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THE STRUCTURE OF 4-CHLORONORTRICYCLENE

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Abstract—The structure of 4-chloronortricyclene in the gas phase was determined by electron diffraction. Interatomic distances and mean square amplitudes of vibration were evaluated. The cyclopropyl ring bonds are 1·510 Å, typical of C_3 rings. A possible correlation between increased cyclopentyl bond lengths and increased flap angle is noted, as is the apparent decrease in these bond lengths with substitution of electronegative groups. A summary of C—Cl bond lengths in a variety of molecular environments completes the discussion.

INTRODUCTION

THE structures of nortricyclene and of its 4-chloro derivative present interesting comparisons of the effects of geometrically imposed constraints on bond lengths and bond angles in 3- and 5-membered carbon atom rings, as well as a unique opportunity to note the effect of a large imposed departure from sp^3 hybridization at the bridge C atom, on the C—Cl bond length. In this paper we report structural data on 4-chloronortricyclene obtained in the gas phase by electron diffraction.

DISCUSSION

There are three interesting structural features in this molecule which merit comparison with related structures. The geometry of 4-chloronortricyclene as shown in Fig. 1 does not differ substantially from that of its parent. The dimensions in the 3-

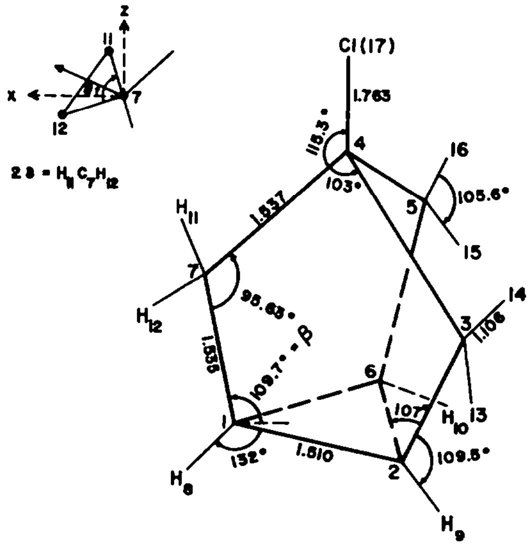


FIG. 1 4-Chloronortricyclene.

membered rings present in nortricyclene, 4-chloronortricyclene and several other compounds containing a cyclopropane ring are summarized in Table 1. The C—C bond distances are close to 1·51 Å except in those systems where the 3-membered ring is attached to a double bond, as in the methylenecyclopropanes, or adjacent to another cyclopropane ring as in spiropentane. The presence of adjacent fused rings does not seem to influence the structure of the C_3 ring.

TABLE 1. COMPARISON OF BOND LENGHTS IN 3-MEMBERED RINGS

Compound	C—C (Å)	Reference
4-chloronortricyclene	1·510 ± 0·008	This Study (ED)
Nortricyclene	1·50 ± 0·02	7 (ED)
Cyclopropane	1·509 ± 0·0015	8 (ED)
Cyclopropylchloride	1·513 ± 0·004	9 (MW)
Methyl cyclopropane	1·514	10 (MW)
Bicyclobutane	1·51 (ring) 1·49 (bridge)	11 (MW)
Spiropentane	1·48 ± 0·03 (central) 1·51 ± 0·03 (periph.)	12 (ED)
Spiropentyl chloride	1·51 (av)	13 (MW)
Methylene cyclopropane	1·484 ± 0·010 (side) 1·535 ± 0·015 (opposite)	14 (ED)
Trimethylene cyclopropane	1·453 ± 0·020	5 (ED)

A comparison of the C–C distances in cyclopentane and in several highly strained derivatives is presented in Table 2. One interesting feature is that in the strained hydrocarbons the C—C separations are consistently larger than in ethane (1·532 ± 0·001).[6] There is a suggestion of a trend towards larger average distances with increasing flap angle but the number of examples is too few and the combined uncertainty in the distances too large to be certain of this. Such an increase would not

