# Conformation and Molecular Structure of 3-Chloropropionitrile and 3-Bromopropionitrile as Determined by Gas-Phase Electron Diffraction and Molecular Mechanics Calculations

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Stavnebrekk, P. J., Stølevik, R., Seip, R., Volden, H. V. and Gundersen, S., 1988. Conformation and Molecular Structure of 3-Chloropropionitrile and 3-Bromopropionitrile as Determined by Gas-Phase Electron Diffraction and Molecular Mechanics Calculations. – Acta Chem. Scand., Ser A 42: 398–408.

Gaseous 3-chloropropionitrile (CPN) and 3-bromopropionitrile (BPN) have been studied by electron diffraction. The ED data for CPN/BPN are best explained in the basis of a mixture of two conformers, *gauche* and *anti*, with a conformational composition of 64(23)/63(17) % *anti*. The results for the more important bond lengths ($r_a$) and bond angles (α) are as follows for CPN/BPN: $r(-C-C-)$ = 1.515(16)/1.512(27), $r(C-C\equiv)$ = 1.478(11)/1.489(22), $r(C\equiv N)$ = 1.160(4)/1.151 (11), $r(C-X)$ = 1.784(5)/1.942(8), ∠CCC = 110.6(1.0)/111.8(1.3), ∠CCX = 110.8(0.8)/111.7(1.3) and $\emptyset_g$ (the *gauche* torsion angle relative to 0° for the syn transition form) = 71(11)/65(8). The values are conformational averages. Uncertainties are given as 2σ, where σ includes uncertainty due to correlation among observations and parameters used in the data reduction.

Molecular mechanics calculations, based on the gas-phase conformational equilibria as determined by ED, have been carried out for both compounds in order to establish new parameter values for the non-bonding interactions H···N≡, Cl···C≡, Br···C≡, Cl···N≡ and Br···N≡ within the Morse potential formulation.

**Dedicated to Professor Otto Bastiansen on his 70th birthday**

Molecules of the type $XH_2C-CH_2-C\equiv N$ may have conformations *gauche* (G) and *anti* (A) as explained in Fig. 1. 3-Chloro- and 3-bromopropionitrile (CNP and BNP, respectively) have been studied in the liquid and solid states. All investigations claim the existence of *anti* and *gauche* conformations.

CPN has been studied by Wyn-Jones and Orville-Thomas[1] using infrared spectroscopy in the liquid and solid states. El Bermani and Jonathan[2] recorded infrared and Raman spectra in the liquid and solid phases. Klaeboe and Grundnes[3] obtained infrared spectra in the vapour, liquid and solid states, and Raman spectra in the liquid phase. Fujiyama[4] recorded infrared and Raman spectra in the liquid and solid phases, and Tanabe[5] measured the infrared spectra in the liquid phase. These authors concluded that in the liquid state the *gauche* form is more stable than the *anti* form, and that the energy difference is in the range 0.4–0.5 kcal $mol^{-1}$. In an NMR study, Chen and Lin[6] state that in the liquid phase *gauche* and *anti* are equally stable in certain types of solvent, while in others the *gauche* conformation is the more stable one.

BPN has been studied in the liquid state by infrared spectroscopy,[1] and has also been the subject of two NMR spectroscopic studies[1,7] the

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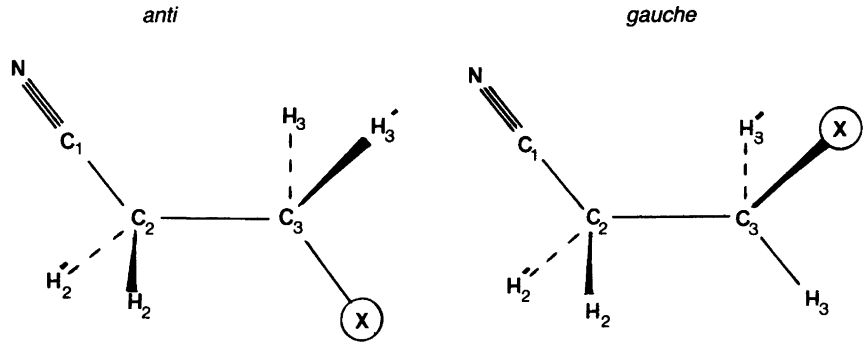


*Fig. 1.* Numbering of atoms in $XH_2C-CH_2-C\equiv N$ (X=Cl or Br) molecules. The *anti*(A) and *gauche*(G) conformers are shown.

latter performed by Deb and Abraham. Their conclusions are that the *gauche* conformers are in the range 0.5–0.6 kcal $mol^{-1}$ more stable than the *anti*.

