D for various monochloroalkanes.

CONCLUSIONS

With the torsional parameters for C—C—C—Cl clearly favoring the equatorial cyclohexyl chloride, it is apparent that the *trans* form of *n*-propyl chloride should be slightly more stable (ΔH) than the *gauche* form. This is also consistent with all levels of *ab initio* calculations on the conformations of *n*-propyl chloride. It is possible that the *gauche* interaction has a favorable or attractive van der Waals interaction of any system with a similar geometry of the *gauche* form of *n*-propyl chloride. However, the effect is small in propyl chloride itself since the Hartree–Fock conformational energy difference changes only negligibly when electron correclation (MP2) is included.

The C—Cl bond lengths depend mainly on the type of alkyl chloride, primary, secondary or tertiary. The average rms difference of the C—Cl bond length

between electron diffraction experiments and MM3 is 0·007 Å (except for *sec*-butyl chloride neopentyl chloride and 1-chloroadamantane), and this appears to be approximately the experimental accuracy. *Ab initio* RHF/6–31G* level results give values very close to our results. With the basis set truncation error, neglect of correlation error and the error due to comparing r_e with r_g fortuitously nearly cancel out. Lower levels of theory overestimate the C—Cl bond lengths (r_e), whereas higher levels, such as MP2/6–31G** *ab initio* methods, appear to calculate correctly the C—Cl bond lengths (r_e).

As utilized for *n*-propyl and isobutyl chloride, our assignments for the vibrational frequencies of stable isomers are straightforward and easily assignable with the help of the graphics program VIBPLT. It should be mentioned that the correct and complete assignments for the vibrational spectra of complicated stable isomers of monochloroalkanes, as well as the assignments of the frequencies for several experimentally non-fully assigned monochloroalkanes, can be made approxi-

mately without serious error by the molecular mechanics programs.

For the correct and precise comparisons of thermodynamic energy parameters, the same temperatures and same quantities are required. Predictions for the energy parameters imply that our approximation of using a bond dipole only for C—Cl not for C—C and C—H is good enough for these the monochloroalkane compounds. For extensive evaluation of electrostatic energies and dipole moments, it will be necessary to extend our studies to polychloroalkanes and other functionalized monochloroalkanes.

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REFERENCES

1. J. March, *Advanced Organic Chemistry*, 4th ed., Chapt. 10. Wiley—Interscience, New York (1992).
2. (a)C. Komaki, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Bull. Chem. Soc. Jpn.* **28**, 330 (1955); (b)Y. Morino and K. Kuchitsu, *J. Chem. Phys.* **28**, 175 (1958); (c)V. K. Kaushik, *Spectrochim. Acta, Part A* **33**, 463 (1977); (d)Y. Ogawa, S. Imazeki, H. Yamaguchi, H. Matsuura, I. Harada and T. Shimanouchi, *Bull. Chem. Soc. Jpn.* **51**, 748 (1978); (e)U. Burkert and N. L. Allinger, *Molecular Mechanics*, ACS Monograph No. 177, p. 205. American Chemical Society, Washington, DC (1982); (f)K. Yamanouchi, M. Sugie, H. Takeo, C. Matsumura and K. Kuchitsu, *J. Phys. Chem.* **88**, 2315 (1984); (g)J. R. Durig, S. E. Godbey and J. F. Sullivan, *J. Chem. Phys.* **80**, 5983 (1984); (h)M. Rasanen and V. E. Bondybey, *J. Phys. Chem.* **90**, 5038 (1986).
3. (a)G. J. Szasz, *J. Chem. Phys.* **23**, 2449 (1955); (b)E. B. Wilson, *Chem. Soc. Rev.* **1**, 293 (1972); (c)J. E. Anderson, C. W. Doecke and H. Pearson, *J. Chem. Soc., Perkin Trans. 2* 336 (1976).
4. C. Tanaka, J. Tanaka and K. Hirao, *J. Mol. Struct.* **146**, 309 (1986).
5. J. Štokr, B. Schneider and J. Jakeš, *J. Mol. Struct.* **15**, 87 (1973).
6. (a)W. Caminati, F. Scappini and D. Damiani, *J. Mol. Spectrosc.* **108**, 287 (1984); (b)D. J. Gardiner, C. J. Littleton, and N. A. Walker, *J. Raman Spectrosc.* **18**, 9 (1987); (c)Q. Shen and J. M. Peloquin, *Acta Chem. Scand., Ser. A* **42**, 367 (1988); (d)D. E. Bugay, C. H. Bushweller, C. T. Danehey, Jr, S. Hoogasian, J. A. Blersch and W. R. Leenstra, *J. Phys. Chem.* **93**, 3908 (1989); (e)J. A. Hirsch, *Top. Stereochem.* **1**, 199 (1967).
7. (a)S. Sykora, *Collect. Czech. Chem. Commun.* **33**, 3514 (1968); (b)N. L. Allinger, J. A. Hirsch, M. A. Miller and I. J. Tyminski, *J. Am. Chem. Soc.* **91**, 337 (1969); (c)R. J. Abraham and K. Parry, *J. Chem. Soc. B* 539 (1970); (d)A. Goursot-Leray and H. Bodot, *Tetrahedron* **27**, 2133 (1971); (e)A. Y. Meyer and N. L. Allinger, *Tetrahedron* **31**, 1971 (1975); (f)A. Y. Meyer, *J. Mol. Struct.* **40**, 127 (1977); (g)A. Y. Meyer, N. L. Allinger and Y. Yuh, *Isr.*

