

Conformational Analysis. 1. The Temperature Effect on the Structure and Composition of the Rotational Conformers of 1,2-Dichloroethane as Studied by Gas Electron Diffraction

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Gaseous 1,2-dichloroethane has been studied by electron diffraction at -13 , 40 , 140 , and 300 °C. The relative amount of the *anti*-conformer as compared to *gauche*, showed a marked variation with the temperature, whereas the structure remained almost invariant, with exception for the long distance u -values. A least-squares fit to the estimated equilibrium constants gave $\Delta E = 1.5(0.2)$ kcal mol $^{-1}$ and $\Delta S = 2.0(0.5)$ cal K $^{-1}$ mol $^{-1}$, which is in good agreement with earlier estimates. The distances

(R_a), corrected for shrinkage, and u -values determined are given in Table 4.

It is well established that internal rotation about carbon-carbon single bonds gives rise to a mixture of different conformers, the amount of each depending on the energy difference. The structure of each conformer differs mainly in their torsional angle about the C—C bond.

Table 1. Experimental conditions and photographic plate data.

Temp. (°C)	-13		40		
Apparatus	Balzer		Oslo		
Nozzle-to-plate distance (mm)	500.00	250.00	481.19	201.19	
Electron wavelength (Å) ^a	0.05848	0.05849	0.06452	0.06452	
Number of plates used	6	5	6	6	
Range of data (s) ^b	1.125—15.625	2.250—29.500	1.500—19.375	7.000—43.500	
Data interval (Δs)	0.125	0.250	0.125	0.250	
Corresponding curves in Figs. 2 and 3	A		B		
140	140 B		300		
Oslo	Balzer		Balzer		
481.19	201.19	500.00	250.00	500.09	248.18
0.06452	0.06452	0.05850	0.05851	0.05850	0.05850
6	6	5	5	4	6
1.500—19.375	7.000—42.250	1.125—15.500	2.250—30.000	1.125—15.500	2.250—30.250
0.125	0.250	0.125	0.250	0.125	0.250
C	D		E		

^a Determined in separate experiments by calibration to CO $_2$. ^b $s = 4\pi/\lambda \sin \theta$; 2θ is the scattering angle.

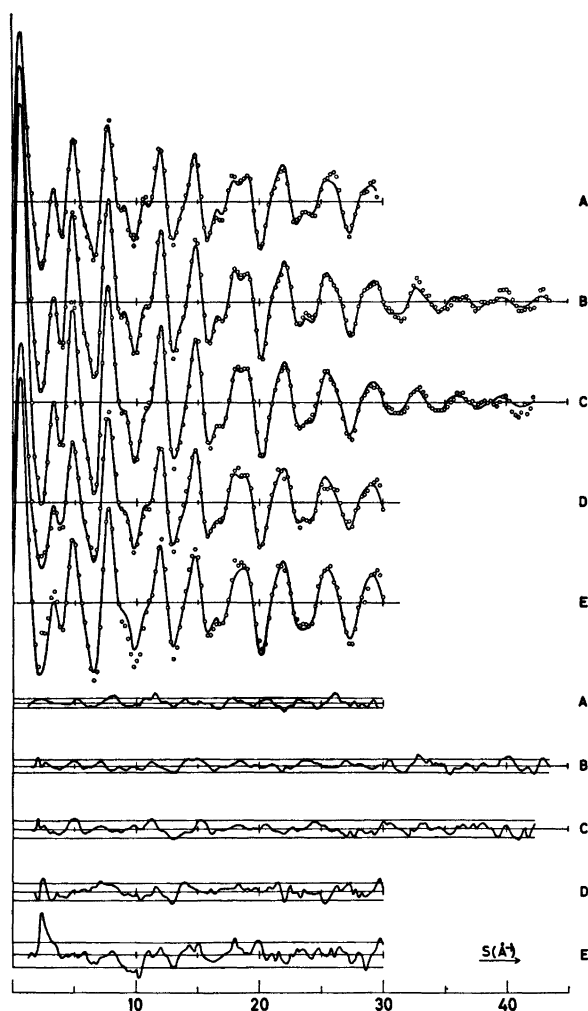


Fig. 1. Intensity and difference curves. The solid curves are theoretically calculated from the parameters given in Table 4. The experimental values are the O. The difference is experimental minus theoretical, and the limits are 3σ , σ being the experimental standard deviation in the observations. The temperature in the different curves are A: -13 , B: 40 , C: 140 , D: 140 and E: 300 ($^{\circ}\text{C}$).

