

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

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Gaseous 1,2-difluoroethane* has been studied by electron diffraction at 25 and 504 °C. The most stable conformer is *gauche*, which contributes with 91 % at 25 °C decreasing to 79 % at 504 °C. From the temperature dependency of the *gauche/anti* ratio thermodynamic differences for the conformational equilibrium, $\Delta E = E_g - E_a$ and $\Delta S = S_g - S_a$, were determined. Assuming the differences to be constant in the actual temperature range gave $\Delta E = -0.93(41)$ kcal mol⁻¹ and $\Delta S = 1.5(8)$ cal mol⁻¹deg⁻¹ (1 cal = 4.184 J). According to experience¹¹ the standard deviation obtained from least squares calculations comes out unrealistically large in ΔE and ΔS . The general experience from electron-diffraction studies as a whole, seems to settle beyond doubt the prevalence of *gauche*.

The bond distances and valence angles remained almost constant with respect to the temperature variations, and the main average parameters (r_a and \angle_a) are:

C–C = 1.502(3), C–F = 1.384(1), C–H = 1.117(3) Å, $\angle CCF = 111.2(2)$ and $\angle CCH = 109.7(12)$ (°). $\phi_g = 71.7(11)^\circ$ at 25 °C and $\phi_g = 65.0(13)^\circ$ at 504 °C.

1,2-Disubstituted ethanes consist of a mixture of two conformers,^{1–3} *anti* and *gauche*. Usually *anti* is the more stable, but for some substituents favourable interactions may give preference to *gauche*. In 1,2-difluoroethane *gauche*^{4–10} has been found to be more stable in all states of aggregation.

The *gauche/anti* ratio (K) may be studied by the gas electron-diffraction method, considering K as

* A concurrent investigation of 1,2-difluoroethane has been carried out by K. Hedberg *et al.* at the University of Oregon, and their manuscript has simultaneously been submitted to *J. Am. Chem. Soc.*

one of the structural parameters in addition to the geometric and vibrational ones. In previous studies of this kind^{11–14} the thermodynamic data deduced from the temperature variation in K have proved to give reasonable results. The main scope of this study of 1,2-difluoroethane is to confirm the accuracy of the method and to give a more detailed discussion of the temperature dependency of the thermodynamic differences ΔE and ΔS for the *anti* ⇌ *gauche* equilibrium in the vapour. In the earlier electron-diffraction studies of 1,2-difluoroethane^{4,5} some discrepancies exist with respect to the geometrical parameters. An additional aim of this study is, therefore, to establish more accurate structural parameters for this basic molecule.

EXPERIMENTAL

The samples of 1,2-difluoroethane were kindly supplied by Prof. R. J. Abraham, University of Liverpool, England, and Prof. W. Lüttke, Universität, Göttingen, BRD. Electron-diffraction photographs were obtained with the Balzers Eldigraph KDG-2 unit.^{15,16} The experimental conditions are summarized in Table 1. The optical densities were measured by a Joyce-Loebl MK 111 C densitometer. The data were corrected in the usual way,¹⁷ giving one intensity curve for each photographic plate. The intensities were modified with the function $s/|f_F|^2$.

The computer drawn background¹⁸ was subtracted separately from each intensity curve on levelled form. The average for each set of plates is presented in Fig. 1.

Due to the limited amount of the compound available, some fairly light plates, in particular the

