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

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Gaseous 1,2-dibromoethane has been studied by electron diffraction at 25, 36, 85, 140 and 200 °C. The most stable conformer is *anti*, which contributes with 95 % at 25 °C decreasing to 82 % at 200 °C in the vapour. 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 $\Delta E = 2.20$ (14) kcal mol^{-1} and $\Delta S = 1.67(30)$ cal mol^{-1} deg^{-1}. The structure remained almost constant with respect to the temperature variations, and the main average parameters (r_a and $\angle_a$) are C – C = 1.506, C – Br = 1.950, C – H = 1.108(Å), ∠CCBr = 109.5, ∠CCH = 110.0 and $\phi_g = 73.0$ (°).

1,2-Disubstituted ethanes consist of a mixture of two conformers,[1-3] *anti* and *gauche*. Due to the difference in energy between the two conformers, the amount of each will vary with the temperature.

The *gauche/anti* ratio (K) may be studied by the gas electron diffraction method, considering K as one of the structural parameters in addition to the geometric and vibrational ones.

In previous studies of this kind,[4-6] the thermodynamic differences deduced from the temperature variations in K proved to give reasonable results. The main scope of this study of 1,2-dibromoethane is to confirm the accuracy of this method and to give a more detailed discussion of the temperature dependency of the thermodynamic quantities ΔE and ΔS.

EXPERIMENTAL

The sample of 1,2-dibromoethane, obtained from Koch-Light Laboratories, (>99 %) was used without further purification. Electron diffraction photographs were obtained with the Balzers Eldigraph KDG-2 unit.[7,8] The experimental conditions are summarized in Table 1. The optical densities at points in a rectangular array covering the plate were measured by a Joyce-Loebl densitometer. For each point in the array the scattering parameter s was calculated, and the final density value obtained by averaging the density for points of very similar s-values.* For this particular molecule it was found necessary to use $\Delta s = 0.125$ Å^{-1} also for the shorter nozzle-to-plate distances.

These data were corrected in the usual way,[9] giving an intensity curve for each photographic plate. The intensities were modified with the function $s/|f_{Br}|^2$.

The background was subtracted separately from each intensity curve. The average for each set of plates was calculated, and composites made at 36 and 200 °C, by scaling a corresponding pair of curves and averaging the intensities in the overlap region. These molecular intensities are given in Fig. 1.

The amount of the two conformers, as well as the structural parameters, are determined by conventional least-squares refinements.

The theoretical molecular intensities were cal-

* In the standard routines applied in this laboratory, the densities were averaged at very similar radii and then converted into densities on the s-scale. These two-step interpolations were smoothing the data too much. This was probably connected with the rapidly oscillating and strongly contributing Br···Br$_a$ distance ($r = 4.6$ Å, $u = 0.072$ Å at 25 °C), and the way it is superposed on the contributions from the other distances.

