Electron-diffraction Studies of Chlorobutatriene and Chlorobut-enynes. III. Molecular Structure of Gaseous 2-Chlorobutenyne

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The molecular structure of 2-chlorobuten-3-yne has been investigated by electron diffraction from the vapour. Normal coordinate calculations based upon an assumed force field supplied amplitudes of vibration which could not be determined from the electron-diffraction data, and correction terms which were used in the geometrically consistent r_α-refinements. The structural parameters (r_a-values are given) were found to be: $C(sp)-H = 1.078(16)$ Å, $C(sp^2)-H = 1.106(16)$ Å, $C\equiv C = 1.220(6)$ Å, $C=C = 1.340(5)$ Å, $C-C = 1.422(5)$ Å, $C-Cl = 1.738(4)$ Å, $\angle C=C-C = 124.7(0.5)°$, $\angle C\equiv C-C = 177.0(5.8)°$, $\angle C=C-Cl = 119.5(2.4)°$, $\angle C=C-H = 122.0(3.2)°$ and $\angle C\equiv C-H = 180.0°$ (assumed). Parenthesized values are 2σ where systematic uncertainties are included.

This electron-diffraction study of 2-chlorobuten-3-yne was initiated as a part of the determination of the molecular structures of C_4H_3Cl-isomers.[1,2]

EXPERIMENTAL AND CALCULATION PROCEDURES

2-Chlorobuten-3-yne was prepared as described previously.[3] The compound was purified[4] by gas liquid chromatography at a temperature of 50 °C using a column packed with diethyl-hexyl sebacate (15 %) absorbed on Chromosorb. The substance was prevented from extensive polymerization by storing the sample at low temperatures (-70 °C) and by using hydroquinone as stabilizer. Electron-diffraction photographs were made in the Oslo Apparatus[5] at nozzle-to-plate distances of 48 and 20 cm, keeping the sample reservoir at about -27 °C. The electron wavelength was 0.06464 Å as calibrated against diffraction patterns of

gaseous benzene. The scattering functions for the 35 kV electrons were those computed for chlorobutatriene.[1] Four plates made at each of the two camera distances were selected for the structure analysis. The experimental modified intensities and the corresponding radial distribution curve were obtained from the distributions of the scattered intensity recorded on the plates by the usual procedure,[6] and they are shown in Figs. 1 and 2, respectively. The structure analysis and supporting calculations were carried out using the standard computer programs and procedures,[6-8] as described previously.[1]

CALCULATIONS AND REFINEMENTS

A general planar model for 2-chlorobutenyne is described by thirteen geometrical parameters; see Fig. 3. By assuming $\angle C\equiv C-H = 180°$, $\angle C=C-H_6 = \angle C=C-H_7$, $r_{C_1H_6} = r_{C_1H_7} = r_{C_4H_8} + 0.027$ Å $= r_{CH}$, the number of variable parameters was reduced to the following nine: r_{CH}, $r_{C\equiv C}$, $r_{C=C}$, r_{C-C}, r_{C-Cl}, $\angle C=C-C$, $\angle C\equiv C-C$ (trans to $\angle C=C-C$), $\angle C=C-Cl$, and $\angle C=C-H$.

The diagonal force field given in Table 1 was designed using force constants taken from similar molecules, and it was used in normal coordinate calculations based upon coordinates consistent with the r_a-model given in Table 3. The resulting D- and l-values[8] are also given in Table 3.

