

# Conformational Analysis. The Structure and Composition of the Rotational Conformers of 1,2-Dicyanoethane (Succinonitrile) as Studied by Gas Electron Diffraction

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Gaseous 1,2-dicyanoethane has been studied by electron diffraction. The more stable conformer in the vapour is *anti*, contributing with 74 (7) % at 170 °C. From the *gauche/anti* ratio and the calculated partition functions  $\Delta E = E_g - E_a = 1.5(3)$  kcal mol<sup>-1</sup> and  $\Delta S = S_g - S_a = 1.4$  cal mol<sup>-1</sup> deg<sup>-1</sup> (1 cal = 4.184 J). The main structural parameters ( $r_a$  and  $\angle_s$ ) are C–C = 1.561(6), C–CN = 1.465(2), C–H = 1.092(10), C≡N = 1.161(2) (Å),  $\angle CCC = 110.4(5)$ ,  $\angle CCH = 107.9(19)$  and  $\phi_g = 75$  (8) (°). When shrinkage corrections were included, the C–C≡N fragment was found to be linear and the symmetry in the CH<sub>2</sub>CN-groups with respect to the angles was C<sub>3</sub>.

1,2-Disubstituted ethanes consist of a mixture of two conformers,<sup>1–3</sup> *anti* and *gauche*. Usually *anti* is the more stable, but for some substituents favourable interactions may give preference to *gauche*. Both 1,2-difluoro<sup>4–10</sup> and 1,2-dicyanoethane<sup>11–15</sup> were found to be more stable as *gauche* conformers in the liquid as well as in the crystalline state. Only *gauche* remains when the solids are cooled, below –50 °C for dicyanoethane and below –180 °C for difluoroethane. In analogy with the findings for 1,2-difluoroethane one may expect that also for 1,2-dicyanoethane *gauche* is the more stable conformer in the gas phase. In order to establish the conformational preference, the microwave spectrum of dicyanoethane has recently been recorded by Harald Møllendal at this institute. But although a spectrum was observed, it could not be satisfactorily assigned.

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<sup>16–19</sup> the thermodynamic data deduced from *K* combined with appropriately calculated partition functions, *Q*, have proved to give reasonable results. The scope of this work is firstly to establish which conformation is the more stable in the gas phase, and secondly to estimate the thermodynamic quantities  $\Delta E$  and  $\Delta S$  for the *anti* ⇌ *gauche* equilibrium.

## EXPERIMENTAL

The sample of 1,2-dicyanoethane, obtained from Fluka A.G. (*puriss*), was used without further purification. Electron-diffraction photographs were obtained with the Balzers Eldigraph KDG-2 unit.<sup>20,21</sup> The experimental conditions were as summarized: Nozzle-to-plate distance 498.56 mm (5 plates) and 248.62 mm (6 plates), wavelength as determined by calibration to benzene 0.058620 Å, the nozzle temperature 170 °C. Range of data were 2.000–14.000 and 5.000–29.500 Å<sup>-1</sup> with  $\Delta s = 0.125$  and 0.250 Å<sup>-1</sup>, respectively. The optical densities were measured by a Joyce-Loebl MK 111 C densitometer.<sup>19</sup> The data were corrected in the usual way,<sup>22</sup> giving one intensity curve for each photographic plate. The intensities were modified with the function  $s/|f_C||f_N|$ .

The computer-drawn background<sup>23</sup> was subtracted separately from each intensity curve. The average for each set of plates is presented in Fig. 1.

The relative amount of the two conformers, as well as the structural parameters, is determined by conventional least-squares refinements on the combined, but not connected, intensity data.

