

## Molecular Structure of Methylcyclopropane and *trans*-1,2-Dimethylcyclopropane as Studied by Gas Electron Diffraction

A. W. KLEIN and G. SCHRUMPF

Organisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 2, D-3400 Göttingen, Germany

The obtained structural parameters for the two compounds are identical and the ring geometries are nearly the same as that of cyclopropane. The CC bond between the three-membered ring and a methyl group is shorter than that in saturated hydrocarbons by about 0.015 Å, which is interpreted in terms of hybridization differences between cyclopropane carbon and carbon in saturated open chain molecules.

The experimentally determined bond distances  $r_a$  are the following: Methylcyclopropane:  $r(\text{C}-\text{H}, \text{ring})=1.089$  (3),  $r(\text{C}-\text{H}, \text{methyl})=1.090$  (4),  $r(\text{C}_1-\text{C}_2)=1.509$  (1) and  $r(\text{C}_1-\text{C}_4)=1.517$  (2) Å; *trans*-1,2-Dimethylcyclopropane:  $r(\text{C}-\text{H}, \text{ring})=1.090$  (6),  $r(\text{C}-\text{H}, \text{methyl})=1.089$  (4),  $r(\text{C}_1-\text{C}_2)=1.508$ (3) and  $r(\text{C}_1-\text{C}_4)=1.519$  (4) Å. Values in parentheses are estimated standard deviations.

It is well-known that a CC-single bond adjacent to a double or triple bond is shorter than that in saturated hydrocarbons. This has been interpreted in terms of differences in hybridization of the carbon atoms involved.<sup>1</sup> In the series propane, propene and propyne, the orbitals forming the single bond are an  $sp^3$  orbital of the methyl group and  $sp^3$ -,  $sp^2$ - and  $sp$ -hybrids, respectively. Increasing  $s$ -character shifts the electron density within the orbital towards the nucleus, and consequently shorter interatomic distances are needed for optimal orbital overlap.

According to the well-established model of bonding in the cyclopropane molecule proposed by Walsh,<sup>2</sup> the exocyclic carbon orbitals are  $sp^2$ -hybridized. Definite shortening of bonds between a cyclopropane carbon and chlorine, nitrogen and phosphorous relative to the corresponding bonds in open chain compounds have been observed.<sup>3–5</sup> Effects from conjugation and from hybridization

changes have been used to explain these results which support the proposed model. Thus, the length of the exocyclic CC bond in methylcyclopropane is expected to be close to the single bond in propene or, at least, definitely shorter than that of propane.

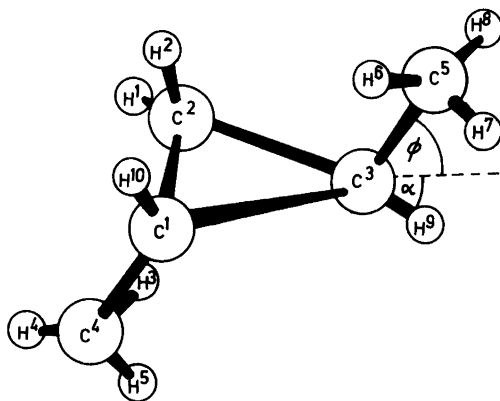
In the only experimental study of the structure of methylcyclopropane, mainly aimed to study the internal rotational barrier of the  $\text{CH}_3$ -group, Ford and Beaudet<sup>6</sup> analyzed the microwave spectrum of the normal isotopic species. The three rotational constants were, however, fit with an exocyclic CC bond length of 1.522 Å. This means only a slight shortening relative to propane<sup>7</sup> if any at all. The determination necessarily involved many assumptions and the result may therefore not be very reliable.

We therefore decided to undertake an electron diffraction study of methylcyclopropane in the gas phase. However, high correlation between the different bond lengths and bond angles was expected to complicate the interpretation of the diffraction data, and the bond lengths might possibly not be determined to a satisfactory precision. Thus, we looked for another molecule having a methyl group linked to a cyclopropane ring. We chose *trans*-1,2-dimethylcyclopropane, because the contribution to the scattered intensity from the exocyclic CC bond is doubled, and its environment essentially the same as in methylcyclopropane.<sup>8</sup>

We decided to investigate the structure of both molecules simultaneously, using the results for the disubstituted cyclopropane to aid the analysis of the diffraction pattern of methylcyclopropane.

Table 1. Photographic plate data.

Camera distance (mm)	No. of plates	$s_{\min}$ ( $\text{\AA}^{-1}$ )	$s_{\max}$ ( $\text{\AA}^{-1}$ )	$\Delta s$ ( $\text{\AA}^{-1}$ )
<b>Methylcyclopropane</b>				
200.78	6	7.00	43.00	0.25
480.78	5	1.50	19.00	0.125
<b><i>trans</i>-1,2-Dimethylcyclopropane</b>				
200.78	4	9.00	43.00	0.25
480.78	6	1.50	19.25	0.125

Fig. 1. *trans*-1,2-Dimethylcyclopropane. Molecular model which shows the numbering of the atoms.

