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MOLECULAR STRUCTURE AND CONFORMATION OF 2,3-DICHLORO-1-PROPENE AS DETERMINED BY GAS-PHASE ELECTRON DIFFRACTION

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ABSTRACT

The molecular structure and conformation of 2,3-dichloro-1-propene have been determined by gas-phase electron diffraction at nozzle temperatures of 24, 90 and 273°C. The molecules exist as a mixture of two conformers with the chlorine atoms *anti* (torsion angle $\angle\phi = 0°$) or *gauche* ($\angle\phi = 109°$) to each other and with the *anti* form the more stable. The composition (mole fraction) of the vapor with uncertainties estimated at 2σ was found to be 0.55 (0.08), 0.49 (0.08) and 0.41 (0.10) at 24, 90 and 273°, respectively. These values correspond to an energy difference with estimated standard deviation $\Delta E°$ = $E_g^0 - E_a^0 = 0.7 \pm 0.3$ kcal mol^{-1} and an entropy difference $\Delta S^0 = S_g^0 - S_a^0 = 0.6 \pm 0.9$ cal mol^{-1} K^{-1}. Some of the diffraction results, together with spectroscopic observations, permit the evaluation of an approximate torsional potential function of the form $2V = V_1 (1 - \cos\phi) + V_2 (1 - \cos 2\phi) + V_3 (1 - \cos 3\phi)$; the results are $V_1 = 4.4 \pm 0.5$, $V_2 = -2.9 \pm 0.5$ and $V_3 = 4.8 \pm 0.2$, all in kcal mol^{-1}. The results at 24°C for the distance (r_a) and angle ($\angle_\alpha$) parameters, with estimated uncertainties of 2σ, are: $r(C_{sp^2}-H)$ = 1.098(0.020)Å, $r(C_{sp^3}-H) = 1.103(0.020)$Å, $r(C=C) = 1.334(0.009)$Å, $r(C-C)$ = 1.504(0.013)Å, $r(C_{sp^2}-Cl) = 1.752(0.021)$Å, $r(C_{sp^3}-Cl) = 1.776(0.020)$Å, $\angle C-C=C$ = 127.6(1.1)°, $\angle C_{sp^3}-C_{sp^2}-Cl$ = 110.2(1.0), $\angle C_{sp^2}-C_{sp^3}-Cl$ = 113.1(1.2)°, $\angle H-C_{sp^3}-H$ = 109.5° (assumed), $\angle C=C-H$ = 120.0° (assumed) and $\angle\phi = 108.9(3.4)°$.

INTRODUCTION

Recently we have studied the molecular structures and conformations of a series of haloacetyl halides [1, 2] CH_2X-COY, and in these molecules observed a mixture of two conformers with the halogen atoms *anti* or *gauche* to each other. 2,3-Dihalo-1-propenes differ from the haloacetyl halides only in that they contain a carbon—carbon instead of a carbon—oxygen double bond. We have therefore started an investigation of a series of 2,3-dihalo-propenes, and in this article we report the results for 2,3-dichloro-1-propene (later called DCLP).

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The existence of rotational isomerism in DCLP was proposed as early as 1948 [3]. This observation has later been confirmed in a large number of spectroscopic works [4—11]. The conformers have been assumed to be *anti* and *gauche*, with the *gauche* form having the lowest energy in the solid and liquid phases, while *anti* has been reported to be the low-energy form in the gas phase.

An investigation of 2,3-difluoro-1-propene [12] showed this compound to be a mixture of *anti* and *gauche* in the gas phase, *anti* being 0.9 ± 0.1 kcal mol^{-1} more stable. In an electron diffraction study of 2-chloro-3-fluoro-1-propene [13] the same conformers were observed; here, the energy difference between *gauche* and *anti* was reported to be 0.42 ± 0.2 kcal mol^{-1}.

For DCLP no determinations of bond distances or bond angles have been published and the torsion angles of the conformers have only been estimated, but not accurately determined. As expected the electron diffraction experiment of DCLP revealed substantial amounts of two different forms (Fig. 1) present in the gas phase, and in order to determine energy and entropy differences between them, complete structure determinations were performed at three different temperatures.