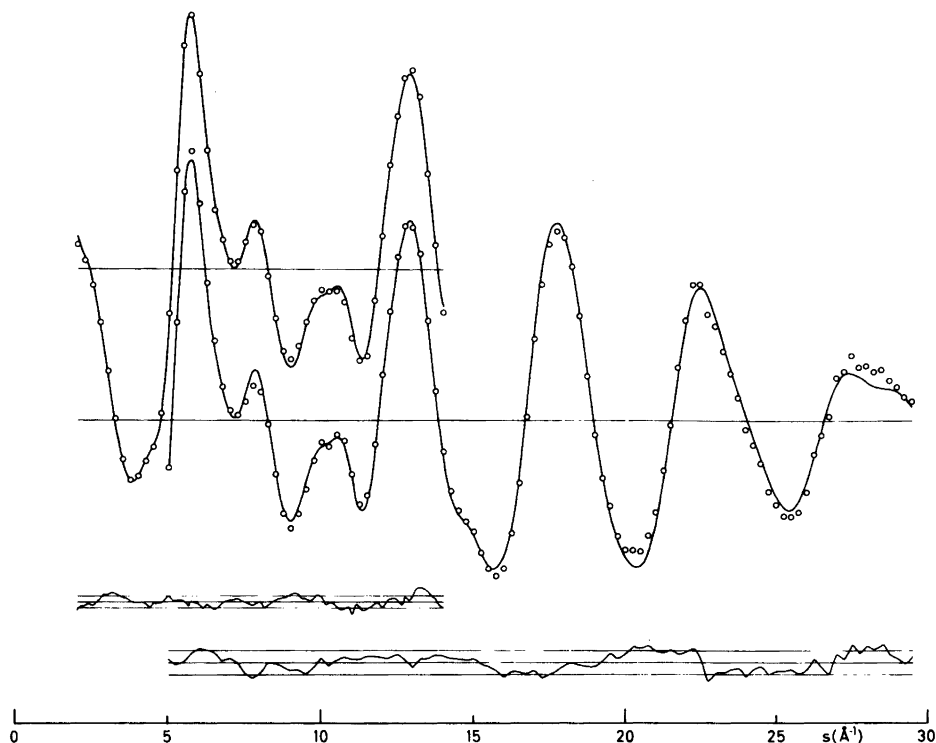


Fig. 1. Intensity curves. 50 cm the upper, 25 cm the lower curve and below, the corresponding difference curves. The solid curves are theoretical, calculated from the parameters in Table 3, c, the open circles are experimental points. The difference is experimental minus theoretical and the limits are  $3\sigma$ ,  $\sigma$  being the experimental standard deviation in the observed points.

The theoretical molecular intensities were calculated according to eqn. 11 of Ref. 22. The scattering amplitudes and phase shifts<sup>22,24</sup> were calculated analytically by a program originally written by Yates,<sup>25</sup> using Hartree-Fock-Slater<sup>24</sup> potentials for C and N, and a molecular bonded potential for H.<sup>26</sup>

#### STRUCTURE ANALYSIS AND REFINEMENT

The radial distribution curve (RD-curve), calculated from the molecular intensities by a Fourier transformation,<sup>22</sup> is shown in Fig. 2. The bond distances contribute to the first two peaks. The peak complex between 2 and 3.5 Å corresponds to all the non-bonded distances, except the torsional dependent  $C_3 \cdots C_7$ ,  $C_3 \cdots N_8$  and  $N_4 \cdots N_8$  distances in *anti*. These distances give rise to a shoulder at

3.7 Å and isolated peaks at 4.8 and 5.8 Å, respectively. The area of these outer peaks varies directly with the amount of *anti* present, and the experimental RD-curve clearly demonstrates the predominance of the *anti* conformer.

In addition to the torsional angle in *gauche*,  $\phi_g$ , the four bond distances,  $r(C_1-C_2)$ ,  $r(C_2-C_3)$ ,  $r(C \equiv N)$  and  $r(C-H)$ , and the angles  $\angle CCC$ ,  $\angle CCH$ ,  $\angle CCN$  and the projected CCH-angle, PV, were chosen as independent geometric parameters.  $\phi$  is defined as  $180^\circ$  in *anti*.  $\angle CCN$  less than  $180^\circ$  implies that the  $C \equiv N$ -groups are bent towards the  $C_1-C_2$ -chain. PV is equal to  $120^\circ$  if there is angular  $C_3$ -symmetry in the  $CH_2CN$ -groups.

To compensate for the shrinkage effect<sup>27,28</sup> the molecular structure was calculated in the geometrically consistent  $r_a$ -picture.<sup>29</sup> The bond distances were transformed by the eqn.  $r_a = r_u + u^2/r - k = r_u + D$ , where  $k$  is the perpendicular amplitude correction