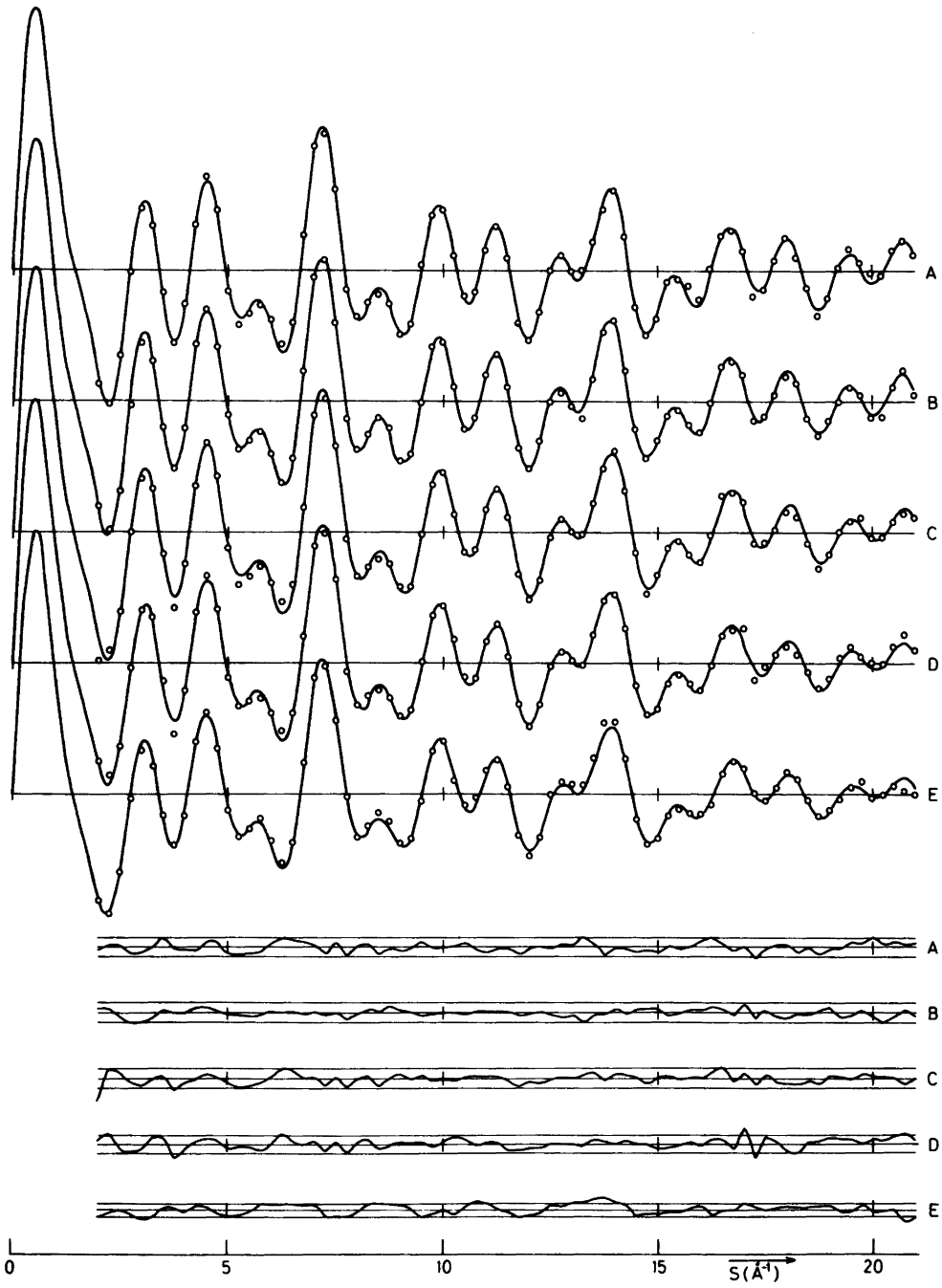

Fig. 1. Intensity and difference curves. The solid curves are theoretical, calculated from the parameters in Table 4, O are experimental values, the difference is experimental minus theoretical and the limits are 3σ, σ being the experimental standard deviation in the observations.
A: 25, B: 36, C: 85, D: 140 and E: 200 °C.

Table 1. Experimental conditions and photographic plate data.

Temperature (°C)	25	36		85	140	200	
Nozzle-to-plate distance (mm)	329.27	578.74	329.27	329.27	329.27	578.91	249.47
Electron wave length (Å)[a]	0.058510	0.058535	0.058510	0.058510	0.058510	0.058524	0.058530
Range of data (s)[b]	2.0–21.0	1.0–13.375	2.0–21.0	2.0–21.0	2.0–21.0	1.0–13.375	2.0–21.0
Data interval (Δs)	0.125	0.125	0.125	0.125	0.125	0.125	0.125
Number of plates used	6	5	6	7	6	6	6
Corresponding curves in Figs.							
Figs. 1 and 2	A	B		C	D	E	

[a] Determined from ZnO diagrams, systematically 0.1 % too low as compared with benzene.
[b] $s=4\pi/\lambda \sin\theta$ (Å^{-1}), 2θ is the scattering angle.