EXPERIMENTAL AND DATA REDUCTION

A commercial sample of DCLP (>98%) was obtained from Aldrich Chemical Company, and was used without further purification. Electron diffraction photographs were made with the Balzers Eldigraph KDG-2 [14, 15] at nozzle temperatures of 24, 90 and 273°C, using a rotating sector with angular opening proportional to r^3 and Kodak Electron Image plates. The experimental conditions are summarized in a supplementary publication [16]. The electron wave length was determined by calibration against diffraction patterns of ZnO and benzene [17]. Reduction of the data was done in the usual way [18, 19], and a calculated background [20] was subtracted from the data for each plate. Composites of the experimental intensity curves after background subtraction (in the form $sI_m(s)$) are shown
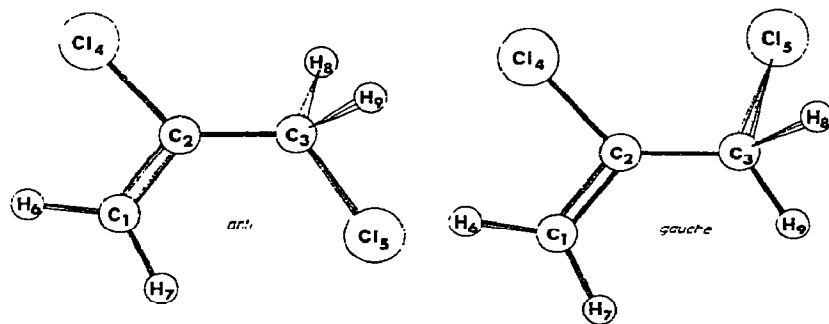

Fig. 1. Diagrams of the *anti* and *gauche* forms of 2,3-dichloro-1-propene with atomic numbering.

in Fig. 2 and the data are available as a supplementary publication [16]. The electron scattering amplitudes and phase shifts [21] were calculated analytically by a program originally written by Yates [22], using Hartree—Fock potentials [23] for C and Cl and molecular bonded potential for H [24].

STRUCTURE ANALYSIS

Radial distribution (RD) curves, calculated from the intensity curves of Fig. 2 are shown in Fig. 3. The origin of the various peaks is indicated by the vertical lines on the high temperature theoretical curve. Approximate values for the geometrical parameters were obtained from the experimental RD-curves, and from structures reported for related molecules [25]. The experimental RD-curves clearly showed the existence of more than one conformer. The area under the peak at 4.3 Å and (less obviously) at 3.1 Å decreased with increasing temperature, while the peak at 3.4—3.8 Å increased with increasing temperature. From the position of the temperature-sensitive peaks it was clear that the two forms present had the chlorine atoms *anti* or *gauche* to each other, and the relative area under the peaks corresponded to approximately equal amounts of these forms at 24°C.

Refinements of the structure were carried out by the method of least squares based on intensity curves [26] in the form $sI_m(s)$, using a unit weight matrix. The gaseous mixtures were assumed to consist of only *anti* and *gauche* conformers having the same structures except for torsion angle. Thus, in addition to a composition parameter the structure of DCLP can be described by thirteen geometrical parameters (the parameters used in our refinements are shown in Table 2) and forty amplitude parameters. One of these is δ, the root-mean-square amplitude of the torsional oscillation of the *anti* form.
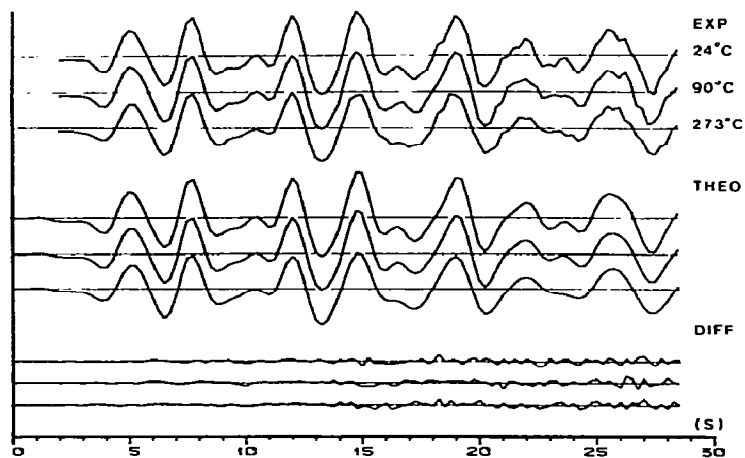