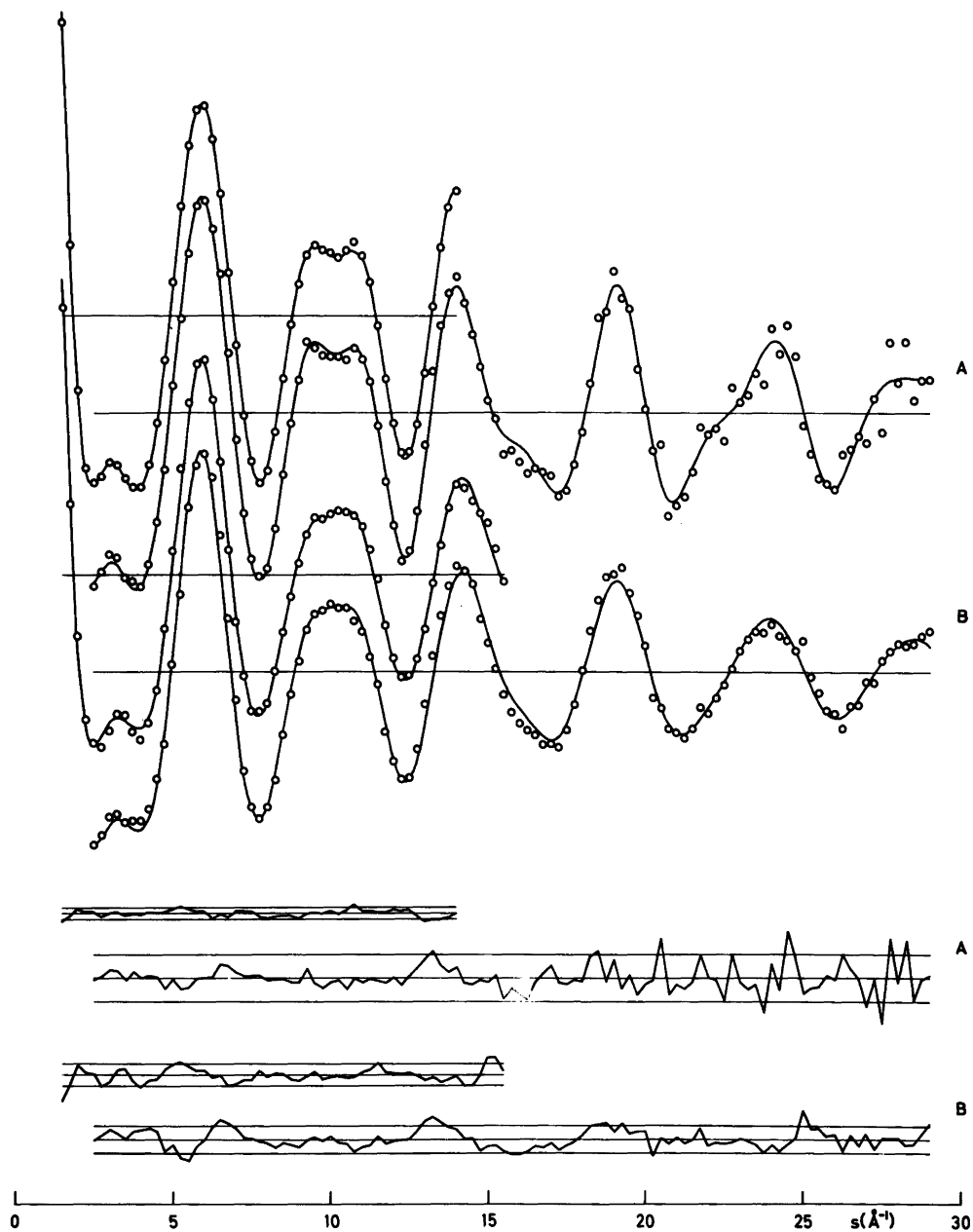


Fig. 1. Intensity and difference curves. The open circles are experimental values, the solid curves are theoretical. The differences, given below, are experimental minus theoretical, and the limits are 3σ , σ being the experimental standard deviation in the observations. A: 25 and B: 504 °C.

Table 1. Experimental conditions and photographic plate data.

Temperature (°C)	25		504	
Nozzle-to-plate distance (mm)	499.27	249.07	499.27	249.07
Electron wave length (Å) ^a	0.05867			
Range of data (s) ^b	1.5–15.5	2.5–29.0	1.5–15.625	2.5–29.0
Data interval (Δs)	0.125	0.250	0.125	0.250
Number of plates used	4	4	5	6
Corresponding curves in Figs. 1 and 2	A		B	

^a As calibrated to benzene, averaged from recordings 3/3–13/4, 10/8–78.³⁹ ^b $s = 4\pi/\lambda \sin \theta (\text{Å}^{-1})$, 2θ is the scattering angle.

25 cm plates at 25 °C, have been applied in this investigation. This is reflected in the unusually large difference curves. The average 3σ levels, given in Fig. 1, exaggerate the experimental noise level in the inner part of the curves, as σ increases with increasing s -values.

The relative amount of each conformer, as well as the structural parameters, were determined by conventional least-squares refinement on the combined, but not connected, intensity data.

