

MOLECULAR STRUCTURE AND CONFORMATIONAL COMPOSITION OF GASEOUS 1,1-DICHLORO-2-BROMOMETHYL-CYCLOPROPANE AND 1,1-DICHLORO-2-CYANOMETHYL-CYCLOPROPANE AS DETERMINED BY ELECTRON DIFFRACTION

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ABSTRACT

The molecular structure of the title compounds have been investigated by gas-phase electron diffraction. Both molecules exist as about equal amounts of the two *gauche* conformers. There is no evidence for the presence of a *syn* conformer, but small amounts of this form cannot be excluded. Some of the important distance (r_a) and angle (\angle_α) parameters for 1,1-dichloro-2-bromomethyl-cyclopropane are: $r(\text{C-H}) = 1.095(19)$ Å, $r(\text{C}_1-\text{C}_2) = 1.476(11)$ Å, $r(\text{C}_2-\text{C}_3) = 1.517(31)$ Å, $r(\text{C}-\text{CH}_2\text{Br}) = 1.543(32)$ Å, $r(\text{C}-\text{Cl}) = 1.752(6)$ Å, $r(\text{C}-\text{Br}) = 1.950(13)$ Å, $\angle\text{C}-\text{C}-\text{Br} = 110.5(1.9)^\circ$, $\angle\text{Cl}-\text{C}-\text{Cl} = 111.9(6)^\circ$, $\angle\text{C}-\text{C}-\text{C} = 117.5(1.3)^\circ$, ϕ_1 (C-C torsion angle between C-Br and the three-membered ring for *gauche*-1) = $116.2(5.6)^\circ$, $\phi_2 = -132.7(7.6)$. For 1,1-dichloro-2-cyanomethyl-cyclopropane the parameter values are: $r(\text{C-H}) = 1.101(16)$ Å, $r(\text{C}_1-\text{C}_2) = 1.498(9)$ Å, $r(\text{C}_2-\text{C}_3) = 1.544(21)$ Å, $r(\text{C}_2-\text{C}_4) = 1.497(33)$ Å, $r(\text{C}-\text{CN}) = 1.466(26)$ Å, $r(\text{C}\equiv\text{N}) = 1.165(8)$ Å, $r(\text{C}-\text{Cl}) = 1.754(5)$ Å, $\angle\text{C}-\text{C}-\text{CN} = 113.7(2.0)^\circ$, $\angle\text{C}-\text{C}-\text{C} = 122.8(1.6)^\circ$, $\text{Cl}-\text{C}-\text{Cl} = 112.5(4)^\circ$, $\phi_1 = 113(13)^\circ$, $\phi_2 = -124(10)^\circ$.

INTRODUCTION

The conformation of halomethyl-cyclopropanes and oxiranes have been studied by spectroscopic methods [1, 2] and by gas-phase electron diffraction [3]. It is fairly well established that the major conformer in the halomethyl-cyclopropanes is the form with the carbon-halogen bond and the three-membered ring *gauche* to each other. The second conformer is the *syn* form, and the population of this form decreases as the size of the halogen atom increases. Wurrey and co-workers [1, 2, 4] studied the vibrational spectra of chloromethyl, bromomethyl, and iodomethyl-cyclopropane and concluded that the abundance of the *syn* form in the liquid state was 5, 2 and $<0.5\%$, respectively. For cyanomethyl-cyclopropane [4] the spectroscopic data were interpreted in terms of a *gauche/syn* equilibrium with the *gauche* form being 3.0 kJ mol^{-1} lower in energy, corresponding to a *syn* population of 13% at room temperature. Reduced steric repulsion and a

possible interaction between the cyano and the cyclopropyl groups are possible reasons for the extra stability of the *syn* form in the cyanomethyl compound.