## Calculations of vibrational quantities

Normal-coordinate calculations[8] have been carried out, and root-mean-square amplitudes ($u$) as well as perpendicular amplitude correction terms ($K$) have been calculated.[9] The valence force field for CPN was transferred from $CH_3-CH_2-C\equiv N$[10] and $(CH_2Cl)_2CH_2$.[11] For BPN the force constants were transferred from $CH_3-CH_2-C\equiv N$[10] and $(CH_2Br)_2CH_2$.[12]

The torsional force constants $F_\phi$ were assigned the value 0.090 mdyn Å $rad^{-2}$ after having tried other values. $K$ and $u$ values were included in the refinements. The $u$ and $K$ values are found in Table 1 for CPN and in Table 2 for BPN, together with internuclear distances, $r_\alpha$.

## Experimental and data reduction

The compounds were obtained from Fluka AG. After purification using preparative gas chromatography the purities were better than 97% (CPN) and 99% (BPN). The ED recordings for CNP were made using the Oslo apparatus[13] at a nozzle-tip temperature of 74 °C. Nozzle-to-plate distances of 48.5 cm and 20.5 cm were used. The number of plates were 4 (LC) and 6 (SC). The ED photographs for BPN were taken with a Balzer Eldigraph KDG-2[14,15] at nozzle temperatures of 85 °C (LC) and 98 °C (SC). Nozzle-to-plate distances of 50 cm and 25 cm were used. Five plates were used for each camera distance.

The electron wavelength was calibrated against benzene.[16] The diffraction photographs were recorded on Kodak Electron Image plates. Optical densities were measured with a Joyce Loebl densitometer.

The data were reduced in the standard way.[17,18] The experimental data were combined to one average curve in the form $sI_m(s)$ for each camera distance. The final intensity curves are shown in Figs. 2 and 3. The electron-scattering amplitudes and phase-shifts were calculated by a program originally written by Yates[19] using Hartree-Fock potentials[20] for C, N, Cl and Br, but a molecular bonded potential for H.[21]

The radial distribution curves in Figs. 4–7 were calculated from the intensities after division with $f'_{Cl}f'_c$ (CPN) and $f'_{Br}f'_c$ (BPN). For CPN, theoretical intensities were used for $s<2.50$ $Å^{-1}$. The corresponding value for BPN was $s<2.25$ $Å^{-1}$. The damping constant was equal to 0.0020 $Å^2$.

## Molecular mechanics calculations

Molecular mechanics calculations have been carried out on chloro- and bromoalkanes in a previous work.[22] Reference values and force constants were taken from this latter work and from Ref. 10. In addition, standard reference values for C≡N, C2–C3 and C1–C2 were used. The parameters for the non-bonded interaction potentials for (X = Cl or Br) C···H, X···H and H···H are given in Ref. 23.

New parameter values for H···N≡, X···C≡

*Table 1.* Internuclear distances ($r_\alpha$), calculated[a] root-mean-square vibrational amplitudes ($u$) and perpendicular amplitude corrections ($K$) in Å at 74 °C for $ClH_2C-CH_2-C\equiv N$.

| Distance (X = Cl) | $r_\alpha$ | $u \cdot 10^3$ | $K \cdot 10^3$ |
|---|---|---|---|
| *Gauche* conformer | | | |
| C3–H | 1.077 | 78 | 20 |
| C2–H | 1.077 | 79 | 29 |
| N≡C | 1.144 | 35 | 19 |
| C2–C1 | 1.461 | 47 | 19 |
| C3–C2 | 1.515 | 52 | 6 |
| X–C | 1.778 | 55 | 5 |
| C1···H2 | 2.08 | 109 | 35 |
| C3···H2 | 2.13 | 111 | 23 |
| C2···H3 | 2.13 | 111 | 14 |
| X···H3 | 2.36 | 109 | 14 |
| C3···C1 | 2.45 | 77 | 8 |
| N···C2 | 2.60 | 50 | 4 |
| C1···H3 | 2.60 | 181 | 13 |
| X···C2 | 2.72 | 71 | 3 |
| X···H2′ | 2.80 | 189 | 13 |
| N···H2 | 3.13 | 142 | 12 |
| X···C1 | 3.20 | 199 | 3 |
| C1···H3′ | 3.37 | 106 | 9 |
| N···H3 | 3.39 | 209 | 5 |
| N···C3 | 3.44 | 105 | 2 |
| X···H2 | 3.66 | 103 | 8 |
| X···N | 3.94 | 168 | 1 |
| N···H3′ | 4.43 | 119 | 6 |
| *Anti* conformer | | | |
| C2–H | 1.077 | 79 | 27 |
| C3–H | 1.085 | 78 | 18 |
| N≡C | 1.144 | 35 | 16 |
| C2–C1 | 1.461 | 47 | 20 |
| C3–C2 | 1.515 | 52 | 2 |
| X–C | 1.778 | 57 | 9 |
| C1···H2 | 2.08 | 108 | 33 |
| C3···H2 | 2.13 | 111 | 12 |
| C2···H3 | 2.15 | 111 | 8 |
| X···H3 | 2.35 | 104 | 14 |
| C3···C1 | 2.45 | 77 | 12 |
| N···C2 | 2.61 | 50 | 7 |
| C1···H3 | 2.71 | 176 | 17 |
| X···C2 | 2.71 | 72 | 6 |
| X···H2 | 2.90 | 185 | 13 |
| N···H2 | 3.13 | 141 | 14 |
| N···C3 | 3.44 | 106 | 41 |
| N···H3 | 3.52 | 106 | 7 |
| X···C1 | 4.03 | 73 | 2 |
| X···N | 5.12 | 88 | 1 |

[a]Ref. 8.

