

# 1,1,2-Trichloro-3,3-difluoro-1-propene. Molecular Structure and Conformation as Determined by Gas Phase Electron Diffraction

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At 20 °C only the  $C_s$  conformer of 1,1,2-trichloro-3,3-difluoro-1-propene was found, although the possibility of a small amount of another form (*ca.* 5 %) could not be excluded. In terms of  $r_a$  distances and  $\angle_a$  angles the following structure was obtained:  $r(\text{C}=\text{C})=1.365(18)$  Å,  $r(\text{C}-\text{C})=1.509(19)$  Å,  $\langle r(\text{C}=\text{C}-\text{Cl}_1) \rangle = 1.713(4)$  Å ( $\langle \rangle$  denotes average),  $r(\text{C}-\text{F})=1.353(11)$  Å,  $\angle\text{C}=\text{C}-\text{C}=124.5(9)^\circ$ ,  $\angle\text{C}=\text{C}-\text{Cl}_1=123.3(6)^\circ$  ( $\text{Cl}_1$  is positioned *cis* to the  $\text{CHF}_2$  group and *trans* to  $\text{Cl}_3$ ),  $\angle\text{C}=\text{C}-\text{Cl}_2=121.8(6)^\circ$ ,  $\angle\text{C}=\text{C}-\text{Cl}_3=120.2(1.0)^\circ$ ,  $\angle\text{C}-\text{C}-\text{F}=111.0(1.2)^\circ$  and the root mean square torsional amplitude is  $10.5(3.2)^\circ$ . Error limits are given as  $2\sigma$ , where  $\sigma$  includes uncertainty due to correlation among observations and uncertainty in parameters used in the data reduction.

The title compound was recently investigated by vibrational spectroscopy,<sup>1</sup> and was found to exist as one single conformer, most likely the form having  $C_s$  symmetry (Fig. 1). Other molecules

having a trichlorovinyl group have been studied by electron diffraction in this laboratory,<sup>2,3</sup> and currently several halogen substituted propenes are being investigated.

*cis*-1-Chloro-3-fluoro-1-propene was found to have a conformation such that none of the 3-positioned atoms were eclipsing the double bond,<sup>4</sup> while an eclipsing of the  $\text{C}=\text{C}$  bond by a 3-positioned hydrogen takes place in *cis*-1,3-dichloro-propene.<sup>5</sup> The more heavily halogenation and the presence of two geminal fluorines in 1,1,2-trichloro-3,3-difluoro-1-propene (TCDFP) makes a  $C_s$  symmetric conformer likely for steric reasons. Such a form has no 3-fluoro-atom which eclipses the double bond and therefore no 1,3-dihalo in-plane arrangement, and both fluorines are in a staggered position relative to the 2-chloro atom. Thus, the twofold intention of the present investigation was to gain additional evidence for the  $C_s$  conformation and to obtain structural information.

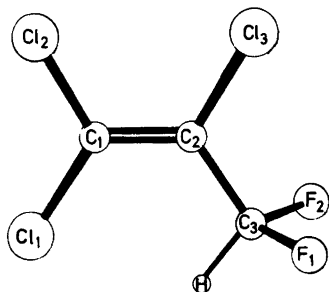


Fig. 1. 1,1,2-Trichloro-3,3-difluoro-1-propene. The conformer of symmetry  $C_s$  with atomic numbering.

## EXPERIMENTAL

A commercial sample of TCDFP from K & K was used. Infrared spectra were recorded and seemed to be identical to those obtained from the purified sample in Ref. 1. Therefore, no purification was carried out. Data were recorded with the Balzers Eldigraph KDG-2<sup>6,7</sup> at 20 °C nozzle temperature. The optical densities of the electron diffraction photographs, recorded on Kodak Electron Image plates, were measured by a Joyce Loebel densitometer. Five and four plates from the 25 and 50 cm (nozzle to plate distance) data, respectively, were selected for analysis. Calibra-

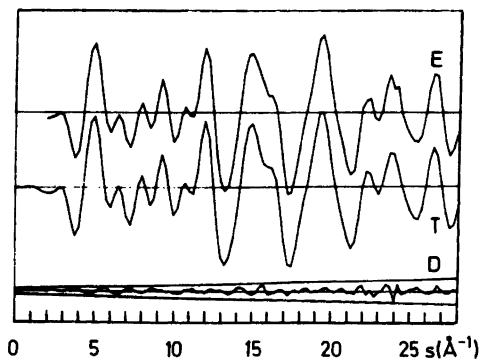


Fig. 2. 1,1,2-Trichloro-3,3-difluoro-1-propene. Intensity curves in the form  $sI_m(s)$ . Experimental curve (E) is the composite at all plates and camera distances. Theoretical curve (T) was calculated from parameters in Table 1. Difference curve (D) is  $E-T$ . All curves are on the same scale.  $\Delta s=0.25 \text{ \AA}^{-1}$ . The straight lines give the experimental uncertainty as three times standard deviation.

tion and data reduction were made as described earlier.<sup>8</sup>

### STRUCTURE ANALYSIS

Least squares refinements were carried out on intensity curves in the form  $sI_m(s)$ <sup>8</sup> (Fig. 2). A unit weight matrix was used. The geometrical structure was calculated from geometry consistent  $r_a$  parameters.<sup>9</sup> Vibrational quantities were calculated from the force field given in Ref. 1.