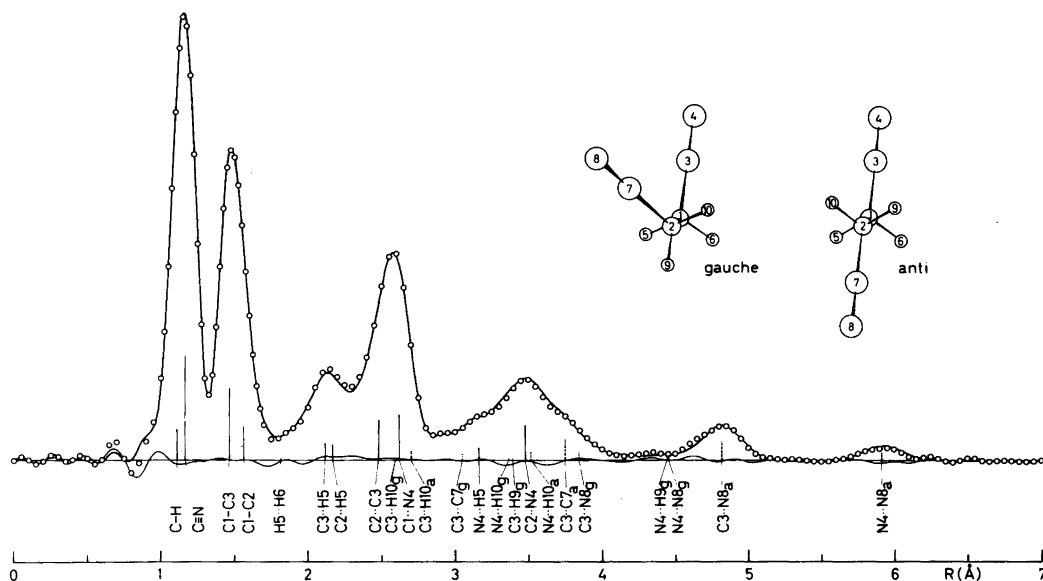


Fig. 2. Radial distribution curve and difference ( $B=0.0015 \text{ \AA}^2$ ).

coefficient<sup>29,30</sup> 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 *anti* correction terms ( $D$ 's), since *anti* was found to be the prevailing conformer. The composition in the vapour is thus determined from the torsion-dependent distances,  $r(C_3 \cdots C_7)$ ,  $r(C_3 \cdots N_8)$  and  $r(N_4 \cdots N_8)$  being most important.

A normal coordinate analysis has been carried out to determine a force field in agreement with the observed vibrational frequencies.<sup>11</sup> The established general valence force field (Table 1) is reasonable compared with related molecules,<sup>31-32</sup> although some of the bending constants and coupling constants particularly are a little different. The calculated  $D$ -values and root-mean-square amplitudes are given in Table 2.

Due to the coupling between the two strong cyano dipoles in the liquid phase the IR-spectrum in the low frequency region consists of a very broad band obscuring the information about the torsional frequency. Since dicyanoethane also has a very low vapour pressure, we have not been able to observe the torsional frequency. The assumed value of the torsional force constant ( $f_t$ ) is somewhat

arbitrarily chosen, although it is supported by assignments of a Raman line ( $l,s$ )<sup>36,37</sup> at  $92-145 \text{ cm}^{-1}$ , varying with temperature and phase.

The comparatively small amount of *gauche* present makes any refinement of the torsional dependent  $u$ -values to determine  $f_t$  impossible. The assumed value of  $0.12 \text{ mdyn \AA rad}^{-2}$  gives a reasonable torsional frequency ( $\nu_t \sim 80 \text{ cm}^{-1}$ ) in comparison with related molecules (e.g. dichloro-

Table 1. Force constants.<sup>a</sup>

Stretch		Interaction	
$f_{C_1C_2}$	4.62	$f_{C_1C_2, C_2CH}$	0.12
$f_{C_2C_3}$	5.47	$f_{C_1C_2, CCC}$	0.23
$f_{CN}$	17.37	$f_{C_3CH, C_3CH}$	-0.039
$f_{CH}$	4.82	$f_{C_3CH, f_{C_2CH}}$	0.015
Bending			
$f_{CC}$	1.09	$f_{C_2CH}$	0.61
$f_{CCN}$	0.36	$f_{HCH}$	0.50
$f_{C_3CH}$	0.67	$f_t$	0.12

<sup>a</sup> Stretching constants in  $\text{mdyn \AA}^{-1}$ , stretch-bending in  $\text{mdyn rad}^{-1}$  and bending in  $\text{mdyn \AA rad}^{-2}$ . An artificial bend of  $1^\circ$  has been introduced in the  $C-C \equiv N$  chain, to enable the program to be used in its present version.