TABLE 2. COMPARISON OF CYCLOPENTYL C—C DISTANCES

Compound	C—C(Average Å)	Flap angle*	Reference ‡
Cyclopentane	1·539 ± 0·003	(puckered)	15
Cyclopentane	1·54†	(180°)	16
Bicyclo[2,1,1]hexane	1·543 ± 0·010	130°	17
Norbornane	1·555 ± 0·015	126°	18
Bicyclo[3,2,0]hept-6-ene	1·560 ± 0·010	115°	19
Tricyclo[3,3,0,$0^{2,6}$]octane	1·551 ± 0·005	117°	20
Nortricyclene	1·54 ± 0·02	125°	7
1,4-Dichloronorbornane	1·551 ± 0·015	126°	18
4-Chloronortricyclene	1·536 ± 0·008§	121°	This work

* Flap angle is defined as the angle the unique carbon atom makes with the other four coplanar carbons.

† No limits cited.

‡ All structures reported in this Table were determined by electron diffraction.

§ Does not include the bonds common with a cyclopropane ring.

be surprising since the larger flap angle may be associated with increased non-bonded interactions in a way that would be partly relieved by increased C—C distances. One might also expect that inclusion of electronegative groups like Cl (or a cyclopropane ring) would shorten adjacent C—C bonds by inducing increased *s*-character. The small decrease of the average C—C cyclopentyl bond distance in 1,4-dichloronorbornane relative to norbornane may be an example of this. Possibly, the 4-chloronortricyclene C—C distances are intermediate because of a balance between the strain and electronegativity effects.

Walsh[21] postulated sp^2 hybridization for the bonds external to a cyclopropane ring and a mixture of p and sp^2 orbitals (equivalent to a pair of sp^5 orbitals) for the internal ring bonds. In nortricyclene this hybridization is disturbed by the geometric requirements for closing the cage. In constraining the C_1—C_7 bond to lie closer to the z axis (refer to Fig. 2) by about 10°, the $C_1 \rightarrow H_8$ orbital must shift towards the x axis. If the fraction of p-character in the internal cyclopropane ring bonds did not change, and if it is assumed that the $C_1 \rightarrow C_7$ orbital points along the bond axis, calculation shows that the C_1—H_8 bond approaches the x axis by about 13°. If a pair of sp^3 orbitals were used instead to describe the internal cyclopropane bonds the same 10° shift would be accompanied by a 24° shift of the $C_1 \rightarrow H_8$ orbital. The observed shift is 20°, which with the above assumptions corresponds to cyclopropane bond hybridization of $sp^{3\cdot 2}$. This is in poor quantitative agreement with the $sp^{4\cdot 1}$ hybridization estimated from the $\angle HCH = 116°$ in cyclopropane. A potential test of the hybridization agreement is to note that the $C_1 \rightarrow H_8$ orbital would be $sp^{1\cdot 2}$ hybridized and the resulting bond should be shorter than the C—H bonds of cyclopropane. Unfortunately current precision is not adequate for such a test.

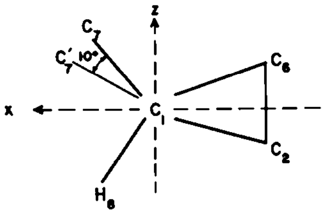
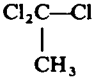
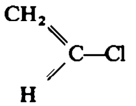
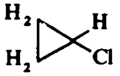
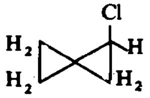


FIG. 2.

An alternative interpretation of the 20° shift of the C_1—H_8 bond axis is that the 10° shift of C_1—C_7 demands a new balance of nonbonded repulsions between H_8 and its neighbors. The change in C—H distance expected for this reorganization is such a small decrease that it is buried in the precision of the experiment. Closer comparison of 4-chloronortricyclene with its parent, nortricyclene, in order to note the effect of substitution of H by Cl is unwarranted because of the low precision claimed for the nortricyclene structure.

