

Electron-diffraction Studies of Chlorobutatriene and Chlorobutenynes. I. Molecular Structure of Gaseous Chlorobutatriene

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Chlorobutatriene has been studied by gas phase electron diffraction. An assumed force field was used to supply correction terms to be used in the r_α -refinements and amplitudes of vibration that could not be determined from the electron diffraction data. The important structural parameters obtained from r_α -refinements on a coplanar model with a linear carbon atom chain and equal terminal C=C bonds are: C=C($sp-sp$) = 1.260(10) Å, C=C($sp-sp^2$) = 1.326(5) Å, C-Cl = 1.733(5) Å, \angle CCCl = 122.2(0.8)°; the r_α -values are given, and the parenthesized values are 2σ with systematic uncertainties included. Different assumptions regarding the CCH-angles did not cause significant changes in the other structural parameters. Determination of the difference between the two terminal C=C bonds was not possible.

Some years ago Vestin *et al.*¹ studied the kinetics and mechanisms of the aliphatic acetylene dimerization in a liquid Cu(I) catalyst. The product of this reaction is vinylacetylene, but by introducing a small flow of O₂ in the entering gas, formation of diacetylene was expected. However, they observed, as it turned out Finlay (du Pont)² had done previously, that instead a chlorohydrocarbon was formed:



Finlay had suggested that the product was 2-chlorobuten-3-yne, and Vestin *et al.* confirmed this by mass spectroscopy and IR- and NMR-spectroscopy.

As an alternative route for preparation of this chlorobutenyne Vestin *et al.*¹ also studied the dehydrochlorination of 1,4-dichloro-2-butyne by alkali. While the end product of this reaction is

diacetylene, Canadian³ and Russian⁴ chemists claimed to have isolated 2-chlorobuten-3-yne as an intermediate. Vestin *et al.*¹ discovered, however, that in fact three C₄H₃Cl-isomers could be isolated, neither of which being identical to the product of the dimerization reaction described above. Two of these were found to be the chlorobutenynes, *trans*- and *cis*-1-chlorobuten-3-yne, the identification being based upon mass spectroscopy, IR-spectroscopy and their relative delay in gas liquid chromatography.¹ Using mass spectroscopy and UV-, IR-, and NMR-spectroscopy the third compound was identified as chlorobutatriene.⁵

We have recently become interested in the molecular structure of the four described C₄H₃Cl compounds as well as the remaining chlorobutenyne, 4-chlorobuten-3-yne.⁶ Since the molecular structures of the corresponding hydrocarbons butatriene⁷ and buten-3-yne⁸ are known, determination of the molecular structure of the C₄H₃Cl-compounds should reveal to which extent monochloro substitution results in significant changes of the carbon skeleton. Also determination of the carbon-chlorine bond length for the varying hybridization state of the carbon atom was of some interest.

The Vestin group initiated studies of the microwave spectra of the compounds,⁹⁻¹³ and the above identifications were confirmed by assignments of the rotational spectra of the substances. Due to low natural ¹³C-concentration, the high cost of ¹³C enriched samples, and the many steps and very low yields of the reactions, complete structure determinations by

microwave spectroscopy was regarded as unrealistic, and only three structure dependent parameters could therefore at the best be obtained from these investigations. It was therefore decided to carry out concurrent electron diffraction studies of the compounds, the result of which we shall now report.

EXPERIMENTAL AND CALCULATION PROCEDURES

The reaction mixture from the dehydrochlorination of 1,4-dichloro-2-butyne by alkali in alcohol was fractionated by gas liquid chromatography at a temperature of 100 °C. The chromatograph column was packed with diethylhexyl sebacate (15 %) absorbed on Chromosorb. Pure chlorobutatriene as well as pure *trans*- and *cis*-1-chlorobuten-3-yne was obtained in this way. Due to extremely low stability toward polymerization, chlorobutatriene had to be stored at low temperatures (−70 °C) and hydroquinone was used as stabilizer. Electron-diffraction photographs were made in the Oslo Apparatus¹⁴ using 48 cm and 28 cm nozzle-to-plate distances. In order to reach a sufficient vapour pressure the sample reservoir was maintained at about −10 °C during the experiment. Simultaneous polymerization was then unavoidable and substantial loss of sample was experienced. Two plates of good quality for the long camera distance and four for the shorter distance were obtained and used in the structure determination. The electron wavelength was 0.06464 Å as calibrated against the diffraction patterns of gaseous benzene.¹⁵

