

Microwave Spectrum, Structure, and ^{35}Cl Nuclear Quadrupole Coupling Constant of 4-Chloronortricyclene

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Abstract: The microwave spectrum of four isotopic species of 4-chloronortricyclene has been studied. Moments of inertia obtained lead to the following substitution structural parameters: $r(\text{C}_1\text{C}_2) = 1.527 \pm 0.005 \text{ \AA}$, $r(\text{C}_1\text{C}_7) = 1.525 \pm 0.016 \text{ \AA}$, $\angle \text{C}_2\text{C}_1\text{C}_7 = 106.6 \pm 0.4^\circ$. With assumption of the CCl bond length to be 1.763 \AA , the following additional parameters are obtained: $r(\text{C}_7\text{C}_4) = 1.538 \pm 0.011 \text{ \AA}$, $\angle \text{ClC}_4\text{C}_7 = 115.7 \pm 1.0^\circ$, $\angle \text{C}_7\text{C}_4\text{C}_3 = 102.6 \pm 0.5^\circ$, $\angle \text{C}_1\text{C}_7\text{C}_4 = 96.2 \pm 0.7^\circ$. The ^{35}Cl nuclear quadrupole coupling constant is found to be $-69.2 \pm 0.2 \text{ MHz}$.

Nortricyclene, tricyclo[2.2.1.0^{2,6}]heptane, is an interesting example of a simple polycyclic hydrocarbon containing a cyclopropane ring. Substantial deviations from the structural parameters normally encountered in hydrocarbons are expected because of the geometrical constraints imposed. These constraints result in considerable angle strain, and accurate structure determinations for nortricyclene and its derivatives should help in understanding the resulting effects on the molecular bonding.

In this work we report the microwave spectrum of several isotopic species of 4-chloronortricyclene and the determination of the heavy atom structure. Because of the nuclear electric quadrupole moment of both naturally occurring isotopes of chlorine, study of the 4-chloro compound also affords an opportunity to investigate the effect of the unusual angles on the electronic distribution at the chlorine nucleus.

Experimental Section

The sample of 4-chloronortricyclene used in this investigation was obtained through the courtesy of Professor P. v. R. Schleyer and was kindly donated by Dr. G. L. Dunn. All isotopic species were studied in their naturally occurring abundance.

Measurements were made both with a conventional 100-kHz Stark modulated spectrometer and with a Hewlett-Packard 8460A K-band spectrometer. Measurements were made at room temperature due to the rather low vapor pressure of the molecule.

Spectrum and Rotational Constants

The spectrum was investigated in the region from 8 to 26 GHz and was characteristic of a rigid symmetric top containing an axial quadrupolar nucleus of spin $3/2$. Except for the lowest frequency transitions, the hyperfine structure due to the quadrupole moment of the chlorine nucleus was unresolved. As a result the higher transitions appeared as quite broad lines. Attention was focused on the $K = 0$ components because of their relatively small hyperfine splittings and the fact that they could be distinguished from other K components through their second-order Stark effect. Interference due to overlap with components of higher K was reduced by biasing the Stark modulation voltage with a small dc component. Rudolph² has shown that in first order the intensity weighted average of frequencies of hyperfine components gives the unperturbed frequency. Thus the peak of an unresolved line tends to the unper-

turbed frequency. Using the peak of the unresolved $K = 0$ lines, values for the rotational constant B_0 are obtained which are very close to the value obtained from the $J = 2$ to $J = 3$ transition where a number of hyperfine components were resolved and where a complete analysis could be made. Both ^{35}Cl and ^{37}Cl species were observed although the ^{37}Cl transitions were too weak to allow a detailed hyperfine analysis.

In the case of both Cl isotopic species the ground-state transitions were accompanied by a rather intense vibrational satellite displaced slightly to low frequency. An accurate determination of the relative intensities was not possible because of considerable overlapping, but the excited state is about one-half the intensity of the ground state at room temperature. The excited state presumably corresponds to the doubly degenerate bending motion involving the C-Cl bond. The pattern of vibrational satellites is quite similar to that observed for 1-chloroadamantane³ and 1-chlorobicyclo[1.1.1]pentane.⁴

In addition to the two most common symmetric top species, two ^{35}Cl species were observed in which one of the off-axis carbons is isotopically substituted. One species has a ^{13}C in the cyclopropane ring while the other has a ^{13}C in one of the methylene groups. These species are denoted as $^{13}\text{C}_1$ and $^{13}\text{C}_7$, respectively (see Figure 1 for the numbering of the atoms). The spectra of these species are those of a very slightly asymmetric rotor. Only the $K = 1$ components are sufficiently split out by the asymmetry to be measured separately. All other K components are grouped in a single broad unresolved absorption with very complex overlapping. Thus accurate frequencies could be obtained only for the $K = 1$ components. The symmetric top species having a ^{13}C at the tertiary carbon C_4 could not be observed. Its transitions are predicted to be very close to those of a vibrational satellite having much more intensity and are presumably masked.