In the halomethyl-oxiranes (one of the CH_2 -groups in the cyclopropyl ring replaced by an oxygen atom) the asymmetry of the oxirane ring makes the two *gauche* forms different. In the liquid state [1, 2, 5], the form with the larger dipole moment (*gauche*-1) is favored while in the gas phase [5, 6] the less polar *gauche* form (*gauche*-2) is the most stable form. The *syn* form has not been observed in these molecules. In the solid phase [5] *gauche*-1 was the only conformer observed for fluoro, chloro and bromomethyl-oxirane. In the gas-phase the *gauche*-2 form has been found to be more stable for chloromethyl-oxirane (epichlorhydrin) [6] and chloromethyl-thiirane (3-chloropropylene sulfide) [7]. The more polar *gauche* form is stabilized in the condensed phases. The relative stability in the gas-phase of the *gauche*-1 and *gauche*-2 forms can shed light on the long range interactions between halogen and oxygen or sulfur atoms. For example, the amount of *gauche*-1 present in chloromethyl-oxirane (33% at 67°C) compared with the amount present in chloromethyl-thiirane (18% at 35°C) suggests greater preference for the *gauche*-2 form in the thiirane. This difference may be a result of a larger repulsion between chlorine and sulfur than between chlorine and oxygen atoms. We wish to explore the non-bond interactions further by observing the relative population of *gauche*-1 and *gauche*-2 in a slightly perturbed cyclopropane system and comparing them with those of the oxiranes and thiiranes. This can be achieved by studying molecules where the symmetry of the three-membered ring is destroyed by substitution. We have therefore initiated gas-phase conformational investigations of 1,1-dichloro-2-cyanomethyl-cyclopropane and 1,1-dichloro-2-bromomethyl-cyclopropane (Fig. 1) and are reporting our findings in this article. No structural or conformational information has been reported available for these two compounds.

EXPERIMENTAL AND DATA ANALYSIS

The samples of 1,1-dichloro-2-cyanomethyl-cyclopropane (DCLC3CN) and 1,1-dichloro-2-bromomethyl-cyclopropane (DCLC3BR) were purchased from Maybridge Chemical Co., and were used without further purification. The electron diffraction photographs were recorded on Kodak Electron Image plates using the Oslo Balzers ED-instrument [8] at nozzle temperatures of 93°C (DCLC3CN) and 65°C (DCLC3BR). The camera distances were 497.73 mm and 247.96 mm for the long and short distances, respectively. Benzene was used for the wavelength calibration ($\lambda = 0.05906 \text{ \AA}$). For DCLC3CN five plates from each of the two camera distances were selected for use, while four plates from each distance were used for DCLC3BR. The intensity data were recorded using a Joyce Loebel microdensitometer. The data range obtained were $2.00 \leq s \leq 14.75$ and $4.00 \leq$

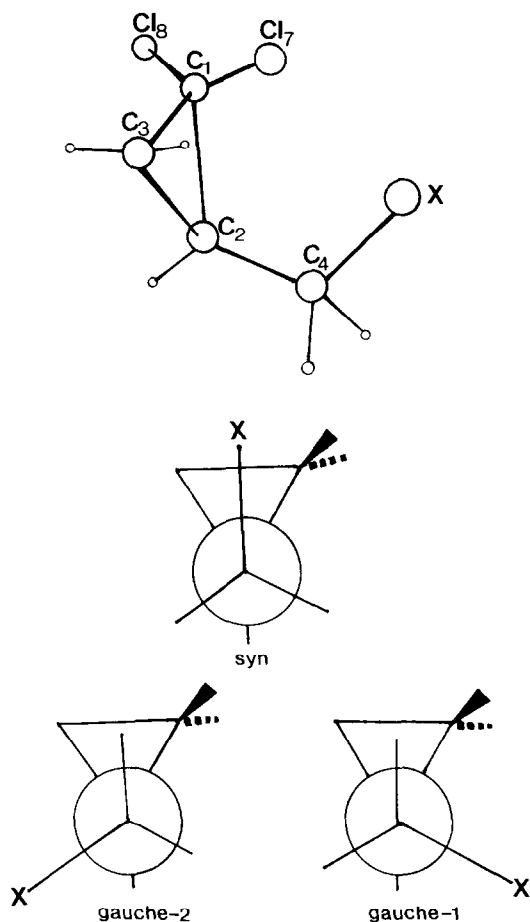


Fig. 1. Diagrams showing the atomic numbering of 1,1-dichloro-2-bromomethyl-cyclopropane ($X = \text{Br}$) and 1,1-dichloro-2-cyanomethyl-cyclopropane ($X = \text{CN}$). Newman projections of *syn*, *gauche-1* and *gauche-2* conformers.

$s \leq 29.00 \text{ \AA}^{-1}$ for the long and short camera experiments, respectively, with $\Delta s = 0.25 \text{ \AA}^{-1}$ ($s = 4\pi\lambda^{-1} \sin \theta$ where 2θ is the scattering angle). The usual data reduction procedures were followed [9, 10] and background curves were subtracted from each individual curve. The intensity data from each camera distance were then averaged together for each compound. These average experimental intensity curves are shown in Figs. 2 and 3, respectively [11]. Least squares procedures outlined by Gundersen and Hedberg [9] are followed using scattering factors tabulated by Schäfer et al. [12].