The photographic plates were analyzed and the data reduced in routine fashion¹⁶ to yield the experimental intensity and radial distribution curves shown in Figs. 1 and 2, respectively. The background corrections were carried out on the individual levelled intensity curves and the resulting curves were transformed to the modified form. The modification function $s/|f'|_C|f'|_C|$ was applied. The modified electron scattering amplitudes, $|f'|_i$, and the phase factors, η_i , were

computed for 35 kV electrons by the partial wave method¹⁷ based upon analytical HF potentials for the C- and Cl-atoms¹⁸ and using the best electron density of bonded hydrogen for H.¹⁹ The deduction of trial models was based upon interpretation of the radial distribution curve, while the structure refinement was carried out by the method of least squares based upon the modified intensity data. The procedure involves the fitting of theoretical curves simultaneously to the two experimental ones by adjustments of geometrical and vibrational parameters and two separate scale factors. To account for correlation among the data²⁰ off-diagonal elements were included in the weight matrix. The standard deviations thus obtained from the least squares refinement, σ_{LS} , should be corrected for systematic uncertainties of 0.1 % for the distance parameters, $\sigma = (\sigma_{LS}^2 + (0.001 r)^2)^{1/2}$.

Closely spaced distances, large number of vibrational parameters, and neglect of shrinkage effects often make the least-squares results ambiguous. However, a modified²¹ program by Gwinn,²² computes root-mean-square amplitudes of vibration (l -values) and perpendicular amplitude correction coefficients (K -values) in addition to vibrational frequencies, from assumed force fields. This provides an important supplement to the electron diffraction investigations, as l -values may be kept fixed at calculated values, and introduction of the correction term $D = l^2/r - K$, in the distance parameters ($r_a = r_a + D$) allows for refinements on a geometrically consistent model (r_a), the problem of shrinkage effects being accounted for.²¹ Even when observed fundamentals are lacking, such calculations by adopting force constants from similar molecules, have proven to be of great value as the l -values and to some extent the K -values, are not too sensitive to the force field chosen. Also, the knowledge of the r_a rather than the r_a -values makes it possible to calculate moments of inertia which are compatible with those obtained from microwave investigations when a similar force field is used to transform r_o into r_a -values.¹⁰

Table 1. Force field for chlorobutatriene, C₄H₃Cl^a.

$K_1 = K_3 = 9.4$	$K_{24} = K_{35} = 0.56$	$\varrho_4^{35} = \varrho_5^{34} = \varrho_6^{17} = 0.20$
$K_2 = 10.1$	$K_{16} = 0.50$	$\varrho_7^{16} = 0.30$
$K_4 = K_5 = 5.5$	$K_{17} = 0.85$	$\chi_{16}^{43} = \chi_{17}^{53} = 0.08$
$K_6 = 5.6$	$K_{46} = 0.25$	$\chi_{17}^{43} = \chi_{16}^{53} = 0.07$
$K_7 = 3.8$	$K_{67} = 0.40$	
	$K_{12} = K_{23} = 0.35^b$	

^a For numbering of the bonds, see Fig. 3. The meaning of the symbols:²¹ K_i , stretching of bond i ; K_{ij} , bending of angle between bonds i and j ; ϱ_k^{ij} , bending of bond k out of ij -plane; χ_{kl}^{ij} , torsion between the ij - and kl -planes. The force constants are given in md/Å and md Å/(rad)². ^b Identical force constants for bending in plane and out of plane are assumed.

Table 2. Refinement conditions for chlorobutatriene.

Curve (camera dist.), cm	48	28
Data range		
s_{\min}	2.25	6.00
s_{\max}	15.00	30.00
Data interval (Δs)	0.125	0.25
Constants of the weight scheme ^{16,20}		
s_1	6.00	6.00
s_2	15.00	22.00
w_1	0.05	0.05
w_2	0.01	0.02
p_2	-0.64	-0.60
p_3	0.146	0.125
w	1.0	1.0

CALCULATIONS AND REFINEMENTS

Restricting all the atoms to one plane and adopting a linear carbon chain, the molecule is described by eight geometrical parameters when all the CH-bond distances are assumed equal and when $\angle\text{CCH}_5 = \angle\text{CCH}_6$. The parameters used were: r_{CH} , $r_{\text{C}_2\text{C}_3}$, $r_{\text{C}_3\text{C}_4}$, $\Delta r_t = r_{\text{C}_3\text{C}_4} - r_{\text{C}_2\text{C}_3}$, r_{CCl} , $\angle\text{CCH}_5 = \angle\text{CCH}_6$, $\angle\text{CCH}_7$, and $\angle\text{CCCl}$. See Fig. 3 for the numbering of the atoms.