Fig. 2. Intensity curves for 2,3-dichloro-1-propene. The experimental curves are composites from several experiments; the theoretical curves were calculated from the parameter values of Table 2. All curves are on the same scale and are in the form $sI_m(s)$.
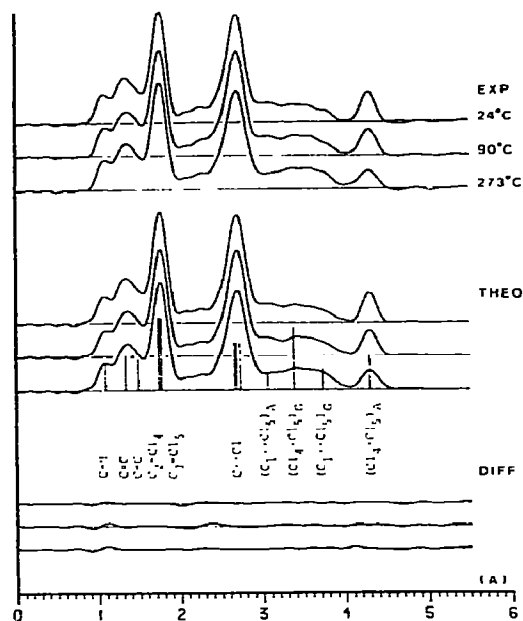
Fig. 3. Radial distribution curves for 2,3-dichloro-1-propene. The curves were calculated by Fourier transformation of the curves in Fig. 2 after multiplication by $z_C z_{Cl}/(A_C A_{Cl})$ with an artificial damping constant $B = 0.0020$ Å². Unobserved or uncertain experimental intensity data from the region $0 < s < 1.75$ were taken from theoretical curves. The vertical lines indicate the important interatomic distances in the final model; the lengths of the lines are proportional to the weights of the distances. All curves are on the same scale.

TABLE 1

Valence force constants for 2,3-dichloro-1-propene

	Anti	*Gauche*		*Anti*	*Gauche*
Stretching (mdyn Å⁻¹)			*Torsion* (mdyn Å)		
C_1—$H_{6,7}$	5.16	5.12	C=C	0.79	0.91
C_3—$H_{8,9}$	4.82	4.97	C—C	0.14	0.15
C=C	7.41	7.50			
C—C	5.66	5.80	*Out-of-plane*[a] (mdyn Å)		
C_2—Cl_4	3.14	3.30	$C_1 H_6 H_7 C_2$	0.36	0.38
C_3—Cl_5	3.10	3.10	$C_2 C_1 C_3 Cl_4$	0.22	0.33
Bending (mdyn Å)			*Stretch/stretch* (mdyn Å⁻¹)		
C=C—C	1.11	1.55	C—C/C—Cl	0.67	0.51
C_2—C_3—Cl_5	1.10	1.00	C—C/C=C	0.27	0.10
C_3—C_2—Cl_4	1.51	0.89			
C_2=C_1—$H_{6,7}$	0.82	0.67	*Bend/bend* (mdyn Å)		
H_6—C_1—H_7	0.42	0.50	C=C—C/C_1—C_2—Cl_4	0.51	0.29
Cl_5—C_3—$H_{8,9}$	0.60	0.45	C=C—C/C_3—C_2—Cl_4	0.51	0.29
H_8—C_3—H_9	0.53	0.49	C=C—C/C_2—C_3—Cl_5	0.35	0.34
C_1=C_2—Cl_4	1.30	1.30			
C_2—C_3—$H_{8,9}$	0.71	0.71	*Stretch/bend* (mdyn)		
			C—C/C_2—C_3—$H_{8,9}$	0.34	0.31
			C=C/C_2—C_1—$H_{6,7}$	−0.06	−0.06

[a]The first atom is the central atom.

Vibrational amplitudes and non-linear shrinkage correction parameters were calculated from the force field shown in Table 1. This force field was derived from the force field developed for 2-chloro-3-fluoro-1-propene [13] with the necessary modification for substitution of a fluorine with a chlorine atom. The calculated values were used for all those amplitudes of vibration that could not be refined in the least squares analysis. In earlier experiments carried out for chloroacetyl chloride [1] and oxalyl chloride [18] we have been able to determine δ (the r.m.s. amplitude for the torsional oscillation of the *anti* form) from the electron diffraction data alone by using a dynamic model [18]. For DCLP these refinements did not converge. From spectroscopy, however, the torsional frequency was known [8], and this made it possible to calculate values for δ at the three temperatures and these values were used in the final refinements.