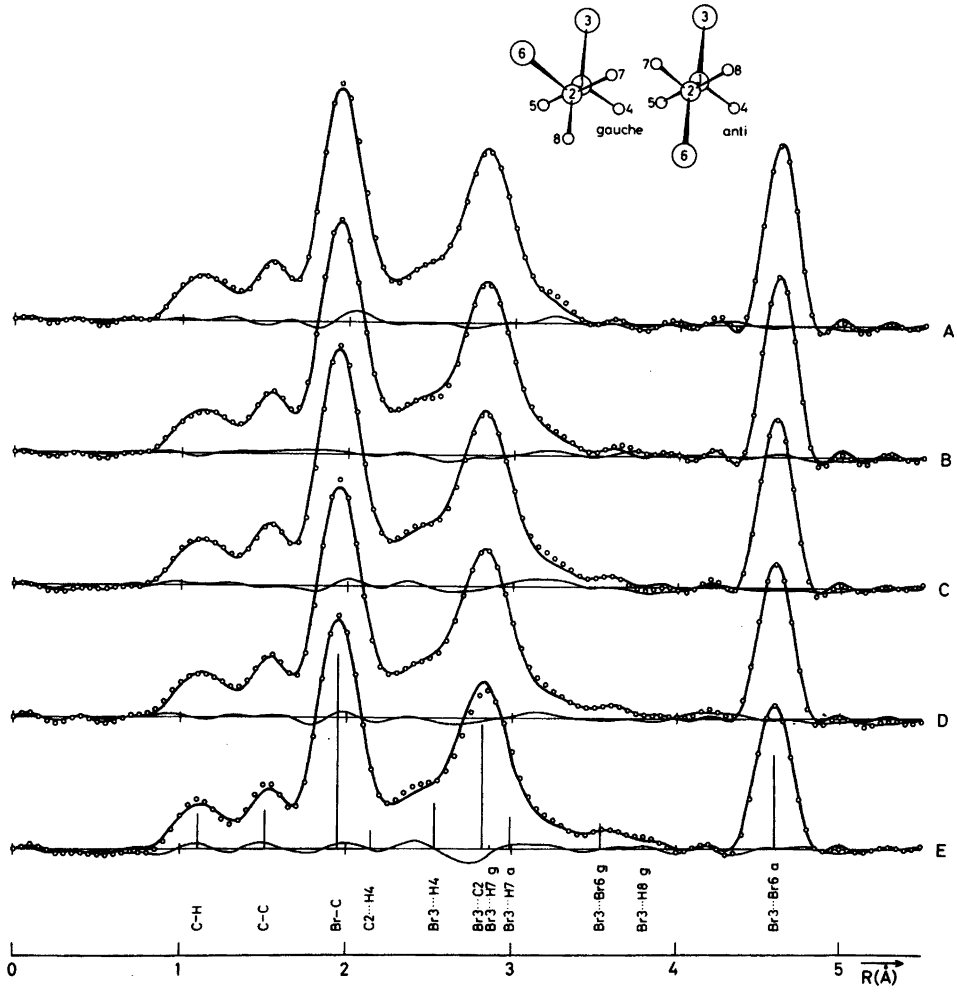

Fig. 2. Radial distribution curves and differences ($B=0.0015$ Å^2).

culated according to eqn. 11 of Ref. 9. The scattering amplitudes and phase shifts[9,10] were calculated analytically by a program originally written by Yates,[11] using Hartree-Fock-Slater potentials[12] for C and Br, and molecular bonded potential[13] for H.

Due to extraneous scattering from the bromine atoms, reproducable intensities were obtained in a more limited s-range than normally achieved, and intensities up to $s=21$ Å^{-1} are used in this study.

STRUCTURE ANALYSIS AND REFINEMENT

Radial distribution curves (RD-curves), calculated from the molecular intensities by a Fourier transformation,[9] are shown in Fig. 2. The bond distances contribute to the first three peaks, together with the short $r(H_4\cdots H_5)$. The peak complex between 2.5 and 4.0 Å corresponds to all the nonbonded distances, except the torsional dependent $r(Br_3\cdots Br_6)$ in *anti*, which gives rise to an isolated peak at 4.60 Å, the area of which varies directly with the amount present.