The atomic numbering scheme used for DCLC3BR is shown in Fig. 1. In principle, all three C—C bonds in the cyclopropyl ring are different. But since the effect of the dichlorosubstitution on the ring geometry is greater than that of a methyl group, we assumed the three-membered ring to be an

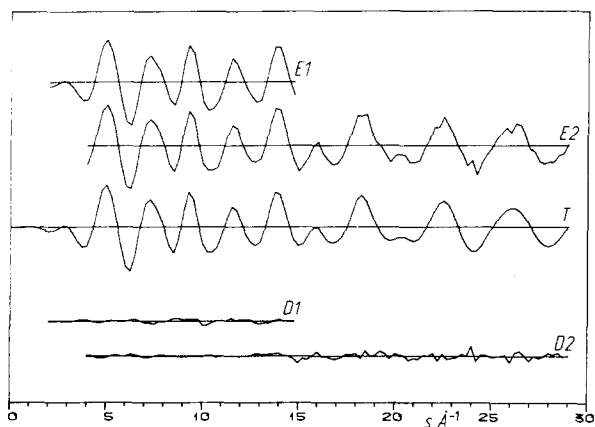


Fig. 2. Intensity curves, $sI_m(s)$ for 1,1-dichloro-2-bromomethyl-cyclopropane. Experimental curves (E1, E2) are averages of all plates for the two camera distances. Theoretical curve (T) was calculated from the structure parameters of Table 1. Difference curves (D1, D2) are $E - T$.

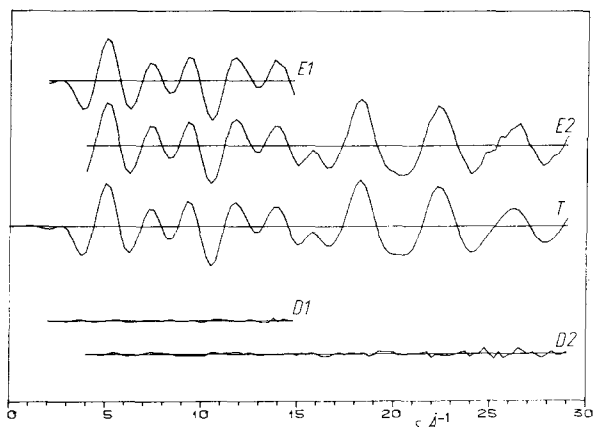


Fig. 3. Intensity curves, $sI_m(s)$ for 1,1-dichloro-2-cyanomethyl-cyclopropane. Experimental curves (E1, E2) are averages of all plates for the two camera distances. Theoretical curve (T) was calculated from the structure parameters of Table 3. Difference curves (D1, D2) are $E - T$.

isosceles triangle with $r(C_1-C_2) = r(C_1-C_3) \neq r(C_2-C_3)$. In our model the following assumptions were also made: (1) all C-H distances have the same length; (2) the different conformers have the same geometry except for the torsion angles. The parameters chosen to define the geometry are: $r(C-H)$, $\langle r(C-C) \rangle = (r(C_1-C_2) + r(C_2-C_3))/2$, $\Delta r(C-C) = r(C_2-C_3) - r(C_1-C_2)$, $r(C_2-C_4)$, $r(C-Cl)$, $r(C-Br)$, $\angle C_2-C_4-H$, $\angle C_1-C_3-H$, $\angle Cl-C-Cl$, $\angle C-C-Br$, $\angle H-C-H$, $H-C-Br, \alpha$ (the angle between C_4-C_2 and the three-membered ring) and ϕ (the torsion angle between C-Br and the bisector of the three-membered ring). A positive value of ϕ corresponds to a clockwise rotation of the bromomethyl group.

The least squares refinements, based on intensity curves, adjusted a single theoretical curve to the two average experimental curves using a unit weight matrix. Vibrational amplitudes and shrinkage corrections were calculated using a force field developed using selected values from the force fields for cyclopropane [13], 1,1-dichloro-cyclopropane [14] and 2,3-dibromopropene [15].