Finally, a summary of various C—Cl distances is presented in Table 3. The first four entries in the top group fit moderately well the correlation that for tertiary chlorides the C—Cl distance decreases as the magnitude of the $\angle$ C—C—C decreases (i.e. increasing *s*-character in the C—Cl orbital). The next four compounds listed show the effect of successive replacement of C—C bonds by C—H bonds. There is a suggestion that the C—Cl distances decrease, but the correlation with bond angle is

TABLE 3. COMPARISON OF C—Cl DISTANCES

Compound	C—Cl	∠CCC	Reference
4-Chloronortricyclene	1·763 ± 0·003	103°	This Study, ED
1,4-dichlorobicyclo[2,2,1]heptane	1·773 ± 0·008	[104·0]	(18), ED
1-Chlorobicyclo[2,2,2]octane	1·781	109·5°	(23), MW
$(CH_3)_3CCl$	1·807	112°	(24), ED
$(CH_3)_2CHCl$	1·798	112·7°	(25), MW
$C_6H_{11}Cl$ (chlorocyclohexane)	1·760		(16), ED
$(CH_3)_3CCH_2Cl$	1·74	∠CCCl = 111°	(26), ED
H_3CCl	1·784	∠HCH 110·5°	(27a), ED
	1·781	110°13′	(27b), MW
	1·781	110°52′	(27c), MW
$(CH_3)_2CCl_2$	1·776 ± 0·020	114·3 ± 3°	(28), ED
 $Cl_2\underset{\displaystyle CH_3}{C}—Cl$	1·7712	109½°	(29), MW
Cl_3CCl	1·765 ± 0·002	∠ClCCl = 109·5°	(30a), ED
	1·763	∠ClCCl = 109·5°	(30b), ED
F_3CCl	1·751	∠FCF = 108·6°	(27a), ED
	1·726	∠ClCC = 122°	(31a), MW
	1·72		(31b), ED
C_6H_5Cl	1·706	120°	(32), MW
$H_3CC{\equiv}C—Cl$	1·6371 ± 0·0002	180°	(33), MW
$(CH_3)_3CC{\equiv}CCl$	1·637 ± 0·005	180°	(34), ED
	1·740	∠CCCl = 118·7°	(9), MW
	1·740 ± 0·010		(13), MW

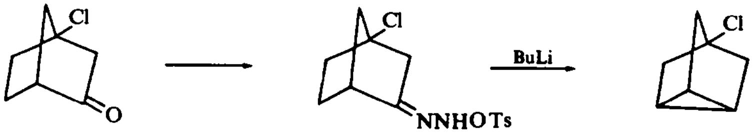
less clear. The next group calls attention to the effect of substitution of C—Cl for C—C. These lead to a decrease in the measured C—Cl bond distances, and the influence of the halogen atom identity is noticeable (CCl_4 *vs* F_3CCl).

When the carbon atom to which the chlorine is attached is sp^2 or sp hybridized due to multiple bonding, a significant decrease in C—Cl distance is apparent, as in group three. In the last catagory chlorine atoms are bonded to carbons incorporated in cyclopropane rings. It is interesting to note again evidence for hybridization changes in that the C—Cl distance in the last two compounds is definitely less than in $(CH_2)_2CHCl$ but larger than in $H_2C = CHCl$.

The nonbonded interactions in chloronortricyclene has been minimized as viewed from the following nonbonded H···H and Cl···H distances; $H_8 \cdots H_9 = 2·994$ Å, $H_8 \cdots H_{11} = 2·548$ Å, $H_{12} \cdots H_{13} = 2·709$ Å; $Cl \cdots H_{11} = 3·118$ Å. If one uses the Van der Waals radii for H = 1·2 Å, Cl = 1·81 Å,[22] he will note that all the nearest nonbonded H···H and Cl···H distances are somewhat longer than the sum of these radii. The strikingly small ∠ HCH angles at C_3, C_5 and C_7 compared with those found in most cycloalkanes cannot be explained. However, the nonbonded C···H distances are comparable: $C_1\cdots H_9$ = 2·396 Å, $C_1\cdots H_{11}$ = 2·225 Å and $C_3\cdots H_9$ = 2·171 Å. The nonbonded repulsions in the carbon skeleton are well balanced, since $C_1\cdots C_3$ = 2·447 Å and $C_3\cdots C_5$ = 2·406 Å do have similar magnitudes.