Substituted ethanes are thoroughly studied both by spectroscopy and diffraction methods,¹ and exist definitely as the two conformers *anti* and *gauche*. Due to the energy difference one must expect that the relative amount of the two conformers varies with the temperature of the experiment. The variation in composition may be used to evaluate both the difference in energy and entropy between the *gauche* and *anti* conformer, the last quantity usually assumed to be $R \ln 2$, only taking into

account the statistical weight of 2 for the *gauche* form.

In a similar study on ethylenechlorohydrin by Bastiansen *et al.*², they were able to evaluate these two quantities. 1,2-Dichloroethane ought to be well suited as the Cl-Cl distance in *anti* is well separated from the rest of the structure, and is also fairly well represented because of the scattering power of the two chlorine atoms.

EXPERIMENTAL

The sample of 1,2-dichloroethane was obtained from British Drug Houses (>98.9%) and used without further purification. Electron diffraction photographs were obtained with the Oslo apparatus³ and the Balzer Eldigraph KDG-2 unit. The experimental conditions are summarized in Table 1. The data were corrected in the usual way,⁴ obtaining an intensity curve for each photographic plate. The intensities were modified with the function⁴

$$s/|f_{cl}|^2$$

The background was subtracted separately from each intensity curve. The average for each set of plates was calculated, and composites made for each temperature by scaling corresponding pair of curves and averaging the intensities in the overlap region. These total intensity curves are drawn in Fig. 1. (The discrepancy at $s=2 \text{ \AA}^{-1}$ in the 300 °C-curve is due to a dust particle in the sector opening.) The amount of the two conformers, as well as the structure, is determined by least squares refinements, carried out either on the composite curves, or simultaneously on data from each nozzle-to-plate distance without connecting them.

