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1-CHLORO-1-(TRICHLOROVINYL)CYCLOPROPANE

MOLECULAR STRUCTURE AND CONFORMATION IN THE GASEOUS PHASE AS DETERMINED BY ELECTRON DIFFRACTION

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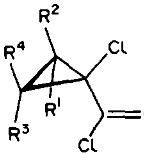
Abstract—A gas phase electron diffraction investigation of 1-chloro-1-(trichlorovinyl)cyclopropane at 65° showed the existence of one conformer having a perpendicular arrangement of the cyclopropyl- and the trichlorovinylgroup, with torsional angle $\tau = 91(3)°$ relative to $\tau = 180°$ for the antiperiplanar conformer (=CCl—CCl *anti* arrangement). Both the experimental data and a molecular mechanics calculation indicate the lower barrier toward the antiperiplanar form, less than 40 kJ · mol^{-1}. The second barrier was by molecular mechanics calculated to 60 kJ · mol^{-1}.

1-Chloro-1-(trichlorovinyl)cyclopropanes (**1**) are readily accessible by addition of thermally ringopened tetrachlorocyclopropene to olefins.[1] Although the correspondingly substituted cyclopropane carboxylic acid **2a** very much resembles the acid part in the highly potent pyrethroid insecticide Permethrin® **3b**, *m*-phenoxybenzyl esters **2b** showed no insecticidal activity whatsoever.



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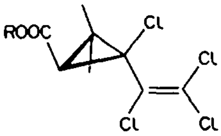

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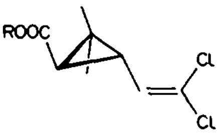

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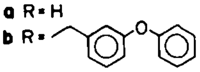

Temperature dependent ^1H- and ^{13}C-NMR spectra of **1** (R^1–R^4 = Me)[2] and **2** (R = Me)[1b,c] revealed torsional barriers $\Delta G^{\neq} = 78$ and 74 kJ · mol^{-1}, respectively, for the rotation around the central single bond. It is conceivable that the lack of insecticidal activity is in some way connected with this unusually high torsional barrier[2] and/or a difference in conformational behaviour of **1**/**2** *vs* **3**. In fact, the acid **2a** was found to crystallize as a single synclinal (sc) conformer with a dihedral angle of 88°,[1b,c] while for unsubstituted vinylcyclopropane (VCP) the antiperiplanar (ap) conformer is favoured over the synclinal—at least in the gaseous and liquid phases—by 4.6 kJ · mol^{-1}.[3,4] Although one can foresee that the serious non-bonded interactions between 1,3-positioned chlorines as well as between a chlorine and the R^1, R^3 substituents would strongly disfavour an antiperiplanar conformation (Cl^3 and Cl^4, Fig. 1, positioned *anti* to each other, torsional angle $\tau = 180°$) and also a normal synclinal conformer (Cl^3 and Cl^4 positioned *gauche* to each other, $\tau = 60°$) in any of the 1-chloro-1-(trichlorovinyl)cyclopropane derivatives **1**/**2**, it was not obvious, whether these derivatives would have a threefold torsional potential curve with a minimum for the ap form. We therefore undertook an electron diffraction structural investigation of **1** (R^1, R^2, R^3, R^4 = H),[7] hereafter denoted as CTCVCP, in the gaseous phase.

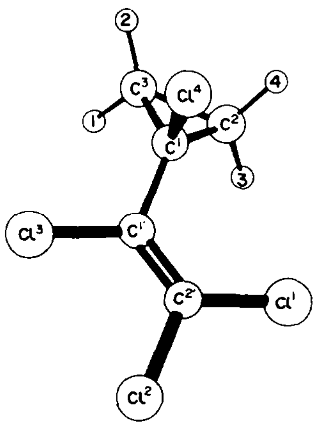

Fig. 1. 1-Chloro-1-(trichlorovinyl)cyclopropane. Atomic numbering. Minimum energy conformation is shown.