Rotational transition frequencies for the two symmetric top species are given in Table I; those for the two asymmetric top species are given in Table II. Table III lists the rotational constants and moments of inertia.

Structure

From the isotopic data available, coordinates for the

(3) D. Chadwick, A. C. Legon, and D. J. Millen, *J. Chem. Soc. A*, 1116 (1968).

(4) K. W. Cox and M. D. Harmony, *J. Mol. Spectrosc.*, **36**, 34 (1970).

(1) This research was supported by a grant from the National Science Foundation.

(2) H. D. Rudolph, *Z. Naturforsch. A*, **23**, 540 (1968).

Table I. Rotational Transitions (MHz)^a of Main Isotopic Species of 4-Chloronortricyclene

Transition ^b	³⁶ Cl		³⁷ Cl	
	Obsd	Obsd - calcd	Obsd	Obsd - calcd
Ground State				
2 → 3 ^c	8,438.73	-0.02		
3 → 4 ^c	11,251.70	+0.03		
6 → 7	19,690.49	+0.07	19,203.53	+0.05
7 → 8	22,503.32	-0.02	21,946.81	-0.02
8 → 9	25,316.26	-0.07	24,690.14	-0.04
Excited Vibrational State				
6 → 7	19,686.10	+0.02	19,199.27	+0.02
7 → 8	22,498.34	-0.04	21,942.04	+0.00
8 → 9	25,310.70	+0.02	24,684.82	-0.02

^a Estimated uncertainty is ± 0.05 MHz. ^b Obtained from $K = 0$ line unless otherwise specified. ^c Hypothetical unsplit frequency obtained from the analysis of hyperfine components.

Table II. Rotational Transitions^a (MHz) of Ground State ¹³C Species of 4-Chloronortricyclene

Transition	¹³ C ₁		¹³ C ₇	
	Obsd	Obsd - calcd	Obsd	Obsd - calcd
6 ₁₆ → 7 ₁₇	19,499.63	+0.03	19,607.7 ^b	-0.16
6 ₁₅ → 7 ₁₆	19,520.11	-0.03	19,659.7 ^b	-0.25
7 ₁₇ → 8 ₁₈	22,285.23	-0.01	22,408.89	-0.02
7 ₁₆ → 8 ₁₇	22,308.75	+0.04	22,468.40	0
8 ₁₈ → 9 ₁₉	25,070.87	-0.01	25,209.92	+0.01
8 ₁₇ → 9 ₁₈	25,097.27	-0.01	25,277.1 ^b	+0.23

^a Estimated uncertainty in measurement is 0.1 MHz unless otherwise specified. In all cases the Cl isotope is ³⁶Cl. ^b These transitions were overlapped by vibrational satellites of the main isotopic species. The uncertainty is estimated to be 0.2 MHz.

Table III. Rotational Constants (MHz) and Moments of Inertia^a (u Å²)

	³⁶ Cl	³⁷ Cl	¹³ C ₁	¹³ C ₇
<i>B</i>	1406.46 ± 0.01	1371.68 ± 0.01	1395.03 ± 0.01	1406.16 ± 0.02
<i>C</i>			1392.10 ± 0.01	1398.72 ± 0.02
<i>I_b</i>	359.326 ± 0.003	368.437 ± 0.003	362.269 ± 0.003	359.403 ± 0.005
<i>I_c</i>			363.033 ± 0.003	361.314 ± 0.005
Excited Vibrational State				
<i>B</i>	1406.15 ± 0.01	1371.38 ± 0.01		
<i>I_b</i>	359.405 ± 0.003	368.518 ± 0.003		

^a Conversion factor 505,377 u Å² MHz.