*Table 2.* Internuclear distances ($r_\alpha$), calculated[a] root-mean-square vibrational amplitudes ($u$) and perpendicular amplitude corrections ($K$) in Å at 91 °C for $BrH_2C-CH_2-C\equiv N$.

| Distance (X = Br) | $r_\alpha$ | $u \cdot 10^3$ | $K \cdot 10^3$ |
|---|---|---|---|
| *Gauche* conformer | | | |
| C3–H | 1.098 | 78 | 19 |
| C2–H | 1.098 | 79 | 34 |
| N≡C | 1.131 | 35 | 26 |
| C2–C1 | 1.468 | 47 | 24 |
| C3–C2 | 1.513 | 51 | 5 |
| X–C | 1.942 | 56 | 4 |
| C1···H2 | 2.09 | 109 | 45 |
| C3···H2 | 2.15 | 111 | 24 |
| C2···H3 | 2.15 | 111 | 13 |
| C3···C1 | 2.48 | 75 | 13 |
| X···H3 | 2.51 | 114 | 10 |
| N···C2 | 2.60 | 50 | 4 |
| C1···H3 | 2.70 | 172 | 17 |
| X···C2 | 2.88 | 80 | 2 |
| X···H2′ | 3.01 | 198 | 14 |
| N···H2 | 3.11 | 156 | 12 |
| X···C1 | 3.32 | 206 | 4 |
| C1···H3′ | 3.42 | 110 | 13 |
| N···C3 | 3.47 | 104 | 2 |
| N···H3 | 3.50 | 208 | 5 |
| X···H2 | 3.86 | 111 | 9 |
| X···N | 3.99 | 134 | 1 |
| N···H3′ | 4.48 | 122 | 5 |
| *Anti* conformer | | | |
| C2–H | 1.098 | 78 | 29 |
| C3–H | 1.108 | 78 | 16 |
| N≡C | 1.131 | 35 | 18 |
| C2–C1 | 1.465 | 47 | 24 |
| C3–C2 | 1.508 | 51 | 2 |
| X–C | 1.936 | 56 | 6 |
| C1···H2 | 2.09 | 109 | 41 |
| C3···H2 | 2.14 | 111 | 14 |
| C2···H3 | 2.17 | 111 | 7 |
| C3···C1 | 2.46 | 75 | 14 |
| X···H3 | 2.51 | 114 | 11 |
| N···C2 | 2.60 | 50 | 8 |
| C1···H3 | 2.73 | 177 | 16 |
| X···C2 | 2.85 | 80 | 4 |
| X···H2 | 3.02 | 200 | 13 |
| N···H2 | 3.12 | 148 | 17 |
| N···C3 | 3.45 | 104 | 5 |
| N···H3 | 3.54 | 188 | 7 |
| X···C1 | 4.19 | 78 | 3 |
| X···N | 5.27 | 87 | 1 |

[a]Ref. 8.

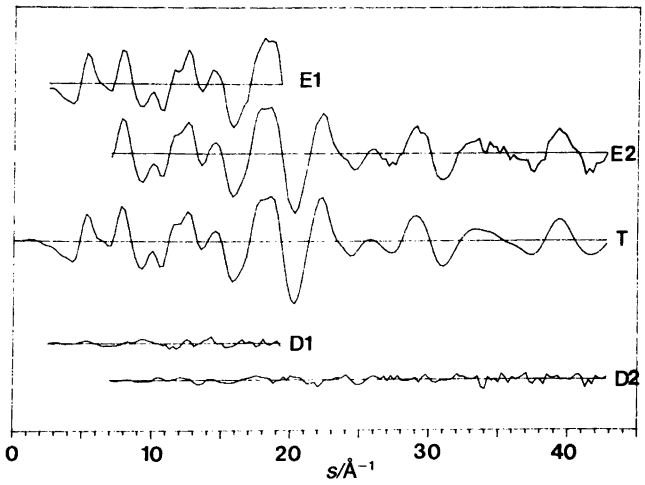


*Fig. 2.* $ClH_2C-CH_2-C\equiv N$. Intensities from the long camera distance (E1) and the short camera distance (E2). The theoretical intensity curve (T), the difference curves D1 = E1−T and D2 = E2−T.