EXPERIMENTAL AND DATA REDUCTION

The sample of CTCVCP[1,7] was investigated at a nozzle temp of 65°. Data were recorded with the Balzer Eldigraph KDG-2[8,9] for nozzle-to-plate distances of 50 and 25 cm. The electron wavelength was calibrated against benzene.[10] Electron diffraction photographs were recorded on Kodak Electron Image plates and optical densities were measured with a Joyce-Loebl densitometer. Four and five plates were selected for analysis from the long and the short camera distances, respectively. The data were reduced in the usual way[11,12] yielding one averaged intensity curve for each camera distance in the form $sI_m(s)$. For the calculation of electron scattering amplitudes and phase shifts[11] Hartree–Fock atomic potentials[13] were used for C and Cl, while molecular bonded potentials were used for H.[14]

STRUCTURE AND CONFORMATION

Vibrational quantities were calculated from a valence force field whose force constants were transferred from 3,3-difluoro-1,1,2-trichloro-1-propene,[15] cyclopropane[16] and (chloromethyl) cyclopropane.[12] The calculated frequencies associated with the cyclopropyl group in the molecule appeared to be reasonable in comparison with those of other substituted cyclopropanes.[17,18] Among the calculated frequencies of the CCl_2=CCl— group only one frequency was considerably dependent on the value of any interaction force constant. With the exception of this particular frequency the calculated frequencies deviated from an observed set of frequencies[2] by an average of 16 cm^{-1} (see Table 1).

In order to test for reasonable conformations and barrier heights of CTCVCP, molecular mechanics (MM) calculations were carried out. The MM calculations relied on the use of non-bonded potential energy functions described as Morse curves[19] with parameters derived for related molecules.[20] According to these calculations the conformation of minimum energy has a torsional angle of 110° with a barrier of 8 kJ · mol^{-1} at $\tau = 180°$ (Fig. 2). The calculations gave another local energy minimum at $\tau = 0$, but this was about 50 kJ · mol^{-1} higher than that at $\tau = 110°$. The second barrier had a maximum of about 60 kJ · mol^{-1} at $\tau = 30°$.

Table 1. 1-Chloro-1-(trichlorovinyl)cyclopropane: observed frequencies (ref. 2), calculated frequencies[a] (cm^{-1}) and an approximate description

Obs.[b]	Calc.	Description[c]
3100[d]	3099	asym. str. CH_2
	3093	asym. str. CH_2
	3056	sym. str. CH_2
3018	3025	sym. str. CH_2
1588	1605	str. C=C
1451	1460	sci. CH_2
1420	1424	sci. CH_2
1340	1328	def. ring
1226[d]	1251	str. =C—C
1173	1160	asym. rock CH_2
1066[d]	976[e]	asym. tw. CH_2
1045[d]	1059	asym. wag CH_2
1020[d]	1023	sym. wag CH_2
951	979	def. ring
940[d]	953	def. ring
914	879	sym. rock CH_2
879	838	str. =C—Cl
800	—[f]	str. =C—Cl
764[d]	779	sym. tw. CH_2
650	683	bend =C—C—C
581	574	bend C=C—C
469	412	str. —C—Cl
440	397	str. =C—Cl
388	388	bend Cl—C—C
367	345	o.o.p. =CCl_2
311	303	bend Cl—C—C
273	271	bend =C—C—C
245	243	bend C=C—Cl
210	182	bend C=C—Cl
166	151	o.o.p. =CCl
150	109	bend C=C—Cl
89	87	tors. C=C
—	41	tors. =C—C

[a] Calculated with a valence force field directly combined from refs 12, 15 and 16, except for the =C—C torsional force constant value of 0.10 (see text).

[b] Raman data except where noted.

[c] The description is highly tentative, since most of the vibrational modes are highly mixed.

[d] Infrared observations.

[e] This particular frequency was also calculated too low for another cyclopropyl ring by use of the corresponding force field, see ref. 12.

[f] The calculation of this particular frequency is very sensitive to the value of the interaction force constant =C—Cl/C—Cl, a value of 1.5 mdyn · rad^{-1} giving 800 cm^{-1}.