Table 2. The differences,  $D = u^2/r - k$  (Å), between  $r_a$  and  $r_b$  and the vibrational amplitudes,  $u$  (Å), as calculated from the valence force field at 170 °C.

Distance <sup>a</sup> type	$r$ (Å)	$D$	$u$	$u_{\text{exp}}^b$
C <sub>1</sub> -C <sub>2</sub>	(1.54)	-0.0007	0.052	
C <sub>1</sub> -C <sub>3</sub>	(1.47)	-0.0120	0.047	0.041(3)
C≡N	(1.16)	-0.0235	0.034	0.039(2)
C-H	(1.11)	-0.0158	0.078	
C <sub>1</sub> ---N <sub>4</sub>	(2.62)	-0.0244	0.051	0.059(4)
C <sub>2</sub> ---C <sub>3</sub>	(2.48)	-0.0058	0.078	0.084(7)
C <sub>2</sub> ---N <sub>4</sub>	(3.49)	-0.0146	0.110	0.125(8)
C <sub>2</sub> ---H <sub>5</sub>	(2.17)	-0.0048	0.113	
C <sub>3</sub> ---H <sub>5</sub>	(2.13)	-0.0176	0.110	
N <sub>4</sub> ---H <sub>5</sub>	(3.18)	-0.0254	0.131	
H <sub>5</sub> ---H <sub>6</sub>	(1.75)	-0.0188	0.129	
(C <sub>3</sub> ---C <sub>7</sub> ) <sub>a</sub>	(3.73)	-0.0008	0.080	0.104
(C <sub>3</sub> ---N <sub>8</sub> ) <sub>a</sub>	(4.80)	-0.0026	0.096	0.120
(N <sub>4</sub> ---N <sub>8</sub> ) <sub>a</sub>	(5.88)	0.0011	0.101	0.125
(C <sub>3</sub> ---H <sub>10</sub> ) <sub>a,g</sub>	(2.70)	-0.0022	0.182	
(N <sub>4</sub> ---H <sub>10</sub> ) <sub>a,g</sub>	(3.52)	-0.0072	0.240	
(H <sub>5</sub> ---H <sub>10</sub> ) <sub>a,g</sub>	(2.53)	-0.0021	0.191	
(H <sub>5</sub> ---H <sub>9</sub> ) <sub>a,a</sub>	(3.04)	-0.0050	0.133	
(C <sub>3</sub> ---C <sub>7</sub> ) <sub>g</sub>	(3.01)	0.0082	0.180	
(C <sub>3</sub> ---N <sub>8</sub> ) <sub>g</sub>	(3.78)	0.0139	0.259	
(N <sub>4</sub> ---N <sub>8</sub> ) <sub>g</sub>	(4.33)	0.0342	0.390	
(C <sub>3</sub> ---H <sub>10</sub> ) <sub>g,g</sub>	(2.67)	-0.0019	0.182	
(C <sub>3</sub> ---H <sub>9</sub> ) <sub>g,a</sub>	(3.39)	-0.0096	0.109	
(N <sub>4</sub> ---H <sub>10</sub> ) <sub>g,g</sub>	(3.46)	0.0026	0.240	
(N <sub>4</sub> ---H <sub>9</sub> ) <sub>g,a</sub>	(4.44)	-0.0059	0.121	
(H <sub>5</sub> ---H <sub>9</sub> ) <sub>g,g</sub>	(2.59)	-0.0200	0.191	
(H <sub>6</sub> ---H <sub>9</sub> ) <sub>g,g</sub>	(2.45)	-0.0270	0.191	
(H <sub>5</sub> ---H <sub>10</sub> ) <sub>g,a</sub>	(3.08)	-0.0204	0.133	

<sup>a</sup> For numbering of atoms see Fig. 2. Suffix *a* refers to *anti*, *g* to *gauche*. In the double suffix, the second gives the type of distance considered. <sup>b</sup> Determined from the electron-diffraction data, the parenthesized value is  $1\sigma$ .

ethane<sup>38</sup>  $\nu_{\tau} \sim 125 \text{ cm}^{-1}$ , bipropargyl,<sup>32</sup> CH<sub>2</sub>-(C≡CH)-CH<sub>2</sub>(C≡CH), estimated to be  $80 \text{ cm}^{-1}$  and *anti* 2-cyanoethanol<sup>33</sup>  $125 (l) \text{ cm}^{-1}$ , although the normal coordinate analysis in Ref. 11 indicates a somewhat lower value ( $\nu_{\tau} \sim 50 \text{ cm}^{-1}$ , which in the GVFF corresponds to  $f_{\tau} = 0.039 \text{ m dyn } \text{Å} \text{ rad}^{-2}$ ).