In addition to the torsional angle, ϕ, the three bond distances, r(C−C), r(C−Br) and r(C−H), and the angles ∠CCBr and ∠CCH, were chosen as independent geometric parameters. ϕ is defined as 180° an *anti*. Since the H-positions are not very well-defined, C_3-symmetry with respect to the angles was assumed in the $CBrH_2$ groups.

The molecular structure was calculated in the geometric consistent r_α-picture, the torsional independent part assumed to be identical in both conformers.[14] The bond distances were transformed by the eqn. $r_\alpha=r_a+u^2/r-k=r_a+D$, where k is the perpendicular amplitude correction coefficient[14,15] and r_a the operative electron diffraction parameter. The dependent structural parameters were then calculated from the geometric restraints, and transformed back to the corresponding r_a-values before the structure was refined. The reported angles correspond to the r_α-structure.

Vibrationally different distances in the two conformers were given different correction terms (D's). The differences are rather small, however, and the composition in the vapour phase is mainly determined from the torsional dependent distances, the

Table 2. The difference, $D=u^2/r-k$ (Å), between r_α and r_a, as calculated from the valence force field established by Schachtschneider and Snyder,[17] with torsional force constants from this work, $f_{\tau,g}=0.360$ and $f_{\tau,a}=0.234$ (mdyn Å rad^{-2}).

The suffix a and g refers to *anti* and *gauche* respectively, the first indicates the conformer, and in the double suffix, the second gives the type of distances considered.

Temp (°C)		25	36	85	140	200
r(C−C)	(1.50)	0	0	0	0	0
r(C−Br)	(1.94)	−0.0046	−0.0047	−0.0055	−0.0064	−0.0073
r(C−H)	(1.12)	−0.0107	−0.0108	−0.0113	−0.0120	−0.0128
$r(Br_3\cdots H_4)$	(2.51)	−0.0064	−0.0066	−0.0076	−0.0087	−0.0100
$r(H_4\cdots H_5)$	(1.79)	−0.0106	−0.0108	−0.0116	−0.0126	−0.0137
$r(C_2\cdots Br_3)$a	(2.83)	−0.0031	−0.0032	−0.0038	−0.0043	−0.0050
$r(C_2\cdots H_4)$a	(2.18)	−0.0020	−0.0020	−0.0022	−0.0025	−0.0028
$r(Br_3\cdots Br_6)$a	(4.60)	0.0011	0.0012	0.0013	0.0015	0.0017
$r(Br_3\cdots H_7)$a,g	(3.03)	0.0008	0.0008	0.0007	0.0007	0.0006
$r(H_4\cdots H_7)$a,a	(3.12)	−0.0028	−0.0028	−0.0030	−0.0031	−0.0034
$r(H_4\cdots H_8)$a,g	(2.56)	0.0011	0.0011	0.0009	0.0008	0.0006
$r(C_2\cdots Br_3)$g	(2.83)	−0.0003	−0.0003	−0.0004	−0.0004	−0.0005
$r(C_2\cdots H_4)$g	(2.18)	−0.0062	−0.0064	−0.0072	−0.0081	−0.0091
$r(Br_3\cdots Br_6)$g	(3.47)	0.0081	0.0084	0.0097	0.0112	0.0128
$r(Br_3\cdots H_7)$g,g	(2.96)	0.0026	0.0026	0.0028	0.0030	0.0033
$r(Br_3\cdots H_8)$g,a	(3.84)	−0.0025	−0.0025	−0.0027	−0.0030	−0.0033
$r(H_4\cdots H_7)$g,g	(2.61)	−0.0044	−0.0046	−0.0055	−0.0064	−0.0075
$r(H_4\cdots H_8)$g,g	(2.52)	−0.0060	−0.0062	−0.0073	−0.0084	−0.0097
$r(H_5\cdots H_7)$g,a	(3.12)	−0.0090	−0.0092	−0.0102	−0.0112	−0.0125

Table 3. The vibrational amplitudes, u(Å) as calculated from valence force field.