The structure was assumed planar around the C=C bond, the CHF<sub>2</sub> group assumed to have local C<sub>s</sub> symmetry and the =C-Cl bonds were refined as an average.  $r(\text{C-H})$  and  $\angle\text{C-C-H}$  had to be kept at assumed values.

Allowing for a mixture of two conformers did not indicate any second conformer in addition to the C<sub>s</sub> symmetric one. However, a small amount (ca. 5 %) of a form with F eclipsing the double bond could be included without significantly worsening the agreement between the experimental and theoretical intensity curves.

By keeping the vibrational amplitudes ( $l$ ) at calculated values, the best result was obtained when the torsional force constant,  $f_t$ , had a value lower than  $0.24 \text{ mdyn \AA rad}^{-2}$  as in Ref. 1. In the final refinement  $f_t=0.12 \text{ mdyn \AA rad}^{-2}$  was used, and a few vibrational amplitudes were allowed to

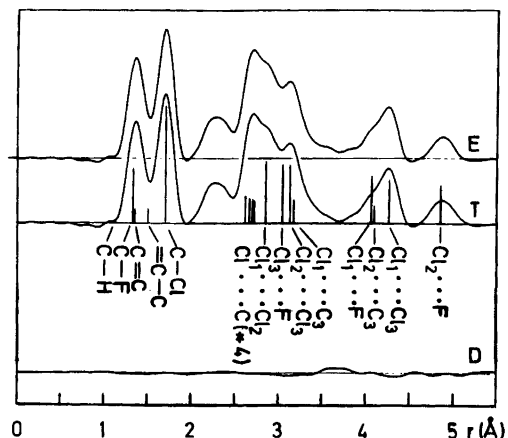


Fig. 3. 1,1,2-Trichloro-3,3-difluoro-1-propene. Radial distribution curves as Fourier transforms of the intensity curves in Fig. 2 after multiplication with  $[f'_{\text{Cl}}(s) \cdot f'_c(s)]^{-1}$ . Theoretical data are used for unobserved area  $s < 2.0 \text{ \AA}^{-1}$ .  $B=0.002 \text{ \AA}^2$ . The vertical lines show the most important distances, height being proportional to weight of distance.

refine. Despite several large correlation coefficients, good convergence was obtained.

### RESULTS AND DISCUSSION

Figs. 2 and 3 show the theoretical and experimental intensity and radial distribution curves. Geometrical parameters and vibrational amplitudes are listed in Table 1. The error estimates are  $2\sigma$ , where  $\sigma$  includes uncertainties due to correlation among observations, electron wavelength and other parameters used in the data reduction (8). The correlation coefficient matrix is given in Table 2.

The conformation of TCDFP is undoubtedly C<sub>s</sub>. The torsional movement around the C-C bond is quite small. Assuming this torsional motion to be harmonic and by using a model with pseudoconformers (excluding torsional contribution to the vibrational quantities) the root mean square torsional amplitude,  $\langle(\Delta\tau)^2\rangle^{1/2}$ , was found to be  $10.5(3.2)^\circ$ . The relation  $V=2RT/\langle(\Delta\tau)^2\rangle$ <sup>10</sup> then gives  $V^*=140(30) \text{ kJ} \cdot \text{mol}^{-1}$  (uncertainty corresponds to  $\sigma_0$ , standard deviation from the least squares refinement). Further,  $f_t=\frac{1}{2}V^*=0.12(3) \text{ mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$ . The corresponding

**Table 1.** 1,1,2-Trichloro-3,3-difluoro-1-propene. Geometrical and vibrational parameters ( $l$  s associated with bonded distances and non-bonded Cl...Cl, Cl...F and Cl...C distances) as found experimentally from the least squares refinements and calculated in the normal coordinate analysis, at 20 °C.  $r_a$  and  $l$  in Å,  $\angle_a$  in degrees and  $R$ -factor in %.