Not all the geometrical parameters could be refined simultaneously, and $\angle H—C—H$, $\angle C=C—H$ and $\angle C_2—C_3—(H_8, H_9)$ (the angle between the plane $C_3H_8H_9$ and C_2C_3) were all kept constant at reasonable values. Several values were tried for the difference between $r(C_{sp^3}—H)$ and $r(C_{sp^2}—H)$ and a good fit was obtained with a value of 0.005 Å. In the final least squares analysis the composition parameter, nine geometrical parameters and seven amplitude parameters were refined simultaneously. The refined amplitude values for the C=C bond distance were unreasonably low, and a systematic error seemed to be present. The proximity of $r(C=C)$ and $r(C—C)$ did not allow for the resolution of their individual peaks in the RD-curve. The consequence of these non-resolved peaks is reflected in the large error-limits on $l(C=C)$ and $l(C—C)$. Attempts to keep the amplitude $l(C=C)$ constant at the value calculated from normal coordinate analysis resulted in a poor fit between experimental and theoretical RD-curves, and because of the high correlation between $l(C=C)$ and $r(C=C)$ we then also obtained unreasonable values for $r(C=C)$. This amplitude was therefore allowed to refine even though the resulting value was too low.

The results are given in Table 2 and 3. The theoretical intensity and radial distribution curves corresponding to these results are shown in Figs. 2 and 3 together with difference curves. The correlation matrix for the refined parameters from the low temperature data is available as a supplementary publication [16]; the other two correlation matrices are similar.

DISCUSSION

Molecular structure

As can be seen from Table 2, the results obtained for DCLP at the three different temperatures are entirely consistent; all geometrical parameters are very nearly constant. In Table 4 some of the important geometrical parameters obtained for DCLP are compared with those for some related molecules. We observed earlier [1, 2] that substitution of an aldehyde proton with a halogen atom significantly decreases the length of the C=O

TABLE 2

Final structural results[a,b] for 2,3-dichloro-1-propene at different temperatures

Parameter	24°C		90°C		273°C	
	$r_a/\angle_\alpha$	l	$r_a/\angle_\alpha$	l	$r_a/\angle_\alpha$	l
$\langle$C–H$\rangle$[c]	1.101(0.020)		1.116(0.022)		1.110(0.020)	
Δ(C–H)[d]	0.005		0.005		0.005	
C=C	1.334(0.009)	0.018(0.022)	1.339(0.010)	0.024(0.021)	1.338(0.009)	0.020(0.023)
C–C	1.504(0.013)	0.056(0.020)	1.499(0.013)	0.047(0.021)	1.497(0.013)	0.048(0.021)
$\langle$C–Cl$\rangle$[e]	1.764(0.006)		1.764(0.006)		1.764(0.006)	
Δ(C–Cl)[f]	0.024(0.039)		0.024(0.045)		0.027(0.042)	
$\angle$C$_3$C$_2$C$_1$	127.6(1.1)		127.1(1.1)		126.9(1.3)	
$\angle$C$_3$C$_2$Cl$_4$	110.2(1.0)		110.9(1.1)		110.7(1.8)	
$\angle$C$_2$C$_3$Cl$_5$	113.1(1.2)		113.2(1.1)		114.3(1.9)	
$\angle$C$_2$C$_3$(H$_8$, H$_9$)[g]	124.0		124.0		124.0	
$\angle$H$_8$C$_3$H$_9$	109.5		109.5		109.5	
$\angle$C$_2$C$_1$H$_7$	120.0		120.0		120.0	
$\angle\phi$[h]	108.9(3.4)		108.8(3.2)		109.8(3.6)	
l_δ[i]	10.4		11.5		14.1	
%anti	54.7(8.2)		48.9(8.4)		41.3(9.9)	
R[j]	0.092		0.098		0.099	

[a]Distances (r_a) and root-mean-square amplitudes (l) in Ångstroms, angles in degrees. [b]Parenthesized values are 2σ and include estimates of correlation in the experimental data and uncertainty in the electron wavelength. [c]$\langle$C–H$\rangle$ = $0.5 \cdot (r(C_3-H_8) + r(C_1-H_6))$. [d]$\Delta$(C–H) = $r(C_3-H_8) - r(C_1-H_6)$. [e]$\langle$C–Cl$\rangle$ = $0.5 \cdot (r(C_3-Cl_5) + r(C_2-Cl_4))$. [f]$\Delta$(C–Cl) = $r(C_3-Cl_5) - r(C_2-Cl_4)$. [g]$\angle$C$_2C_3$(H$_8$, H$_9$) is the angle between the plane C$_3$H$_8$H$_9$ and C$_2$C$_3$. [h]$\angle\phi$ is the gauche torsion angle relative to 0° for the anti form. [i]$l_{\angle\delta}$ is the r.m.s. amplitude for the torsional oscillation in the anti form. [j]$R = |\Sigma w_i \Delta_i^2/(w_i I_i (\text{obs.}))^2|^{1/2}$ where $\Delta_i = I_i(\text{obs.}) - I_i(\text{calc.})$.