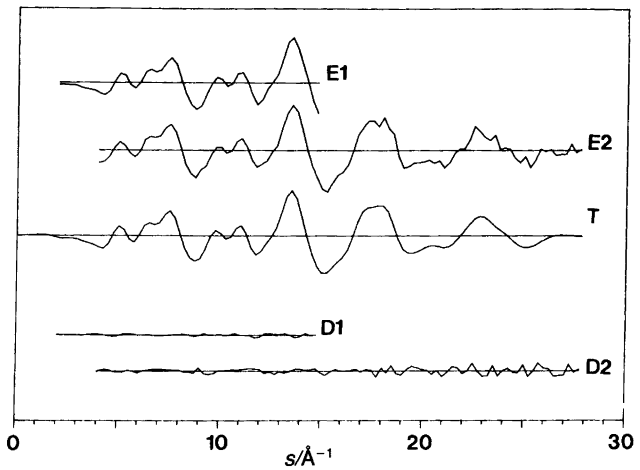


*Fig. 3.* $BrH_2C-CH_2-C\equiv N$. Intensities from the long camera distance (E1) and the short camera distance (E2). The theoretical intensity curve (T), the difference curves D1 = E1−T and D2 = E2−T.

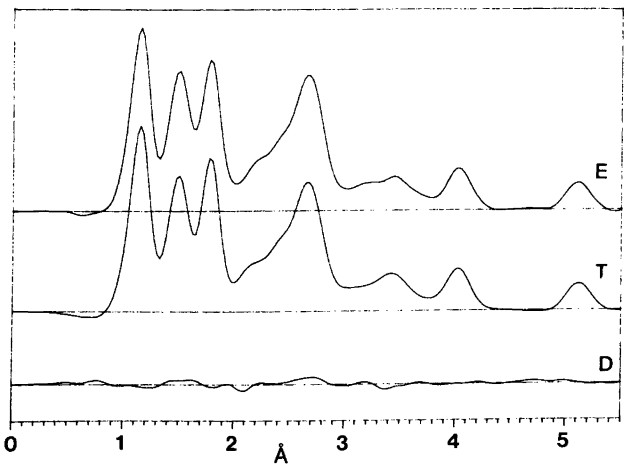


*Fig. 4.* $ClH_2C-CH_2-C\equiv N$. Experimental (E) and theoretical (T) radial distribution curves, the difference curve D= E−T. The damping constant was 0.0020 Å².

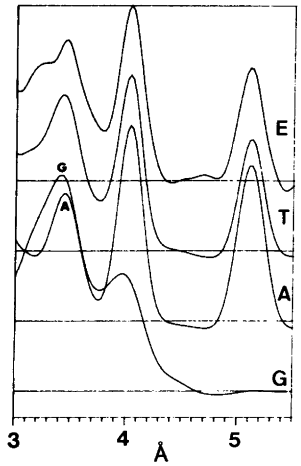


*Fig. 5.* $ClH_2C-CH_2-C\equiv N$. Radial distribution curves in the conformationally sensitive range 3.0–5.5 Å. Experimental curve (E), theoretical curve (T) and curves for the individual conformers *gauche* (G) and *anti* (A).

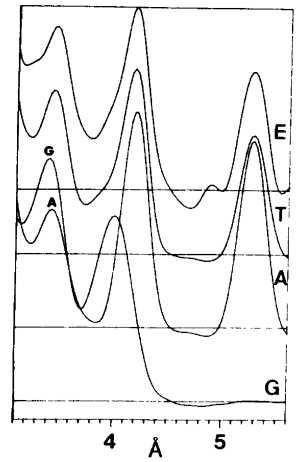


*Fig. 7.* $BrH_2C-CH_2-C\equiv N$. Radial distribution curves in the conformationally sensitive range 3.1–5.6 Å. Experimental (E), theoretical curve (T) and curves for the individual conformers *gauche* (G) and *anti* (A).

and X···N≡ were established in order to fit the experimental conformational compositions from the ED analysis in this work on CPN and BPN. The new parameter values are given in Table 3. It has been assumed that X···C≡ and X···N≡ have equal values of the parameters $R_o$, $R_m$ and ε. It was also assumed that ε for these interactions had the same value as for X···C($sp^2$).[24, 25].

The method of calculation is explained in Refs. 26, 27 and 28.

An intrinsic potential term equal to 3.0 kcal. $mol^{-1}$ was used for rotation around C2–C3. The excess charges on the atoms were calculated according to the method given in Ref. 29, and modified by division by 1.6 (CPN) and 1.3 (BPN). The parameter values $D$ of the electrostatic energy terms $D/R$ are given in Table 4.