C₁, C₇, and Cl atoms can be calculated⁵ and are given in Table IV. Since only $K = 1$ components could be

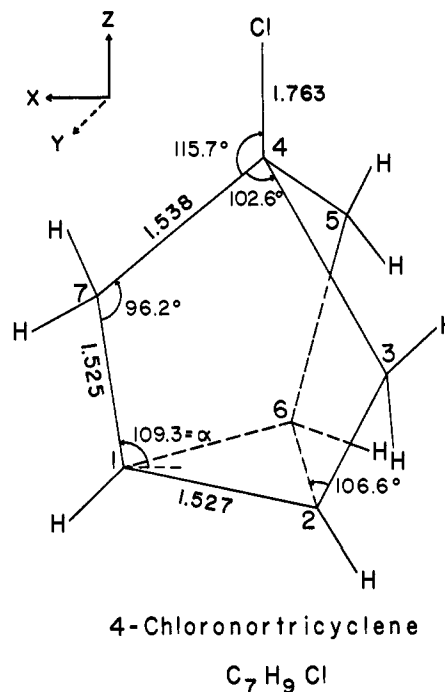
Table IV. Atomic Coordinates^a (Å)

Atom	<i>x</i>	<i>z</i>
Cl	0	2.153 ± 0.001
C ₄	0	0.390 ^b ± 0.004
C ₇	1.386 ± 0.003	-0.277 ± 0.014
C ₁	0.881 ± 0.003	-1.716 ± 0.001

^a The symmetry axis is *z* and *xz* is the plane of symmetry containing Cl, C₄, C₇, and C₁. ^b Obtained from the value $r(\text{C}_4\text{Cl}) = 1.763 \pm 0.003$ Å (ref 8).

measured accurately for the ¹³C species, only the rotational constants *B*₀ and *C*₀ could be obtained. How-

(5) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

**Figure 1.** Numbering of C atoms and heavy atom structural parameters for 4-chloronortricyclene.

ever, the coordinates are very insensitive⁶ to *I_a* and an approximate value was sufficient for the calculations. It was assumed in all calculations that the molecule possesses C_{3v} symmetry.⁷ From the available coordinates, the structural parameters associated with the

cyclopropane ring and its adjacent CC bond can be calculated. To obtain the structural parameters associated with the remaining CC bond and the CCl bond, however, it is necessary to make an assumption which provides the location of the one nonvanishing C₄ coordinate. The most reasonable assumption would seem to be that of the CCl bond length from a recent electron diffraction study.⁸ This parameter is the best determined distance reported in that investigation with a stated uncertainty of 0.004 Å. Also, the Cl coordinate obtained in this study should be quite accurate with an

(6) Of course, the off-axis coordinates could be well determined from values for *I_a* if they were known, but an expression involving *I_b* and *I_c* which is very insensitive to *I_a* also exists. See J. E. Wollrab, "Rotational Spectra and Molecular Structure," Academic Press, New York, N. Y., 1957, p 98.

(7) Since the existence of a symmetric top spectrum only establishes C₃ symmetry, a slightly twisted form is not unequivocally ruled out.

(8) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969).

experimental uncertainty of 0.001 Å. Thus, assumption of the CCl bond length should locate the C₄ atom reasonably well. The resulting coordinate is given in Table IV.

Geometrical parameters obtained from diffraction investigations are not exactly equivalent to those obtained spectroscopically because of the differing effects of molecular vibrations. Hence, combination of a CCl bond length obtained by diffraction with spectroscopic data is subject to uncertainties in addition to those purely experimental. To check the compatibility of the electron diffraction and spectroscopic results for C and Cl parameters, a distance which is *experimentally* well determined in both the diffraction and spectroscopic investigations can be compared. The electron diffraction value for the distance of the Cl atom to one of the carbons in the cyclopropane ring is reported to be⁸ 3.962 ± 0.008 Å. In this study we find 3.968 ± 0.002 Å. In addition a number of comparisons can be made between less precisely determined heavy atom distances, and in all cases the diffraction and spectroscopic values agree within experimental error. For example, the electron diffraction and spectroscopic values for the distance of the Cl from the methylene carbons are 2.790 ± 0.007 and 2.795 ± 0.012 Å, respectively. It seems likely, therefore, that no substantial inconsistency is introduced in this case by mixing a diffraction parameter with spectroscopic data.

Another possible route to the determination of the C₄ coordinate is to assume the *H* parameters from the electron diffraction study and to then use the center of mass condition. This procedure leads to an unreasonable result, indicating an inconsistency between the diffraction and spectroscopic data in the case of *H* parameters. Such a result is not unexpected, however, since *H* parameters are especially susceptible to vibrational effects⁹ because of the large vibrational amplitudes involved.

Structural parameters for the heavy atoms are given in Table V together with the corresponding electron diffraction values.