Taking support in force constants from similar molecules the force field given in Table 1 was designed for chlorobutatriene, and the resulting l - and D -values are given in Table 3.

Table 3. Computed D - and l -values, and r_a -structure for chlorobutatriene.^a

Parameters ^b	D -values	l -values	r_a -structure ^c
C-H	4,5	-0.0194	0.074 ₁
	4,6	-0.0226	0.074 ₂
	1,7	-0.0131	0.074 ₃
C=C	2,3	-0.0047	0.039 ₃
	1,2	-0.0053	0.040 ₄
	3,4	-0.0116	0.040 ₅
C-Cl	1,8	-0.0033	0.047
C...C	1,3	-0.0072	0.048
	2,4	-0.0086	0.048
	1,4	-0.0020	0.054
C...Cl	2,8	-0.0035	0.066
	3,8	+0.0005	0.096
	4,8	+0.0028	0.128
Cl...H	7,8	-0.0068	0.106
	5,8	+0.0062	0.235
	6,8	-0.0027	0.130
C...H	2,7	-0.0121	0.096
	3,5	-0.0187	0.097
	3,6	-0.0246	0.097
	3,7	-0.0046	0.113
	2,5	-0.0123	0.114
	2,6	-0.0172	0.114
	4,7	-0.0004	0.129
	1,5	-0.0042	0.130
	1,6	-0.0060	0.130
	1,7	-0.0305	0.124
H...H	5,6	-0.0305	0.124
	7,6	+0.0015	0.216
	7,5	-0.0046	0.145
$\angle\text{CCH}_5 = \angle\text{CCH}_6$	-	-	[1.225]
$\angle\text{CCH}_7$	-	-	[122.5]
$\angle\text{CCCl}$	-	-	121.5(0.3)
R_w^d (%)	-	-	8.6

^a Correction terms (D -values), amplitudes (l -values) and distances (r_a) in Å; angles in degrees. The r_a -structure gives the result of r_a -refinement (no D -value correction) using the calculated l -values. Quantities in brackets are assumed values. ^{b,c,d} See corresponding comments under Table 4.

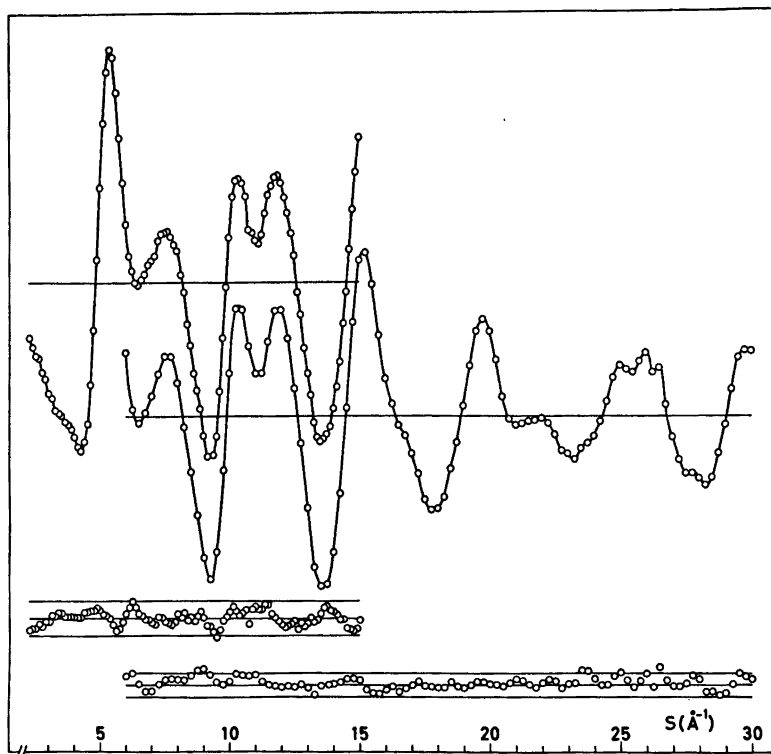


Fig. 1. Experimental intensity data for chlorobutatriene from the 48 cm ($\Delta s = 0.125 \text{ \AA}^{-1}$) and 28 cm ($\Delta s = 0.25 \text{ \AA}^{-1}$) camera distances, and the corresponding difference between the experimental intensities and the theoretical ones computed according to the parameter values of model IV (Table 4). The full lines given along with the difference points indicate the estimated uncertainties (three standard deviations) of the experimental intensity points.