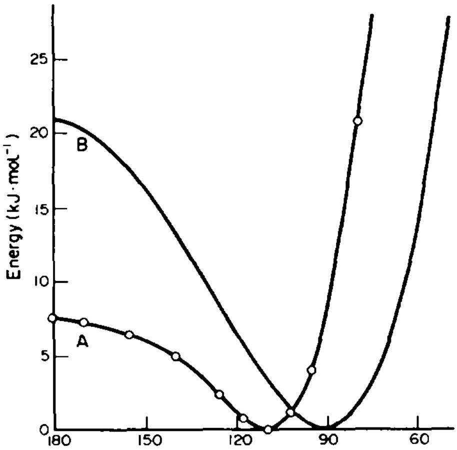

Fig. 2. 1-Chloro-1-(trichlorovinyl)cyclopropane. Torsional potential energy curves as calculated by a molecular mechanics model (A) and as obtained from the electron diffraction data (B) by use of the model $V(\tau) = V_0(1 - 2(\tau/\tau_0)^2 + (\tau/\tau_0)^4)$, $V_0 = 21$ kJ · mol^{-1} with $\tau_0 = 91.0°$.

The least squares refinements were carried out on intensity curves in the form $sI_m(s)$. A unit weight matrix was used. Geometrical parameters were calculated from the geometry consistent r_α-values.[21] The experimentally obtained radial distribution (RD) curve is shown in Fig. 3. Preliminary calculated RD curves, using geometry parameters from related molecules,[3,22] showed that a mixture of the conformers with $\tau = 180°$ (with an in-plane 1,3-dichloro propene-like eclipsing positioning of the atoms) and $\tau = 60°$ could not reproduce the experimental curve. The average torsional angle turned out to be close to 90°.

Because of the large number of geometrical parameters it was desirable to maintain all vibrational amplitudes (l) at calculated values during the least

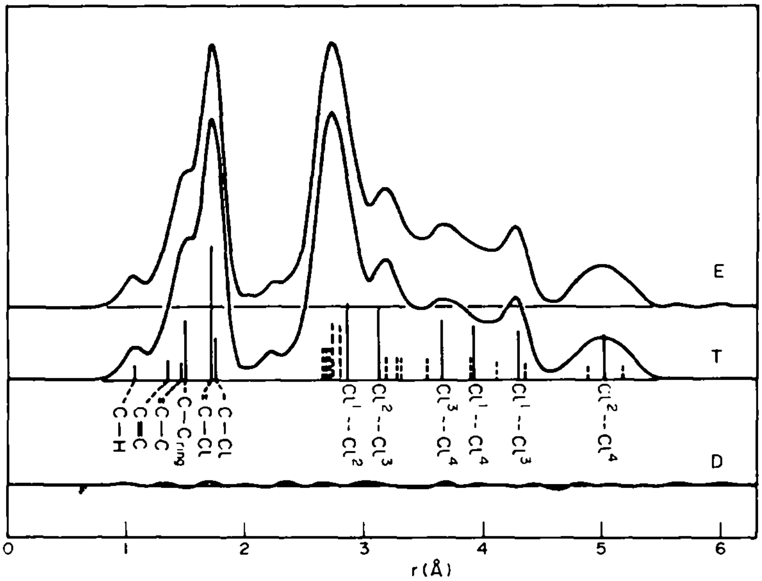

Fig. 3. 1-Chloro-1-(trichlorovinyl)cyclopropane. Radial distribution curves as Fourier transforms of the intensity curves in Fig. 4, using a modification function $(f'_{Cl}(s) \cdot f'_{C}(s))^{-1}$, theoretical data for $s < 2.0$ Å and $B = 0.002$ Å^2. The vertical lines show the most important distances (height proportional to weight of distance). Dotted lines refer to Cl..C distances. All curves are on the same scale.

squares refinement. To avoid uncertainty in the vibrational quantities due to dependency on the torsional force constant, a dynamic model simulating the torsional movement by the use of pseudo-conformers was introduced. Accordingly, the torsional movement was excluded in the calculation of vibrational quantities. Such l_{ij}'s corresponding to $\tau = 90°$ are listed in Table 2.