Table V. Structural Parameters of 4-Chloronortricyclene

	This work	Electron diffraction ^a
<i>r</i> (C ₄ Cl)	(1.763 ^b Å)	1.763 ± 0.003 Å
<i>r</i> (C ₁ C ₄)	1.538 ± 0.011 Å	1.537 ± 0.005 Å
<i>r</i> (C ₁ C ₇)	1.525 ± 0.016 Å	1.535 ± 0.010 Å
<i>r</i> (C ₁ C ₂)	1.527 ± 0.005 Å	1.510 ± 0.016 Å
∠C ₁ C ₄ C ₇	115.7 ± 1.0°	115.3° ^c
∠C ₇ C ₄ C ₃	102.6 ± 0.5°	103° ^c
∠C ₁ C ₇ C ₄	96.2 ± 0.7°	95.6° ^c
∠C ₂ C ₁ C ₇	106.6 ± 0.4°	107° ^c
∠α ^d	109.3 ± 0.4°	109.7° ^c

^a Reference 8. ^b Assumed from electron diffraction. ^c No error limits given. ^d α is the angle between the C₁-C₇ bond and the plane of the cyclopropane ring.

³⁵Cl Nuclear Quadrupole Coupling

For the ³⁵Cl species, it was possible to resolve and accurately measure most of the hyperfine components for the *J* = 2 → 3 transition. Also in the *J* = 3 → 4 transition the components with the largest splittings

(9) V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, **37**, 1687 (1962).

could be resolved although most components overlapped and were not measured. The value of the coupling constant *eQq* obtained is -69.2 ± 0.2 MHz. Observed and calculated hyperfine frequencies are given in Table VI.

Table VI. Quadrupole Splitting of ³⁵Cl in 4-Chloronortricyclene

<i>J</i> → <i>J'</i>	<i>F</i> → <i>F'</i>	<i>K</i>	Calcd <i>ν</i>	Obsd <i>ν</i>	
2 → 3	5/2 → 7/2	2	8,426.39	8,426.41	
	3/2 → 5/2	0	8,435.29		
	1/2 → 3/2	0	8,435.29	8,435.38	
	5/2 → 7/2	1	8,436.28		
	3/2 → 5/2	1	8,436.19	8,436.30	
	3/2 → 5/2	2	8,438.75		
	7/2 → 9/2	0	8,439.57	8,439.57	
	5/2 → 7/2	0	8,439.57		
	7/2 → 9/2	1	8,440.60	8,440.55	
	1/2 → 3/2	1	8,440.48		
3 → 4	7/2 → 9/2	2	8,443.69	8,443.73	
	1/2 → 3/2	2	8,456.06	8,456.00	
	7/2 → 9/2	3	11,241.11	11,241.12	
	3/2 → 5/2	3	11,264.65	11,264.70	
					<i>a</i>

^a Interference of vibrational satellite.

Discussion

For purposes of comparison, CC bond lengths from related molecules are given in Table VII.

Table VII. Comparison of CC Bond Lengths in Related Molecules

Molecule	Bond	Value
Cyclopropane	CC	1.509 ± 0.002, ^a
		1.514 ± 0.002 ^b
Cyclopropyl chloride	C ₁ C ₂	1.513 ± 0.004 ^c
	C ₂ C ₃	1.515 ± 0.001 ^c
Cyclopentane	CC	1.539 ± 0.003 ^d
Norbornane	CC (av)	1.549 ± 0.003 ^e
4-Chloronortricyclene	C ₁ C ₂	1.527 ± 0.005
	C ₁ C ₇	1.525 ± 0.016
	C ₄ C ₇	1.538 ± 0.011

^a O. Bastiansen, F. N. Frisch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964). ^b W. J. Jones and B. P. Stoicheff, *Can. J. Phys.*, **42** (11), 2259 (1964). ^c Reference 13. ^d A. Almennigen and O. Bastiansen, *Acta Chem. Scand.*, **15**, 711 (1961). ^e A. Yokeziki and K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **44**, 2356 (1971).

One question of interest is the effect on the distances in the three-membered ring of 4-chloronortricyclene caused by inclusion in a strained tricyclic system. From Table VII it can be seen that an elongation of the cyclopropyl bonds relative to those of cyclopropane itself seems to have occurred. Such an elongation would serve to lessen angle strain at C₄ and C₇ although counterbalanced somewhat by increased strain at C₁.