Temp (°C)		25	36	85	140	200
$u(C-C)$	(1.50)	0.0506	0.0506	0.0510	0.0515	0.0522
$u(C-Br)$	(1.94)	0.0534	0.0538	0.0554	0.0574	0.0597
$u(C-H)$	(1.12)	0.0780	0.0780	0.0780	0.0780	0.0780
$u(Br_3\cdots H_4)$	(2.51)	0.1112	0.1114	0.1125	0.1141	0.1161
$u(H_4\cdots H_5)$	(1.79)	0.1263	0.1263	0.1264	0.1267	0.1272
$u(C_2\cdots Br_3)$	(2.83)	0.0745	0.0754	0.0794	0.0838	0.0885
$u(C_2\cdots H_4)$a	(2.18)	0.1074	0.1075	0.1082	0.1091	0.1103
$u(Br_3\cdots Br_6)$a	(4.60)	0.0718	0.0730	0.0779	0.0832	0.0887
$u(Br_3\cdots H_7)$a,g	(3.03)	0.1656	0.1670	0.1737	0.1812	0.1893
$u(H_4\cdots H_7)$a,a	(3.12)	0.1267	0.1268	0.1271	0.1276	0.1283
$u(H_4\cdots H_8)$a,g	(2.56)	0.1708	0.1712	0.1731	0.1758	0.1793
$u(C_2\cdots Br_3)$g	(2.83)	0.0745	0.0754	0.0794	0.0838	0.0885
$u(C_2\cdots H_4)$g	(2.18)	0.1074	0.1075	0.1082	0.1091	0.1103
$u(Br_3\cdots Br_6)$g	(3.47)	0.1645	0.1674	0.1799	0.1930	0.2064
$u(Br_2\cdots H_7)$g,g	(2.96)	0.1597	0.1609	0.1665	0.1730	0.1802
$u(Br_3\cdots H_8)$g,a	(3.84)	0.1028	0.1032	0.1053	0.1078	0.1106
$u(H_4\cdots H_7)$g,g	(2.61)	0.1674	0.1678	0.1695	0.1719	0.1750
$u(H_4\cdots H_8)$g,g	(2.52)	0.1666	0.1669	0.1688	0.1713	0.1744
$u(H_5\cdots H_7)$g,a	(3.12)	0.1266	0.1267	0.1270	0.1274	0.1282

Br···Br distance in *gauche* (3.5 Å) and *anti* (4.6 Å) being most important.

D-Values and root-mean-square amplitudes (u-values) as calculated[15,16] from the established valence force field[17] and the cartesian displacement coordinates are given in Table 2 and 3, respectively. The torsional force constants were varied to reproduce the observed frequencies at 80 cm^{-1} in *gauche* (observed at 91 cm^{-1} in liquid[18,19]) and 118 cm^{-1} in *anti*. The values obtained are similar to those previously obtained for 1,2,3-tribromopropane.[20] The torsional force constant in *anti* was found to be slightly smaller than in *gauche*, similar to the difference previously found for 1,2-dichloroethane.

The absolute magnitude of all the calculated *D*-values is somewhat larger than found for 1,2-dichloroethane.[4,5] The estimated u-values are somewhat smaller than the corresponding ones in 1,2-dichloro- and 1,1,2,2-tetrafluoroethane,[21] whereas the others, which involve halogens generally are increasing in going from F to Br.

The vibrational amplitudes that did not refine, were given the calculated values, although refinements at the different temperatures of $u(C-Br)$, $u(C_2\cdots Br_3)$ and $u(Br_3\cdots Br_6)_a$ gave slightly lower values. Since the refined u-values were somewhat dependent of the subtracted experimental background, we chose to let the average refined values determine the level of these u-values, and estimated a new set assuming the same temperature slope as obtained from the force field calculations.

It was also quite obvious from the preliminary refinements that the shrinkage corrections based upon the harmonic force field calculations, were much too small for Br···Br *anti* distance, and it was decided to refine this distance as an independent parameter as well.

Repeated least-squares refinements revealed a slight dependency of some of the geometry parameters on the experimental background, whereas $r(C-Br)$, $\angle CCBr$ and $r(Br_3\cdots Br_6)_a$ were practically invariant, and almost identical at the different temperatures. Inspection of Tables 2 and 3 shows that of the parameters refined only the u-values for the long non-bonded distances and the *gauche/anti* ratio vary significantly with the temperature, in accordance with general experiences.