Some constraints had to be made among the geometrical parameters. Equal values were used within each of the following groups of parameters: $r\,(\mathrm{C{-}C})_{\mathrm{ring}}$, $r(\mathrm{C{-}H})$, $\angle$ C—C—H, $\angle$ Cl—C—$\mathrm{C_{ring}}$, $\angle$ C—C—$\mathrm{C_{ring}}$, and $r(\mathrm{{=}C{-}Cl})$ (see Fig. 1 for the molecular model). The $\mathrm{CCl_2{=}CCl{-}C}$ fragment was assumed to be planar. The C=C bond length could not be refined together with the other geometrical parameters and was therefore set equal to the value found in perchlorodivinylacetylene.[22] The effect of the latter constraint was tested, but only the C=C—Cl(CCl) angle changed noticably with a change in $r(\mathrm{C{=}C})$, a variation in $r(\mathrm{C{=}C})$ of 0.02 Å altering $\angle$ C=C—Cl(CCl) by 1.5°. Simultaneous refinement of the —C—Cl and =C—Cl distances was possible, suggesting a difference of 0.03 Å between the two

Table 2. 1-Chloro-1-(trichlorovinyl)cyclopropane: the most important distances and root mean square amplitudes of vibration (in Å) calculated without contribution from the torsional movement

Distance	r_a	l	Distance	r_a	l
C—H	1.06	0.077	$Cl^2..C^1$	4.11	0.060
C=C	1.35	0.045	$Cl^1..C^3$	4.37	0.122
=C—C	1.47	0.049	$Cl^3..C^2$	4.88	0.121
$\mathrm{C{-}C_{ring}}$	1.52	0.051	$Cl^2..C^3$	5.18	0.075
=C—Cl	1.73	0.052	$C^1..C^{2'}$	2.51	0.057
—C—Cl	1.75	0.052	$C^{2,3}..C^{1'}$	2.59	0.074
$Cl^1..Cl^2$	2.88	0.065	$C^2..C^{2'}$	3.24	0.113
$Cl^2..Cl^3$	3.12	0.104	$C^3..C^{2'}$	3.71	0.080
$Cl^3..Cl^4$	3.65	0.110	$Cl^4..H^{2,4}$	2.82	0.156
$Cl^1..Cl^4$	3.91	0.117	$Cl^1..H^3$	3.01	0.235
$Cl^1..Cl^3$	4.30	0.058	$Cl^3..H^1$	3.03	0.211
$Cl^2..Cl^4$	5.01	0.119	$Cl^4..H^{1,3}$	3.68	0.117
$Cl^3..C^{2'}$	2.65	0.054	$Cl^1..H^4$	3.71	0.254
$Cl^4..C^{1'}$	2.67	0.055	$Cl^3..H^2$	3.94	0.191
$Cl^3..C^1$	2.70	0.071	$Cl^3..H^3$	4.11	0.161
$Cl^{1,2}..C^{1'}$	2.72	0.055	$Cl^2..H^3$	4.58	0.225
$Cl^4..C^{2,3}$	2.78	0.075	$Cl^1..H^1$	4.73	0.164
$Cl^1..C^1$	3.18	0.099	$Cl^3..H^4$	4.81	0.123
$Cl^3..C^3$	3.26	0.132	$Cl^2..H^1$	5.09	0.210
$Cl^1..C^2$	3.30	0.175	$Cl^1..H^2$	5.21	0.155
$Cl^4..C^{2'}$	3.51	0.091	$Cl^2..H^4$	5.77	0.168
$Cl^3..C^2$	3.91	0.086	$Cl^2..H^2$	6.11	0.125

Table 3. 1-Chloro-1-(trichlorovinyl)cyclopropane. Structural parameters at 65° obtained for a pseudoconformational model around $\tau_0 = 91°$, the position of minimum energy[a]