## EXPERIMENTAL

Both compounds used in this study were synthesized by modifications of established routes.<sup>9</sup>

The electron diffraction data were recorded on the Oslo electron diffraction unit<sup>10</sup> at two different nozzle-to-plate distances. The exposures were made at about 18 °C and at an electron wavelength of 0.06463 Å.

The photographic plate data of the two compounds are summarized in Table 1. For each camera distance, the four best plates were selected and the intensities corrected in the usual way.<sup>11</sup> Due to a little uncertainty in the blackness correction particularly affecting the darkest intensity points, the values below  $s=1.5 \text{ \AA}^{-1}$  were dropped. An empirical background was subtracted from the data of each plate before averaging the intensity data for

each camera distance. The intensities were modified<sup>11</sup> by  $s/|f'_c(s)|^2$ . The scattering amplitudes and phases ( $|f'_j(s)|$  and  $\eta_j(s)$ ) were calculated by the partial wave method<sup>12</sup> using the Hartree-Fock atomic potential for C-atoms<sup>13</sup> and the potential for molecular bonded H-atoms.<sup>14</sup> Radial distribution functions were calculated by Fourier inversions of experimental and theoretical intensity curves after multiplication with the artificial damping function  $\exp(-ks^2)$ . For  $s$ -values below  $1.5 \text{ \AA}^{-1}$ , theoretical intensity data obtained from a molecular model were included.

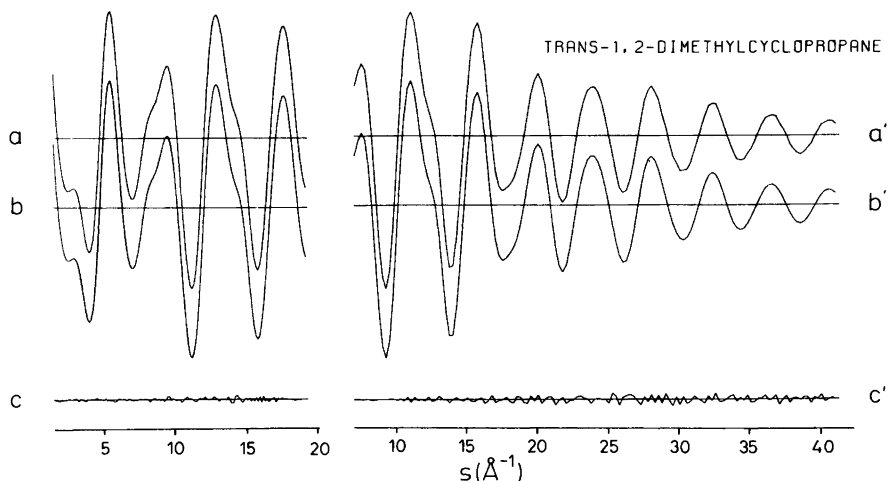


Fig. 2. (a) Experimental and (b) calculated molecular intensity curve for nozzle to photographic plate distance of 48 cm; (c) difference curve (a) – (b) multiplied by a factor of 2. (a'), (b') and (c') are the corresponding curves for the 20 cm distance.

## STRUCTURE ANALYSIS AND FINAL RESULTS

*trans*-1,2-Dimethylcyclopropane. A molecular model of *trans*-1,2-dimethylcyclopropane is shown in Fig. 1 which also gives the numbering of the atoms. In order to reduce the number of parameters to be refined to a practical limit, the following assumptions about the molecular structure were made: (a) The molecule possesses  $C_2$  symmetry, (b) the carbon carbon bonds within the cyclopropyl group are equal, (c) the hydrogen atoms of the methyl groups are staggered to the ring hydrogen atoms, (d) the four carbon hydrogen bond lengths of the ring are equal and (e) the  $CH_2$ -group has local  $C_{2v}$  symmetry.

With these assumptions, the geometry of the molecular model could be completely defined by eight parameters only. These include four bond lengths  $r(C-H, ring)$ ,  $r(C-H, methyl)$ ,  $r(C_1-C_2)$ ,  $r(C_1-C_4)$  and four bond angles  $HCH(ring)$ ,  $C_1C_3H_9$ ,  $C_1C_4H_3$ ,  $C_1C_3C_5$ .

Preliminary values for the bond distances and bond angles were obtained from the experimental radial distribution curve (Fig. 3). The peaks at about 1.1 and 1.5 Å correspond to the ten carbon hydrogen and five carbon carbon bond distances, respectively. Nonbonded carbon hydrogen distances over one bond angle are found at about 2.2 Å. The peak at about 2.6 Å contains contributions from nonbonded carbon carbon distances over one angle. Preliminary root-mean-square amplitudes of vibration ( $u$ -values) were assigned by using experimental data obtained from similar molecules.<sup>15-19</sup>

The molecular structure was then refined by least squares calculations on the intensity data<sup>20</sup> using a non-diagonal weight-matrix<sup>21</sup> with the parameters summarized in Table 2. The data of the 20 and 48 cm curves were given equal weight. The computations involved strongly damped iterations using 0.5 times the calculated shift of the current iteration cycle and

Table 2. Constants of the weighting schemes used in the structure refinements.<sup>a</sup>

Camera distance (mm)	$s_1$	$s_2$	$w_1$	$w_2$	$p_2$	$p_3$
48	2.0	18.0	0.2	0.2	-0.64	0.146
20	8.0	40.0	0.2	0.2	-0.60	0.125

<sup>a</sup> For the meaning of the symbols see Refs. 11 and 21.