The theoretical molecular intensities were calculated according to eqn. 11 of Ref. 17. The scattering amplitudes and phase shifts^{17,19} were calculated analytically by a program originally written by Yates,²⁰ using Hartree-Fock-Slater potentials¹⁹ for C and F, and a molecular bonded potential for H.²¹

STRUCTURE ANALYSIS AND REFINEMENT

Radial distribution curves (RD-curves), calculated from the molecular intensities by a Fourier transformation,¹⁷ are presented in Fig. 2. The bond distances contribute to the first two peaks, together with the short $r(\text{H}_4 \cdots \text{H}_5)$. The peak complex between 1.8 and 2.5 Å corresponds to the torsion-independent, non-bonded distances. The torsional dependent distances contribute to the peak complex between 2.5 and 4 Å, the area and shape of which varies directly with the conformational ratio.

The following parameters were chosen as independent structural parameters. The three bond distances, $r(\text{C}-\text{C})$, $r(\text{C}-\text{F})$ and $r(\text{C}-\text{H})$, the angles $\angle \text{CCF}$, $\angle \text{CCH}$, the projected H_4CH_5 -angle (PV)

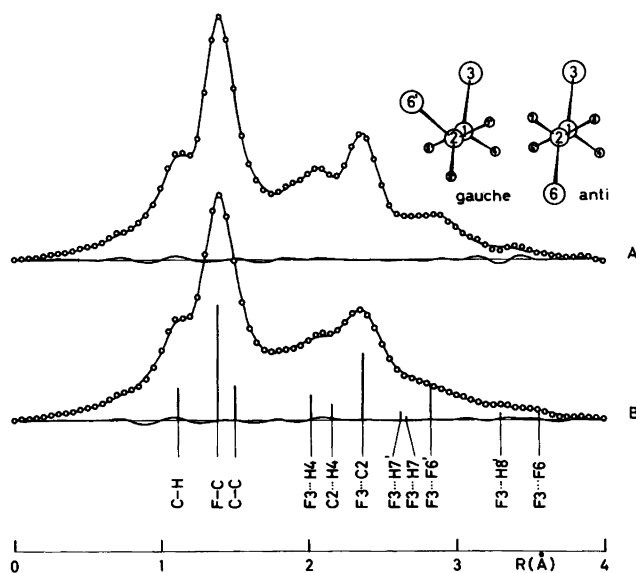


Fig. 2. Radial distribution curves and differences. ($B = 0.0020 \text{ Å}^2$).

and the torsional angle about the C–C axis (ϕ). ϕ is defined as 180° in *anti* and PV is equal to 120° if there is angular C_3 symmetry in the CFH_2 -group.

To compensate for the shrinkage effect,^{22,23} the molecular structure was calculated in the geometric consistent r_x -picture.²⁴ The bond distances were transformed to r_x before calculating the dependent distances by eqn. $r_x = r_a + u^2/r - k = r_a + D$. u is the root-mean-square vibrational amplitude, k the perpendicular amplitude correction coefficient,^{24,25} and r_a the operative electron diffraction parameter.

The torsion independent part of the molecule was assumed to be identical in both conformers, and the common distances were given the *gauche* correction terms (D 's), since *gauche* was found to be the prevailing conformation. The composition in the vapour phase is thus determined from the torsion-dependent distances, the F...F distance in *gauche* (2.8 Å) and *anti* (3.6 Å) being the most important.

D -values and u -values as calculated^{26,27} from the established valence force field⁸ are given in Table 2. Using the same value for the torsional force constant in the two conformers, the torsional frequencies in *gauche* ($\nu_{\tau,g} = 130 \text{ cm}^{-1}$) and *anti*

($\nu_{\tau,a} = 145 \text{ cm}^{-1}$) as assigned by Klæboe *et al.*⁸ were reproduced. Previous experience^{11,14} has indicated that this force constant should be slightly smaller in *anti*, as would have been obtained if these frequencies had been interchanged, as assigned by others.^{9,10}

The absolute magnitude of the calculated D -values for the torsion insensitive distances are somewhat larger than the corresponding ones in 1,2-dichloro-^{11,12} and 1,2-dibromoethane.¹⁴ This reflects the fact that 1,2-difluoroethane has *gauche* as the more stable form, and that the given D -values are calculated for this conformation. The calculated u -values are somewhat smaller than found in the chloro and bromo analogs, but agree excellently with the corresponding reported values for 1,1,2,2-tetrafluoro-²⁸ and hexafluoroethane.^{29,30}

The vibrational amplitudes that did not refine, were fixed at the spectroscopic values. The final results are presented in Table 3. The projected H_4CH_5 -angle could not be refined, and is kept constant at 120° . Only diagonal elements have been included in the weight matrix^{31,32} in the least-squares refinements, as including non-diagonal elements resulted in unacceptable fit and structural parameters at both temperatures. The obtained

Table 2. The differences, $D = u^2/r - k$ (Å), between r_x and r_a and the vibrational amplitudes u (Å), as calculated from the valence force field.⁸ For numbering of atoms see Fig. 2, the primed values refer to *gauche*. The refined u -values at 504°C (u^{exp}) are included for comparisons, 1σ is given in parentheses.