The interpretation of the experimental radial distribution curve was straightforward as indicated by the approximate positions for the important interatomic distances shown in Fig. 2 (see Table 3). Least-squares refinements
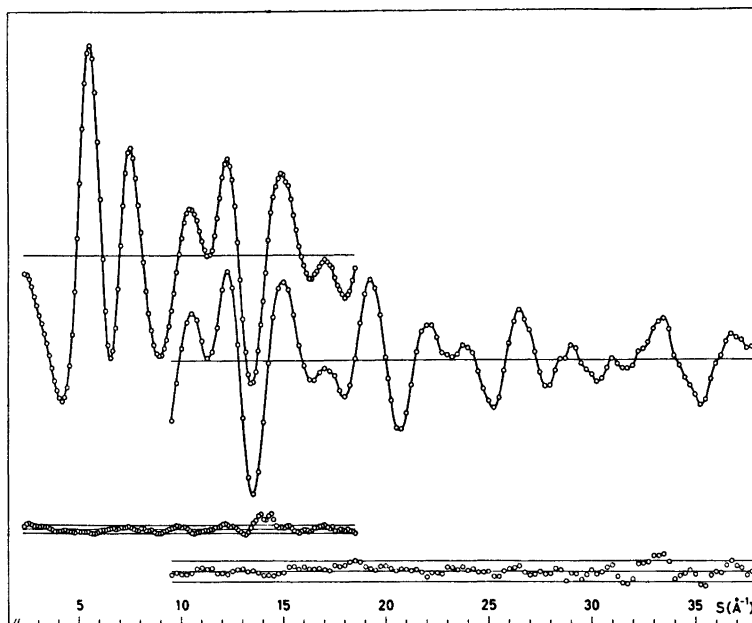
Fig. 1. Experimental intensity data for 2-chlorobutenyne from the 48 cm ($\Delta s = 0.125$ Å^{-1}) and 20 cm ($\Delta s = 0.25$ Å^{-1}) camera distances, and the corresponding difference between the experimental intensities and the theoretical ones computed according to the parameter values of Table 4. The full lines given along with the differences indicate the estimated uncertainties (three standard deviations) of the experimental intensity points.
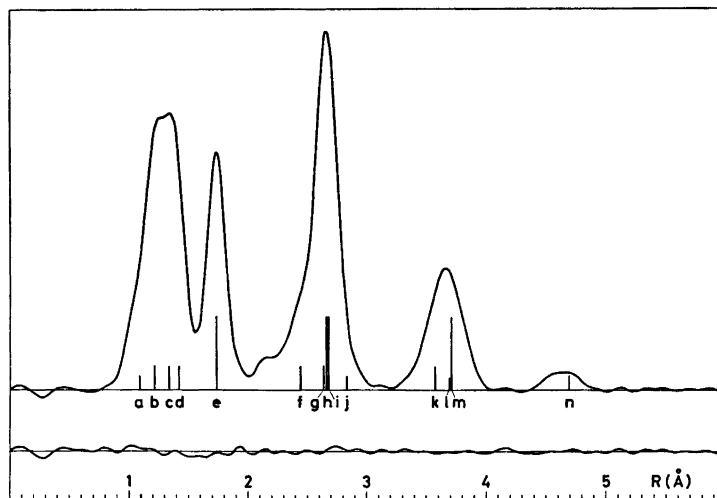

Fig. 2. Experimental radial distribution curve for 2-chlorobutenyne calculated for the artificial dampling constant $k = 0.0015$ Å^2. The approximate positions of the important interatomic distances are indicated: a, $C(sp) - H$ and $C(sp^2) - H$; b, $C \equiv C$; c, $C = C$; d, $C - C$; e, $C - Cl$; f, $C_1 \cdots C_3$; g, $C_2 \cdots C_4$; h, $C_3 \cdots Cl$; i, $C_1 \cdots Cl$; j, $Cl \cdots H_7$; k, $C_1 \cdots C_4$; l, $Cl \cdots H_6$; m, $C_4 \cdots Cl$; n, $Cl \cdots H_5$.

The difference between the experimental and theoretical radial distribution curves calculated according to the parameter values in Table 4 is also given.
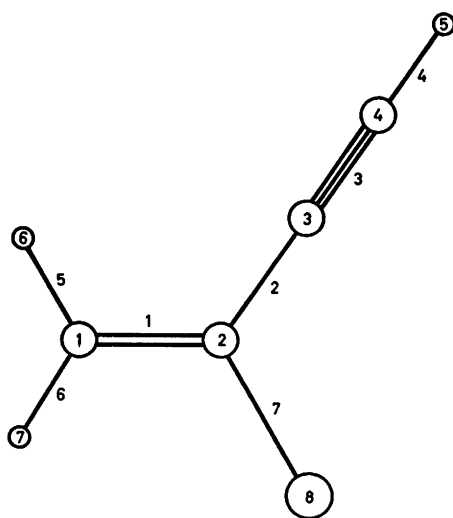
Fig. 3. Numbering of the atoms and bonds in 2-chlorobutenyne, C_4H_3Cl.