The calculated torsional potentials are given in Figs. 8 and 9 for CPN and BPN, respectively. The potentials were obtained by simultaneously adjusting the bond lengths and the bond angles for each value of ø. According to these calculations,

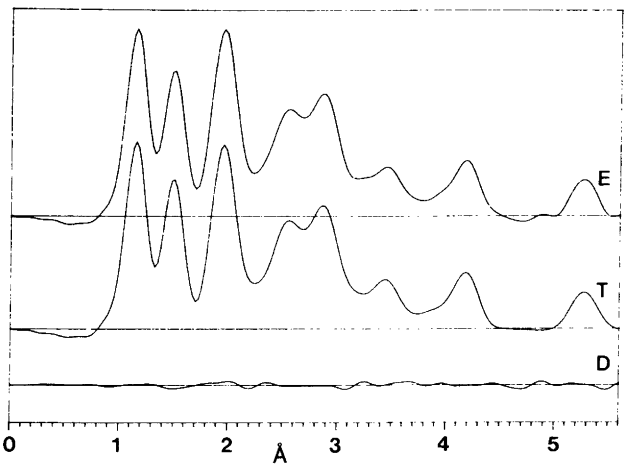


*Fig. 6.* $BrH_2C-CH_2-C\equiv N$. Experimental (E) and theoretical (T) radial distribution curves, the difference curve D = E–T. The damping constant was 0.0020 $Å^2$.

*Table 3.* Parameter values for non-bonding atom···atom interactions in the Morse potential ($V$) formulation.[a]

| | $R_o$/Å | $R_m$/Å | ε/kcal mol$^{-1}$ |
|---|---|---|---|
| H···N≡ | 2.90 | 3.30 | 0.043 |
| Cl···C≡ | 3.15 | 3.82 | 1.22 |
| Cl···N≡ | 3.15 | 3.82 | 1.22 |
| Br···C≡ | 3.25 | 3.92 | 1.22 |
| Br···N≡ | 3.25 | 3.92 | 1.22 |

[a]The parameters are related as follows: $V(R_o) = 0$, $V(R_m) = -\varepsilon$, corresponding to minimum of $V$(R); see Ref. 24 for details.

the amounts of the *anti* conformer are 65 % (CPN) and 64 % (BPN) when equal vibrational and rotational partition functions are assumed.

The effect of ignoring the electrostatic terms in the calculations, which is not too dramatic, is also shown in Figs. 8 and 9.

Results from the MM calculations are listed in Table 5. The calculations did not show conformational differences for the following parameters: $r$(C−H), $r$(C≡N), ∠C−Cl−H, ∠H−C−H and ∠C−C≡N.

## Structural assumptions

The C−C≡N angle was assumed to be 180°, which means that the atoms N≡C−C−C are coplanar. All C−H bonds had equal lengths. Local $C_s$ symmetry was assumed for the group C−$CH_2$X. The bonds C2−C3 and C1−C2 had different lengths, as indicated in Table 6.

For CPN it was assumed that the bond lengths and bond angles in the two conformers are equal. For BPN the conformational differences within the parameters calculated from MM were included in the least-squares refinements. A

*Table 4.* Coulomb parameters $D = 332qq^*$ in kcal mol$^{-1}$. $q$ and $q^*$ are excess charges.

| | H···H | C···H | H···X[a] | H···N≡ | X···N≡ | X···C≡ |
|---|---|---|---|---|---|---|
| $ClH_2C-CH_2C{\equiv}N$ | 0.83 | 0.19 | −2.39 | −1.47 | 4.27 | −0.54 |
| $BrH_2C-CH_2C{\equiv}N$ | 0.98 | 0.13 | −2.20 | −2.08 | 4.69 | −0.28 |

[a]X = Cl or Br.

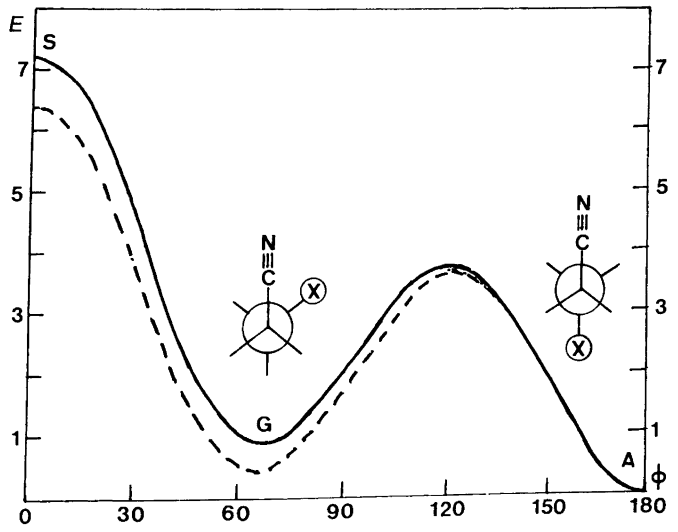


*Fig. 8.* Torsional potential curve $E(\varphi)$ in kcal mol$^{-1}$ for $ClH_2C-CH_2-C{\equiv}N$. The letters S, G and A signify *syn, gauche* and *anti,* respectively. The torsion angle (φ) is N≡C1−C2−C3−Cl. φ = 10 corresponds to a *syn* arrangement of the N≡C1−C2−C3−Cl-skeleton. The dotted curve was obtained without excess charges on the atoms.

