Electron-diffraction Studies of Chlorobutatriene and Chlorobutenynes. IV. Molecular Structure of Gaseous 4-Chlorobutenyne

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The molecular structure of 4-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-refinement. The structural parameters (r_a-values are given) were found to be: $C-H = 1.078(16)$ Å, $C\equiv C = 1.213(5)$ Å, $C=C = 1.332(7)$ Å, $C-C = 1.429(5)$ Å, $C-Cl = 1.637(4)$ Å, $\angle C=C-C = 125.3(1.2)°$, $\angle C\equiv C-C = 181.0(3.8)°$, $\angle C\equiv C-Cl = 182.9(5.2)°$, $\angle C=C_1-H = 126.9(5.4)°$ and $\angle C=C_2-H = 114.61(5.2)°$. Parenthesized values are 2σ where estimates of systematic uncertainties are included.

This electron-diffraction investigation of 4-chlorobuten-3-yne concludes the structural studies of the five isomeric C_4H_3Cl species by this method.[1-3]

EXPERIMENTAL AND CALCULATION PROCEDURES

4-Chlorobuten-3-yne was prepared by adding monovinyl acetylene to a potassium hypochlorite solution.[4,5] The substance was isolated and purified by gas liquid chromatography at a temperature of 100 °C, using a column packed with diethyl-hexyl sebacate (15 %) absorbed on Chromosorb. The compound was prevented from polymerization by storing the sample at $-70°C$. Diffraction photographs were made in the Oslo Apparatus [6] at nozzle-to-plate distances of 48 cm and 20 cm, keeping the sample reservoir at about -30 °C. The electron wavelength was

0.06464 Å as calibrated against diffraction patterns of gaseous benzene. The scattering functions for the 35 kV electrons used were those computed for chlorobutatriene.[1] Four plates for each of the two camera distances were selected for the structure analysis. The data reduction, structure analysis, and supporting calculations were carried out in routine fashion [7-9] as described for chlorobutatriene.[1] The modified intensities and radial distribution curves obtained are shown in Figs. 1 and 2, respectively.

CALCULATIONS AND REFINEMENTS

A general planar model of 4-chlorobutenyne is described by thirteen parameters; see Fig. 3. Assuming all $C(sp^2)-H$ bond distances to be equal and $\angle C=C_1-H_7 = \angle C=C_1-H_6$, the number of adjustable parameters was, however, reduced to the following ten: r_{C-H}, $r_{C\equiv C}$, $r_{C=C}$, r_{C-C}, r_{C-Cl}, $\angle C=C_1-H$, $\angle C=C_2-H$, and defined alternately *trans* with respect to each other $\angle C=C-C$, $\angle C-C\equiv C$, and $\angle C\equiv C-Cl$.

The diagonal force field given in Table 1 was designed by adopting force constants from similar molecules, and it was used in normal coordinate calculations [9] based upon coordinates consistent with the r_a-model given in Table 3. The resulting D- and l-values are also given in Table 3.