TABLE 3

Dependent distances and root-mean-square amplitudes of vibration for 2,3-dichloro-1-propene[a]

Distances	24°C		90°C		273°C	
	r_a	l	r_a	l	r_a	l
C_1—H_6	1.098(0.020)	0.077	1.112(0.021)	0.077	1.107(0.020)	0.077
C_3—H_8	1.103(0.020)	0.078	1.117(0.021)	0.078	1.110(0.020)	0.078
C_2—Cl_4	1.752(0.021)	0.049	1.752(0.023)	0.053	1.750(0.022)	0.054
C_3—Cl_5	1.776(0.020)	0.050	1.776(0.023)	0.055	1.777(0.021)	0.056
$C_2 \cdots Cl_5$	2.739(0.023)	0.069 ⎫	2.736(0.024)	0.073 ⎫	2.750(0.033)	0.082 ⎫
$C_3 \cdots Cl_4$	2.673(0.025)	0.069 ⎬(0.007)	2.679(0.027)	0.072 ⎬(0.006)	2.671(0.035)	0.082 ⎬(0.010)
$C_1 \cdots Cl_4$	2.704(0.013)	0.057 ⎭	2.707(0.014)	0.059 ⎭	2.707(0.017)	0.067 ⎭
$C_2 \cdots H_6$	2.102(0.016)	0.098	2.120(0.018)	0.099	2.113(0.016)	0.102
$C_2 \cdots H_8$	2.129(0.016)	0.107	2.134(0.017)	0.108	2.126(0.016)	0.112
$C_1 \cdots C_3$	2.545(0.018)	0.059	2.539(0.019)	0.064	2.532(0.019)	0.071
$C_3 \cdots H_6$	3.516(0.017)	0.096	3.524(0.018)	0.096	3.512(0.017)	0.100
$C_3 \cdots H_7$	2.801(0.026)	0.142	2.799(0.027)	0.147	2.787(0.029)	0.162
$H_6 \cdots Cl_4$	2.856(0.023)	0.142	2.861(0.027)	0.147	2.863(0.032)	0.163
$H_7 \cdots Cl_4$	3.709(0.015)	0.096	3.725(0.016)	0.097	3.718(0.016)	0.103
$H_8 \cdots H_9$	1.795(0.033)	0.128	1.818(0.035)	0.128	1.806(0.032)	0.130
$H_6 \cdots H_7$	1.893(0.034)	0.119	1.918(0.037)	0.119	1.908(0.034)	0.120
$Cl_5 \cdots H_8$ ⎫	2.360(0.019)	0.116	2.369(0.021)	0.118	2.357(0.022)	0.125
$C_1 \cdots H_8$ ⎪	3.221(0.016)	0.132	3.226(0.017)	0.136	3.221(0.016)	0.150
$C_1 \cdots Cl_5$ ⎪	3.066(0.024)	0.086(0.016)	3.055(0.022)	0.076(0.016)	3.072(0.041)	0.102(0.029)
$Cl_4 \cdots Cl_5$ ⎬(A)	4.312(0.013)	0.059(0.006)	4.317(0.013)	0.064(0.008)	4.319(0.015)	0.083(0.012)
$H_6 \cdots Cl_5$ ⎪	4.152(0.027)	0.135	4.154(0.026)	0.145	4.163(0.044)	0.166
$H_7 \cdots Cl_5$ ⎪	2.624(0.048)	0.193	2.604(0.045)	0.206	2.620(0.083)	0.240
$H_8 \cdots Cl_4$ ⎭	2.842(0.028)	0.171	2.855(0.030)	0.181	2.840(0.042)	0.207
$C_1 \cdots Cl_5$ ⎫	3.733(0.020)	0.130(0.044)	3.728(0.021)	0.148(0.055)	3.748(0.023)	0.119(0.029)
$C_1 \cdots H_8$ ⎪	3.276(0.020)	0.120	3.284(0.021)	0.124	3.267(0.021)	0.133
$C_1 \cdots H_9$ ⎪	2.676(0.027)	0.142	2.670(0.028)	0.145	2.657(0.030)	0.158
$H_8 \cdots Cl_9$ ⎬(G)	2.754(0.047)	0.165	2.766(0.048)	0.172	2.761(0.067)	0.196
$H_9 \cdots Cl_4$ ⎪	3.630(0.020)	0.105	3.647(0.021)	0.109	3.634(0.025)	0.116
$H_6 \cdots Cl_5$ ⎪	4.600(0.023)	0.146	4.610(0.024)	0.156	4.623(0.028)	0.178
$H_7 \cdots Cl_5$ ⎪	3.972(0.029)	0.196	3.968(0.030)	0.210	3.979(0.028)	0.245
$Cl_4 \cdots Cl_5$ ⎭	3.385(0.030)	0.151(0.023)	3.396(0.028)	0.159(0.026)	3.395(0.032)	0.166(0.022)