It was therefore felt appropriate in this case to determine an average geometry from the best fit at all temperatures. The final backgrounds were adjusted to the intensity differences obtained with this mean structural model, and the quality was judged by the smoothness of particularly the inner part of

Table 4. 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 deviation (1σ) in parentheses.

Temp (°C)	Average [a]	25	36	85	140	200
r(C−C)	1.506	(7)	(6)	(7)	(7)	(7)
r(C−Br)	1.950	(3)	(2)	(3)	(3)	(3)
r(C−H)	1.108	(8)	(7)	(8)	(8)	(8)
$r(Br_3\cdots Br_6)_a$		4.611(5) *	4.612(5) *	4.600(5) *	4.605(2) *	4.603(5) *
∠CCBr	109.5	(4)	(3)	(4)	(4)	(4)
∠CCH	110.0	(11)	(9)	(11)	(12)	(13)
ϕ_g	73.0	(46)	(32)	(27)	(22)	(20)
u(C−Br)	0.0534	0.049(3)	0.050(3)	0.051(4)	0.053(4)	0.056(4)
$u(C_2\cdots Br_3)$	0.0745	0.065(4)	0.066(4)	0.070(5)	0.075(6)	0.079(7)
$u(Br_3\cdots Br_6)_a$	0.0718	0.064(2)	0.065(2)	0.070(2)	0.075(2)	0.081(2)
n_a (%)		95.1(18) *	93.7(16) *	89.9(19) *	86.2(19) *	82.5(30) *
R_2 (%) [b]		10.3	8.9	11.0	11.4	12.3
$\rho(r$(C−C),∠CCBr)		−0.88	−0.88	−0.87	−0.87	−0.86
$\rho(\gamma$,∠CCH)		0.63	0.63	0.63	0.64	0.64
$\rho[\gamma,u$(C−Br)]		0.67	0.67	0.68	0.68	0.68
$\rho[\gamma,u(C_2\cdots Br_3)]$		0.50	0.53	0.60	0.65	0.68
$\rho(\gamma,n_a)$		−0.78	−0.78	−0.77	−0.76	−0.75
$\rho[n_a,u(C_2\cdots Br_3)]$		−0.54	−0.53	−0.54	−0.54	−0.54
$\rho[n_a,u(C_2\cdots Br_3)]$		−0.49	−0.53	−0.64	−0.71	−0.77

[a] See text, calculated u-values at 25 °C. 0.1 % r is added to the refined values to account for the systematic error in the wavelength. [b] $R_2=(\Sigma w\Delta^2/\Sigma wI^2)^{\frac{1}{2}}\times 100$.

the final RD-curves.

To get some information about the uncertainty introduced by fixing the structure to a mean, all the estimated values were refined one cycle, and corresponding standard deviations and correlation coefficients were calculated. These are given in Table 4, together with the mean structural parameters, the refined $r(Br_3\cdots Br_6)_a$ and the percentage of *anti* (n_a). The standard deviations are those obtained from diagonal[22,23] least-squares refinements, corrected for a uncertainty of 0.1 % in the wavelength. Refinements with fixed mean structure are marked.* Previous experience[4] seems to indicate that this estimate of σ_{n_a} probably is negligibly smaller than one would have obtained from a full individual structural refinement.

RESULTS AND DISCUSSION

The structural parameters (Table 4) are quite normal and agree very well with previously reported results,[20,24,25] except that u(C−Br) and $u(C_2\cdots Br_3)$ as estimated by Brunvoll[24] are definitely too large. Because of the relatively small *gauche* contribution, the torsional angle (ϕ_g) was difficult to determine. Several refinements, especially at the higher temperature recordings, indicated that 73° was a reasonably good values, as also is indicated by the relatively normal standard deviations in the first cycle refinements. This value is also identical to the angle previously reported by Brunvoll.[24] Although larger than the corresponding angle in 1,2,3-tribromopropane[20] (where 65.3° must be considered as a compromise between the Br/Br repulsions in the 1,2 and 1,3-positions) it agrees reasonably well with the torsional angle in 1,2-dichloroethane[4,5] [$\bar{\phi}_g=75.3(9)°$].