The interpretation of the main features of the radial distribution curve was straightforward as indicated by the approximate positions of the important interatomic distances shown in Fig. 2. Least-squares refinements were carried out under conditions given in Table 2, and the
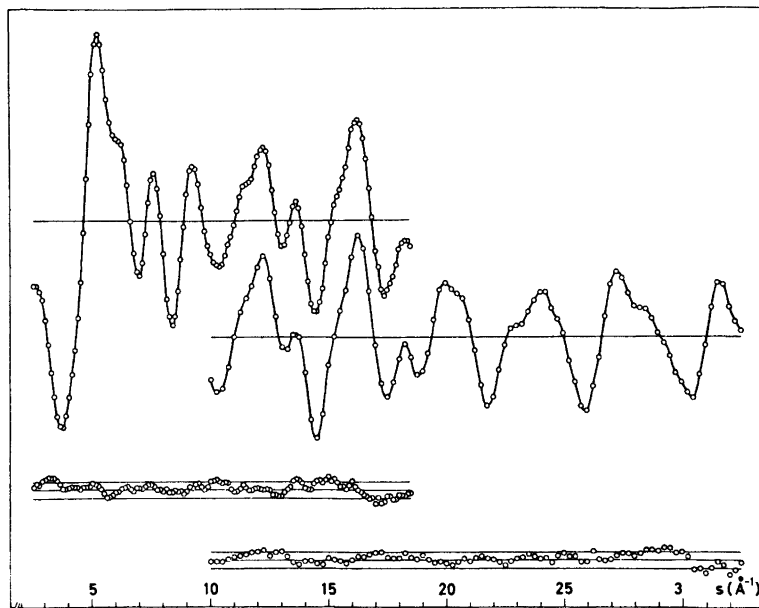
Fig. 1. Experimental intensity data for 4-chlorobutenyne from the 48 cm ($\Delta s = 0.125$ Å^{-1}) and 20 cm ($\Delta s = 0.25$ Å^{-1}) camera distances, and the corresponding differences between experimental and theoretical intensities computed according to the parameter values of Table 4(II) The full lines given along with the differences indicate the estimated uncertainties (three standard deviations) of the experimental intensity points.
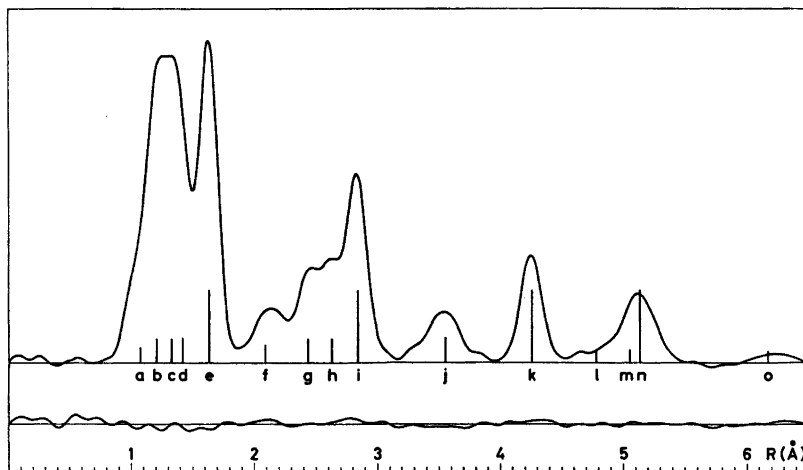
Fig. 2. Experimental radial distribution curve for 4-chlorobutenyne calculated for the artificial damping constant $k = 0.0015$ Å^2. The approximate positions of the important interatomic distances are indicated: a, $C-H$; b, $C\equiv C$; c, $C=C$; d, $C-C$; e, $C-Cl$; f, four $C\cdots H$; g, $C_1\cdots C_3$; h, $C_2\cdots C_4$; i, $C_3\cdots Cl$; j, $C_1\cdots C_4$; k, $C_2\cdots Cl$; l, $Cl\cdots H_5$; m, $Cl\cdots H_6$; n, $C_1\cdots Cl$; o, $Cl\cdots H_7$. The difference between the experimental and theoretical radial distribution curves calculated according to the parameter values in Table 4 (Model II) is also shown.
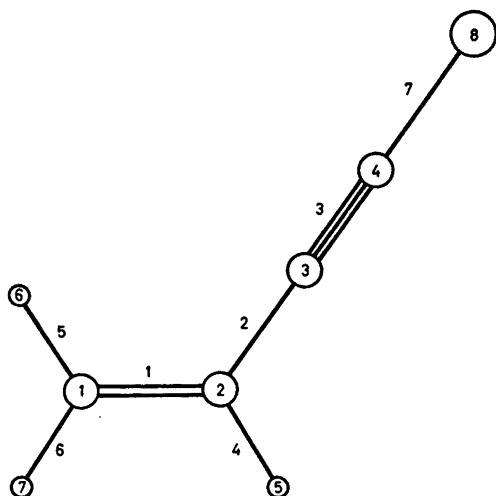
Fig. 3. Numbering of atoms and bonds in 4-chlorobutenyne, C_4H_3Cl.

Table 1. Force field for 4-chlorobuten-3-yne.[a]

$K_1 = 9.10$	$K_{16} = 0.59$	$\varrho_5^{16} = 0.20$
$K_2 = 4.60$	$K_{15} = 0.59$	$\varrho_6^{15} = 0.20$
$K_3 = 15.70$	$K_{56} = 0.25$	$\varrho_4^{11} = 0.20$
$K_4 = 5.40$	$K_{14} = 0.53$	$\varrho_2^{14} = 0.25$
$K_5 = 5.50$	$K_{12} = 0.84$	$\chi_{12}^{16} = \chi_{14}^{15} = 0.16$
$K_6 = 5.50$	$K_{24} = 0.25$	$\chi_{12}^{15} = \chi_{14}^{16} = 0.13$
$K_7 = 5.16$	$K_{23}^{b} = 0.32$	
	$K_{37}^{b} = 0.28$	