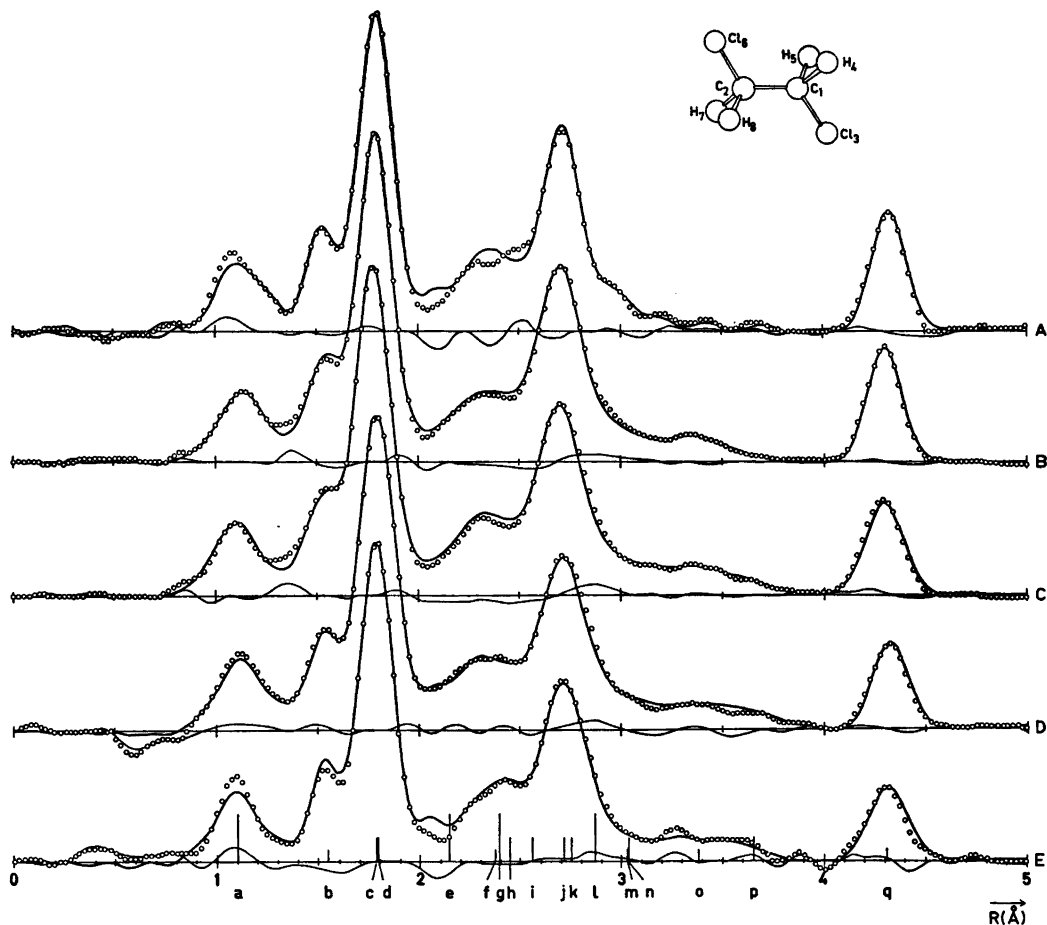


Fig. 2. Radial distribution and difference curves ($k=0.0015 \text{ \AA}^2$). The solid curves are those theoretically calculated from the parameters given in Table 4. The experimental values are the O. The difference is experimental minus theoretical. The temperature in the different curves are A: -13, B: 40, C: 140, D: 140 and E: 300 (°C).

a C_1-H_4 ; b C_1-C_2 ; c C_1-Cl_3 ; d $H_4 \cdots H_5$; e $C_1 \cdots H_7$; f $H_5 \cdots H_7, g, g$; g $Cl_3 \cdots H_4$; h $H_4 \cdots H_8, a, g$; i $H_4 \cdots H_7, g, g$; j $C_1 \cdots Cl_6$; k $Cl_3 \cdots H_8, g, g$; l $Cl_3 \cdots H_7, a, g$; m $H_4 \cdots H_8, a, g$; n $H_4 \cdots H_7, a, a$; o $Cl_3 \cdots Cl_6, g$; p $Cl_3 \cdots H_7, a, g$; q $Cl_3 \cdots Cl_6, a$.

The theoretical molecular intensities were calculated according to eqn. (10) of Ref. 4. The scattering amplitudes were calculated by the partial wave method,^{4,5} using Hartree-Fock atomic potentials.⁶

STRUCTURE ANALYSIS AND REFINEMENT

Radial distribution curves (RD-curves) calculated from the composities by a Fourier transformation, are shown in Fig. 2. The bond distances contribute to the first three peaks, together with the short $r(\text{H}\cdots\text{H})$. The peak complex between $R=2 \text{ \AA}$ and $R=4 \text{ \AA}$ corresponds to all the non-bonded distances, except for the torsional dependant $r(\text{Cl}\cdots\text{Cl})$ in *anti*, which gives rise to an isolated peak in the outer part of the curve, the area of which varies with the temperature.

All bond distances, the angles CCCI and CCH and the torsional angle ϕ were chosen as independent parameters. ϕ is defined as 180° in *anti*. For the *gauche* conformation ϕ was refined for each temperature. The torsional

independent part of the structure is assumed to be the same for the two conformers. The composition in the gas phase is thus determined from the two torsional dependant $r(\text{Cl}\cdots\text{Cl})$ -distances, as the contribution from the long $r(\text{Cl}\cdots\text{H})$ is comparatively small.

The molecular structure was calculated in the geometrical consistent R_α -picture, the bond distances transformed by eqn. (1)

$$R_\alpha = R_a + u^2/R - K = R_a + D \quad (1)$$

K is perpendicular amplitude correction coefficient (see Ref. 8). The distances thus determined are transformed to R_a -values before refining to the intensities by least-squares procedure. The calculated angles will correspond to R_α -structure.

D -values and root-mean-square vibrational amplitudes (u -values) calculated^{7,8} from the established valence force field⁹ and cartesian displacement coordinates, are given in Table 2 and Table 3, respectively. Both parameters vary considerably with the temperature, with the smallest dependency for the bond distances.

Table 2. The difference, $D(\text{\AA})$, between R_α and R_a . The difference is calculated from the valence force field established by Schachtschneider and Snyder, with the torsional force constants from this work; $f_{t,g} = 0.253 \text{ mdyn \AA rad}^{-2}$ and $f_{t,a} = 0.174 \text{ mdyn \AA rad}^{-2}$.