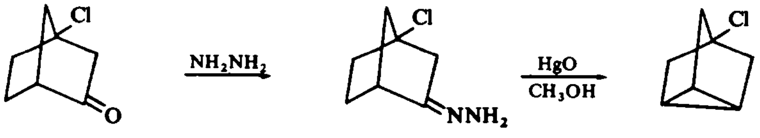
EXPERIMENTAL

Sample sources. One sample of 4-chloronortricyclene used in this investigation was kindly sent to us by Dr. R. S. Sauers.[1] Its synthesis started with the known ketone (I). For compound III, b.p.: 142–144°,



I II III

n_D^{25} = 1·4814; its NMR spectrum consists of two singlets of relative area 2:1 at 1·6 and 1·2 ppm, respectively. Two strong bands appear in the IR spectrum at 8·03 and 9·95 μ. Another sample was generously provided by Dr. G. L. Dunn,[2] and was prepared by a somewhat different route, in which the last two steps followed a procedure described by Reusch, *et al.*[3]



I VII III

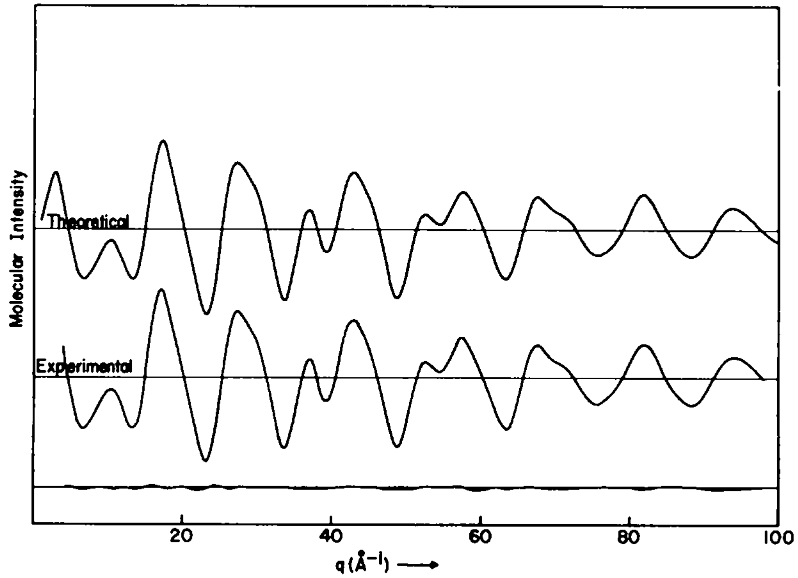


FIG. 3 Reduced experimental and theoretical intensity curves for 4-chloronortricyclene; $q = (40/\lambda)\sin\theta/2$.