Figure 4 shows the torsion-sensitive section of the experimental radial distribution (RD) curve together with the theoretical RD-curves for *syn*, *gauche-1*, *gauche-2* and for a mixture of the last two of these conformers. The *gauche-1* conformer has no important interatomic distances longer than 4.8 Å and the experimental peak at 5.6 Å clearly shows the presence of the *gauche-2* conformer. However, the area under this peak in the experimental curve shows that a significant amount of a second conformer is present. This is also shown by the experimental RD-curve at about 4.6 Å. A theoretical RD-curve calculated with about equal amounts of *gauche-1* and *gauche-2* conformers gave good agreement with the experimental curve, and least squares refinements were made using this two-conformer model. A model with three conformers (*gauche-1*, *gauche-2* and *syn*) was also tested. Our experiment gave no indications of a *syn* form being present, but based on the ED-results alone the presence of up to 10% *syn* cannot be excluded. In the refinements a value of 2% *syn* was obtained. In the final refinement the two-conformer model was used and the detailed results are summarized in Table 1.

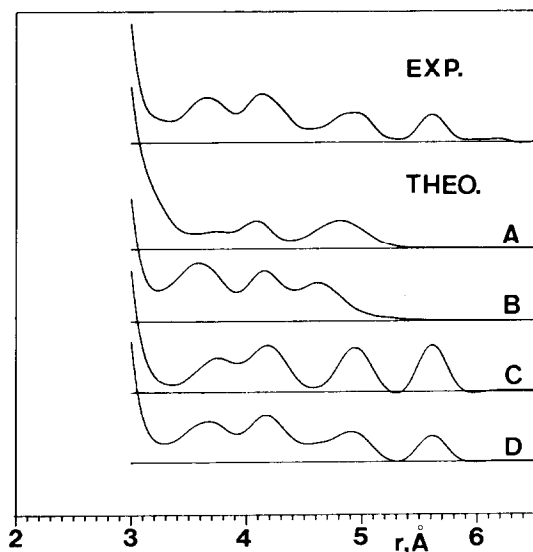


Fig. 4. Experimental radial distribution curve for 1,1-dichloro-2-bromomethyl-cyclopropane together with theoretical curves for the *syn* (A), *gauche-1* (B), and *gauche-2* (C) conformers and a mixture of 45% *gauche-1* and 55% *gauche-2* (D). Only the conformationally important parts of the curves are shown. All curves are on the same scale.

TABLE 1

Final parameter values for 1,1-dichloro-2-bromomethyl-cyclopropane^a

Parameter	r_a/L_α	l	Parameter	r_a	l
$r(\text{C—H})$	1.095(19)	0.067	<i>Dependent distances:</i>		
$\langle r(\text{C—C}) \rangle^b$	1.496(14)		$r(\text{C}_1\text{—C}_2)$	1.476(11)	0.046
$\Delta r(\text{C—C})^c$	0.041(36)		$r(\text{C}_2\text{—C}_3)$	1.517(31)	0.046
$r(\text{C}_2\text{—C}_4)$	1.543(32)	0.051	$r(\text{C}_2\cdots\text{Br})$	2.871(24)	0.077
$r(\text{C—Cl})$	1.752(6)	0.049	$r(\text{C}_1\cdots\text{C}_4)$	2.560(61)	0.070
$r(\text{C—Br})$	1.950(13)	0.053	$r(\text{Cl}\cdots\text{Cl})$	2.900(11)	0.069
$\angle \text{C}_4\text{—C}_2\text{—C}_1$	117.5(1.3)		$r(\text{C}_3\cdots\text{Cl})$	2.780(8)	0.070
$\angle \text{C—C—Br}$	110.5(1.9)		$r(\text{C}_4\cdots\text{Cl}_8)$	4.095(17)	0.089
$\angle \text{Cl—C—Cl}$	111.9(6)		$r(\text{C}_4\cdots\text{Cl}_7)$	3.036(21)	0.094
$\angle \text{H—C—H}$	[109.0]		<i>gauche-2</i>		
$\angle \text{C}_4\text{—C}_2\text{—H}$	[110.0]		$r(\text{C}_3\cdots\text{Br})$	3.789(64)	0.156
$\angle \text{C}_2\text{—C}_4\text{—H}$	[111.4]		$r(\text{C}_1\cdots\text{Br})$	4.244(19)	0.082
ϕ_1^d	116.2(5.6)		$r(\text{Cl}_8\cdots\text{Br})$	5.607(20)	0.110
ϕ_2^d	-132.7(7.6)		$r(\text{Cl}_7\cdots\text{Br})$	4.941(24)	0.137
% <i>gauche-2</i>	55(11)		<i>gauche-1</i>		
			$r(\text{C}_3\cdots\text{Br})$	4.225(23)	0.096
			$r(\text{C}_1\cdots\text{Br})$	3.581(39)	0.147 ^e (50)
			$r(\text{Cl}_8\cdots\text{Br})$	4.641(34)	0.192
			$r(\text{Cl}_7\cdots\text{Br})$	3.624(87)	0.290 ^e (50)