[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 are assumed for bending in plane and out of plane.

result of an r_a-refinement where the amplitudes were fixed at the calculated values and all CCH angles at 122.0° is given in Table 3. No changes in the distance parameters were observed when $\angle C \equiv C - C$ and $\angle C \equiv C - Cl$ were included in the refinement. The values obtained for the angles were then $\angle C = C - C = 124.6(0.3)°$, $\angle C \equiv C - C = 177.2(1.6)°$, and $\angle C \equiv C - Cl = 176.5(2.1)°$ and the least-squares fit improved somewhat ($R_w = 9.71 \%$). The D-values given in Table 3 were now used to obtain a geometrically consistent model, and the corresponding r_α-refinements were carried out. This resulted in a significantly better least-squares fit as the a-greement factors were 8.94 and 8.60 %, respectively, for the models with linear and non-linear $Cl - C \equiv C - C$ chains. The bond distances in these two models did not differ significantly and the refined valence angles were for the linear one $\angle C = C - C = 125.1(1.3)°$ and for the non-linear one $\angle C = C - C = 124.6(0.6)°$, $\angle C = C - C = 180.1(1.7)°$, and $\angle C \equiv C - Cl = 182.5(2.3)°$. The r_α-results do not suggest any significant deviation from linearity of the $Cl - C \equiv C - C$ chain contrary to the implications of the r_a-results. Also, the bond distances from the r_α-refinements are significantly longer than those obtained from the r_a-refinements of the structure (cf. values in Table 3 and 4). Comparisons of experimental and theoretical radial distribution curves for the described models revealed that the r_a-results gave poor agreement in the region where the bond distances are located.

The r_α-refinement of the structure was continued by including amplitudes of vibration and the CCH-angles in the refinement. As the values obtained for the CCH-angles seemed somewhat unreasonable, refinements were also carried out

Table 2. Refinements conditions for 4-chlorobuten-3-yne.

Curve Camera distance (cm)	Data range		Data interval Δs	Constants of the weight scheme [7,8]						
	s_{min}	s_{max}		s_1	s_2	w_1	w_2	p_1	p_2	W
48	2.50	18.50	0.125	6.00	15.00	0.05	0.01	−0.64	0.146	1.0
20	10.00	32.50	0.250	10.00	24.00	0.05	0.02	−0.60	0.125	0.5

Table 3. Computed *D*- and *l*-values, and r_a-structure for 4-chlorobutenyne.[a]

Parameters[b]		*D*-Values	*l*-Values	r_a-Structure[c]
C−H	2,5	− 0.0216	0.075	1.070(7)
	1,6	− 0.0209	0.074	1.070(7)
	1,7	− 0.0211	0.074	1.070(7)
C≡C	3,4	− 0.0050	0.036	1.204(2)
C=C	1,2	− 0.0058	0.041	1.326(3)
C−C	2,3	− 0.0097	0.048	1.417(2)
C−Cl	4,8	− 0.0123	0.042	1.635(1)
C⋯C	2,4	− 0.0058	0.051	2.621(2)
	1,3	− 0.0089	0.065	2.435(3)
	1,4	− 0.0047	0.085	3.553(4)
C⋯Cl	3,8	− 0.0066	0.046	2.838(2)
	2,8	+ 0.0001	0.056	4.255(2)
	1,8	+ 0.0023	0.113	5.134(4)
Cl⋯H	8,5	+ 0.0003	0.147	4.773(7)
	8,6	+ 0.0068	0.231	5.047(8)
	8,7	− 0.0022	0.120	6.173(8)
C⋯H	1,5	− 0.0150	0.098	2.099(7)
	3,5	− 0.0229	0.108	2.081(7)
	4,5	− 0.0130	0.126	3.192(7)
	2,6	− 0.0154	0.097	2.099(7)
	3,6	− 0.0059	0.141	2.720(6)
	4,6	+ 0.0003	0.179	3.619(7)
	2,7	− 0.0151	0.097	2.099(7)
	3,7	− 0.0203	0.097	3.407(7)
	4,7	− 0.0137	0.104	4.569(8)
H⋯H	5,6	− 0.0281	0.119	3.057(13)
	5,7	− 0.0082	0.161	2.460(8)
	6,7	− 0.0342	0.122	1.815(11)
∠C=C−C		−	−	125.2(0.3)
∠C−C≡C		−	−	180.0
∠C≡C−Cl		−	−	180.0
∠C=C_1−H		−	−	122.0
C=C_2−H		−	−	122.0
∠R_w[d] (%)		−	−	9.98