Temp. ($^\circ\text{C}$)	-13	40	140	300
$r(\text{C}-\text{C})$	0.00010	0.00005	-0.00005	-0.00020
$r(\text{C}-\text{Cl})$	-0.00304	-0.00370	-0.00494	-0.00694
$r(\text{C}-\text{H})$	-0.01009	-0.01054	-0.01160	-0.01534
$r(\text{C}\cdots\text{Cl})_a^a$	-0.00155	-0.00191	-0.00258	-0.00363
$r(\text{C}\cdots\text{Cl})_g$	-0.00016	-0.00027	-0.00046	-0.00073
$r(\text{C}\cdots\text{H})_a$	-0.00122	-0.00137	-0.00170	-0.00228
$r(\text{C}\cdots\text{H})_g$	-0.00450	-0.00511	-0.00636	-0.00850
$r(\text{Cl}\cdots\text{H})$	-0.00506	-0.00593	-0.00765	-0.01046
$r(\text{H}\cdots\text{H})$	-0.00963	-0.01030	-0.01186	-0.01489
$r(\text{Cl}\cdots\text{Cl})_a$	0.00096	0.00109	0.00135	0.00180
$r(\text{Cl}\cdots\text{H})_{a,g}^b$	0.00147	0.00149	0.00157	0.00179
$r(\text{Cl}\cdots\text{H})_{a,g}$	0.00147	0.00149	0.00157	0.00179
$r(\text{H}\cdots\text{H})_{a,a}$	-0.00238	-0.00247	-0.00269	-0.00321
$r(\text{H}\cdots\text{H})_{a,g}$	0.00240	0.00230	0.00222	0.00231
$r(\text{H}\cdots\text{H})_{g,g}$	0.00240	0.00230	0.00222	0.00231
$r(\text{Cl}\cdots\text{Cl})_g$	0.00534	0.00635	0.00827	0.01138
$r(\text{Cl}\cdots\text{H})_{g,g}$	0.00275	0.00288	0.00323	0.00396
$r(\text{Cl}\cdots\text{H})_{g,a}$	-0.00194	-0.00210	-0.00244	-0.00307
$r(\text{H}\cdots\text{H})_{g,g}$	-0.00268	-0.00334	-0.00460	-0.00661
$r(\text{H}\cdots\text{H})_{g,g}$	-0.00363	-0.00458	-0.00641	-0.00936
$r(\text{H}\cdots\text{H})_{g,a}$	-0.00636	-0.00697	-0.00828	-0.01064

^a the suffix *a* and *g* means *anti* and *gauche*, respectively. ^b in the double suffix the first letter gives the conformation, the second the type of distance involved.

Table 3. Vibrational amplitudes, u (Å), calculated from the valence force field.

Temp. (°C)	-13	40	140	300
$u(\text{C}-\text{C})$	0.052	0.052	0.054	0.056
$u(\text{C}-\text{Cl})$	0.052	0.053	0.056	0.061
$u(\text{C}-\text{H})$	0.078	0.078	0.078	0.078
$u(\text{C}\cdots\text{Cl})$	0.067	0.070	0.076	0.086
$u(\text{C}\cdots\text{H})$	0.109	0.110	0.112	0.116
$u(\text{Cl}\cdots\text{H})$	0.109	0.109	0.111	0.116
$u(\text{H}\cdots\text{H})$	0.128	0.128	0.129	0.131
$u(\text{Cl}\cdots\text{Cl})_a^a$	0.064	0.068	0.075	0.087
$u(\text{Cl}\cdots\text{H})_{a,g}$	0.160	0.167	0.180	0.200
$u(\text{Cl}\cdots\text{H})_{a,g}$	0.160	0.167	0.180	0.200
$u(\text{H}\cdots\text{H})_{a,a}$	0.131	0.131	0.132	0.135
$u(\text{H}\cdots\text{H})_{a,g}$	0.173	0.175	0.180	0.191
$u(\text{H}\cdots\text{H})_{a,g}$	0.173	0.175	0.180	0.191
$u(\text{Cl}\cdots\text{Cl})_g$	0.141	0.153	0.175	0.205
$u(\text{Cl}\cdots\text{H})_{g,g}$	0.158	0.163	0.174	0.193
$u(\text{Cl}\cdots\text{H})_{g,a}$	0.102	0.104	0.107	0.113
$u(\text{H}\cdots\text{H})_{g,g}$	0.170	0.172	0.177	0.187
$u(\text{H}\cdots\text{H})_{g,g}$	0.173	0.175	0.180	0.191
$u(\text{H}\cdots\text{H})_{g,a}$	0.129	0.129	0.130	0.133

^a See captions to Table 2.

Vibrational amplitudes which did not refine, are given the calculated value (see discussion).

The (Cl \cdots Cl)-vibrational amplitudes in *gauche* are, contrary to $u(\text{Cl}\cdots\text{Cl})_a$, dependent on the torsional force constant, $f_{t,g}$, which is varied to reproduce the experimental u -value. At 300 °C it was found that $f_{t,g}=0.253$ mdyne Å/rad² gave the experimental u -value. The calculated torsional frequency of 117 cm⁻¹ is also in excellent agreement with the experimental value of 125 cm⁻¹,¹⁰⁻¹² measured in liquid Raman, where a shift to lower frequency may be expected in the gas phase.