The absolute magnitudes of the calculated *D*-values are generally somewhat larger than found in related halogenated molecules.<sup>16,17,19</sup> The correction terms found for the longer distances are large in these types of molecules, and the shrinkage<sup>27,28</sup> corrections here play a much more important role.

The obtained *D*-values are strongly dependent on  $f_{\tau}$ . The shrinkage effect obtained with  $f_{\tau} = 0.12$

mdyn Å rad<sup>-2</sup>, although not a very sensitive criterium, agreed excellently with the observed positions of the C<sub>3</sub>---N<sub>8</sub> and N<sub>4</sub>---N<sub>8</sub> peaks in *anti* (the parameters given in Table 3, column b, c and d), whereas no such corrections gave theoretical peaks beyond the experimental positions (Table 3, a). Introducing *D*-values calculated with  $f_{\tau} = 0.039 \text{ m dyn } \text{Å} \text{ rad}^{-2}$ , on the other hand, gave a too large shrinkage effect and shifted these peaks correspondingly too much to smaller values.

An indication that  $f_{\tau} = 0.12 \text{ m dyn } \text{Å} \text{ rad}^{-2}$  is a fairly good value, is also that it was possible to refine  $\phi_g$  when the corresponding perpendicular amplitudes were introduced, whereas  $\phi_g$  had to be assumed otherwise.

The estimated *u*-values are, when comparable, very similar to the values obtained for 1,2-dichloroethane.<sup>16</sup> The vibrational amplitudes that did not refine were given the calculated values, although the refined values were generally, but not significantly, higher than the calculated ones. A disturbing factor in this relation is that the percentage of *anti* is rather sensitive to the magnitude of the *anti* *u*-values (varying from 64.1(32) to 73.7(52) %, whether these *u*-values are kept at the calculated values or refined in a group, Table 3, c and d). This problem is also reflected in the comparatively large correlation between  $u(\text{C}_3\cdots\text{C}_7)$  and  $n_a$ . Similar difficulties have been experienced in the corresponding electron-diffraction study of bipropargyl.<sup>39</sup>

The final results are presented in Table 3, c. The standard deviations ( $1\sigma$ ) as obtained from the least-squares refinement using non-diagonal elements in the applied weight matrix<sup>40,41</sup> and corrected for a uncertainty of 0.1 % in the wavelength, are given in column e.

## RESULTS AND DISCUSSION

The set of parameters determined from an *ab initio* calculation<sup>42</sup> is identical to the experimentally obtained values. In general the obtained structural parameters agree with the structurally related bipropargyl.<sup>39</sup> Also compared with such related cyano compounds as Cl<sub>3</sub>C-CN,<sup>43</sup> (CH<sub>3</sub>)<sub>3</sub>C-CN<sup>44</sup> (ED) and CH<sub>3</sub>CH<sub>2</sub>CN (MW)<sup>45,46</sup> the parameters are quite normal. The lengthening of  $r(\text{C}_1 - \text{C}_2)$  is enhanced, which may be rationalized from the effect of two substituted cyano-groups. Due to the fairly large correlation coefficient between  $r(\text{C}_1 - \text{C}_2)$  and  $u(\text{C}_2 - \text{C}_3)$ , however, this lengthening

Table 3. Molecular parameters, distances ( $r_a$ ) and vibrational amplitudes ( $u$ ) in Å, angles ( $\angle_a$ ) in degrees, and estimated correlation coefficients ( $\rho$ ) larger than 0.5. Standard deviations ( $1\sigma$ ) in parentheses.  $R_2 = (\sum w\Delta^2 / \sum w)^{1/2} \times 100$ .

a, Without shrinkage corrections; b–e, shrinkage estimated with  $f_r = 0.12$  mdyn Å rad<sup>-2</sup> (see text). a–b,  $\phi_g$  is fixed; d,  $u$ -values in *anti* are fixed; e, standard deviations with a non-diagonal weight matrix.