[a] Correction terms (*D*-values), amplitudes (*l*-values) and distances (r_a) in Ångströms; angles in degrees. The r_a-structure gives the result of a r_a-refinement (no *D*-value correction) using the calculated *l*-values. [b,c,d] See corresponding comments under Table 4.

keeping these parameters fixed at 122.0°. In both models l_{C-H} and $l_{Cl\cdots H_8}$ were kept at the calculated values given in Table 3 as they refined to unreasonable values with large standard deviations, as was also the case for $l_{Cl\cdots H_8}$ [0.41(27) Å] when the CCH-angles were kept at 122.0°. The results of both refinements are given in Table 4. The differences between the experimental and theoretical intensities and radial distribution curves are given in Figs. 1

and 2, respectively, for the less restricted model (Table 4, II) and Table 5 comprises the elements of the error matrix from the corresponding least-squares refinement.

The r_a-values given in Table 4 were transformed to the corresponding r_α-values and the moments of inertia were calculated for the two models. The results are given in Table 4 together with those obtained from microwave data (r_z-values).[10] The uncertainty limits for the electron-diffraction values are probably at least 0.5 % as estimated from calculations based upon parameter values given increments according to their standard deviations.

DISCUSSION

The failure of the r_a-model to represent the data in a satisfactory manner was not surprising as the location of the heavy chlorine atom at the end of the rather flexible −C≡C-chain should suggest that large shrinkage effects would be encountered for the non-bonded interactions which are responsible for a major contribution to the scattered intensity. In fact, as calculated from the *D*-values used in this investigation, the shrinkage effects for the $C_3\cdots Cl$, $C_2\cdots Cl$, and $C_1\cdots Cl$ distances respectively were 0.010, 0.027, and 0.033 Å. A least-squares r_a-refinement would therefore result in a compromise yielding too short bond distances. The results of the geometrically consistent r_α-refinement should therefore be more reliable, although the correction terms applied originate from an assumed force field. The difference curve in Fig. 2 does not, however, suggest that any serious problems due to shrinkage effects are remaining and the good agreement between calculated and refined amplitudes of vibration is reassuring. On the other hand, the moments of inertia calculated from the electron-diffraction data are smaller than those obtained from the microwave data [10] (*cf.* Table 4), which may suggest that the shrinkage effect is somewhat underestimated. The differences are, however, probably not significant, at least not for the less restricted model. This model exhibits what we at first sight considered to be unreasonable values for the CCH-angles. However, the facts that it seems to conform better to the microwave moments of inertia and also gave amplitudes of

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

Parameters [b]		I $r_a{}^c$	l^c	II $r_a{}^c$	l^c
C−H	2,5⎫ 1,6⎬ 1,7⎭	1.086(7)	[0.075]	1.078(8)	[0.075]
C≡C	3,4	1.214(2)	0.038(4)′	1.213(2)	0.036(4)′
C=C	1,2	1.333(3)	0.043(4)′	1.332(3)	0.041(4)′
C−C	2,3	1.428(2)	0.050(4)′	1.429(2)	0.048(4)′
C−Cl	4,8	1.638(1)	0.038(1)	1.637(1)	0.039(3)
C···C	2,4	2.633(3)	0.060(6)	2.632(3)	0.054(6)
	1,3	2.438(6)	0.069(6)	2.447(6)	0.064(6)
	1,4	3.557(8)	0.090(8)	3.558(8)	0.091(8)
C···Cl	3,8	2.840(2)	0.047(3)	2.838(2)	0.047(3)
	2,8	4.251(2)	0.058(3)	4.250(2)	0.058(3)
	1,8	5.133(5)	0.105(4)	5.135(5)	0.104(5)
Cl···H	8,5	4.762(8)	[0.147]	4.861(36)	0.144(48)
	8,6	5.046(10)	[0.231]	5.142(47)	[0.231]
	8,7	6.169(9)	0.137(33)	6.181(41)	0.136(33)
∠C=C−C		124.4(0.6)		125.3(0.6)	
∠C≡C−C		179.7(1.9)		181.0(1.9)	
∠C≡C−Cl		182.1(2.6)		182.9(2.6)	
∠C=C$_1$−H		[122.0]		126.9(2.7)	
∠C=C$_2$−H		[122.0]		114.6(2.6)	
$R_w{}^d$ (%)		8.51		8.05	
$I_a{}^e$ (−)[10]		11.5		11.5	
I_b (358.49)		356.2		357.3	
I_c (370.60)		367.7		368.8	