[a]Distance (r_a) and root-mean-square amplitudes (l) are in Ångstroms. Parenthesized values are 2σ and include estimates of correlation in the experimental data and uncertainty in the electron wavelength.

bond. Such a substitution effect, if present at all, is much smaller for the C=C bond. The C—C bond seems to have almost the same length in propene, 2-chloro-3-fluoro-1-propene and DCLP. The two C—Cl bonds are not very well determined in DCLP since electron diffraction is not suited to determine bonds which are only slightly different (the average C—Cl bond is accurately determined, however). It is therefore difficult to know how reliable the observation that $r(C_{sp^2}$—Cl) < $r(C_{sp^3}$—Cl) is. The opposite effect is, however, observed in 2,3-dibromo-1-propene [28] where the effect is significant. In chloroacetyl chloride [1] the two C—Cl distances were found to be almost equal, but the error-limits were large.

As reported earlier, DCLP was found to be a mixture of two forms with the halogen atoms *anti* and *gauche* to each other. The *gauche* form had a torsion angle of $\angle\phi = 108.9 \pm 3.4°$, close to the value ($\angle\phi = 111.5 \pm 3.6°$) observed in 2-chloro-3-fluoro-1-propene. It is significantly smaller than the

TABLE 4

Comparison of parameter values for 2,3-dichloro-1-propene and some related molecules[a]

Parameter	CH₃—CH=CH₂	CH₂F—CCl=CH₂	CH₂Cl—CCl=CH₂	CH₂Cl—CCl=O
$r(C=C)$	1.342(0.002)	1.338(0.006)	1.334(0.009)	
$r(C-C)$	1.506(0.003)	1.505(0.005)	1.504(0.013)	1.514(0.009)
$r(C_{sp^3}\cdots Cl)$			1.752(0.021)	1.778(0.029)
$r(C_{sp^2}-Cl)$		1.743(0.003)	1.776(0.020)	1.774(0.027)
$\angle C-C=C$ (O)	124.3(0.4)	125.6(0.6)	127.6(1.1)	126.7(1.3)
$\angle C_{sp^3}-C_{sp^2}-X$		111.4(0.7)	110.2(1.0)	110.8(1.1)
$\angle C_{sp^2}-C_{sp^3}-X$		111.2(0.8)	113.1(1.2)	112.9(1.3)
$\angle\phi$[b]		111.5(3.6)	108.9(3.4)	120.2(9.6)
Method	ED, MW (r_g)	ED (r_g)	ED (r_a)	ED (r_a)
Ref.	27	13	This work	1

[a]Distances (r) are in Ångstroms, angles in degrees. The reported error limits from different investigations do not necessarily have the same meaning. [b]Torsion angle of the high energy conformer relative to 0° for the *anti* form.

torsion angle observed in chloroacetyl chloride ($\angle\phi$ = 116.4 ± 7.7°, 120.2 ± 9.6° and 121.5 ± 6.5° at 18, 110 and 215°C, respectively).