To reproduce the torsional frequency in *anti* at 125 cm⁻¹, measured in gas phase IR, the force constant was found to be $f_{t,a}=0.174$ mdyne Å/rad², a bit smaller than in *gauche*.

An attempt to estimate the ratio between the two torsional force constants from the extended van der Waals potential curve¹³ (as suggested by R. Stølevik), gave the same results as found above. The magnitude agrees with an estimate from the second derivatives of the assumed cosine potential at $\phi=60^\circ$ and 180° , also assuming harmonic motion with small amplitudes. Using an earlier estimate of ΔH , this method gave $f_{t,g}=f_{t,a}=0.17$ mdyne Å/rad². The graphs in Fig. 3 show the excellent over

all agreement between the calculated and refined torsional u -values, as well as the linear dependency of $T^{\frac{1}{2}}$.

To get some information about the uncertainty introduced by the parameters kept at fixed values, all parameters were refined one cycle and corresponding standard deviations, σ , were calculated. The fixed parameters were varied in the region of $\pm 3\sigma$ without

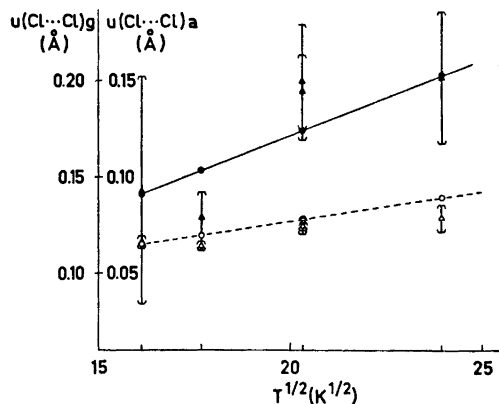


Fig. 3. $u(\text{Cl}\cdots\text{Cl})$ as a function of $T^{\frac{1}{2}}$. Δ : experimental values, \circ : calculated values. Open marks in *anti*, closed in *gauche*.

Table 4. Molecular parameters for 1,2-dichloroethane. Distance (r_a) and amplitudes in Å, angles ($\angle \alpha$) in degrees.

Temp. (°C)	-13	40	140	140B	300	^c
$r(\text{C}-\text{C})$	1.528(6) ^a	1.533(3)	1.533(4)	1.521(8)	1.541(8)	1.531(3)
$r(\text{C}-\text{Cl})$	1.796(3)	1.785(2)	1.786(2)	1.795(3)	1.790(3)	1.790(2)
$r(\text{C}-\text{H})$	1.120(10)	1.128(6)	1.101(6)	1.111(10)	1.100(10)	1.112(5)
$\angle \text{CCCl}$	108.9(3)	108.8(2)	108.6(2)	109.5(4)	109.1(4)	109.0(2)
$\angle \text{CCH}$	113.0(1.3)	114.5(1.6)	114.0(1.2)	116.0(3.0)	108.4(1.6)	113.2(1.3)
ϕ_g	78.2(4.6)	76.4(1.3)	75.5(2.0)	77.6(3.1)	74.4(3.0)	76.4(7)
$u(\text{C}-\text{C})$	0.032(10)	0.043(4)	0.053(4)	0.043(9)	0.035(14)	
$u(\text{C}-\text{Cl})$	0.044(3)	0.047(2)	0.050(3)	0.054(3)	0.038(5)	
$u(\text{C}\cdots\text{Cl})$	0.057(4)	0.073(3)	0.080(3)	0.088(5)	0.076(6)	
$u(\text{Cl}\cdots\text{H})$	0.102(14)	0.151(19)	0.115(11)	0.134(25)	0.076(14)	
$u(\text{Cl}\cdots\text{Cl})_a$	0.066(5)	0.074(5)	0.074(6)	0.074(6)	0.078(7)	
$u(\text{Cl}\cdots\text{Cl})_g$	0.143(59)	0.129(13)	0.194(19)	0.199(30)	0.201(34)	
% <i>anti</i>	89.4(4.4)	78.7(3.4)	67.9(3.6)	67.0(5.1)	63.9(5.8)	
% <i>anti</i> ^b	87.6(3.1)	77.0(1.7)	67.5(2.2)	65.1(3.4)	64.7(4.3)	
% <i>gauche</i>	15.4(4.1)	20.6(2.4)	32.1(3.6)	38.9(5.6)	43.7(6.4)	

^a The distances are corrected for shrinkage. Standard deviations obtained from the refinement using off diagonal elements in the weight matrix, are given in parenthesis. ^b The % of *anti* and *gauche* are individually refined, the rest of the structural parameters is kept constant. ^c This column gives the average and calculated standard deviations in parenthesis for the geometry parameters.

causing any significant changes in the rest of the refined structure.