[a] Results of r_α-refinements (the distances given are r_a-values). Different restrictions are imposed on the two models as indicated by the brackets. 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_{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. Primed amplitudes are refined in groups. [d] Agreement factor $R_w = [\sum w_i \Delta_i{}^2 / \sum w_i I_i{}^2(\text{obs})]^{\frac{1}{2}}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{th})$. [e] Moments of inertia ($r_\alpha$values); parenthesized values are microwave results (r_z-values). See text for estimates of uncertainties.

vibration in closer agreement with the calculated ones, gives it more credibility than the electron diffraction data alone would have done. In particular we would like to point out that the problems with the Cl···H$_5$ amplitude of vibration suggested that the position of the H$_5$-atom was wrong when the C=C−H$_5$ = 122.0° was assumed, while it refined to a value close to the calculated one when this angle was included in the refinement. We will therefore choose the less restricted model to represent the final structure of 4-chlorobutenyne (Table 4, II). Apart from the location of the hydrogen atoms this has otherwise only minor consequences for the molecular structure as the other structural parameters do not differ significantly in the two models.

The C(sp)−Cl bond in 4-chlorobutenyne is found to be 1.637(2) Å. The parenthesized value corresponds to 2σ where σ is corrected for systematic uncertainties. This bond, as well as the triplebond of 1.213(5) Å, is in agreement with the corresponding bond in *tert*-butylchloroacetylene, $(CH_3)_3C−C≡C−Cl$ [1.637(5) and 1.210(5) Å].[11] The C≡C bonds in acetylene and butenyne are 1.212(1) Å and 1.213(1) Å, respectively, which indicate that chlorine substitution does not affect this bond significantly contrary to what seems to be the case for the C(sp^2) = C(sp^2) bond.[12]

The carbon skeleton found for 4-chlorobutenyne is compared to those of the three other chlorobutenynes [2,3] and the unsubstituted hydrocarbon [13] in Table 6. The acetylene chain in

Table 5. Correlation matrix for parameters of 4-chlorobutenyne. (Model II, Table 4).

$r_{C\equiv C}$	r_{C-C}	$r_{C=C}$	$\angle C=C-C$	$\angle C\equiv C-C$	r_{C-Cl}	$\angle C\equiv C-Cl$	r_{C-H}	$\angle C=C_2-H$	$\angle C=C_1-H$	l_{C-C}
1.0										
−0.22	1.0									
0.54	−0.11	1.0								
−0.02	0.02	−0.34	1.0							
0.43	0.16	0.09	0.62	1.0						
−0.37	0.04	−0.13	−0.06	0.01	1.0					
0.50	0.15	0.19	0.28	0.87	0.09	1.0				
0.52	−0.11	0.42	−0.05	0.17	−0.15	0.22	1.0			
0.05	−0.05	−0.03	−0.24	−0.02	0.04	−0.04	0.01	1.0		
−0.15	0.13	−0.23	0.32	0.30	−0.07	0.13	−0.35	0.26	1.0	
0.25	−0.26	0.43	−0.16	0.04	0.19	0.13	0.21	−0.01	−0.24	1.0
0.20	−0.16	0.13	−0.26	−0.22	0.04	−0.16	0.11	0.09	−0.27	0.15
0.00	0.04	0.00	0.09	0.10	0.02	0.07	0.04	−0.01	0.12	0.14
0.09	−0.09	0.12	−0.19	−0.13	0.08	−0.07	0.04	0.05	−0.25	0.14
−0.05	−0.01	−0.05	−0.02	−0.09	−0.19	−0.13	−0.25	−0.05	0.02	−0.05
−0.13	−0.03	0.02	−0.08	−0.10	−0.01	−0.09	−0.19	−0.03	−0.04	0.09
−0.06	0.05	0.00	−0.01	−0.04	−0.09	−0.07	−0.17	−0.04	0.02	0.04
−0.03	0.04	0.07	−0.07	−0.05	−0.01	−0.04	−0.02	−0.01	−0.10	0.05
−0.07	0.02	0.03	−0.08	−0.13	0.08	−0.15	0.07	−0.01	−0.13	0.05
−0.09	0.01	−0.04	0.01	−0.05	0.05	−0.09	−0.03	−0.06	0.01	0.01
−0.27	0.01	−0.07	−0.07	−0.14	0.09	−0.14	−0.40	0.04	0.07	0.03
−0.01	0.11	0.06	−0.03	−0.02	−0.20	−0.03	−0.22	−0.11	−0.04	0.06

Table 5. Continued.