No.	Parameter	$r_a/\angle_\alpha$ I	$r_a/\angle_\alpha$ II
1	$\langle r(\mathrm{C{-}C})_{\mathrm{ring}}\rangle$	1.522(8)[b]	1.518(11)
2	$r(\mathrm{{=}C{-}C})$	1.457(18)	1.473(21)
3	$r(\mathrm{C{=}C})$	1.353[c]	1.353[c]
4	$\langle r(\mathrm{{=}C{-}Cl})\rangle$	1.733(9)	1.727(7)
5	$r(\mathrm{{-}C{-}Cl})$	1.735(27)	1.752(23)
6	$\langle r(\mathrm{{-}C{-}H})\rangle$	1.066(67)	1.060(72)
7	$\angle\,\mathrm{C{=}C{-}C}$	124.6(1.0)	126.4(1.4)
8	$\angle\,\mathrm{C{=}C{-}Cl^{1d}}$	121.4(0.7)	123.5(0.3)
9	$\angle\,\mathrm{C{=}C{-}Cl^{2d}}$	125.7(0.9)	
10	$\angle\,\mathrm{C{=}C{-}Cl^{3d}}$	117.9(1.0)	117.6(0.9)
11	$\langle\angle\,\mathrm{C{-}C{-}C_{ring}}\rangle$	121.1(1.1)	120.9(1.2)
12	$\langle\angle\,\mathrm{Cl{-}C{-}C_{ring}}\rangle$	116.1(1.0)	116.8(1.0)
13	$\langle\angle\,\mathrm{C{-}C{-}H}\rangle$	117.3(3.0)	122.0(4.2)
14	τ_0	91.0(2.6)	89.5(2.8)
	$R^{\mathrm{lc}}/R^{\mathrm{sc}}$ [e]	3.5/13.2	6.4/13.4

Model I: three distinct C=C—Cl angles. Model II: C=C—Cl assumed to be equal.

[a] The pseudoconformational distribution is described by $V(\tau) = V_0(1-2(\tau/\tau_0)^2+(\tau/\tau_0)^4)$, where $V_0 = 21(16)\ \mathrm{kJ \cdot mol^{-1}}$.

[b] Results given in Å and deg., for type of error limit see text.

[c] Value from ref. 23.

[d] Atomic numbering in Fig. 1.

[e] lc and sc denote long and short camera distance, respectively; *R*-factor given in %.

distances, $r(\mathrm{{-}C{-}Cl}) > r(\mathrm{{=}C{-}Cl})$. When the difference was kept at a larger value or when $r(\mathrm{{-}C{-}Cl}) \geq 1.76$ Å, a good fit between theoretical and observed data could be obtained only with unreasonable values of $l(\mathrm{C{-}Cl})$. The three C=C—Cl angles could be refined simultaneously, resulting in a better *R*-factor than when the C=C—Cl(CCl$_2$) angles were restricted to equal values.

In the dynamic models pseudoconformers were distributed at intervals of $\Delta\tau = 12.5°$. A gaussian function described the distribution quite well. However, the RD curve suggested a slightly asymmetric distribution around the position of minimum energy, $\tau = \tau_0$, with a lower barrier towards increasing τ-values. Therefore, a function of the form $V(\tau) = V_0(1-2(\tau/\tau_0)^2+(\tau/\tau_0)^4)^{23}$ was used to describe the potential energy distribution. Such an approach was successful in obtaining a better RD curve, but the value of $V_0 = 21(16)\ \mathrm{kJ \cdot mol^{-1}}$, the barrier at $\tau = 180°$, came out with a high degree of uncertainty, while the position of the energy minimum $\tau_0 = 91.0(2.6)°$ seemed to be well determined.

RESULTS AND DISCUSSION

The geometrical parameters of CTCVCP (**1a**) resulting from the least squares refinements are listed in

Table 4. 1-Chloro-1-(trichlorovinyl)cyclopropane: correlation matrix for the geometrical parameters

No.	1	2	4	5	6	7	8	9	10	11	12	13	14
2	0.03												
4	0.25	0.11											
5	0.33	0.00	−0.73										
6	0.72	0.28	0.19	0.41									
7	0.24	0.07	0.08	0.11	0.16								
8	0.12	0.14	−0.40	0.48	0.22	−0.09							
9	0.00	−0.19	0.77	−0.73	−0.12	0.05	0.80						
10	0.16	0.13	−0.73	0.81	0.31	−0.05	0.47	−0.76					
11	0.10	0.03	−0.29	0.42	0.10	−0.28	0.38	−0.32	0.30				
12	−0.05	0.37	−0.38	0.33	0.15	0.17	0.36	−0.58	0.60	−0.20			
13	0.78	0.18	0.40	0.22	0.73	0.09	0.05	0.13	0.05	0.02	−0.11		
14	0.29	−0.13	0.31	−0.18	0.44	−0.38	−0.30	0.38	−0.13	0.22	−0.21	0.32	
σ_0	0.0020	0.0046	0.0022	0.0069	0.0022	0.34	0.23	0.31	0.33	0.38	0.33	1.4	0.88

σ_0 is standard deviation from the least square refinement in units of Å and deg. Parameter numbering corresponds to Table 2.