Table 1. Force field for 2-chlorobuten-3-yne.[a]

$K_1 = 9.1$	$K_{16} = 0.50$	$\varrho_5^{16} = 0.20$
$K_2 = 4.6$	$K_{15} = 0.50$	$\varrho_6^{15} = 0.20$
$K_3 = 15.7$	$K_{56} = 0.50$	$\varrho_7^{12} = 0.30$
$K_4 = 6.3$	$K_{17} = 0.85$	$\varrho_2^{17} = 0.25$
$K_5 = 5.5$	$K_{12} = 0.84$	$\chi_{12}^{16} = \chi_{15}^{17} = 0.12$
$K_6 = 5.5$	$K_{27} = 1.03$	$\chi_{12}^{15} = \chi_{16}^{17} = 0.14$
$K_7 = 3.9$	$K_{23}^b = 0.32$	
	$K_{34}^b = 0.23$	

[a] For numbering of the bonds, see Fig. 3. The meaning of the symbols: 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.

were carried out under conditions given in Table 2. The result of a r_a-refinement where the amplitudes of vibration (*l*-values) were fixed at the calculated values, is given in Table 3. The C≡C−C angle was fixed at 180° since, when allowed to refine, it oscillated about 180° and no improvement of the least-squares fit was observed for deviation from 180°. A corresponding r_α-refinement where the calculated *D*-values given in Table 3, were used to obtain a geometrically consistent model, was carried out. This did not result in any significant changes in the refined parameter values nor in the least-squares fit. Further r_α-refinements of the structure were carried out including amplitudes of vibration. Amplitudes for overlapping distances were refined in groups. Attempts to refine the group of amplitudes corresponding to the C,C bond distances resulted in unreasonable values, as was also the case for the Cl···H non bonded amplitudes. Adjustments of amplitudes for the C···H and H···H non-bonded distances were never implemented. The simultaneous refinement of the amplitudes did not cause any significant changes in the geometrical parameters. In the r_α-refinements the C≡C−C angle converged to 177.0(2.9)° when allowed to refine. This did not, however, affect the other parameters nor the least-squares fit significantly. The final results are given in Table 4, and Table 5 comprises the elements of the corresponding correlation matrix. The differences between the experimental and theoretical intensities and radial distribution curves calculated according to these results are shown in Figs. 1 and 2, respectively.

The r_a-values given in Table 4 were transformed to the corresponding r_α-values and the

Table 2. Refinement conditions for 2-chlorobuten-3-yne.

Curve Camera distance (cm)	Data range		Data interval	Constants of the weightscheme [6,7]						
	s_{min}	s_{max}	Δs	s_1	s_2	w_1	w_2	p_1	p_2	W
48	2.25	18.50	0.125	6.00	15.00	0.05	0.01	−0.64	0.146	1.0
20	9.50	38.00	0.25	9.50	24.00	0.05	0.02	−0.60	0.125	0.5

Table 3. Computed *D*- and *l*-values, and r_a-structure for 2-chlorobutenyne.[a]