The calculation was carried out using coordinates consistent with the r_a -model also given in Table 3. Only a diagonal force field was used since the designing of a more sophisticated force field was, in the absence of observed fundamentals, judged meaningless. The calculated l -values for the distance types that also occur in butatriene are in fair agreement with those calculated for this molecule.²⁴

The interpretation of the main features of the radial distribution curve was straight forward as indicated by the approximate positions of the important interatomic distances (*cf.* Table 3) shown in Fig. 2.

Least squares refinements of the model were carried out under conditions given in Table 2.

Comparison of the r_a - and r_α -structure for the molecule was carried out for $\Delta r_t = 0$ and $\angle CCH_5 = \angle CCH_6 = \angle CCH_7 = 122.5^\circ$. The

results of r_a -refinements using the calculated l -values are given in Table 3, while model I in Table 4 is the result of the corresponding r_α -refinement where the D -values are used to obtain a geometrically consistent model. The results of further r_α -refinements on models where $\Delta r_t = 0$ are also given in Table 4, where quantities in brackets are assumed values and indicate different restrictions on the vibrational parameters and the CCH angles. The goodness of the least-squares fit for the four models of Table 4 is demonstrated by the agreement-factors given in the table and by the difference between experimental and theoretical radial distribution curves shown in Fig. 2. The correlation matrix for the less restricted model (IV) is given in Table 5, and the corresponding differences in observed and calculated intensity points are shown in Fig. 1.

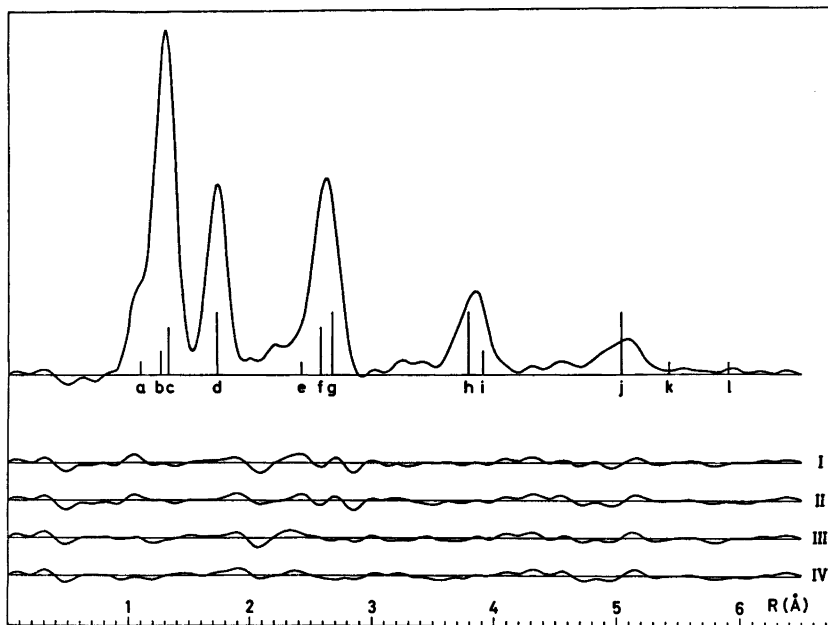


Fig. 2. Experimental radial distribution curve for chlorobutatriene calculated for the artificial damping constant $k = 0.0015 \text{ \AA}^2$. The approximate positions of the important interatomic distances are indicated: a, C-H; b, C=C (central); c, C=C (terminal); d, C-Cl; e, Cl \cdots H₇; f, C₁ \cdots C₃; g, C₂ \cdots Cl; h, C₃ \cdots Cl; i, C₁ \cdots C₄; j, C₄ \cdots Cl; k, Cl \cdots H₈; l, Cl \cdots H₆. The differences between the experimental and theoretical radial distribution curves are shown for models I-IV, Table 4.