$l_{C_3C_4}$	$l_{C_1C_4}$	$l_{C_1C_3}$	l_{C_3Cl}	l_{C_2Cl}	l_{C_4Cl}	l_{ClH_5}	l_{ClH_6}	l_{ClH_7}	Scales 48 cm	20 cm
1.0										
−0.04	1.0									
0.54	−0.07	1.0								
−0.03	0.04	0.12	1.0							
0.09	0.03	0.08	0.51	1.0						
−0.02	0.05	0.06	0.47	0.36	1.0					
0.03	0.04	0.02	0.26	0.18	0.20	1.0				
0.07	0.01	−0.02	0.03	0.02	0.02	0.58	1.0			
0.00	0.01	−0.03	0.06	0.06	0.04	−0.04	−0.02	1.0		
−0.04	0.05	0.06	0.41	0.33	0.32	0.17	−0.02	0.04	1.0	
−0.02	0.05	0.13	0.78	0.60	0.58	0.29	0.02	0.07	0.38	1.0

Table 6. The carbon skeleton in butenyne and chlorobutenynes.[a]

	C=C	C−C	C≡C	$\angle C=C-C$	$\angle C\equiv C\cdots C$
Butenyne [13]	1.344(4)	1.434(3)	1.215(3)	123.1(0.5)	177.9(1.2)
cis-1-Chlorobytenyne [2]	1.345(7)	1.426(6)	1.212(6)	123.9(0.6)	178.0(2.2)
trans-1-Chlorobytenyne [2]	1.356(7)	1.436(6)	1.220(8)	120.7(1.0)	180.2(2.4)
2-Chlorobutenyne [3]	1.340(5)	1.422(5)	1.220(6)	124.7(0.5)	177.0(5.8)
4-Chlorobutenyne [b]	1.332(7)	1.429(5)	1.213(5)	125.2(1.2)	181.0(3.8)

[a] Distances, r_a, in Å; angles in degrees. Parenthesized values correspond to 2σ where systematic uncertainties are included. [b] This work.

butenyne appears to be slightly bent. The determination of the $C-C\equiv C$ angle in the chlorobutenynes are associated with large standard deviations which makes it impossible to determine small deviations from linearity, and *cis*-chlorobutenyne seems to be the only chlorobutenyne where a similar trend is observed. The variations of the carbon skeletons in the five butenynes considered are small. The only systematic trend apparent to us is that the average carbon-carbon bond length is longer and the $C=C-C$ angle smaller in *trans*-chlorobutenyne than in the other chlorobutenynes, while the corresponding values for butenyne are intermediate to these.

The chlorine atom should interact with the rest of the molecule both by the inductive effect and by the competing resonance effect as one lone pair of the chlorine atom will participate in the π-electron delocalization in the conjugated system. We can, however, see no obvious ways to relate the structures of the carbon skeletons in the five butenynes to such effects. For example, no systematic lengthening of the $C=C$ bond as compared to butenyne is observed in the three pertinent chlorobutenynes, contrary to what is observed in chloro-substituted ethylenes.[12] A similar lengthening of the $C=C$ bond in ethylenes is, however, also observed by methyl substitution.[14] This suggests that this effect could be rationalized by considering non-bonded repulsions rather than in terms of inductive and resonance effects, which also seems to be consistent with the apparent invariance toward chlorine substitution of the $C\equiv C$ bond. We feel that the observed variations of the structural parameters for the carbon skeletons in the five butenynes considered are too small to be a subject for extensive discussions about their origins. However, the previous arguments and the notion that these parameters seem to adjust in such a manner as to give $C\cdots C$ and $C\cdots Cl$ non-bonded interactions across one valence angle in the ethylenic groups in narrow ranges (2.42 – 2.45 Å and 2.67 – 2.70 Å, respectively) suggest that non-bonded repulsions should be included in any such discussion.

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