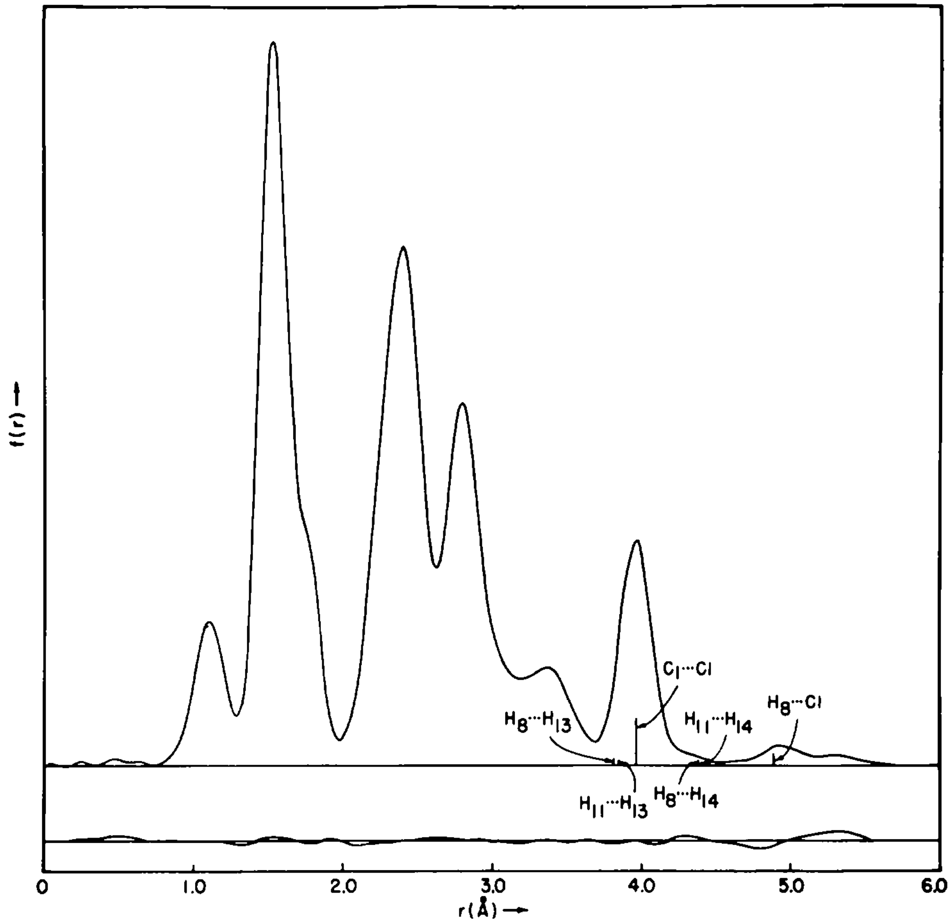


FIG. 4 Radial distribution and difference curves for 4-chloronortricyclene.

Electron diffraction details. Sectored electron diffraction patterns were taken with the new apparatus, with a 70 kV electron beam at two sample-plate distances [262 and 129 mm]. The sample was maintained at room temp. MgO diffraction patterns were recorded concurrently to establish the scale factor. The patterns were microphotometered with a double beam Jarrell-Ash microdensitometer and the recorder tracings were converted to intensities at unit intervals of q according to the procedures previously described.[4]

Analysis of the diffraction patterns. The reduced and final theoretical molecular intensity curves $[qM(q)]$ are shown in Fig. 3. The refined radial distribution plot and the difference curve between the experimental and the theoretical $f(r)$ functions for the best model are plotted in Fig. 4. C_{3v} symmetry was assumed with C—Cl to lie along the principal threefold rotational axis. Theoretical models were computed in terms of the following eight geometrical structural parameters: C_1—C_2, C_2—C_3, C_1—C_7, C—H, C—Cl, β, θ, δ; β is defined as the angle between C_1—C_7 and the 3-member ring plane; θ is the angle between the plane of $C_7H_{11}H_{12}$ and the xy-plane; and δ is the half value of $\angle H_{11}C_7H_{12}$ (Fig. 1).

Fig. 5 shows the second peak of $f(r)$ on an enlarged scale with the vertical scale decreased to half the value used in Fig. 4. This peak is due mainly to the bonded C—C and C—Cl distances; i.e. C_1—C_2 = 1·510 Å, C_1—C_7 = 1·535 Å, C_3—C_4 = 1·537 Å and C—Cl = 1·762 Å. The third and fourth peaks are replotted in Fig. 6, resolved into three sets of nonbonded C—C distances: C_1—C_3 = 2·447 Å, C_1—C_4 = 2·276 Å, and C_3—C_5 = 2·406 Å; one nonbonded C_3—Cl = 2·790 Å and four sets of C—H nonbonded distances. The fourth peak is contributed mainly by C_3—Cl = 2·790 Å and C_3—H_{12} = 3·782 Å. The shoulder between