The amplitudes of vibration for the group of C=C distances could not be determined and they were kept at the calculated values after checking that assignments to smaller or larger values did not improve the least-squares fit. In particular it should be mentioned that in order to obtain a $sp-sp^2/sp-sp$ bond distance splitting comparable to the one found in butatriene the amplitudes had to be increased by about 0.007 Å.

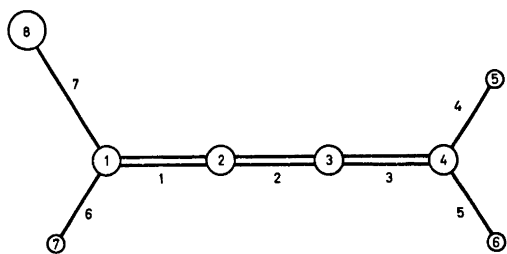


Fig. 3. Numbering of the atoms and bonds in chlorobutatriene, C₄H₅Cl.

Chlorine substitution is known to cause a slight lengthening of the C=C bond in ethylenes.²⁵⁻²⁷ We could, however, not determine the difference between the two terminal bonds (Δr_t) in chlorobutatriene. Introduction of Δr_t equal to small positive values (0.01, 0.02 Å) made the least-squares fit poorer while negative values improved it. Refinements of this parameter resulted in one $sp-sp^2$ double bond longer than the sp^2-sp^2 double bond in ethylene ($\Delta r_t < -0.04 \text{ \AA}$), but this did not cause significant changes in the central C=C bond length nor in the CCH angles.

Finally, models with non-linear carbon chains were considered. Two models with *cis*- and two with *trans*-configuration were tested, neither of which improved the least-squares fit nor refined to models significantly different from the linear ones.

The r_a -values given for the four models in Table 4 were transformed to r_α -values, using the *D*-correction terms of Table 3. The corresponding moments of inertia, I_a , I_b , and I_c ,

Table 4. Important parameter values and corresponding moments of inertia for chlorobutatriene.^a

Parameters ^b	Model I		Model II		Model III		Model IV	
	r_a^c	l^c	r_a^d	l^c	r_a^d	l^c	r_a^d	l^c
C-H	1.106(10)	[0.074]	1.099(11)	[0.074]	1.089(9)	[0.074]	1.082(10)	0.064(9)
C _a =C ₃	1.268(4)	[0.039 _a]	1.267(4)	[0.039 _a]	1.263(5)	[0.039 _a]	1.260(5)	[0.039 _a]
C ₁ =C ₂	1.327(2)	{[0.040 _a]	1.327(2)	{[0.040 _a]	1.326(2)	{[0.040 _a]	1.326(2)	{[0.040 _a]
C ₃ =C ₄	1.734(2)	{[0.040 _b]	1.734(2)	{[0.040 _b]	1.733(2)	{[0.040 _b]	1.733(2)	{[0.040 _b]
C...C	2.587(3)	[0.047]	2.586(3)	[0.047]	2.581(2)	[0.047]	2.578(4)	0.050(3)
	1,3	[0.048]	2.586(3)	[0.048]	2.581(2)	[0.048]	2.578(4)	0.052(7)
	2,4	[0.054]	3.900(3)	[0.054]	3.895(4)	[0.054]	3.892(5)	0.056(8)
C...Cl	2.679(3)	[0.066]	2.681(3)	[0.066]	2.676(5)	[0.066]	2.682(4)	0.053(6)
	2,8	[0.096]	3.793(4)	[0.096]	3.786(5)	[0.096]	3.792(5)	0.106(7)
	3,8	[0.128]	5.033(5)	[0.128]	5.021(4)	[0.128]	5.028(6)	0.140(8)
Cl...H	5.029(5)	[0.106]	2.455(32)	[0.106]	2.408(10)	[0.106]	2.433(33)	[0.106]
	7,8	[0.235]	5.592(47)	[0.235]	5.402(8)	[0.235]	5.580(47)	[0.235]
	5,8	[0.130]	5.996(26)	[0.130]	5.878(10)	[0.130]	5.977(26)	[0.130]
$\angle CCH_3 = \angle CCH_6$		[122.5]	133.2(3.1)	[122.5]		[122.5]		133.4(3.0)
$\angle CCH_7$		[122.5]	119.4(3.0)	[122.5]		[122.5]		119.5(2.6)
$\angle CCCI$		121.9(0.3)	122.1(0.3)	122.1(0.3)		121.8(0.4)		122.2(0.4)
R_W^d (%)		8.44	8.17	8.17		7.82		7.70
$I_a^e(-)^{10}$		20.6	20.2	20.2		20.5		20.1
$I_b^e(326.01)$		324.1	326.8	326.8		322.9		325.8
$I_c^e(346.20)$		344.8	347.0	347.0		343.4		345.8