No.	Parameter	$r_a/\angle_a$	$R_{\text{calc.}}$	$l_{\text{ref.}}$
1	$r(\text{C}=\text{C})$	1.365(18) <sup>b</sup>	0.045	
2	$r(\text{C}-\text{C})$	1.509(19)	0.049	
3	$\langle r(\text{C}-\text{Cl}) \rangle^c$	1.713(4)	0.051	
4	$r(\text{C}-\text{F})$	1.353(11)	0.048	
5	$r(\text{C}-\text{H})$	1.090 <sup>d</sup>	0.078	
6	$\angle \text{C}=\text{C}-\text{C}$	124.5(.9)		
7	$\angle \text{C}=\text{C}-\text{Cl}_1$	123.3(.6)		
8	$\angle \text{C}=\text{C}-\text{Cl}_2$	121.8(.6)		
9	$\angle \text{C}=\text{C}-\text{Cl}_3$	120.2(1.0)		
10	$\angle \text{C}-\text{C}-\text{F}$	111.0(1.2)		
11	$\angle \text{C}-\text{C}-\text{H}$	109.5 <sup>d</sup>		
12	$p(\text{FCF})^e$	120.0(2.6)		
13	$\langle (\Delta\tau)^2 \rangle^{1/2}$ $R^{\text{lc}}/R^{\text{scg}}$	10.5(3.2) 6.5/7.8		
14	Cl <sub>1</sub> ...Cl <sub>2</sub>	2.885	0.064	0.058(4)
15	Cl <sub>2</sub> ...Cl <sub>3</sub>	3.126	0.103	0.106(7)
16	Cl <sub>1</sub> ...Cl <sub>3</sub>	4.293	0.063	0.060(3)
17	Cl <sub>3</sub> ...F	3.070	0.142	
18	Cl <sub>1</sub> ...F	4.080	0.164	
19	Cl <sub>2</sub> ...F	4.884	0.104	0.121(10)
20	Cl <sub>3</sub> ...C <sub>1</sub>	2.670	0.059	
21	Cl <sub>2</sub> ...C <sub>2</sub>	2.693	0.056	
22	Cl <sub>1</sub> ...C <sub>2</sub>	2.710	0.057	
23	Cl <sub>3</sub> ...C <sub>3</sub>	2.720	0.068	
24	Cl <sub>1</sub> ...C <sub>3</sub>	3.160	0.087	
25	Cl <sub>2</sub> ...C <sub>3</sub>	4.121	0.061	
26	F...F	2.192	0.061	
27	F...C <sub>2</sub>	2.356	0.064	
28	F...C <sub>1</sub>	3.440	0.098	
29	C <sub>1</sub> ...C <sub>3</sub>	2.541	0.060	

<sup>a</sup> Vibrational amplitudes calculated by using torsional force constant of 0.12 mdyn Å rad.<sup>-2</sup> <sup>b</sup> Definition of error limits, see text. <sup>c</sup>  $\langle \rangle$  denotes average. <sup>d</sup> Assumed value. <sup>e</sup> Angle between projections of the C-F bonds on a plane perpendicular to the =C-C bond. <sup>f</sup> Root mean square torsional amplitude at the actual temperature. <sup>g</sup> lc and sc denote long and short camera distance, respectively.

torsional frequency is 67 cm<sup>-1</sup>, which does not necessarily contradict the somewhat higher experimental value,<sup>1</sup> since no C-C torsional frequency was observed in the gaseous phase. The most interesting result within the trichlorovinyl group is the relative size of the C=C-Cl angles. The results indicate an increase in the order  $\angle \text{C}=\text{C}-\text{Cl}_3 < \angle \text{C}=\text{C}-\text{Cl}_2 < \angle \text{C}=\text{C}-\text{Cl}_1$ . Earlier works on similar molecules have mostly assumed the C=C-Cl angles of the =CCl<sub>2</sub> group to be identical.<sup>2,11,3</sup>

The C=C bond length are well within error limits not different from  $r(\text{C}=\text{C})$  in other heavily

chloro-substituted vinyl fragments, as are  $r(\text{C}-\text{Cl})$ .<sup>2,3,11,12</sup> Also the C-F bond has a length which compares well with earlier observations for corresponding geminal difluoro-substitution.<sup>13,14</sup> However,  $r(\text{C}=\text{C})$  and  $r(\text{C}-\text{F})$  have values very close to each other, and both parameters show large uncertainties. Especially the C=C distance was easily subject to changes resulting from small alterations in refinement conditions.

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Table 2. 1,1,2-Trichloro-3,3-difluoro-1-propene. Correlation matrix for the refined parameters (for numbering see Table 1), given as  $\rho \cdot 10^2$ . Standard deviation from least squares refinement given in Å and degrees.

No.	$\sigma_0$	1	2	3	4	6	7	8	9	10	12	13	14	15	16
1	0.0045														
2	0.0048	-72													
3	0.0007	-65	54												
4	0.0027	-90	79	63											
6	0.31	60	-50	-24	-54										
7	0.21	-18	18	8	13	27									
8	0.19	-31	7	35	30	-38	-79								
9	0.32	-81	68	38	80	-71	-7	35							
10	0.39	79	-83	-57	-82	66	9	-37	-79						
12	0.90	80	-73	-59	-83	68	12	-44	-78	94					
13	1.03	-45	46	42	58	-41	-24	52	64	-61	-61				
14	0.0013	-55	38	29	47	-17	22	8	38	-37	-39	13			
15	0.0036	-40	17	18	39	-42	-20	46	46	-28	-33	59	25		
16	0.0016	-7	-1	-2	0	-9	10	-11	-2	1	1	-21	3	-4	
19	0.0048	-2	7	7	7	0	5	-1	8	-4	-3	-4	0	10	-6

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