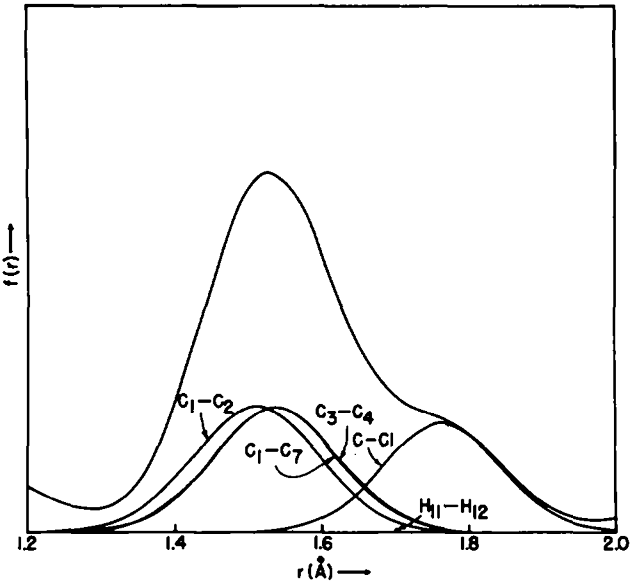


FIG. 5 Expanded scale of the 1·2–2·0 Å region of Fig. 4

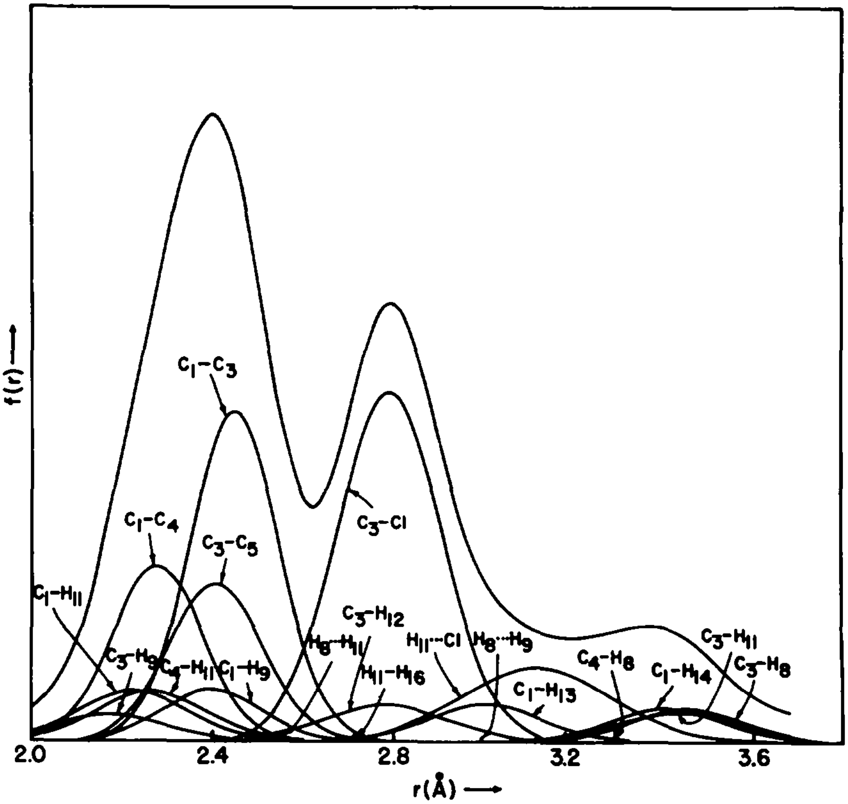


FIG. 6 Expanded scale of the 2·0–3·6 Å region of Fig. 4.

TABLE 4.
STRUCTURAL PARAMETERS FOR 4-CHLORONORTRICYCLENE
(C_{3v} Symmetry)

Type	r_{ij} (Å)	l_{ij} (Å)
C_1—C_2	1·510 ± 0·016	0·055 ± 0·003*
C_1—C_7	1·535 ± 0·010	0·055 ± 0·003*
C_3—C_4	1·537 ± 0·005	0·055 ± 0·003*
C—H	1·106 ± 0·006	0·078 ± 0·004
C—Cl	1·762 ± 0·004	0·048 ± 0·003
Nonbonded Internuclear Distances†		
$C_1\cdots C_3$	2·447 ± 0·010	0·072 ± 0·005
$C_1\cdots C_4$	2·276 ± 0·009	0·073 ± 0·008
$C_3\cdots C_5$	2·406 ± 0·006	0·080 ± 0·016
$C_1\cdots Cl$	3·962 ± 0·008	0·080
$C_3\cdots Cl$	2·790 ± 0·007	0·094
$C_1\cdots H_9$	2·396 ± 0·009	0·085
$C_1\cdots H_{11}$	2·225 ± 0·011	0·100
$C_1\cdots H_{14}$	3·407 ± 0·010	0·100
$C_1\cdots H_{13}$	3·006 ± 0·001	0·100
$C_3\cdots H_9$	2·171 ± 0·009	0·100
$C_3\cdots H_8$	3·452 ± 0·010	0·100
$C_3\cdots H_{11}$	3·440 ± 0·010	0·120
$C_3\cdots H_{12}$	2·782 ± 0·010	0·120
$C_4\cdots H_8$	3·292 ± 0·011	0·090
$C_4\cdots H_{11}$	2·264 ± 0·008	0·100
$H_8\cdots Cl$	4·880 ± 0·007	0·120
$H_{11}\cdots Cl$	3·118 ± 0·006	0·150

* The l_{ij}'s for bonded C—C were assumed equal.