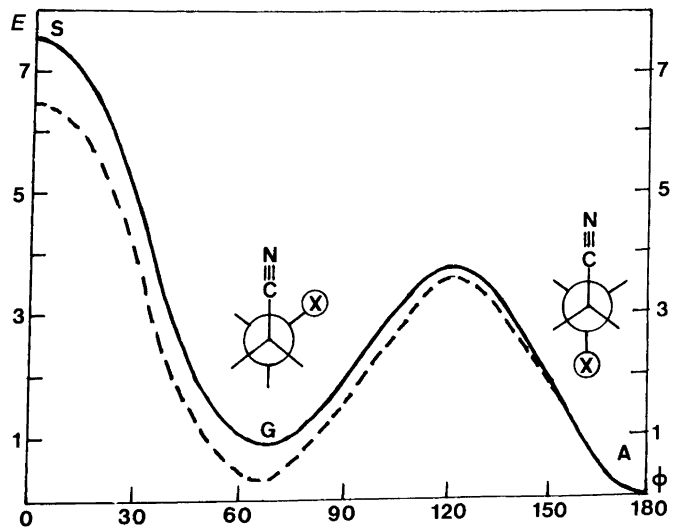


*Fig. 9.* Torsional potential curve $E(\varphi)$ in kcal mol$^{-1}$ for $BrH_2C-CH_2-C\equiv N$. The letters S, G and A signify *syn, gauche* and *anti*, respectively. The torsion angle ($\varphi$) is N≡C1−C2−C3−Br. $\varphi = 0$ corresponds to a *syn* arrangement of the N≡C1−C2−C3−Br skeleton. The dotted curve was obtained without excess charges on the atoms.

slightly better fit of theoretical to experimental intensities was obtained for BPN when these differences were included. In contrast, the reverse was true for CPN.

The transition state syn (S), possess a syn relationship between the X-atom and the N≡C−C fragment with a torsion angle ($\varphi$) of 0°. When $\varphi$ is about 60° the conformation is *gauche* (G) with $C_1$ symmetry, and for $\varphi = 180°$ the conformation is *anti* (A) with $C_s$ symmetry.

The calculated vibrational amplitudes ($u$ and $K$) from NORCOR[9] are given in Table 1 for CPN

*Table 5.* Results from molecular mechanics calculations for 3-chloropropionitrile (CPN) and 3-bromopropionitrile (BPN).

| | CPN | | BPN | |
|---|---|---|---|---|
| | *gauche* | *anti* | *gauche* | *anti* |
| **Bond lengths/Å** | | | | |
| C2−C3 | 1.539 | 1.535 | 1.539 | 1.534 |
| C1−C2 | 1.462 | 1.459 | 1.462 | 1.459 |
| C−X[a] | 1.785 | 1.780 | 1.965 | 1.959 |
| **Valence angles/°** | | | | |
| ∠C−C−X | 111.2 | 109.9 | 111.2 | 109.8 |
| ∠C−C−C | 112.9 | 111.7 | 112.8 | 111.6 |
| ∠H−C−X | 108.9 | 109.2 | 108.9 | 109.2 |
| ∠C3−C2−H | 108.6 | 108.7 | 108.6 | 108.7 |
| Energy/kcal mol$^{-1}$ | 0.9 | 0.0 | 0.9 | 0.0 |
| $\varphi$/° [b] | 68.1 | 180.0 | 68.5 | 180.0 |
| $F_\varphi$/mdyn Å rad$^{-2}$ [c] | 0.14 | 0.12 | 0.15 | 0.12 |

[a] X = Cl or Br. [b] $\varphi$ denotes the torsional angle at minimum energy; [c] $F_\varphi$ denotes the torsional force constant at this minimum.

*Table 6.* Final structural parameters for $XH_2C-CH_2-C\equiv N$. The error limits ($2\sigma$) are given in parentheses.

| Parameter | X=Cl[a] | X=Br | |
|---|---|---|---|
| | | *gauche* | *anti* |
| Bond lengths, $r_a$/Å | | | |
| C–H (average) | 1.097(17) | 1.119(31) | 1.120(31) |
| C≡N | 1.160(4) | 1.156(11) | 1.148(11) |
| C1–C2 | 1.478(11) | 1.490(22) | 1.488(22) |
| C2–C3 | 1.515(16) | 1.517(27) | 1.509(27) |
| C–X | 1.784(5) | 1.944(5) | 1.941(8) |
| Bond angles α/° | | | |
| C–C–C | 110.6(1.0) | 112.6(1.3) | 111.3(1.3) |
| C–C–X | 110.8(0.8) | 112.6(1.1) | 111.2(1.1) |
| C–C–H | 109.47[b] | 109.47[b] | 109.47[b] |
| C–C≡N | 180.0[b] | 180.0[b] | 180.0[b] |
| Torsion angle, φ (*gauche*)/° | 71(11) | 65(8) | 180[b] |
| *R*(LC)/*R*(SC)[c] | 11.5/13.9 | 6.0/17.2 | |
| Mol % (*gauche*) | 36(23) | 37(17) | |

[a]The values for CPN are conformational averages. [b]Assumed values. [c]*R*-factor (in %) for long camera (LC) distance and short camera (SC) distance.

and Table 2 for BPN. However, some of the *u* values were refined, and the calculated and refined values are compared in Table 9.