Energy and entropy differences of the conformers

The measurements of sample composition as a function of nozzle-temperature can be used in a thermodynamic study of the conformational equilibrium. If we consider the conformational equilibrium *anti* ⇌ *gauche*, the difference in energy $\Delta E^0 = E_g^0 - E_a^0$, and the difference in entropy, $\Delta S^0 = S_g^0 - S_a^0$, between the two conformers, may be obtained from the temperature variation of the *gauche/anti* ratio K by use of the formula

$$K = N_g/N_a = 2e^{\Delta S^0/R}e^{-\Delta E^0/RT}$$

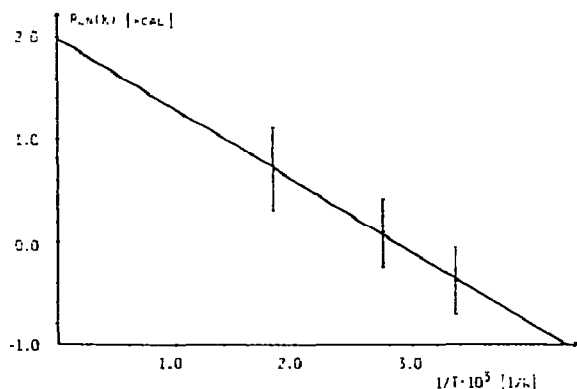where N_g and N_a are the fractions of the two conformers and 2 is the ratio

Fig. 4. Van't Hoff plot of composition data. $K = N_g/N_a$. The half-lengths of the vertical bars indicate 1σ. Least-squares straight line.
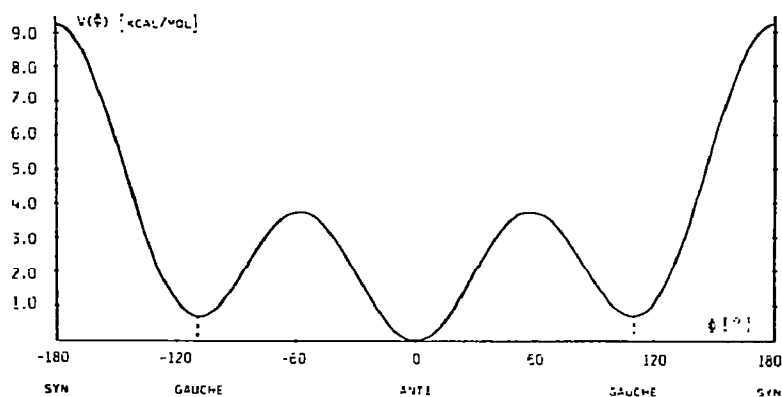
Fig. 5. Form of torsional potential for 2,3-dichloro-1-propene.

of the statistical weights of the two forms. Assuming ΔE° and ΔS° to be temperature independent in the temperature-interval of this investigation, these parameters are determined from a straight line fitted to the ($R \ln(K)$, $1/T$) points (see Fig. 4). The best-fit (least squares) line leads to the values with estimated standard deviations $\Delta E^\circ = 0.7 \pm 0.3$ kcal mol^{-1} and ΔS° $= 0.6 \pm 0.9$ cal mol^{-1} K^{-1}. The value for ΔE° is in good agreement with the value reported by Whipple (0.9 kcal mol^{-1}) from NMR-experiments in different solvents [6]. For comparison ΔE° for 2-chloro-3-fluoro-1-propene [13] and 2,3-difluoro-1-propene [12] are 0.9 ± 0.1 and 0.4 ± 0.2 kcal mol^{-1}, respectively, while in chloroacetyl chloride [1] a value of 1.3 ± 0.4 kcal mol^{-1} was observed.

Rotational potential function

The potential function for torsion about a C—C single bond may be written as

$$V(\phi) = \tfrac{1}{2}(V_1 (1 - \cos \phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi) + \cdots)$$

From the investigations of DCLP, three conditions can be identified that may be used in determining the torsional potential function. These conditions are the torsional frequency observed in IR spectroscopy [8], the value of the torsional angle at which $V(\phi)$ has a minimum ($\angle\phi_g = 109.2$ ($\sigma = 1.0$)) and the value of $V(\phi)$ at this angle ($V(\phi_g) = \Delta E^\circ = 0.7$ ($\sigma = 0.3$)). The total torsional potential can then be determined if it is assumed that the first three terms in the function given above adequately describe the total function (higher order terms are neglected). Results from other related molecules [12, 29] have indicated that three terms may not be sufficient, and this should be kept in mind when the total potential and the individual terms are discussed. Using this assumption the obtained results (with estimated standard deviations calculated from the standard deviations for ΔE° and $\angle\phi_g$) are: $V_1 = 4.4$ ($\sigma = 0.5$) kcal mol^{-1}, $V_2 = -2.9$ ($\sigma = 0.5$) kcal mol^{-1} and $V_3 = 4.8$ ($\sigma = 0.2$) kcal mol^{-1}. The potential function is shown in Fig. 5. The barrier separating the *anti* from the *gauche* conformer is calculated to