	a	b	c	d	e
$r(C_1 - C_2)$	1.564(4)	1.560(3)	1.561(3)	1.560(3)	(6)
$r(C_1 - C_3)$	1.463(2)	1.465(2)	1.465(2)	1.465(2)	(2)
$r(C \equiv N)$	1.161(1)	1.161(1)	1.161(1)	1.161(1)	(2)
$r(C - H)$	1.093(4)	1.091(4)	1.092(4)	1.092(4)	(10)
$\angle CCC$	110.1(3)	110.4(3)	110.4(3)	110.5(3)	(5)
$\angle CCH$	108.2(10)	107.8(10)	107.9(10)	107.7(10)	(19)
VP <sup>a</sup>	119.4(8)	120.6(8)	120.5(8)	120.7(8)	(16)
$\angle CCN^a$	178.7(8)	180.5(8)	180.7(8)	181.0(8)	(13)
$\phi_g$	70. —	70. —	74.8(59)	74.0(39)	(81)
$u(C_1 - C_3)$	0.040(2)	0.041(2)	0.041(2)	0.041(2)	(3)
$u(C \equiv N)$	0.041(1)	0.039(1)	0.039(1)	0.039(1)	(2)
$u(C_1 \cdots N_4)$	0.055(3)	0.059(3)	0.059(3)	0.059(3)	(4)
$u(C_2 \cdots C_3)$	0.073(4)	0.083(4)	0.084(4)	0.083(4)	(7)
$u(C_2 \cdots N_4)$	0.127(5)	0.128(5)	0.125(5)	0.122(5)	(8)
$u(C_3 \cdots C_7)_a$	0.103)	0.105)	0.104)	0.080)	(10)
$u(C_3 \cdots N_8)_a$	0.120)	0.121)	0.120)	0.096)	
$u(N_4 \cdots N_8)_a$	0.125)	0.126)	0.125)	0.101)	
$n_a$ ( <sup>o</sup> )	71.4(57)	73.6(51)	73.7(52)	64.1(32)	(66)
$R_2$ ( <sup>o</sup> )	7.56	6.73	6.69	6.83	
$\rho(r(C \equiv N), r(C - H))$	-0.64	-0.64	-0.63	-0.63	-0.61
$\rho(r(C_1 - C_2), \angle CCC)$	-0.73	-0.66	-0.65	-0.65	-0.74
$\rho(r(C_1 - C_2), VP)$	-0.51	-0.51	-0.50	-0.50	-0.45
$\rho(\angle CCC, VP)$	0.59	0.62	0.60	0.58	0.54
$\rho(\angle CCH, \angle CCN)$	-0.50	-0.54	-0.44	-0.47	-0.55
$\rho(r(C_1 - C_2), u(C_1 - C_3))$	-0.56	-0.61	-0.61	-0.61	-0.65
$\rho(u(C_1 \cdots N_4), u(C_2 \cdots C_3))$	0.69	0.61	0.61	0.61	0.72
$\rho(u(C_3 \cdots C_7), n_a)$	0.72	0.71	0.70	—	0.70
$\rho(u(C \equiv N), \gamma_2)$	0.75	0.76	0.76	0.76	0.72

<sup>a</sup> For explanation see text.

may not be real. The split between the two C–C distances will depend on the assumed  $u(C_1 - C_2)$ , which was kept at the calculated value, since it did not refine reasonably.

The predominance of *anti* in the vapour, agrees with the findings both for bipropargyl,<sup>32,39</sup> the 1-bromo<sup>47</sup> and 1,6-dibromo<sup>48,49</sup> analogs, and 1-cyano-4-butyne<sup>50</sup> (CH<sub>2</sub>CN–CH<sub>2</sub>(C≡CH)), as well as for 1,2-dichloro<sup>16,17</sup> and 1,2-dibromoethane.<sup>19</sup> The fact that in the solid and liquid phases *gauche* dicyanoethane is the more favourable species must therefore be due to favourable intermolecular dipole contacts.

Due to the relatively small *gauche* contribution together with the comparatively large  $u$ -values for

the *gauche* distances, the torsional angle was difficult to determine. But, as mentioned above, when a reasonable shrinkage correction was introduced, even this angle could be determined, and the obtained value (75(8)°), is quite reasonable (1,2-dichloroethane,<sup>16,17</sup>  $\phi_g = 75.3(9)^\circ$  in bipropargyl,<sup>39</sup>  $\phi_g = 78 \pm 10^\circ$ ).