Temp. ($^\circ\text{C}$)	(r)	D		u		u^{exp}
		25	504	25	504	504
C–C	(1.50)	–0.0012	–0.0038	0.055	0.066	
C–F	(1.38)	–0.0054	–0.0148	0.046	0.053	0.054(1)
C–H	(1.12)	–0.0133	–0.0256	0.078	0.079	
F ₃ ...H ₄	(2.02)	–0.0111	–0.0285	0.104	0.115	0.145(8)
H ₄ ...H ₅	(1.80)	–0.0147	–0.0328	0.129	0.136	
F ₃ ...C ₂	(2.37)	–0.0000 ₂	–0.0009	0.074	0.106	0.095(2)
C ₂ ...H ₄	(2.16)	–0.0065	–0.0164	0.107	0.120	
F ₃ ...F ₆	(3.56)	0.0015	0.0032	0.074	0.109	
F ₃ ...H ₇	(2.66)	–0.0000 ₇	–0.0018	0.160	0.220	0.230 ^a
H ₄ ...H ₇	(3.06)	–0.0019	–0.0031	0.129	0.138	
H ₄ ...H ₈	(2.50)	0.0009	–0.0015	0.180	0.222	
F ₃ ...F ₆	(2.83)	0.0071	0.0183	0.148	0.237	0.247 ^a
F ₃ ...H ₇	(2.63)	0.0012	0.0004	0.161	0.218	0.228 ^a
F ₃ ...H ₈	(3.31)	–0.0021	–0.0048	0.106	0.127	
H ₄ ...H ₇	(2.54)	–0.0051	–0.0149	0.175	0.215	
H ₄ ...H ₈	(2.50)	–0.0113	–0.0322	0.175	0.215	
H ₅ ...H ₇	(3.07)	–0.0053	–0.0112	0.131	0.142	

^a Refined in one group.

Table 3. Molecular parameters, distances (r_a) and vibrational amplitudes (u) in Å, angles (\angle_a) in degrees, and estimated correlation coefficients larger than 0.5 (ρ). Standard deviations (1σ) in parentheses.

Temp. (°C)	25	504	Average
$r(\text{C}-\text{C})$	1.504(4)	1.500(4)	1.502(3)
$r(\text{C}-\text{F})$	1.386(2)	1.382(2)	1.384(1)
$r(\text{C}-\text{H})$	1.116(4)	1.117(4)	1.117(3)
$\angle \text{CCF}$	110.8(3)	111.5(3)	111.2(2)
$\angle \text{CCH}$	110.3(2)	109.1(24)	109.7(12)
ϕ_g	71.7(11)	65.0(13)	68.4(9)
$u(\text{C}-\text{F})$	0.045(1)	0.054(1)	
$u(\text{F}_3 \cdots \text{H}_4)$	0.100(10)	0.145(8)	
$u(\text{F}_3 \cdots \text{C}_2)$	0.063(2)	0.095(2)	
$u(\text{F}_3 \cdots \text{F}_{6'})^a$	0.127(8)	0.247(18)	
n_a (%)	9.0(31)	20.6(36)	
R_2 (%)	10.10	8.97	
$\rho(r(\text{C}-\text{C}), \angle \text{CCF})$	-0.82	-0.75	
$\rho(\angle \text{CCH}, u(\text{F}_3 \cdots \text{H}_4))$	-0.72	-0.91	
$\rho(\angle \text{CCH}, u(\text{F}_3 \cdots \text{F}_{6'}))$		0.64	
$\rho(\phi_g, \angle \text{CCF})$	-0.60		
$\rho(\phi_g, \angle \text{CCH})$	0.63		
$\rho(\phi_g, u(\text{F}_3 \cdots \text{H}_4))$	-0.52		
$\rho(\phi_g, u(\text{F}_3 \cdots \text{F}_{6'}))$		-0.65	
$\rho(u(\text{F}_3 \cdots \text{H}_4), u(\text{F}_3 \cdots \text{F}_{6'}))$		-0.55	

^a All torsion sensitive *gauche* u -values refined in one group.

standard deviations (1σ), including the uncertainty of 0.1 % in the wavelength, are given in parentheses.