^aDistances (r_a) and vibrational amplitudes (l) are in Ångströms, angles (\angle_α) are in degrees. Parenthesized uncertainties are 2σ and include estimates of systematic errors and correlation in the experimental data. Quantities in brackets were kept constant in the least squares refinements. ^b $\langle r(\text{C—C}) \rangle = 0.5(r(\text{C}_1\text{—C}_2) + r(\text{C}_2\text{—C}_3))$. ^c $\Delta r(\text{C—C}) = r(\text{C}_2\text{—C}_3) - r(\text{C}_1\text{—C}_2)$. ^d ϕ_1 , and ϕ_2 are the C—C torsion angles between the C—Br bond and the three-membered ring for *gauche-1* and *gauche-2* conformers, respectively. A positive value of ϕ corresponds to a clockwise rotation of the C—Br bond in the Newman projections shown in Fig. 1. ^eRefined as a group.

Some of the valence angles involving hydrogen could not be determined in the refinements and they were therefore given reasonable values and kept constant. In the preliminary refinements a value of 0.040 Å, as reported for 1,1-dichloro-cyclopropane [14], was assumed for $\Delta r(\text{C—C})$. This restriction was removed in the final refinement and a value of 0.041(36) Å was obtained. Figure 5 shows the experimental radial distribution curve together with the difference curve. Table 2 gives the correlation matrix for the refined parameters.

The parameters used to define the DCLC3CN-molecules are basically the same as those used for DCLC3BR. The parameters $r(\text{C—Br})$ and $\angle \text{C—C—Br}$ are replaced by $r(\text{C—CN})$ and $\angle \text{C—C—CN}$, and $r(\text{C}\equiv\text{N})$ is an additional parameter. It was assumed that $\angle \text{C—C}\equiv\text{N} = 180^\circ$. For DCLC3CN the amplitudes of vibration and shrinkage corrections are calculated using force constants selected from force fields of cyclopropane [13], 1,1-dichloro-cyclopropane [14] and allyl cyanide [16].

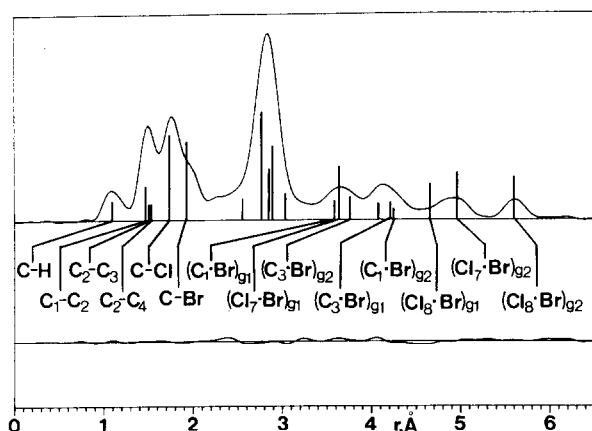


Fig. 5. Radial distribution curves for 1,1-dichloro-2-bromomethyl-cyclopropane. The vertical lines indicate the locations and weights for the most important interatomic distances in the molecule. Difference curve is experimental minus theoretical. Artificial damping coefficient $B = 0.0020 \text{ \AA}^2$.

TABLE 2

Correlation matrix ($\times 100$) for the parameters of 1,1-dichloro-2-bromomethyl-cyclopropane