The measurements of the *gauche/anti* ratio as a function of the temperature have been used in a thermodynamic study of the conformational equilibrium. If we consider the conformational equilibrium *anti* ⇌ *gauche*, the difference in energy, $\Delta E=E_g-E_a$, and the difference in entropy, $\Delta S=S_g-S_a$, between the two conformers, may be obtained from the temperature variation of the *gauche/anti* ratio K[4,5,26], by use of the formula

$$K=\frac{n_g}{n_a}=e^{-(\Delta E-T\Delta S)/RT}=\frac{2\,Q_g}{Q_a}e^{-\Delta E^0/RT} \qquad (1)$$

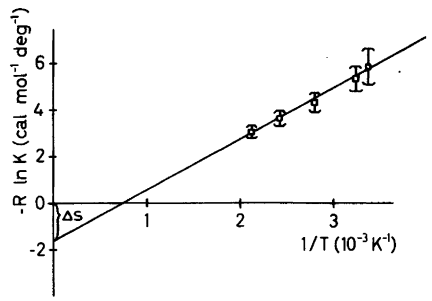

Fig. 3. $-R \ln K$ as a function of $1/T$. The standard deviations marked at each point by vertical lines, are calculated from σ_{n_a}.

n is the percentage of the conformers *gauche* (g) and *anti* (a). Q is the vibrational/rotational partition function and $\Delta E°$ is the energy difference between *gauche* and *anti* at the absolute zero point. The factor 2 is the statistical weight for the two identical *gauche* forms, and is included in ΔS. Thus $\Delta S = R \ln 2 + \Delta S_c$, where ΔS_c may be considered as the difference in conformational entropy.

These differences may be obtained in two ways. Firstly, if ΔE and ΔS are assumed to be temperature independent, they may be determined from the slope and intersection, respectively, of the straight line fitted to the observed $(-R \ln K, 1/T)$ points (see Fig. 3). Secondly, if the appropriate vibrational-rotational partition functions, as calculated from the valence force field, are combined with the observed K-values an average estimate of ΔE and ΔS may be calculated. As in the earlier papers[4-6] both approaches were used in this investigation, and the results are given in Table 5.

Columns A demonstrate that both ΔE and ΔS are practically constant in the actual temperature interval, indicating that the assumed linearity of $-R \ln K$ as a function of $1/T$ is valid. The constancy of ΔS is obviously due to the opposite temperature effect of the $R \ln Q_g/Q_a$ and $RT\,\partial/\partial T \ln Q_g/Q_a$ functions. The table also reveals, as previously found for 1,2-dihaloethanes,[5,18] that the deviation of ΔS from $R \ln 2$ is rather small (insignificant compared with the estimated standard deviation, 0.3 cal mol^{-1} deg^{-1}), but that both $R \ln Q_g/Q_a$ and $RT\,\partial/\partial T \ln Q_g/Q_a$ have to be included if more accurate calculations are to be made.

The discrepancy between the estimates of ΔS may be connected with the assumption that the internal rotation also is a harmonic motion as well as with the uncertainty in the assigned torsional frequencies: Shimanouchi[19] gives 91(l) and 118 (g) cm^{-1} in *gauche* and *anti* respectively, whereas Tanabe *et al.*[18] give ~70(l) and 126(l), the latter in much better agreement with the "pure" electron diffraction results (column B). In 1,2-dichloroethane[5] the conformational entropy was estimated to be less than zero ($\Delta S_C = \Delta S - R \ln 2 = -0.48$ cal mol^{-1} deg^{-1}). In 1,2-dibromoethane we obtain $\Delta S_C = 0.29$

Table 5. Thermodynamic terms, (A) calculated from estimated mol fractions ($K = n_g/n_a$) and partition functions (Q),[a] (B) from a least-squares fitted straight line to the observed $(-R \ln K, 1/T)$ points. Standard deviation (1σ) in parentheses.