RESULTS AND DISCUSSION

The set of parameters determined from an *ab initio* calculation³³ is in perfect agreement with the obtained electron-diffraction values. The structural parameters are identical with those previously reported by Brunvoll,⁴ as well as with the results of a parallel reinvestigation by K. Hedberg *et al.*³⁴ made known to the authors after this study had been started. The obtained $r(\text{C}-\text{C})$ and $r(\text{C}-\text{F})$ are significantly smaller than the values ($r(\text{C}-\text{C}) = 1.535(2)$ and $r(\text{C}-\text{F}) = 1.394(0_6)$ Å) obtained by van Schaick *et al.*⁵ This difference may be related to the somewhat too large $u(\text{C}-\text{C})$ and $u(\text{C}-\text{F})$ obtained in the latter investigation, although the relevant correlation coefficients in that investigation are all smaller than 0.5. Also their assumption of more than 98 % *gauche* at room temperature, as well as the somewhat larger torsional angle ($\phi = 74.4(3)^\circ$), may be the reasons for the apparent increase in bond lengths.

Also when compared with the related compounds fluoroethane³⁵ (MW) ($r(\text{C}-\text{C}) = 1.505(4)$, $r(\text{C}-\text{F}) = 1.398(5)$), 1,1,2,2 tetrafluoroethane²⁸ ($r(\text{C}-\text{C}) = 1.518(5)$, $r(\text{C}-\text{F}) = 1.350(2)$), hexafluoroethane²⁹ ($r(\text{C}-\text{C}) = 1.545(6)$, $r(\text{C}-\text{F}) = 1.326(2)$ (Å)), the parameters obtained in this investigation seem the more probable ones. Two substitution effects are observed in fluorinated ethanes. Comparisons with 1,2-difluoroethane, ethane⁴⁰ ($r(\text{C}-\text{C}) = 1.532$ Å) and the above series of molecules reveal that increasing fluorine substitution strengthens all bonds in the molecular system. Two or more substituents at both C-atoms lead to steric effects that tend to increase the central C-C bond, although even in 1,1,2,2-tetrafluoroethane $r(\text{C}-\text{C})$ remains significantly shorter than observed in ethane.

The decrease (72 to 65°) in ϕ_g with increasing temperature is significant with respect to the obtained standard deviations. A possible artifact, introduced by the assumed two rigid conformers model, has been tested for by introducing a more flexible model in *gauche*. The obtained shift in the distance distribution, however, was insignificant, and the observed decrease in the torsional angle

remains. The low temperature value is in good agreement with 73(4)° reported in a MW-study.³⁶

The decrease in ϕ_g is compatible with a hypothetical possibility of a *syn* barrier that is lower than the *gauche/anti* barrier at 120°, as obtained from spectroscopy,⁹ or a torsional potential that is more open towards *syn* in the *gauche* well. But this is in contradiction with a potential calculated *ab initio*. Although this calculation gave *anti* 0.7 kcal mol⁻¹ more stable than the *gauche* conformation,³³ it seems unreasonable that the energy in *syn* ($V^*(0)=8.8$ kcal mol⁻¹) should be in error by 6 kcal mol⁻¹. The barrier at 120° was estimated to 3.1 kcal mol⁻¹. Barriers as low as $V^*(0)=1.33$ kcal mol⁻¹, as predicted from a spectroscopic study⁹ seem unreasonable, as both conformers in the present study are satisfactorily described by rigid molecular models.³⁸ The origin of the reported difficulties⁹ in reproducing satisfactorily the obtained frequencies by a three terms Fourier series expanded torsional potential, may be related to three major points: (a) misassignment of the torsional overtones and hot bands,^{8,10} (b) information from different states of aggregation have been combined and finally (c) including only three Fourier terms in the potential expansion is insufficient when the torsional angle deviates substantially from the idealized 60° *gauche* angle.³⁸

The refined u -values agree satisfactorily with the calculated ones.