Parameter	σ^a	r_1	r_2	r_3	r_4	L_5	L_6	L_7	L_8	r_9	L_{10}	l_{11}	%
1 $r(\text{C-H})$	0.0051	100	-9	8	9	9	-2	10	-8	-1	5	-4	2
2 $r(\text{C}_2-\text{C}_4)$	0.0067		100	-71	29	-58	-38	-34	5	36	-54	1	-13
3 $\langle r(\text{C-C}) \rangle$	0.0022			100	-31	41	13	30	-2	-41	69	1	11
4 $\Delta r(\text{C-C})$	0.0031				100	-19	-56	10	11	50	-27	14	-3
5 $\angle \text{C}_4-\text{C}_2-\text{C}$	0.55					100	38	38	-10	-10	21	-2	2
6 $\angle \text{C-C-Br}$	0.51						100	-13	-29	-60	2	-23	-7
7 ϕ_1	2.56							100	-16	6	24	43	18
8 ϕ_2	1.95								100	19	-4	4	-29
9 $r(\text{C-Cl})$	0.0013									100	-42	11	-2
10 $\angle \text{Cl-C-Cl}$	0.17										100	11	7
11 $l(\text{C}_1 \cdots \text{Br})$	0.027											100	-24
12 % <i>gauche</i> -2	3.9												100

^aStandard deviations from least squares refinements.

Figure 6 shows the torsion-dependent part of the experimental RD-curve together with theoretical curves for *syn*, *gauche*-1, *gauche*-2 and a mixture of the last two conformers.

In *gauche*-1 all important interatomic distances are shorter than 5.2 Å while *gauche*-2 has longer non-bonded distances between the cyano group and the chlorine atoms. This is reflected in the RD-curves of Fig. 6. The area under the peaks at 4.15, 4.9, 5.6 and 6.2 Å clearly shows the presence of

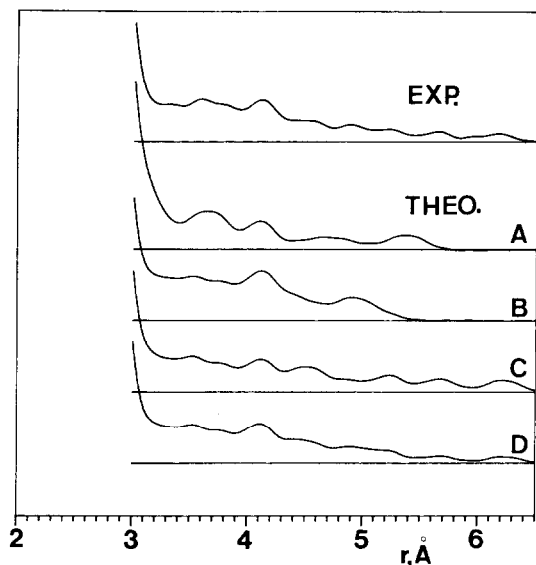


Fig. 6. Experimental radial distribution curve for 1,1-dichloro-2-cyanomethyl-cyclopropane together with theoretical curves for *syn* (A), *gauche*-1 (B) and *gauche*-2 (C) and a mixture of 45% *gauche*-1 and 55% *gauche*-2 (D). All curves are on the same scale.

both *gauche* conformers. Also for this molecule we can find no evidence for the *syn* form being present, but small amounts (up to 15%) of this conformer cannot be excluded. In the final least squares refinement a two-conformer model was used and the results are shown in Table 3. Table 4 gives the correlation matrix for the parameters and the final RD-curves for DCLC-3CN are shown in Fig. 7.

DISCUSSION

Table 5 summarizes the major geometrical parameters for some substituted cyclopropanes. The ring structure obtained for DCLC3CN agrees very well with that reported for 1,1-dichloro-cyclopropane [14]. One has to bear in mind, however, that we assumed an isosceles triangle for the cyclopropane ring. The external C—C bond (i.e. $r(\text{C}_2\text{---C}_4)$) in DCLC3CN is identical to that reported for methylcyclopropane [17]. The bonds in DCLC3BR are not very accurately determined, but the structures of these two molecules are consistent with each other and with related molecules.

The *gauche*-2 form is slightly favored in the gas phase for both DCLC3BR and DCLC3CN and this suggests a very small difference in energy between the two *gauche* conformers. Thus, perturbation of the cyclopropane ring by the two chlorine atoms makes little difference in the preference of one *gauche* conformer over the other. A much larger energy difference was observed between the *gauche*-1 and the *gauche*-2 conformers in chloro-