J. Chem. **20**, 57 (1980); (h)R. J. Abraham and R. Stølevik, *Chem. Phys. Lett.* **77**, 181 (1981); (i)R. Stølevik, *J. Mol. Struct.* **291**, 301 (1993).
8. N. L. Allinger, Y. H. Yuh and J.-H. Lii, *J. Am. Chem. Soc.* **111**, 8551, 8566, 8576 (1989).
9. R. G. Snyder and J. H. Schactschneider, *J. Mol. Spectrosc.* **30**, 290 (1969).
10. A. Yokozeki and S. H. Bauer, *Top. Curr. Chem.* **75**, 71 (1975).
11. H. A. Bent, *Chem. Rev.* **61**, 275 (1961).
12. N. L. Allinger, M. R. Imam, M. R. Frierson, Y. H. Yuh and L. Schafer, in *Mathematics and Computational Concepts in Chemistry*, edited by N. Trinajstic, p. 8. Ellis Horwood, Chichester (1986).
13. M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, *Gaussian 90 (Revision 1)*. Gaussian, Pittsburgh, PA (1990).
14. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, *Gaussian 92 (Revision D.2)*. Gaussian, Pittsburgh, PA (1992).
15. L. S. Bartell and O. Brockway, *J. Chem. Phys.* **23**, 1860 (1955).
16. J. L. Duncan, *J. Mol. Struct.* **6**, 447 (1970).
17. J. L. Duncan, D. C. McKean, P. D. Mallinson, and R. D. McCulloch, *J. Mol. Spectrosc.* **46**, 232 (1973).
18. P. Jensen and S. Brodersen and G. Guelachuili, *J. Mol. Spectrosc.* **88**, 378 (1981).
19. M. Hirota, T. Iijima and M. Kimura, *Bull. Chem. Soc. Jpn.* **51**, 1594 (1978).
20. T. Hayashi and T. Inagusa, *J. Mol. Struct.* **220**, 103 (1990).
21. T. Iijima, S. Seki, and M. Kimura, *Bull. Chem. Soc. Jpn.* **50**, 2568 (1977).
22. (a)M. Hayashi and C. Ikeda, *J. Mol. Struct.* **223**, 207 (1990); (b)F. L. Tobiason and R. H. Schwendeman, *J. Chem. Phys.* **40**, 1014 (1964); (c)M. Meyer, J.-U. Grabow and H. Dreizler, *J. Mol. Spectrosc.* **151**, 217 (1992).
23. S. Fagerland, T. Rydland, R. Stølevik and R. Seip, *J. Mol. Struct.* **96**, 339 (1983).
24. (a)T. Ukaji and R. A. Bonham, *J. Am. Chem. Soc.* **84**, 3627 (1962); (b) **84**, 3631 (1962).
25. W. V. F. Brooks, J. A. Gosselin, M. A. Mohammadi and J. D. Thibault, *J. Mol. Struct.* **72**, 17 (1981).
26. S. H. Schei and R. L. Hilderbrandt, *J. Mol. Struct.* **128**, 181 (1985).
27. G. H. Pauli, F. A. Momany and R. A. Bonham, *J. Am. Chem. Soc.* **86**, 1286 (1964).
28. M. Yamaha and M. Igarashi, *Bull. Chem. Soc. Jpn.* **34**, 733 (1961).
29. (a)F. A. Momany, R. A. Bonham, and M. L. Druelinger, *J. Am. Chem. Soc.* **85**, 3075 (1963); (b)D. R. Lide, Jr and M. Jen, *J. Chem. Phys.* **38**, 1504 (1963); (c)R. L. Hilderbrandt and J. D. Wieser, *J. Chem. Phys.* **55**, 4648 (1971); (d)W. Braun, H. Gunther, H. Umbrecht and W. Zeil, *Z. Phys. Chem.* **93**, 247 (1974).

30. V. W. Laurie and W. M. Stigliani, *J. Am. Chem. Soc.* **95**, 4154 (1973).
31. D. Chadwick, A. C. Legon and D. J. Millen, *J. Chem. Soc. A* 1116 (1968).
32. J. M. Hastings and S. H. Bauer, *J. Chem. Phys.* **18**, 13 (1950).
33. R. L. Hilderbrandt and Q. Shen, *J. Phys. Chem.* **86**, 587 (1982).
34. R. C. Loyd, S. N. Mathur and M. D. Harmony, *J. Mol. Spectrosc.* **72**, 359 (1978).
35. P. Groner, M. J. Lee and J. R. Durig, *J. Chem. Phys.* **94**, 3315 (1991).
36. D. Damiani and L. Ferretti, *Chem. Phys. Lett.* **21**, 592 (1973).
37. G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas* **88**, 1221 (1969).
38. J. J. Shipman, V. L. Folt and S. Krimm, *Spectrochim. Acta* **18**, 1603 (1962).
39. Y. Huang, R. M. Paroli, D. F. R. Gilson and I. S. Butler, *Can. J. Chem.* **71**, 1890 (1993).