^a Results of r_a -refinements (the distances given are r_a -values), where Δr for the terminal C=C distances is zero. Quantities in brackets are assumed values and the brackets indicate the different restrictions on the vibrational parameters and the CCH angles in Models I-IV. Distances, r_a , amplitudes, l , in Å; angles in degrees; moment of inertia, I , in u Å². ^b See Fig. 3 for numbering of the atoms. ^c Parenthesized values are standard deviations obtained from the least-squares refinement (σ_{I_a}) and they refer to the last digit given. For the distance parameters they should be corrected for systematic uncertainties according to $\sigma = (\sigma_{I_a}^2 + (0.001 \tau)^2)^{1/2}$. ^d Agreement factor $R_W = [\sum w_i \Delta_i^2 / \sum w_i I_i^2(\text{obs})]^{1/2}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{th})$. ^e Moments of inertia (r_a -values); parenthesized values are microwave results (r_a -values). See text for estimates of uncertainties.

Table 5. Correlation matrix for parameters of chlorobutatriene (Model IV).

$r_{C,C}$	r_{C,C_s}	r_{CH}	$\angle CCH_s$	r_{C-Cl}	$\angle CCCI$	$\angle CCH_7$	t_{CH}	t_{C,C_s}	$t_{C_1C_s}$	$t_{C_2C_1}$	$t_{C_3C_1}$	$t_{C_4C_1}$	t_{C-Cl}	Scale Long	Middle
1.0															
-0.49	1.0														
-0.08	0.58	1.0													
-0.02	-0.13	-0.18	1.0												
0.02	-0.02	0.06	-0.11	1.0											
-0.25	-0.28	-0.19	0.37	-0.40	1.0										
0.03	-0.26	-0.26	-0.27	0.18	-0.13	1.0									
0.17	0.07	0.16	-0.06	-0.02	-0.10	0.08	1.0								
0.09	0.48	0.22	-0.25	-0.06	-0.65	-0.16	0.06	1.0							
-0.01	-0.05	-0.07	0.09	-0.05	0.30	-0.03	0.00	-0.19	1.0						
0.02	-0.06	-0.10	0.01	-0.01	0.07	-0.10	-0.02	-0.01	0.04	1.0					
-0.09	-0.39	-0.38	-0.08	0.00	0.02	0.17	-0.12	-0.18	0.05	0.07	1.0				
0.13	0.50	0.26	-0.22	-0.04	-0.56	-0.13	0.12	0.77	-0.10	-0.01	-0.24	1.0			
0.17	-0.31	-0.26	0.05	-0.02	0.10	0.16	-0.05	-0.10	0.07	0.03	0.17	-0.05	1.0		
0.20	-0.41	-0.39	-0.06	-0.12	0.06	0.18	-0.17	0.06	0.12	0.09	0.31	0.04	0.35	1.0	
0.45	-0.59	-0.44	0.17	-0.08	0.13	0.14	-0.07	-0.07	0.14	0.07	0.28	-0.01	0.47	0.43	1.0

were calculated using a program written by H. Møllendal. The results are given in Table 4 along with the values calculated from microwave data.¹⁰ The program did not estimate the standard deviations. However, a change of 0.1 % for all the distance parameters (systematic uncertainty) resulted in about 0.2 % changes in the moments of inertia, while addition of $\sigma_{\text{I,S}}$ to the geometrical parameters caused changes of 0.1–0.3, 0.6–1.1, and 0.6–1.1 %. Models with Δr_t about -0.04 \AA gave I_b and I_c values 0.3–0.4 % higher than the corresponding $\Delta r_t = 0$ models of Table 4.

DISCUSSION

The agreement-factors given in Table 4 and the difference curves shown in Figs. 1 and 2 demonstrate that the four models are in fair agreement with the experimental data. The refined amplitudes agree within two standard deviations with those calculated from the assumed force field.