TABLE 3

Final parameter values for 1,1-dichloro-2-cyanomethyl-cyclopropane^a

Parameter	r_a/L_α	l		r_a	l
$r(\text{C}-\text{H})$	1.101(16)	0.067	<i>gauche-2</i>		
$\langle r(\text{C}-\text{C}) \rangle^b$	1.521(12)		$r(\text{C}_3 \cdots \text{C}_5)$	3.436(59)	0.155
$\Delta r(\text{C}-\text{C})^c$	0.046(23)		$r(\text{C}_3 \cdots \text{N})$	4.296(84)	0.200
$r(\text{C}\equiv\text{N})$	1.165(8)	0.035	$r(\text{C}_1 \cdots \text{C}_5)$	3.851(22)	0.082
$r(\text{C}-\text{CN})$	1.466(26)	0.052	$r(\text{C}_1 \cdots \text{N})$	4.902(30)	0.102
$r(\text{C}_2-\text{C}_4)$	1.497(33)	0.051	$r(\text{C}_5 \cdots \text{Cl}_8)$	5.232(25)	0.111
$r(\text{C}-\text{Cl})$	1.754(5)	0.049	$r(\text{N} \cdots \text{Cl}_8)$	6.221(36)	0.144
$\angle \text{C}_4-\text{C}_2-\text{C}$	122.8(1.6)		$r(\text{C}_5 \cdots \text{Cl}_7)$	4.546(38)	0.136
$\angle \text{C}_2-\text{C}_4-\text{C}_5$	113.7(2.0)		$r(\text{N} \cdots \text{Cl}_7)$	5.659(51)	0.146
$\angle \text{Cl}-\text{C}-\text{Cl}$	112.5(4)		<i>gauche-1</i>		
$\angle \text{H}-\text{C}-\text{H}$	[109.0]		$r(\text{C}_3 \cdots \text{C}_5)$	3.862(35)	0.096
$\angle \text{C}_4-\text{C}_2-\text{H}$	[110.0]		$r(\text{C}_3 \cdots \text{N})$	4.897(47)	0.120
$\angle \text{C}_2-\text{C}_4-\text{H}$	[111.4]		$r(\text{C}_1 \cdots \text{C}_5)$	3.315(71)	0.164
ϕ_1^d	113(13)		$r(\text{C}_1 \cdots \text{N})$	4.135(99)	0.212
ϕ_2^d	-124(11)		$r(\text{C}_5 \cdots \text{Cl}_7)$	3.521(156)	0.217
% <i>gauche-2</i>	55(26)		$r(\text{N} \cdots \text{Cl}_7)$	4.135(99)	0.197
<i>Dependent distances:</i>			$r(\text{C}_5 \cdots \text{Cl}_8)$	4.456(45)	0.193
$r(\text{C}_1-\text{C}_2)$	1.498(9)	0.046	$r(\text{N} \cdots \text{Cl}_8)$	5.021(69)	0.279
$r(\text{C}_2-\text{C}_3)$	1.544(21)	0.046			
$r(\text{C}_5 \cdots \text{C}_2)$	2.473(25)	0.077			
$r(\text{C}_2 \cdots \text{N})$	3.487(22)	0.102			
$r(\text{C}_1 \cdots \text{C}_4)$	2.629(24)	0.069			
$r(\text{Cl} \cdots \text{Cl})$	2.912(8)	0.069			
$r(\text{C}_3 \cdots \text{Cl})$	2.797(7)	0.070			
$r(\text{C}_4 \cdots \text{Cl}_8)$	4.094(15)	0.089			
$r(\text{C}_4 \cdots \text{Cl}_7)$	3.158(26)	0.121			

^aDistances (r_a) and vibrational amplitudes (l) are in Ångströms, angles (\angle_α) are in degrees. Parenthesized uncertainties are 2σ and include estimates of errors in the wavelength and data correlation. Quantities in brackets were kept constant in the least squares refinements. ^b $\langle r(\text{C}-\text{C}) \rangle = 0.5(r(\text{C}_1-\text{C}_2) + r(\text{C}_2-\text{C}_3))$. ^c $\Delta r(\text{C}-\text{C}) = r(\text{C}_2-\text{C}_3) - r(\text{C}_1-\text{C}_2)$. ^d ϕ_1 and ϕ_2 are the C-C torsion angles between C-C≡N and the three-membered ring for the *gauche-1* and *gauche-2* conformers, respectively. A positive value of ϕ corresponds to a clockwise rotation of the C-C≡N group in the Newman projections shown in Fig. 1.