Table 4 gives the results obtained from refinements at the different temperatures on average curves. The distances are all R_a -values, the angles correspond to α -values. The standard deviations, given in parenthesis, are those calculated by the least-squares procedure, using non-diagonal elements in the applied weight matrix,¹⁴ and adding 0.1 % R as systematic error.

THERMODYNAMICS

The equilibrium between the two conformers (*anti* \rightleftharpoons *gauche*) is described by eqn. (2)

$$K = \frac{n_g}{n_a} = 2 \frac{Q_g}{Q_a} e^{-\Delta E^\circ/RT} = e^{-(\Delta E - T\Delta S)/RT} \quad (2)$$

where n is the percentage of the conformer, Q is the partition function, and ΔE° is the difference in energy between *gauche* and *anti* at the absolute zero point. $\Delta E = \Delta H$ and ΔS are the ordinary thermodynamical quantities for the reaction. The factor 2 is the statistical weight of the *gauche* form.

It is quite common to assume $Q_g = Q_a$, and

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one aim of this investigation is to test this assumption.

The partition function can be calculated from the moments of inertia, I , and vibrational frequencies, ν , by eqn. (3), as the translational functions are equal in the two forms

$$Q = Q_{\text{rot}} Q_{\text{vib}} = \frac{1}{\sigma_r h} 8\pi^2 (8\pi^2 I_A I_B I_C)^{1/2} (kT)^{3/2} \times \prod [1 - \exp(-h\nu_j/kT)]^{-1} \quad (3)$$

The torsional frequency is included in the vibrational contribution to Q . σ_r is here the rotational symmetry number, equal to 2 for both conformers.

In the investigation by electron diffraction K is determined as a function of the temperature. Fig. 4 shows how $R \ln (2/K)$ varies with the inverse, absolute temperature, $1/T$.

The straight line fitted to these values by least squares, has an angle coefficient of ΔE° and cuts the $R \ln (2/K)$ -axis in $-R \ln (Q_g/Q_a)$. This is true as long as Q_g/Q_a does not vary with the temperature. The fraction $(Q_g/Q_a)_{\text{rot}}$ is independent of the temperature, thus Q_g/Q_a is temperature dependant only if $(Q_g/Q_a)_{\text{vib}}$ varies with the temperature.

From eqn. (2) and the statistical expression for ΔE and ΔS [eqn. (4)] it is seen that assuming

ΔE and ΔS constant in the reaction interval, implies that Q_g/Q_a is temperature independent, and therefore $\partial/\partial T(\ln Q_g/Q_a) = 0$. And then $\Delta E = \Delta E^\circ$ and $\Delta S = R \ln (Q_g/Q_a) + R \ln 2$. If $\partial/\partial T(\ln Q_g/Q_a)$ differs from zero, then assuming $R \ln (2/K)$ as a linear function of $(1/T)$ implies that the calculated $\ln (Q_g/Q_a)$ is the mean value in the actual temperature interval. The calculation of the thermodynamic quantities then requires a knowledge of $\partial/\partial T(\ln Q_g/Q_a)$. Then

$$\Delta E = \Delta E^\circ + RT^2 \frac{\partial}{\partial T} (\ln Q_g/Q_a)$$

$$\Delta S = R \ln (Q_g/Q_a) + RT \frac{\partial}{\partial T} (\ln Q_g/Q_a) + R \ln 2 \quad (4)$$

RESULTS AND DISCUSSION

From Table 3 it is seen that the temperature dependency is of major importance in the u -values for the non-bonded distances. This is also confirmed by the refined values in Table 4, though some fluctuations due to experimental errors are seen here. In general, the discrepancies are within one to two standard deviations. But especially $u(C-C)$ from the Balzer plates refines to a much smaller value, probably due to the shorter observation interval ($S_{MAX} \approx 30 \text{ \AA}^{-1}$ contrary to 42 \AA^{-1}) and thereby the greater uncertainty introduced in the bond distances. It is also believed that the blackness correction was too small, and therefore generally made the amplitudes too small.

The structural parameters change very little with respect to the temperature (see Table 4). Thus the temperature effect, as demonstrated on the R.D.-curves (Fig. 2) causes a broadening of the peaks, whereas the positions remain constant.