Chiang, *et al.*,⁸ concluded from their electron diffraction study that the cyclopropyl bond lengths of 4-chloronortricyclene were similar to those in unstrained molecules and that the structure of the three-membered ring was uninfluenced by inclusion in the tricyclic system. Although the value 1.510 Å which they obtained is very close to the values observed in cyclopropane (see Table VII), their data are not inconsistent with the greater value found in this work because of their rather large error limits of 0.016 Å. However, it is difficult to see how the spectroscopic data could be

consistent with any value much smaller than the one reported here. For example, vibration-rotation effects should tend to bias the reported distance toward a low value rather than a high one.⁹ Thus, it is concluded that the higher value reported here is the more nearly correct one and that the apparent expansion of the cyclopropyl ring is probably real.

Although their rather large uncertainties preclude a definitive comparison, the other two CC bond lengths in 4-chloronortricyclene do not appear to be appreciably longer than the value found in cyclopentane. On the other hand, in the related molecule norbornane a significant lengthening of the CC bonds is reported (see Table VII for values of bond lengths). This lengthening may be due to the eclipsed methylenes present in norbornane but absent in nortricyclene.

Table VIII compares CCl bond lengths and ³⁵Cl

Table VIII. Comparison of CCl Bond Lengths and ³⁵Cl Quadrupole Coupling Constants

Molecule	r_{CCl} , Å	eQq , MHz
<i>tert</i> -Butyl chloride ^a	1.803 ± 0.002	-66.9
CH ₃ Cl ^b	1.781 ± 0.001	-75.1
1-Chlorobicyclo[1.1.1]- pentane ^c	1.761 ± 0.012	-66.6
Cyclopropyl chloride ^d	1.740 ± 0.003	-71.4 ^e
4-Chloronortricyclene	1.763 ± 0.003 ^f	-69.2

^a Reference 10. However, the CCl bond may be substantially longer. See R. L. Hilderbrandt and J. D. Wieser, *J. Chem. Phys.*, **56**, 1143 (1972). ^b C. C. Costain, *ibid.*, **29**, 864 (1958). ^c Reference 4. ^d Reference 13. ^e The value obtained assuming the CCl bond to coincide with a principal axis of the quadrupole tensor. ^f Reference 8.

quadrupole coupling constants in a number of molecules. It can be seen that the CCl bond is considerably shorter than that in *tert*-butyl chloride. This can be ascribed in part to decreased ionic character, but presumably changes in the hybridization of the C₄ orbitals are also involved. The small apex angle of 102.6° should cause more p character in the orbitals involved in the C₄C bonds and correspondingly greater s char-

acter in the orbital involved in the C₄Cl bond. This increased s character in turn should lead to a shortened CCl bond. In addition, the greater p character in the other C₄ orbitals should facilitate greater π overlap with the Cl p_x and p_y orbitals which also would contribute to a shorter CCl bond. A similar shortening is observed in 1-chlorobicyclo[1.1.1]pentane.⁴

For the simple alkyl halides a monotonic correlation between CCl bond length and the Cl quadrupole coupling constant has been pointed out.^{10,11} According to the simplified theory of Dailey and Townes,¹² the coupling constant is given by the relation

$$eQq = -109.7 \text{ MHz}(1 - s^2 + d^2 - \Pi - I) \quad (1)$$

where -109.7 MHz is the quadrupole coupling constant of atomic Cl, s^2 and d^2 are the fraction of s and d character of the Cl σ p_z orbital primarily involved in the CCl bond, Π is a measure of the participation of the nominally nonbonding p_x and p_y orbitals of the Cl, and I is the ionic character of the CCl bond. For a homologous series where H is being successively replaced by CH₃, it is plausible to assume that changes in the Cl quadrupole coupling constant and the CCl bond length would be primarily due to changes in the ionic character and thus that these changes would be monotonically related. However, for strained cyclic systems no such simple relation is found. As has been pointed out for the case of cyclopropyl chloride,¹³ an additional factor which must be considered is the extent of the Π participation of the Cl p_x and p_y orbitals. Also eq 1 neglects any effects on the quadrupole coupling constant from electrons associated with the C orbitals, whereas the CCl bond length obviously is sensitive to such changes. Thus, it is not surprising that no simple monotonic relation between the Cl quadrupole coupling constant and the CCl bond length is found for strained ring systems.

(10) D. R. Lide and M. Jen, *J. Chem. Phys.*, **38**, 1504 (1963).

(11) F. L. Tobiason and R. H. Schwendeman, *J. Chem. Phys.*, **40**, 1014 (1964).

(12) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

(13) R. H. Schwendeman, G. D. Jacobs, and T. M. Krigas, *J. Chem. Phys.*, **40**, 1022 (1964).