Temp (°C)	A						B
	25	36	85	140	200	Average	
n_a (%)	95.1(18)	93.7(16)	89.9(19)	86.2(19)	82.5(20)		
$R \ln (Q_g/Q_a)$ (cal mol^{-1} deg^{-1})	0.072	0.056	−0.009	−0.067	−0.118	−0.013	0.71
$RT\,\partial/\partial T \ln (Q_g/Q_a)$ (cal mol^{-1} deg^{-1})	−0.457	−0.450	−0.422	−0.394	−0.362	−0.417	−0.42
$\Delta E°$ (kcal mol^{-1})	2.19(23)[b]	2.10(8)	2.05(15)	2.05(13)	2.05(13)	2.09(3)[c]	
ΔE (kcal mol^{-1})[d]	1.95	1.95	1.94	1.93	1.92	1.94	2.20(14)
ΔS (cal mol^{-1} deg^{-1})[e]	0.99	0.98	0.95	0.92	0.90	0.95	1.67(30)[f]

[a] Calculated from the valence force field[17] [$\nu_{\tau,g} = 80$ and $\nu_{\tau,a} = 118$ (cm^{-1})] and the products of the principal moments of intertia ($(I_A I_B I_C)_g = 2.056762 \times 10^7$ and $(I_A I_B I_C)_a = 1.335220 \times 10^7$ (a.w.Å^2)). Q is the rotational/vibrational partition function. [b] Standard deviations calculated according to $\sigma_{\Delta E°} = \partial/\partial n_a \Delta E° \sigma_{n_a}$. [c] Standard deviations calculated from the squared deviations from the mean. [d] $\Delta E = \Delta E° + RT^2 \partial/\partial T \ln (Q_g/Q_a)$,[26] the mean value, $\Delta E° = 2.09$, is used. [e] $\Delta S = R \ln 2 + R \ln (Q_g/Q_a) + RT\partial/\partial T \ln (Q_g/Q_a)$. [f] This ΔS corresponds to $\nu_{\tau,g}/\nu_{\tau,a} = 0.45$, giving $\nu_{\tau,g} = 53$ cm^{-1} if $\nu_{\tau,a} = 118$ cm^{-1} is assumed to be correct. The standard deviations are obtained from the least squares fitting.

cal mol^{-1} deg^{-1} from the straight line fit (column B, Table 5), whereas the estimated partition functions give $\Delta S_C = -0.42$ cal mol^{-1} deg^{-1} (column A, Table 5). Although these values are not significantly different from zero, the reasons for a positive value for ΔS_C in 1,2-dibromoethane may be that increased halogen/halogen interactions lead to a relatively broader minimum in *gauche* 1,2-dibromoethane than in *gauche* 1,2-dichloroethane. We therefore believe that the estimate by the straight line fit is the most reliable in this case.

The two estimates of ΔE are slightly, although not significantly, different, but definitely higher than previous estimates (*e.g.* 1.6 [ED(*g*)],[24] 1.5 [IR(*g*)],[29] 0.9 [IR,R(*l*)],[18] 0.75 [R(*l*)] estimated 1.6 (*g*),[27] 0.9 [R(*l*)][28] [kcal mol^{-1}]).

Because of the stabilization of the more polar form (*i.e., gauche*) in the liquid state, it is generally expected that ΔE in the liquid state should be smaller than the vapour phase value.[3] The difference in the case of 1,2-dibromoethane, approximated from dielectric constants and dipole moments to 0.9 kcal mol^{-1},[27] and from experiment[29] to 0.8 kcal mol^{-1}, is reducing the apparent discrepancy, but the straight line estimate (column B, Table 5) is still the highest observed value for this conformational energy difference.

The estimated standard deviation ($1\sigma = 0.14$ kcal mol^{-1}) is rather small, but covers, of course, only random errors in ΔE. The critical point in this type of thermodynamic study is the assumption that the nozzle temperature is identical to the gas temperature[30,31] at the scattering point. Previous experiences[4,5,32] seem to indicate that this assumption is sufficiently accurate at the present level of accuracy of the electron diffraction method. However, applying the formula $T_{sample} = 0.8\ T_{nozzle}$[33] reduces the estimate in this case to $\Delta E' = 1.76$ kcal mol^{-1}, which is significantly lower. This suggests that for larger ΔE the uncertainty in the temperature may be of greater importance, provided Bauer's formula gives the correct temperature, and that the equilibrium was established at this temperature.

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