Parameters[b]		*D*-Values	*l*-Values	r_a-Structure[c]
C−H	4,5	−0.0325	0.072	1.067(7)
	1,6	−0.0121	0.074	1.094(7)
	1,7	−0.0127	0.074	1.094(7)
C≡C	3,4	−0.0099	0.036	1.217(2)
C=C	1,2	−0.0024	0.041	1.336(2)
C−C	2,3	−0.0014	0.048	1.421(2)
C−Cl	2,8	−0.0011	0.046	1.737(1)
C···C	2,4	−0.0024	0.052	2.639(3)
	1,3	−0.0014	0.063	2.440(4)
	1,4	+0.0006	0.083	3.571(5)
C···Cl	1,8	−0.0001	0.064	2.659(4)
	3,8	−0.0004	0.067	2.682(4)
	4,8	+0.0018	0.098	3.709(4)
Cl···H	8,7	+0.0010	0.145	2.832(25)
	8,6	−0.0036	0.096	3.695(9)
	8,5	−0.0047	0.148	4.695(7)
C···H	3,5	−0.0282	0.077	2.284(8)
	2,5	−0.0139	0.085	3.706(8)
	1,5	−0.0068	0.123	4.598(10)
	2,6	−0.0062	0.098	2.108(14)
	3,6	−0.0003	0.139	2.701(24)
	4,6	+0.0044	0.176	3.598(27)
	2,7	−0.0074	0.098	2.108(14)
	3,7	−0.0059	0.097	3.424(11)
	4,7	−0.0021	0.103	4.601(10)
H···H	6,7	−0.0169	0.116	1.894(33)
	5,6	−0.0005	0.226	4.511(27)
	5,7	−0.0067	0.131	5.647(15)
∠C=C−C		−	−	124.7(0.2)
∠C−C≡C		−	−	[180.0]
∠C=C−Cl		−	−	121.0(0.3)
∠C=C−H		−	−	120.1(1.4)
R_w^d(%)		−	−	6.42

[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.
[b,c,d] See corresponding comments under Table 4.

Table 4. Important parameter values and corresponding moments of inertia for 2-chlorobutenyne.[a]

Parameters[a]		r_a^c	l^c
C−H	4,5	1.078(8)	0.073(7)′
	1,6 } 1,7 }	1.106(8)	0.075(7)′
C≡C	3,4	1.220(3)	[0.036]
C=C	1,2	1.340(3)	[0.041]
C−C	2,3	1.422(2)	[0.048]
C−Cl	2,8	1.738(1)	0.049(2)
C···C	2,4	2.634(4)	0.049(2)″
	1,3	2.445(5)	0.059(5)
	1,4	3.584(18)	0.088(16)
C···Cl	1,8	2.663(16)	0.061(2)″
	3,8	2.680(18)	0.064(2)″
	4,8	3.701(12)	0.109(9)
Cl···H	8,7	2.833(34)	[0.145]
	8,6	3.696(15)	[0.096]
	8,5	4.664(21)	[0.148]
∠C=C−C		124.7(0.2)	
∠C−C≡C		177.0(2.9)	
∠C=C−Cl		119.5(1.2)	
∠C=C−H		122.0(1.6)	
R_w^d(%)		5.95	
I_a^e(73.63)[e]		73.5	
I_b(163.41)		163.2	
I_c(237.05)		236.7	

[a] Results of r_α-refinements (the distances given are r_a-values). 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-squarer refinement (σ_{LS}) and they refer to the last digits given. For the distance parameters they should be corrected for systematic uncertainties according to $\sigma=[\sigma_{LS}^2+(0.001\ r)^2]^{\frac{1}{2}}$. Quantities in brackets are assumed values and primed amplitudes are refined in groups.
[d] Agreement factor $R_w=[\sum w_i\varDelta_i^2/\sum w_i I_i^2(\text{obs})]^{\frac{1}{2}}$ where $\varDelta_i=I_i(\text{obs})-I_i(\text{th})$.
[e] Moments of inertia (r_α-values); parenthesized values are microwave results (r_s-values). See text for estimates of uncertainties.

moments of inertia for the molecule were calculated. The results are given in Table 4 along with those obtained from the microwave data (r_s-values).[4] The uncertainty limits for the values obtained from the electron-diffraction data are probably at least 0.5 % as estimated from calculations based upon parameter values given increments according to their standard deviations.

DISCUSSION

The agreement factor ($R_w=5.95$ %) and the difference curves shown in Figs. 1 and 2 demonstrate that the final model (Table 4) is in good agreement with the experimental data. The refined amplitudes of vibration agree well with those calculated from the assumed force field (*see* Tables 3 and 4). The moments of inertia based upon the electron-diffraction

Table 5. Correlation matrix for parameters of 2-chlorobutenyne.