Since one aim of this investigation is to estimate the thermodynamic data of the conformational equilibrium, the uncertainty in the *gauche/anti* ratio is a serious defect. Several refinements, based upon different assumptions, indicate strongly that the percentage found when the  $u$ -values in *anti* are refined gives the best agreement with the observed data. The arguments are particularly based upon

Table 4. Thermodynamic data obtained from estimated mol fraction ( $K = n_g/n_a$ ) and partition functions ( $Q$ ), calculated from the valence force field ( $\nu_{\tau,g} = 77 \text{ cm}^{-1}$  and  $\nu_{\tau,a} = 83 \text{ cm}^{-1}$ ) and the products of the principal moments of inertia [ $(I_A I_B I_C)_g = 4.02223 \cdot 10^6$  and  $(I_A I_B I_C)_a = 2.37792 \cdot 10^6 \text{ amu}^3 \text{ \AA}^6$ ].

$R \ln(Q_g/Q_a)$ ; cal mol <sup>-1</sup> deg <sup>-1</sup>	0.191
$RT \partial/\partial T \ln(Q_g/Q_a)$ ; cal mol <sup>-1</sup> deg <sup>-1</sup>	-0.158
$\Delta E$ ; kcal mol <sup>-1</sup>	1.53(25)
$\Delta S$ ; cal mol <sup>-1</sup> deg <sup>-1</sup>	1.41

analysis of the shape of the RD-difference curve in the outer region. To estimate the conformational energy difference the measured *gauche/anti* ratio ( $K$ ) has been combined with the appropriate vibrational-rotational partition functions ( $Q$ ), as calculated from the valence force field and the products of the principal moments of inertia. The results based upon the parameters given in Table 3, c are presented in Table 4. The formulas applied<sup>16,17,51</sup> are

$$K = \frac{n_g}{n_a} = \exp -(\Delta E - T\Delta S)/RT$$

$$= \frac{2Q_g}{Q_a} \exp -\Delta E^\circ/RT$$

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

$$\Delta S = R \ln 2 + R \ln(Q_g/Q_a) + RT \partial/\partial T \ln(Q_g/Q_a)$$

Here  $\Delta = \textit{gauche-anti}$ ,  $n$  the percentage of the conformers *gauche* ( $g$ ) and *anti* ( $a$ ) and  $\Delta E^\circ$  the energy difference at the absolute zero point. The factor 2 accounts for the two indistinguishable *gauche* forms, and is included in  $\Delta S$ . Thus  $\Delta S = R \ln 2 + \Delta S_c$  where  $\Delta S_c$  is the difference in conformational entropy.

The obtained  $\Delta E$  value is in slightly better agreement with the *ab initio* estimate than originally stated,<sup>42</sup> although the theoretical value is still too small. Applying  $n_a = 64.1\%$ , as obtained when the  $u$ -values in *anti* were kept at the calculated values, gives  $\Delta E = 1.14 \text{ kcal mol}^{-1}$ . This indicates that the agreement may be even better, although such a low value gives an unreasonable shape in the outer RD-curve difference.

It is also interesting to note that correcting the spectroscopically<sup>12</sup> obtained energy difference in the liquid [ $\Delta E(l) = -0.36 \text{ kcal mol}^{-1}$ ] with the

dielectric constants and dipole moments, gave  $\Delta E(g) = 1 \text{ kcal mol}^{-1}$ . Although predicting a somewhat low value, these corrections gave a correct conformational preference in the vapour.

Both in dichloro and dibromoethane the torsional force constant had to be given different values for the two conformations to reproduce the observed torsional frequencies (dichloroethane<sup>16,17</sup>  $f_{\tau,g} = 0.25$  and  $f_{\tau,a} = 0.17 \text{ m dyn \AA rad}^{-2}$ ). A similar approach in the dicyano case would lead to  $\Delta S = 1.04 \text{ cal mol}^{-1} \text{ deg}^{-1}$ , and give only a minor shift in  $\Delta E$ , although  $\Delta S_c$  will have opposite sign [ $\Delta S_c = 0.034$  when  $f_{\tau,g} = f_{\tau,a}$  and  $-0.290 \text{ cal mol}^{-1} \text{ deg}^{-1}$  when

$$f_{\tau,g} = \frac{0.25}{0.17} f_{\tau,a}$$

The temperature applied in these calculations is measured at the nozzle tip.<sup>52-54</sup> Previous experiences<sup>16,17,19</sup> have justified that within the present level of accuracy, the nozzle temperature may be used as the temperature of the gaseous mixture.

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