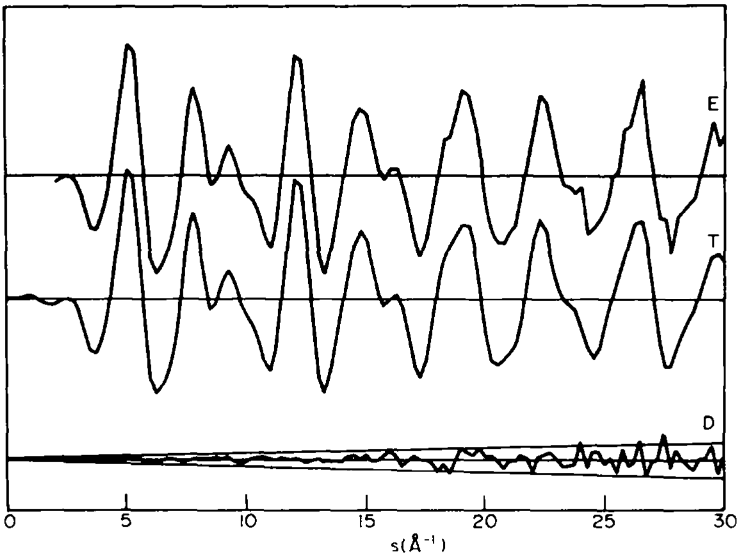

Fig. 4. 1-Chloro-1-(trichlorovinyl)cyclopropane. Intensity curves in the form $sI_m(s)$. Experimental curve (E) is the composite curve for all plates and camera distances. The theoretical curve (T) was calculated from parameters in Tables 2 and 3. The straight lines in D give the experimental uncertainties (3σ). All curves are on the same scale. $\Delta s = 0.25$ Å^{-1}.

Table 3. Alternative I gives the results from the refinement with three distinct C=C—Cl angles, while alternative II shows the results obtained when the C=C—Cl angles in the =CCl_2 group were assumed to be equal. The correlation matrix with respect to the geometrical parameters is presented in Table 4.

The theoretical intensity and RD curves (Figs 3 and 4) correspond to alternative I, and the pseudoconformational distribution is the nonsymmetric one described above.

The single conformation with minimum energy has a torsional angle $\tau = 91(3)°$ which differ by about 30° from that of the normal synclinal (*gauche*, $\tau = 60°$) form observed in vinylcyclopropane[4] and 2-cyclopropylpropene.[24] The fact that CTCVCP does not exist in the antiperiplanar form may not be surprising because of the serious 1,3-propene-like non-bonded interactions, but the unusual torsional angle is noteworthy. However, a similar conformation has earlier been observed for perchlorobutadiene,[25] for which the torsional angle differed about 20° from the synclinal form indicated in butadiene.[26] For perchlorobutadiene there was observed a Cl..Cl distance smaller than the sum of the van der Waals radii, as was also the case in the corresponding form of 2,3-dichloro-1-propene.[27] The shortest conformationally dependent Cl..Cl distance in CTCVCP (**1a**) was $r(\mathrm{Cl}^3..\mathrm{Cl}^4) = 3.65$ Å when $\tau = \tau_0$, thus barely avoiding van der Waals contact.

The torsional potential energy distribution function $V(\tau) = V_0(1-2(\tau/\tau_0)^2+(\tau/\tau_0)^4)$, with $\tau_0 = 91°$ and $V_0 = 21$ kJ·mol^{-1}, is shown in Fig. 2. For positions more than 20–30° away from the minimum this can only be taken as a qualitative picture. The actual experimentally determined barrier to rotation in CTCVCP is 33 kJ·mol^{-1}.[2] Within the very wide limits of uncertainty, however, the two values do agree nevertheless.