methyl-oxirane (2.1 kJ mol⁻¹) [7]. The *gauche-2* population in the thiirane compound was observed to be 82% at 35°C. This larger energy difference cannot be the result of a much higher steric repulsion in the *gauche-1* form of chloromethyl-thiirane compared with that in DCL3BR. Both the shortest Br \cdots Cl distance in DCLC3BR and the S \cdots Cl distance in chloromethyl-thiirane are slightly shorter than the sum of the van der Waals radii (3.62 vs. 3.75 Å and 3.46 vs. 3.65 Å, respectively). These distances could also be easily increased by a small increase in the value of ϕ_1 . The conformational difference between the oxirane/thiirane and the dichloro-cyclopropyl

TABLE 4

Correlation matrix ($\times 100$) for the parameters of 1,1-dichloro-2-cyanomethyl-cyclopropane

Parameter	σ^a	r_1	r_2	r_3	r_4	r_5	x_6	\angle_7	\angle_8	\angle_9	\angle_{10}	\angle_{11}	r_{12}	%
1 $r(\text{C-H})$	0.0039	100	-1	-20	-21	16	19	14	4	8	-7	1	-46	-4
2 $r(\text{C}_2-\text{C}_4)$	0.0082		100	-77	-44	-70	-48	-28	-35	-8	-13	-4	4	5
3 $\langle r(\text{C-C}) \rangle$	0.0028			100	74	42	22	21	24	-5	23	-3	21	-2
4 $\Delta r(\text{C-C})$	0.0058				100	47	-29	-13	1	-5	60	-58	19	2
5 $r(\text{C-CN})$	0.0064					100	7	-6	17	14	35	-41	-23	-2
6 $\angle \text{C}_4-\text{C}_2-\text{C}$	0.69						100	62	38	-1	-16	50	-18	-4
7 $\angle \text{C}_2-\text{C}_4-\text{C}_5$	0.66							100	32	-40	-13	32	1	-4
8 ϕ_1	3.52								100	0	2	17	-2	-1
9 ϕ_2	4.32									100	2	-3	-15	-31
10 $r(\text{C-Cl})$	0.0009										100	-67	9	-1
11 $\angle \text{Cl-C-Cl}$	0.15											100	-1	-4
12 $r(\text{C}\equiv\text{N})$	0.0019												100	3
13 % <i>gauche</i> -2	8.7													100

^aStandard deviations from least squares refinements.

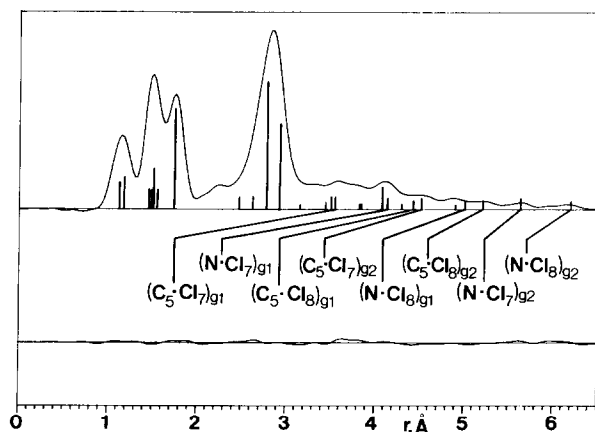


Fig. 7. Radial distribution curves for 1,1-dichloro-2-cyanomethyl-cyclopropane. The vertical lines indicate the locations and weights for the most important inter-atomic distances in the molecule. $B = 0.0020 \text{ \AA}^2$.

TABLE 5

Comparison of the geometry of some substituted cyclopropanes^a

	1,1-Dichloro- cyclopropane	Methyl-cyclopropane	1,1-Dichloro- 2-bromo- methyl-cyclo- propane	1,1-Dichloro- 2-cyano- methyl-cyclo- propane
$r(\text{C}_1-\text{C}_2)$	1.497(3)	1.509(3)	1.476(11)	1.498(9)
$r(\text{C}_2-\text{C}_3)$	1.538(9)	1.509(3)	1.517(31)	1.544(21)
$r(\text{C}-\text{CH}_2\text{X})$		1.517(6)	1.543(32)	1.497(33)
$r(\text{C}-\text{Cl})$	1.759(2)		1.752(6)	1.754(5)
$\angle \text{Cl}-\text{C}-\text{Cl}$	112.6(2)		111.9(6)	112.5(4)
Dist. type	r_g	r_a	r_a	r_a
Ref.	14	17	This work	This work

^aDistances are in Ångstroms, angles in degrees.

compounds must therefore have other origins, for example differences in dipole/dipole interactions or inherent differences in the rotation about those C_2-C_4 bonds.

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