The structural parameters show quite normal values, and agree very well with earlier investigations by Brunvoll¹⁵ and Karle.¹⁶ The CCH-angles seem to be a bit too large. But the determination of both this angle and $r(C-H)$ is to some extent coupled to the uncertainties in the experimental background.

The torsional angle in *gauche*, ϕ_g , is considerably larger than 60° , which is understood from the relatively strong Cl...Cl-repulsion in this form. Calculations of the van der Waals energy,¹⁷ also including dipol repulsions, gave

a minimum at 78° , in excellent agreement with the experimental values.

The agreement between the parameters given in column 140 and 140 B (Table 4), (the latter is the Balzer-recording), shows that there are no camera effects in the structure determination.

As expected, the percentage of the two conformers, *gauche* and *anti*, varies most markedly with the temperature. The presence of the *anti*-form decreases strongly as the temperature increases, in accordance with the increasing population of *gauche*, having higher energy than *anti* but favoured by the statistical weight, equal to 2.

The uncertainties in $R \ln (2/K)$, marked as vertical lines in Fig. 4, are calculated from the least squares standard deviations, σ , in n . These uncertainties are likely to be too great. By varying the percentage within $\pm \sigma$, the visual change in Cl...Cl-peak is much too great to be acceptable. This implies that the errors in the total structure overestimate the error in the percentage determination.

Also individual refinements at -13 and 300°C on single plates, and thereby estimation of the means and standard deviations from distribution of the parameters (see Table 5), give much smaller σ 's in n , whereas the overall

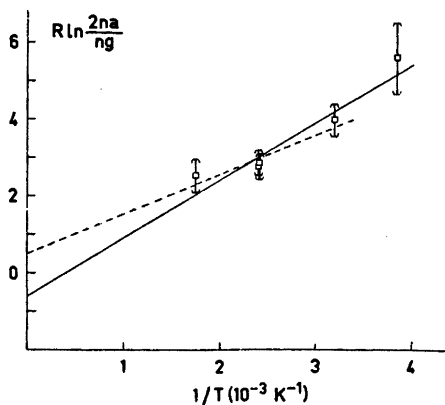


Fig. 4. $R \ln (2/K) = R \ln (2n_a/n_g)$ as a function of $1/T$. The standard deviations marked in each point by vertical lines are calculated from those obtained on n_a in the least squares refinement on the total structure. The solid line is calculated from all five observations, the broken line from four observations excluding the point at -13°C .

Table 5. Average molecular parameters for 1,2-dichloroethane. Distance (r_a) and amplitudes in Å, angles (\angle_a) in degrees.

Temp. (°C)	-13	300
$r(\text{C}-\text{C})$	1.528(4) ^a	1.535(2)
$r(\text{C}-\text{Cl})$	1.793(1)	1.789(7)
$\angle \text{CCCl}$	109.1(.3)	108.9(.5)
ϕ_g	73.8(3.0)	74.6(.8)
$u(\text{C}-\text{C})$	0.030(6)	0.039 -
$u(\text{C}-\text{Cl})$	0.043(2)	0.044(11)
$u(\text{C}\cdot\text{Cl})$	0.056(4)	0.083(6)
$u(\text{C}\cdot\text{H})$	0.210(45)	0.110(10)
$u(\text{Cl}\cdot\text{H})$	0.116(14)	0.089(13)
$u(\text{Cl}\cdot\text{Cl})_a$	0.064(3)	0.085(13)
$u(\text{Cl}\cdot\text{Cl})_g$		0.196(1)
% <i>anti</i>	89.6(2.5)	62.7(.7)

^a Standard deviations calculated from the individual differences from the mean $\sigma_p^2 = \sum_n (p - \bar{p})^2 / n(n-1)$ are given in parenthesis. The mean is calculated from 5, respectively 4, individual refinements.

agreement between the structural parameters and standard deviations is very good.

The two bottom rows of Table 4 give the percentage with standard deviations, individually refined, when the rest of the structure is kept constant. Still the σ 's are greater than obtained from refinement on individual plates.

The accuracy in the nozzle temperature is at least better than 3°C. If this temperature reflects the gas temperature, this is sufficiently accurate to assume that the uncertainty due to errors in the temperature can be neglected in the thermodynamic calculations. The overall agreement between the investigations by

the Oslo- and the Balzer-apparatus also verifies the this.

The gas is definitely cooled when it comes into vacuum, but this temperature fall in the gas jet is assumed to be only in the translational energy. This is supported by earlier investigations where electron diffraction data agree very well with other experiments,¹⁷ and the reproducibility of the results from the two Oslo-apparatus, as well as the reproducibility reported by Bastiansen/Hedberg.³ A recent paper by Bauer¹⁸ seems to indicate a temperature fall of as much as 50°C.