Qualitatively the trend of the above function is also

Table 5. Comparison between geometrical parameters of molecules related to 1-chloro-1-(trichlorovinyl)cyclopropane; all parameters obta from electron diffraction studies

Molecule		r(=C—Cl)	r(—C—Cl)	r(=C—C)	∠ C=C—C	∠ C=C^1—Cl	∠ C=C^2—Cl	Re
$\mathrm{CCl_2{=}CCl{-}Cl\overline{C{-}CH_2{-}C}H_2}$	r_a	1.727	1.752	1.473	126.4	123.5	117.5	this w
$\mathrm{CCl_2{=}CCl{-}CCl{=}CCl_2}$	r_a	1.715		1.483	123.4	122.5	122.0	2
$\mathrm{CCl_2{=}CCl{-}C{\equiv}C{-}CCl{=}CCl_2}$	r_a	1.715		1.415	123.6	123.6	120.5	2
$\mathrm{CH_2{=}CH{-}H\overline{C{-}CH_2{-}C}H_2}$	r_a			1.475	126.2			
$\mathrm{CH_2{=}C(CH_3){-}H\overline{C{-}CH_2{-}C}H_2}$	r_g			1.485	123.2			2
$\mathrm{CCl_2{=}CCl_2}$	r_a	1.718				122.4		3
$\mathrm{Cl_2\overline{C{-}CH_2{-}C}H_2}$	r_g		1.759					31
$\mathrm{CH_2{=}CCl{-}CH_2Cl}$	r_a	1.752	1.776	1.504	127.6		122.2	2
cis $\mathrm{CHCl{=}CH{-}CH_2Cl}$	r_g	1.726	1.806	1.508	124.6			

[a] Uncertainties are not given, since they are not comparable throughout the table.

suggested by molecular mechanics calculations, though the energy minimum was calculated at an angle *ca* 20° too large.

Although the rotational barrier for CTCVCP **1** (R^1–R^4 = H) is considerably lower than that for the dimethylsubstituted carboxylate **2** (R = Me), the torsional angles of the most stable conformers are essentially the same, even in the gaseous [**1**(R^1–R^4 = H)] and crystalline phases [**2**(R = Me)]. The perpendicular arrangement between the 1-chlorocyclopropyl and the trichlorovinyl groups in molecules of type **1** may be a reason for the ease with which they undergo a nucleophilic substitution with allylic rearrangement (S_N2') to yield highly strained methylenecyclopropane derivatives.[2,28]

The second (higher) barrier to internal rotation in CTCVCP could not be experimentally determined. Approximating the energy distribution in curve B (Fig. 2) around $\tau = 91°$ as Gaussian,[29] $V^* = 120(60)$ kJ$\cdot$mol^{-1} was calculated for the barrier. Thus, assuming the torsional movement around the =C—C bond to be harmonic, one can estimate the torsional force constant as 0.10(4) mdyn$\cdot$Å$\cdot$rad^{-2}, and the corresponding torsional frequency as 41(10) cm^{-1}.

Since it has been customary to report average C=C—Cl angles for the =CCl_2 group[22,25] the results from refinement II were used for comparison with other molecules in Table 5. The main features of bonded distances and bond angles compare well with related molecules. Discrepancies of as much as 0.02Å and 2° between models I and II (Table 3) together with some quite large uncertainties make it unreasonable to compare details.

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REFERENCES

[1a] W. Weber and A. de Meijere, *Angew. Chem.* **92**, 135 (1980); *Ibid. Int. Ed. Engl.* **19**, 138 (1980); [b] W. Weber and A. de Meijere, *Chem. Ber.* **117** (1984) in press; [c] W. Weber, Dissertation, Universität Göttingen (1980).

[2] Th. Liese, Dissertation, Universität Hamburg (1983).

[3] The torsional barrier of unsubstituted vinylcyclopropane is only in the order of 16 kJ$\cdot$mol^{-1}. Cf. L. A. Carreira, T. G. Towns and T. B. Malloy Jr., *J. Am. Chem. Soc.* **100**, 385 (1978); E. G. Codding and R. H. Schwendeman, *J. Mol. Spectrosc.* **49**, 226 (1974); G. R. DeMaré and M. R. Peterson, *J. Mol. Struct.* **89**, 213 (1982).