	$r_{C\equiv C}$	r_{C-C}	$r_{C=C}$	$\angle C=C-C$	$\angle C\equiv C-C$	r_{C-Cl}	$\angle C=C-Cl$	r_{C-H}	$\angle C=C-H$	l_{CH}	$l_{C_3C_4}$	$l_{C_2C_4}$	$l_{C_1C_3}$	l_{C_3Cl}	l_{C-Cl}	Scales 48 cm	20 cm
$r_{C\equiv C}$	1.0																
r_{C-C}	-0.3	1.0															
$r_{C=C}$	0.45	-0.36	1.0														
$\angle C=C-C$	0.38	0.33	0.26	1.0													
$\angle C\equiv C-C$	0.04	0.01	0.01	0.10	1.0												
r_{C-Cl}	-0.12	-0.14	-0.14	0.40	-0.04	1.0											
$\angle C=C-Cl$	0.18	0.10	0.04	0.11	0.90	-0.08	1.0										
r_{C-H}	0.47	-0.12	0.54	0.26	0.01	-0.02	0.11	1.0									
$\angle C=C-H$	-0.21	0.20	-0.23	0.04	-0.20	-0.03	-0.18	-0.42	1.0								
l_{CH}	-0.62	0.04	-0.09	-0.10	0.02	0.13	-0.09	-0.17	0.09	1.0							
$l_{C_3C_4}$	0.19	0.26	-0.12	0.08	0.67	-0.19	0.78	-0.08	-0.05	-0.11	1.0						
$l_{C_2C_4}$	0.07	0.15	0.02	0.10	-0.66	0.02	-0.35	0.00	0.21	-0.07	-0.19	1.0					
$l_{C_1C_3}$	0.22	0.04	0.15	0.05	0.28	0.04	0.31	0.21	-0.26	-0.17	0.30	-0.16	1.0				
l_{C_3Cl}	0.17	0.19	0.07	0.18	-0.82	0.01	-0.65	0.06	0.24	-0.11	-0.39	0.72	-0.19	1.0			
l_{C-Cl}	-0.13	0.23	-0.24	-0.07	0.01	-0.09	0.06	-0.34	0.32	0.00	0.38	0.13	-0.12	0.12	1.0		
Scales 48 cm	-0.30	0.21	-0.36	-0.19	0.07	-0.12	0.11	-0.49	0.42	0.10	0.34	0.10	-0.14	0.02	0.48	1.0	
20 cm	-0.17	0.33	-0.31	-0.12	-0.03	-0.17	0.06	-0.41	0.32	0.04	0.49	0.19	-0.06	0.18	0.70	0.53	1.0

data are in good agreement with those obtained from the microwave data [4] as compared with the estimated uncertainty limits.

The carbon, chlorine bond length is found to be 1.738(4) Å; the parenthesized value is 2σ where systematic uncertainties are included (see note *c* in Table 4). This is significantly longer than those found for the $C(sp^2) - Cl$ bond in *cis*- and *trans*-1-chlorobutenyne [1.716 (5) Å, 1.717(4) Å],[2] but within the range usually found for this distance type. In 2-chloro-butenyne the C−Cl bond is adjacent to a conjugated single bond and opposite a relatively large C=C−C angle. Its environment is therefore similar to that of the C−Cl bonds in 2,3-dichlorobutadiene [9] [$\angle C = C - C = 126.9(0.2)°$] where also the $C(sp^2) - Cl$ bond is relatively long [$r_{C-Cl} = 1.747(2)$ Å].

A slight bend of the C≡C−C chain was observed in butenyne [$\angle C \equiv C - C = 177.9$ (1.2)°].[10] A similar value for the C≡C−C angle is found in 2-chlorobutenyne, but due to the lower accuracy of the determination, the deviation from linearity of the C≡C−C chain is not significant in this compound. The chlorine subtitution has resulted in a small opening of the C=C−C angle and a slight shortening of the C−C bond as compared to the unsubstituted hydrocarbon [$\angle C = C - C = 123.1(0.5)°$ and $r_{C-C} = 1.431(3)$ Å],[10] while the other structural parameters are not significantly different in the two compounds. Comparison of the carbon skeleton in monochloro substituted butenynes will be carried out and related to the unsubstituted hydrocarbon in more detail in the last paper of this series.

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