## Results for CPN and BPN

From the radial distribution (RD) curves for CPN in Fig. 4 and for BPN in Fig. 6 the contributions from the internuclear distances may be seen. All internuclear distances are listed in

*Table 7.* 3-Chloropropionitrile. Correlation matrix (×100) for the geometrical parameters. $\sigma_o$ is standard deviation from the least-squares refinement in units of Å and ° (X=Cl).

| Parameter | $\sigma_o$ | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C2–C3 | 0.0040 | 100 | | | | | | | | | | | | | | |
| C–X | 0.0009 | −3 | 100 | | | | | | | | | | | | | |
| C–H | 0.0041 | 2 | −2 | 100 | | | | | | | | | | | | |
| ∠CCX | 0.2565 | 4 | −13 | −1 | 100 | | | | | | | | | | | |
| C1–C2 | 0.0027 | −69 | 6 | 11 | 55 | 100 | | | | | | | | | | |
| ∠CCC | 0.3200 | −36 | −6 | 1 | 35 | 15 | 100 | | | | | | | | | |
| $\varphi_g$ | 2.7770 | 4 | 10 | 2 | −4 | −5 | −8 | 100 | | | | | | | | |
| C≡N | 0.0008 | 25 | −7 | −32 | −14 | −33 | −4 | −8 | 100 | | | | | | | |
| *u*(2–3) | 0.0016 | −53 | 11 | −8 | 44 | 45 | 19 | −10 | −11 | 100 | | | | | | |
| *u*(3–X) | 0.0010 | 4 | 0 | −21 | 5 | −15 | 4 | −3 | 11 | 19 | 100 | | | | | |
| *u*(C≡N) | 0.0009 | 3 | −1 | 15 | 3 | −4 | 1 | −7 | 2 | 13 | 24 | 100 | | | | |
| *u*(2–N) | 0.0026 | 2 | 1 | 3 | −27 | −4 | −3 | 1 | 0 | −1 | 3 | 2 | 100 | | | |
| $u(1-X)_g$ | 0.0299 | 19 | 4 | 6 | −31 | −24 | −42 | 12 | −1 | −14 | 3 | 2 | 8 | 100 | | |
| $u(1-X)_a$ | 0.0064 | 7 | −21 | 0 | −10 | −8 | −9 | −20 | 16 | −2 | −9 | 1 | 3 | −15 | 100 | |
| α | 0.0758 | −9 | 25 | −6 | 15 | 8 | 13 | 37 | −17 | 8 | 18 | 5 | −3 | 14 | −79 | 100 |

*Table 8.* 3-Bromopropionitrile. Correlation matrix (×100) for the geometrical parameters. $\sigma_o$ is standard deviation from the least-squares refinement in units of Å and ° (X=Br).

| Parameter | $\sigma_o$ | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C2–C3 | 0.0066 | 100 | | | | | | | | | | | | | |
| C–X | 0.0017 | 6 | 100 | | | | | | | | | | | | |
| C–H | 0.0078 | −23 | 19 | 100 | | | | | | | | | | | |
| ∠CCX | 0.3716 | −79 | −22 | 14 | 100 | | | | | | | | | | |
| C1–C2 | 0.0053 | −85 | −7 | 20 | 71 | 100 | | | | | | | | | |
| ∠CCC | 0.4494 | −6 | −12 | 9 | 3 | −14 | 100 | | | | | | | | |
| $\varphi_g$ | 2.6117 | −16 | 2 | 6 | 7 | 16 | −23 | 100 | | | | | | | |
| C≡N | 0.0026 | 46 | −7 | −72 | −32 | −39 | −15 | −15 | 100 | | | | | | |
| $u$(3–X) | 0.0030 | 22 | −13 | −22 | −15 | −25 | 1 | −6 | 24 | 100 | | | | | |
| $u$(3–N) | 0.0096 | 6 | 1 | −2 | 1 | −5 | 6 | 13 | 3 | 9 | 100 | | | | |
| $u$(2–N) | 0.0079 | 18 | 6 | 7 | −12 | −17 | 37 | −3 | 0 | 8 | 10 | 100 | | | |
| $u(1-X)_g$ | 0.0296 | −2 | −4 | 4 | −14 | −3 | −35 | 43 | −8 | 3 | −9 | −13 | 100 | | |
| $u(1-X)_a$ | 0.0209 | 21 | 9 | −4 | −13 | −17 | −17 | 3 | 14 | 5 | 3 | −6 | 9 | 100 | |
| α | 0.0583 | −28 | −15 | 5 | 9 | 21 | 1 | 55 | −22 | 2 | 7 | 7 | 50 | −45 | 100 |

Table 1 (CPN) and Table 2 (BPN). Figs. 5 (CPN) and 7 (BPN) show the conformationally sensitive range outside about 3 Å. This part of the RD curve is shown for each conformer together with the experimental and the theoretical curves in these two figures.