[4] A. de Meijere and W. Lüttke, *Tetrahedron* **25**, 2047 (1969); M. Trætteberg, unpublished results.

[5] G. R. DeMaré and J. S. Martin, *J. Am. Chem. Soc.* **88**, 5033 (1966); G. R. DeMaré and S. Lapaille, *Org. Magn. Reson.* **13**, 75 (1980); H. Günther, H. Klase and D. Wendisch, *Tetrahedron* **25**, 1531 (1969).

[6] Q. Shen, *J. Mol. Struct.* **75**, 75 (1981).

[7] Th. Liese, G. Splettstösser and A. de Meijere, *Tetrahedron Lett.* **23**, 3341 (1982).

[8] M. Zeil, J. Haase and L. Wegman, *Z. Instrumentenkd.* **74**, 84 (1966).

[9] O. Bastiansen, R. Graber and L. Wegman, *Balzers High Vacuum Rep.* **24**, 1 (1969).

[10] K. Tamagawa, I. Iijima and M. Kimura, *J. Mol. Struct.* **30**, 243 (1976).

[11] B. Andersen, H. M. Seip, T. G. Strand and R. Stølevik, *Acta Chem. Scand.* **23**, 3224 (1969).

[12] S. H. Schei, *Acta Chem. Scand.* **A37**, 15 (1983).

[13] T. G. Strand and R. A. Bonham, *J. Chem. Phys.* **40**, 1686 (1964).

[14] R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.* **42**, 3175 (1965).

[15] P. Klæboe, G. Nerland and S. H. Schei, *Spectrochim. Acta* **38A**, 1025 (1982).

[16] M. Spiekermann, D. Bougeard and B. Schrader, *J. Mol. Struct.* **60**, 55 (1980).

[17] V. F. Kalasinsky and C. J. Wurrey, *J. Raman Spectrosc.* **9**, 315 (1980).

[18] J. Maillots and V. Tabacik, *Spectrochim. Acta* **35A**, 1125 (1979).

[19] R. J. Abraham and R. Stølevik, *Chem. Phys. Lett.* **58**, 622 (1978).

[20] R. Stølevik and Ø. Thingstad, *J. Mol. Struct. Theochem.* **106**, 333 (1984).

[21] K. Kuchitsu and S. J. Cyvin, *Molecular Structures and Vibrations* (Edited by S. J. Cyvin), Chap. 12. Elsevier, Amsterdam (1982).

[22] A. Almenningen, E. Gogstad, K. Hagen, S. H. Schei, R. Stølevik, Ø. Thingstad and M. Trætteberg, *J. Mol. Struct.* **116**, 131 (1984).

[23] S. H. Schei, Q. Shen, R. F. Cunico and R. L. Hilderbrandt, *J. Mol. Struct.* **63**, 59 (1980).

[24] S. Konaka, H. Suga and M. Kimura, *J. Mol. Struct.* **98**, 133 (1983).

[25] G. Gundersen, *J. Am. Chem. Soc.* **97**, 6342 (1975).

[26] O. Bastiansen, K. Kveseth and H. Møllendal, *Topics in Current Chemistry*. Springer, Berlin (1979).

[27] Ø. Trongmo, Q. Shen, K. Hagen and R. Seip, *J. Mol. Struct.* **71**, 185 (1981).

[28] Th. Liese, G. Splettstösser and A. de Meijere, *Angew. Chem.* **94**, 799 (1982); *Ibid. Int. Ed. Engl.* **21**, 790 (1982); *Ibid.* Suppl. 1715 (1982).

[29] W. G. Fately, R. K. Harris, F. A. Miller and R. E. Witkowski, *Spectrochim. Acta* **21**, 231 (1965).

[30] T. G. Strand, *Acta Chem. Scand.* **21**, 2112 (1967).

[31] L. Hedberg, K. Hedberg and J. E. Boggs, *J. Chem. Phys.* **77**, 2996 (1982).