Table 6 shows the calculated values for ΔE and ΔS , assuming the $\partial/\partial T(\ln Q_g/Q_a)$ is negligible, calculated by least squares using all 5 observation points in column A, and only the 4 highest temperature points in column B. If the calculated frequency in *gauche*, 117 cm⁻¹, is correct, the torsional frequency in *anti* is calculated from comparing the theoretical expression for the partition function [eqn. (3)] and the $R \ln (Q_g/Q_a)$ quantity from the least-squares fit.

Fig. 4 gives the five corresponding ($R \ln (2/K)$, $1/T$) values as well as the two least-squares fitted straight lines, the solid line fitted to all five points, the broken excluding the $t = -13^\circ\text{C}$ observation. The figure reveals that the observation at $t = -13^\circ\text{C}$ ($1/T = 3.846 \times 10^{-3} \text{ K}^{-1}$) is off the line about which the other observations are grouped. I believe this is due to some condensing phenomena in the nozzle, favouring the *anti* conformer, since the external bath temperature and the nozzle temperature here vary very close to each other. To check this

Table 6. Thermodynamical differences between *gauche* and *anti*, and the torsional frequencies of the two conformers.

	a	b	c	d
ΔE (kcal/mol)	1.5(0.2) ^e	1.0(0.2)		0.89 - 1.27 ^{15,16,19,20}
ΔS (cal/K mol)	2.0(0.5)	0.8(0.5)	1.4 ^f	~ 1.4 ²¹
ν_g (cm ⁻¹)	117	117	117 ^g	125 ¹³
ν_a (cm ⁻¹)	198(84)	96(28)	125 ^g	123 ¹³

^a Least-squares result from electron diffraction data, also including the observation at -13°C . ^b Least-squares result from electron diffraction data, excluding the observation at -13°C . ^c Calculated values from normal coordinates and frequencies. ^d Earlier observations. ^e Standard deviations are given in parenthesis. ^f The average in the observation interval ($\Delta S = R \ln 2 + R \ln (Q_g/Q_a)$) ^g The calculated torsional frequencies, $f_{t,g} = 0.253 \text{ m dyn } \text{Å} \text{ rad}^{-2}$ and $f_{t,a} = 0.174 \text{ m dyn } \text{Å} \text{ rad}^{-2}$.

a new experiment with a slightly higher nozzle temperature is performed.

The normal coordinate calculations have given values for the partition functions and their temperature derivatives, and it shows that the temperature dependency is much too small to explain the apparent non-linearity ($\partial/\partial T(\ln Q_g/Q_a) = 0.36 \times 10^{-3}$).

The apparent non-linearity could be a result of the above mentioned drop in the vibrational temperature.¹⁸ If this is assumed to be constant, and approximately 50 C°, the shift in the 1/T-scale will be greatest for the lowest temperature point, and thereby making the points closer to a straight line. This shift in the 1/T-scale, however, will cause very little change in the value of the determined quantities, compared to the calculated standard deviations.

The value $\Delta E^\circ = 1.0$ kcal/mol agrees very well with earlier estimates, while the value calculated from all five observations seems to be too high. But compared with the calculated van der Waals energy difference, $\Delta E_{vdw} = 1.4$ kcal/mol, and adding the difference in zero point energy between the two conformers, 0.23 kcal/mol [calculated in the force field program, $\Delta E^\circ = \Delta E_{vdw} + \frac{1}{2}h \sum_k (\nu_{k,g} - \nu_{k,a})$], the agreement is better with the result in column A.

From this investigation it is quite clear that the partition functions in the two conformers are very similar, and therefore ΔS is very close to $R \ln 2$. Also the assumed temperature invariance of ΔE and ΔS is established within the experimental error limits. Within the calculated standard deviations it is not possible to tell whether ΔS should be smaller or greater than $R \ln 2$. But if the torsional frequency should be smaller in *gauche*, $\nu_g < \nu_a$, there seems to be a discrepancy between the calculated entropy difference from the partition functions (C) and the value estimated from the four best electron diffraction points (B), the latter revealing an entropy smaller than $R \ln 2$ in *gauche*, and therefore $\nu_g > \nu_a$.

Conclusion. This structure determination of 1,2-dichloroethane at different temperatures, has shown that such a temperature study of conformational equilibria by electron diffraction is a suitable tool to estimate energy and entropy values with reasonable certainty.

From the estimated entropy value and the observed frequencies the ratio between the torsional frequencies of the conformers can be determined.

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