Based on the usual formulas^{11,12,37} the conformational energy difference, $\Delta E=E_g-E_a$, and entropy difference, $\Delta S=S_g-S_a$, have been determined. Two approaches have been applied. Firstly, if ΔE and ΔS are assumed to be temperature independent, they may be determined from the slope and

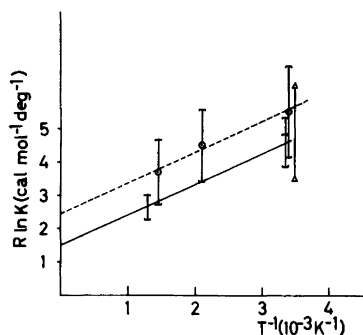


Fig. 3. $R \ln K$ as a function of $1/T$. The solid curve represents the data obtained in this investigation, the dotted line those of Hedberg *et al.*³⁴ The two triangles mark the limits observed by Brunvoll. The standard deviations, marked at each point by vertical lines, are calculated from σ_{n_a} .

intersection, respectively, of the straight line connecting the two observation points ($R \ln K$, $1/T$) (see Fig. 3). Secondly, the observed K -values may be combined with the appropriate vibrational/rotational partition functions (Q). Q has been calculated from the valence force field and the products of the moments of inertia (I). The results of both approaches are presented in Table 4.

Columns A demonstrate that both ΔE and ΔS for all practical reasons may be treated as temperature independent, even within this large temperature interval. As has been found previously,^{12,14} the constancy of ΔS is due to the opposite temperature effect in $R \ln Q_g/Q_a$ and $RT\partial/\partial T \ln Q_g/Q_a$. The table also reveals, as previously found for 1,2-dichloro-¹² and 1,2-dibromoethane,¹⁴ that the deviation of ΔS

Table 4. Thermodynamic terms, (A) calculated from the estimated mol fractions ($K=n_g/n_a$) and partition functions (Q),^a (B) from the line through the two observed ($R \ln K$, $1/T$) points.

Temp (°C)	A			B
	25	504	Average	
n_a (%)	9.0(31)	20.6(36)		
$R \ln(Q_g/Q_a)$ (cal mol ⁻¹ deg ⁻¹)	0.130	0.055	0.092	
$RT \partial/\partial T \ln(Q_g/Q_a)$ (cal mol ⁻¹ deg ⁻¹)	-0.093	-0.054	-0.074	
ΔE° (kcal mol ⁻¹)	-0.92(22)	-0.97(33)	-0.95(20)	
ΔE (kcal mol ⁻¹) ^b	-0.98	-0.99	-0.99	-0.93(41)
ΔS (cal mol ⁻¹ deg ⁻¹)	1.41	1.38	1.40	1.5(8)

^a Calculated from the valence force field and the products of the principal moments of inertia ($I_A I_B I_C$)_g = 3.530528 × 10⁵ and ($I_A I_B I_C$)_a = 3.072044 × 10⁵ (au.Å²)³. Q is the rotational/vibrational partition function. ^b The mean value $\Delta E^\circ = -0.95$ is used.

from $R \ln 2$ is rather small (insignificant compared with the estimated standard deviation).

Comparisons between columns A and B (Table 4), demonstrate the excellent agreement between the results obtained from the electron diffraction data alone (B), and the results obtained when K is combined with the partition functions. The consistency of the obtained results with those of Brunvoll⁴ and Hedberg³⁴ is demonstrated in Fig. 3, and in light of the indicated error limits the agreement is remarkable. Hedberg *et al.*³⁴ report $\Delta E = -0.99(0.81)$ kcal mol⁻¹ and $\Delta S = 2.3(1.7)$ cal mol⁻¹ deg⁻¹. The slightly larger ΔS value obtained in the latter investigation, must reflect a systematic difference, possibly the difference in the fixed torsion-dependent u -values.

The obtained ΔE agrees reasonably with other estimates ($-1.98[\text{R,IR(l)}]$,⁹ $\sim -0.6[\text{IR(g)}]$,⁸ $-0.6[\text{IR(Ar-matrix)}]$,¹⁰ $-0.6[\text{NMR(g)}]$,⁷ $-2.6[\text{NMR(l)}]$, taken into account the additional stabilization of the more polar form (*i.e. gauche*) in the liquid phase. Although the absolute value of ΔE determined by the electron diffraction method is slightly higher than those obtained from vapour phase spectroscopy, the difference is not significant. Taking the large standard deviations into consideration, the energy difference seems insignificantly different from zero. However, according to earlier experience¹¹ the errors seem to exaggerate uncertainties in the conformational ratio. In the present case this effect is enhanced by the increased uncertainties in the outer part of the experimental intensities. Despite the large formal standard deviation the present electron diffraction study settles beyond doubt the prevalence of *gauche*.

The temperature applied in these calculations is measured at the nozzle tip. Previous experience³⁸ has justified that within the present level of accuracy the nozzle temperature is that of the gaseous mixture.

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