For CPN, the X···Cl and X···N distances for *anti* are found at 4.0 and 5.1 Å, and for *gauche* at 3.2 and 3.9 Å.

For BPN, the X···Cl and X···N distances for *anti* are found at 4.2 and 5.3 Å, and for *gauche* at 3.3 and 4.0 Å.

Final results are given in Table 6. Standard deviations (σ) have been corrected for correlation[30] and an uncertainty in the $s$ scale (0.14 %) has been included in the standard deviations for bond lengths. The correlation matrices for CPN and BPN are given in Table 7 and Table 8, respectively.

*Table 9.* Root-mean-square amplitudes ($u$-values) in Å. Calculated values from NORCOR[a] (C) are compared to values from the least-squares refinement (R). The values are multiplied by $10^3$.

| Distance | CPN | | BPN | |
|---|---|---|---|---|
| | $u$(C) | $u$(R)[b] | $u$(C) | $u$(R)[c] |
| C2–C3 | 52 | 65(6) | | |
| C1–C2 | 47 | 60(6) | | |
| C–X | 55 | 44(4) | 56 | 46(12) |
| C≡N | 35 | 33(4) | | |
| C3···N | | | 104 | 75(19) |
| N···C2 | 50 | 51(8) | 50 | 76(24) |
| X···C1(G) | 199 | 211(60) | 206 | 230(59) |
| X···N(G) | 168 | 180(60) | 134 | 157(59) |
| X···C1(A) | 73 | 73(13) | 78 | 57(21) |
| X···N(A) | 88 | 89(13) | | |

[a]Ref. 9. [b]The following pairs of $u$-values were refined in groups: C1–C2 and C2–C3, X–C1(G) and X–N(G), X–C1(A) and X–N(A). [c]The following pair of $u$-values was refined in a group: X–C1(G) and X–N(G).

## Discussion and conclusions

As explained earlier in this work, previous investigators concluded that *gauche* is more stable than *anti* in the liquid phase. Using simple Boltzmann statistics with multiplicities 1 and 2 for *anti* and *gauche*, respectively, we found that for both CPN and BPN, *anti* has a lower potential energy than *gauche* in the gas phase.

The *anti* mol fractions [0.64(0.23) for CPN and 0.63(0.17) for BPN] have large uncertainties in α(*anti*). However, least-squares calculations where α(*anti*) was kept at values much different

*Table 10.* Some structure parameters for CPN and BPN compared to other related molecules (distances $r_\alpha$ and angles $\alpha$).

| Molecule | C≡N/Å | C–CN/Å | C–C/Å | C–C–C/° | Ref. |
|---|---|---|---|---|---|
| $ClH_2C-CH_2-C\equiv N$ | 1.160(4) | 1.478(11) | 1.515(16) | 110.6(1.0) | This work |
| $BrH_2C-CH_2-C\equiv N$[a] | 1.151(11) | 1.489(22) | 1.512(27) | 111.8(1.3) | This work |
| $N\equiv C-CH_2-CH_2-C\equiv N$ | 1.161(1) | 1.465(2) | 1.561(6) | 110.4(0.5) | 31 |
| $CH_2=CH-CH_2-C\equiv N$ | 1.162(7) | 1.460(5) | 1.508(5) | 114.0(1.0) | 32 |
| $CH_3-CH_2-C\equiv N$[b] | 1.159(1) | 1.459(1) | 1.537(1) | 112.0(0.1) | 33 |

[a]Average values are used for BPN. [b]This work is a MW study, while the other four are ED studies.

from these showed definite misfits between experimental and theoretical RD curves.

The comparable structure parameters for CPN and BPN are consistent within the error limits.

According to the MM calculations the *gauche* bond lengths C2–C3, C1–C2 and C–X are about 0.005 Å longer than those for *anti*. In addition, the C–C–C and C–C–X bond angles are 1.0–1.5° larger for the *gauche* form than for *anti*. The latter numbers are of the same order as the uncertainties in these angles from the ED analysis. For BPN, the fit between experimental and theoretical intensities was better when the conformational differences in the parameter values from MM were included in the least-squares refinements. This was not the case for CPN. However, for both CPN and BPN, the inclusion or not of these conformational differences meant relatively little for the fit between the theoretical and the experimental intensities. In Table 10 some structural parameters for CPN and BPN are compared to those of other nitriles. The $r$(C≡N) bond lengths agree within the error limits, but the $r$(C–CN) bond lengths are somewhat longer than those in the other nitriles. The values 110.4(0.5)° from Ref. 31 and 112.0(0.1)° from Ref. 33 for ∠CCC are almost in agreement with the values for CPN and BPN when the error limits are considered.

*Acknowledgements.* As scientific children and grandchildren of Otto Bastiansen we dedicate this work to him on his 70th birthday as an expression of gratitude.

Financial support from *Norges Almenvitenskapelige Forskningsråd* (NAVF) is gratefully acknowledged.

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Received January 7, 1988.