The values obtained for the important structural parameters ($C_1 = C_2$, $C_2 = C_3$, and C–Cl bond distances, and $\angle \text{CCCl}$) do not differ significantly in the four models given in Table 4, although there is a trend towards a somewhat shorter central C=C bond in the models where the amplitudes are refined. Model IV is chosen to represent the final results of this investigation. The CCH-angles are unreasonable, but if one chooses not to believe in these, the other structural parameters would not be different (model III). It shall be mentioned that similar problems with the determination of the CCH-angles and the fit in the 2.0–2.5 Å region appear to have been encountered in the electron diffraction investigations of chloro-²⁷ and *cis*-1,2-dichloro-ethylene.²⁸

It was hoped that the moments of inertia obtained from the microwave investigation¹⁰ would supply the additional information needed to make a clear choice between different models obtained from the electron diffraction study. However, the I_b - and I_c -values obtained from the electron diffraction data are probably associated with uncertainty limits of about 1 %. Therefore, although comparisons with the microwave results tend to favour models which gave the better least-squares fit, but which were considered unacceptable (unreasonable CCH

angles and $\Delta r_t = -0.04 \text{ \AA}$), this support is not significant and it will not reverse our previous judgements.

The carbon chlorine bond which is adjacent to a sp^2 - sp double bond, is found to be 1.733(5) Å which is within the range usually found for C(sp^2)-Cl bonds adjacent to sp^2 - sp^2 double bonds. For example, electron diffraction studies of chloro-,²⁷ *cis*-1,2-dichloro-,²⁸ and tetrachloro-ethylene,²⁵ 2,3-dichloro-,²⁸ and hexachloro-1,3-butadiene,²⁹ have given the following results: 1.728(7), 1.718(7), 1.718(3), 1.747(3), and 1.715(2) Å, respectively. The variations in the bond length could be due to small deviations from sp^2 -hybridization of the carbon atom and to different amount of double bond character in the C–Cl bond. It is interesting to note that in chlorobutatriene the C...Cl non-bonded interaction across one bond angle is 2.682(4) Å, which conforms to the 2.67–2.70 Å values usually found for such distances.

The average carbon-carbon bond lengths in chlorobutatriene and butatriene⁷ are in good agreement. The results of r_a -refinements on a linear model for butatriene gave the following parameter values: $C_1 = C_2 = 1.327 \text{ \AA}$, $C_2 = C_3 = 1.257 \text{ \AA}$, C–H = 1.083 Å and $\angle \text{CCH} = 122.5^\circ$, while due to shrinkage effects the best values for the carbon-carbon bonds were estimated to 1.318 and 1.283 Å, respectively. This means that the chlorine substitution has not resulted in any significant change in the total length of the carbon chain. However, while the r_a -models for the two molecules also are in agreement with respect to the individual C=C bonds, this is not the case for the models where attempts to account for the shrinkage effects were made. To which extent this difference is real and caused by the chlorine substitution, or related to improper treatment of the shrinkage effect for either molecule has to be considered.

The D -values used in the r_a -refinements for chlorobutatriene were based upon an assumed force field. A complete spectroscopic investigation of chlorobutatriene upon which a rigorous normal coordinate analysis could be based would clarify the effect of this assumption. However, in our judgement, the small differences in the parameter values obtained in this investigation for corresponding r_a - (Table 3) and r_α -models (Table 4, model I) suggest that this effect would be small.

The method of D -value correction was not available when butatriene was investigated,⁷ and the shrinkage problem could only be handled in a round-about manner. We feel that the differences between the parameter values of the r_a -model and those cited as the final results are larger than usually encountered. A reanalysis of the electron diffraction data for butatriene, utilizing the D -value correction method and the results of a new normal coordinate analysis now available,³⁴ is therefore planned by one of us (G.G.) in cooperation with the earlier investigators.

The $sp-sp^2$ double bonds in chlorobutatriene and in butatriene are both longer than the corresponding bond in allene [1.312(1) Å].³⁰ A similar trend is observed for the terminal $sp-sp$ triple bonds in diacetylene [1.218(1) Å]³¹ as compared to acetylene. At the first sight the short $sp-sp$ double bond found in chlorobutatriene was surprising. However, we feel that more information about such bonds is needed before a possible effect from the substituted chlorine atom should be discussed. It was found to be beyond the capability of the method to determine a possible difference between the two terminal double bonds in chlorobutatriene. The attempts to refine the Δr_t parameter, however, indicated that abnormal bonding conditions might be present. This suggests that also further studies on the bonding in chlorobutatriene would be worthwhile.

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