be 3.8 (σ = 0.4) kcal mol^{-1} and that separating the two *gauche* forms 8.5 (σ = 0.6) kcal mol^{-1}. These values are much higher than those calculated for chloroacetyl chloride [1] (1.8 ± 0.4 and 0.7 ± 0.5 kcal mol^{-1}) and they are also somewhat higher than the values found in 2,3-difluoro-1-propene [12] (2.9 ± 0.3 and 2.9 ± 0.3 kcal mol^{-1}). The barrier separating the two *gauche* forms is expected to be higher in DCLP than in 2,3-difluoro-1-propene since chlorine atoms have larger van der Waals' radii than fluorine atoms.

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REFERENCES

1 O. Steinnes, Q. Shen and K. Hagen, J. Mol. Struct., 64 (1980) 217.
2 O. Steinnes, Q. Shen and K. Hagen, J. Mol. Struct., 66 (1980) 181.
3 A. Kirrman, Bull. Soc. Chim. Fr., (1948) 170.
4 H. Gerding and H. G. Haring, Rec. Trav. Chim. Pays-Bas, 74 (1955) 957.
5 E. B. Whipple, J. H. Goldstein and G. R. McClure, J. Am. Chem. Soc., 82 (1960) 3811.
6 E. B. Whipple, J. Chem. Phys., 35 (1961) 1039.
7 T. Torgrimsen and P. Klæboe, J. Mol. Struct., 20 (1974) 229.
8 G. A. Crowder, J. Mol. Spectrosc., 20 (1966) 430.
9 G. A. Crowder, J. Mol. Spectrosc., 23 (1967) 1.
10 G. A. Crowder, J. Mol. Spectrosc., 23 (1967) 103.
11 L. H. L. Chia, E. Huang and H. H. Huang, J. Chem. Soc. Perkin Trans. 2, (1973) 766.
12 A. D. English, L. H. Scharpen, K. M. Ewool, H. L. Strauss and D. O. Harris, J. Mol. Spectrosc., 60 (1976) 210.
13 S. Samdal, H. M. Seip and T. Torgrimsen, J. Mol. Struct., 42 (1977) 153.
14 W. Zeil, J. Haase and L. Wegmann, Z. Instrumentenkd., 74 (1966) 84.
15 O. Bastiansen, R. Graber and L. Wegmann, Balzer's High Vacuum Rep., 25 (1969) 1.
16 Available as Supplementary Publication No. SUP 26175 (7 pages). See J. Mol. Struct., 34 (1976) 322 for further details.
17 K. Tamagawa, T. Iijima and M. Kimura, J. Mol. Struct., 30 (1976) 243.
18 K. Hagen and K. Hedberg, J. Am. Chem. Soc., 95 (1973) 1003.
19 G. Gundersen and K. Hedberg, J. Chem. Phys., 51 (1969) 2500.
20 L. Hedberg, Abstracts, 5th Austin Symposium on Gas Phase Molecular Structure, Austin, TX, 1974, p. 37.
21 B. Andersen, H. M. Seip, T. G. Strand and R. Stølevik, Acta Chem. Scand., 23 (1969) 3224.
22 A. C. Yates, Comput. Phys. Commun., 2 (1971) 175.
23 T. G. Strand and R. A. Bonham, J. Chem. Phys., 40 (1964) 1686.
24 R. F. Stewart, E. R. Davidson and W. T. Simpson, J. Chem. Phys., 42 (1965) 3175.
25 J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki and C. S. Pote, Structure Data of Free Polyatomic Molecules, Landolt-Børnstein, New Series, Vol. 7, Springer-Verlag, Berlin, 1976.
26 K. Hedberg and M. Iwasaki, Acta Crystallogr., 17 (1964) 529.
27 I. Tokue, T. Fukuyama and K. Kuchitsu, J. Mol. Struct., 17 (1973) 207.
28 O. I. Søvik, Ø. Trongmo, Q. Shen, R. Seip and K. Hagen, unpublished results.
29 O. Bastiansen, K. Kveseth and H. Møllendal, Top. Curr. Chem., 81 (1979) 99.