† All the nonbonded interatomic distances were calculated from above least squares values and bond angles.

3·0 Å and 3·6 Å is due to C_1—H_{13} = 3·006 Å, C_4—H_8 = 3·292 Å, C_1—H_{14} = 3·407 Å, C_3—H_{11} = 3·440 Å, C_3—H_8 = 3·452 Å and H_{11}—Cl = 3·118 Å. The last peak in Fig. 4 is due to C_1—Cl = 3·962 Å, H_8—H_{13} = 3·821 Å and H_{11}—H_{13} = 3·825 Å. The longest nonbonded distance in the molecule is H_8—Cl = 4·880 Å. A small peak which appears at r = 5·32 Å has no physical interpretation, and is probably due to an error in the form factor for chlorine which cannot be removed.

The values for the geometric parameters were refined by a least squares analysis of the reduced molecular intensity curve, following a conventional procedure.[4] Thirteen parameters were allowed to vary and the analysis converged to the values listed in Table 4. The corresponding error matrix is reproduced in Table 5. Those l_{ij} values which are not listed in this Table were assigned reasonable magnitudes, corresponding to known values in similar compounds. The limits of error cited in Table 4 are twice (in some cases three times) the standard deviations which are listed along the diagonal of the error matrix. Significance of the error matrix has been stated in the previous publication.[4, 5] No large correlations are indicated for any pairs of parameters.

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TABLE 5. ERROR MATRIX FOR C_7H_9Cl

(Distances in Å units; angle in radian)

	C_1—C_2	C_1—C_7	C_3—C_4	C—H	C—Cl	β	θ	δ	l_{12}	l_{13}	l_{14}	$l_{C—Cl}$	l_{35}
C_1—C_2	0·0078												
C_1—C_7	−0·0063	0·0053											
C_3—C_4	−0·0041	0·0031	0·0025										
C—H	0·0020	−0·0017	−0·0010	0·0018									
C—Cl	0·0017	−0·0011	−0·0011	−0·0001	0·0015								
β	−0·0056	0·0045	0·0032	−0·0014	−0·0011	0·0042							
θ	0·0042	−0·0035	−0·0022	−0·0004	−0·0014	−0·0034	0·0185						
δ	−0·0064	0·0049	0·0040	0·0013	−0·0017	0·0049	0·0068	0·0145					
l_{12}	0·0032	−0·0025	−0·0017	0·0008	0·0008	−0·0023	0·0016	−0·0027	0·0013				
l_{13}	−0·0034	0·0027	0·0020	−0·0008	0·0007	0·0027	−0·0032	0·0023	−0·0013	0·0026			
l_{14}	0·0019	−0·0015	−0·0016	0·0006	−0·0012	−0·0020	0·0015	−0·0059	0·0007	−0·0009	0·0040		
$l_{C—Cl}$	−0·0016	0·0011	0·0007	0·0002	−0·0007	0·0010	0·0005	0·0015	−0·0007	−0·0004	0·0005	0·0016	
l_{35}	0·0057	−0·0047	−0·0035	0·0016	−0·0017	−0·0047	0·0034	−0·0078	0·0022	−0·0039	0·0045	0·0009	0·0079

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APPENDIX

Cartesian Coordinates for Least Squares Model

4-Chloronortricyclene

	x	*y*	*z*
C_1	0·8717	0	0
C_2	−0·4357	0·7549	0
C_3	−0·6945	1·2030	1·4452
C_4	0	0	2·1028
C_5	−0·6945	−1·2030	1·4452
C_6	−0·4357	−0·7549	0
C_7	1·3891	0	1·4452

H_8	1·7285	0	−0·6988
H_9	−0·8643	+1·4969	−0·6988
H_{10}	−0·8643	−1·4969	−0·6988
H_{11}	2·0551	−0·8506	1·6806
H_{12}	2·0551	0·8506	1·6806
H_{13}	−0·2909	2·2050	1·6806
H_{14}	−1·7642	1·3544	1·6806
H_{15}	−1·7642	−1·3544	1·6806
H_{16}	−0·2909	−2·2050	1·6806
Cl	0	0	3·8653