Table 3. *trans*-1,2-Dimethylcyclopropane. Molecular parameters obtained from least squares refinements of the molecular intensities.<sup>a</sup>

	$r_a$	$u$
$C_1-C_4$	1.519 (4)	0.049 (4)
$C_1-C_2$	1.508 (3)	0.047 (2)
$C-H(ring)$	1.090 (6)	0.080 (25)
$C-H(methyl)$	1.089 (4)	0.076 (15)
$\rho_{14,12}$	-0.87	
Angles		
$\phi^b$	56.8 (0.2)	
$\alpha^b$	59.9 (2.2)	
$\angle HCH(ring)$	116.9 (1.3)	
$\angle CCH(methyl)$	112.1 (0.4)	

<sup>a</sup> Bond distances ( $r_a$ ) and mean square amplitudes ( $u$ ) are given in Å, angles are in degrees. Parenthesized values are the standard deviations. <sup>b</sup> See text and Fig. 1 for the definition of  $\phi$  and  $\alpha$ .

0.2 times the shift of the previous cycle.

It was possible to refine all geometrical parameters together with the  $u$ -values for the bond distances and those for the nonbonded  $C\cdots C$  distances simultaneously. The least squares refinement yielded an  $R$ -factor of 1.7%. The final parameters are given in Table 3, and the corresponding theoretical radial distribution and intensity functions are shown in Figs. 2 and 3 together with their experimental counterparts.

*Methylcyclopropane*. A molecular model of methylcyclopropane is shown in Fig. 4, which also gives the numbering of the atoms. In addition to the

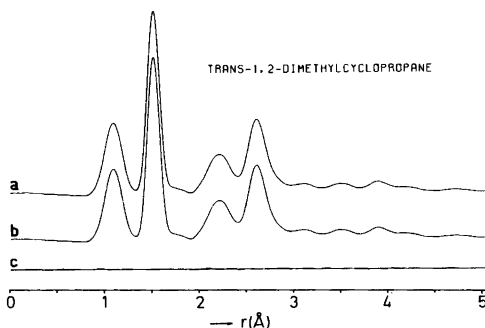


Fig. 3. (a) Experimental and (b) calculated radial distribution curve with an artificial damping factor  $k = 0.0015 \text{ \AA}^2$ ; (c) difference curve (a) - (b) multiplied by a factor of 2.

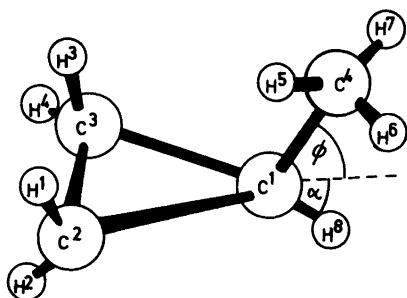


Fig. 4. Methylcyclopropane. Molecular model which shows the numbering of the atoms.

obvious supposition of molecular  $C_s$  symmetry, all assumptions about the molecular structure were made according to those made for *trans*-1,2-dimethylcyclopropane.

Preliminary values for the bond distances, bond angles, and the vibrational amplitudes ( $u_{ij}$ ) were obtained from our results for *trans*-1,2-dimethylcyclopropane. Except for the two bond angles  $C_2C_1C_4$  and  $C_2C_1H_8$ , it was possible to refine all geometrical parameters together with the  $u$ -values for the bond distances and those for the nonbonded  $C \cdots C$  distances simultaneously. In order to get the values of the  $C_2C_1C_4$  and  $C_2C_1H_8$  bond angles (or rather the angle of inclination  $\phi$  of the  $C_1C_4$  bond against the plane of the cyclopropane ring) as exactly as possible, a combined trial and

Table 4. Methylcyclopropane. Molecular parameters obtained from least squares refinements of the molecular intensities.<sup>a</sup>

	$r_a$	$u$
$C_1-C_4$	1.517 (2)	0.049 (5)
$C_1-C_2$	1.509 (1)	0.047 (2)
C-H(ring)	1.089 (3)	0.082 (7)
C-H(methyl)	1.090 (4)	0.074 (11)
$\rho_{14,12}$	-0.97	

Angles	
$\phi^b$	56.7 (0.1) <sup>c</sup>
$\alpha^b$	60.0 (0.3) <sup>c</sup>
$\angle HCH(\text{ring})$	116.4 (0.6)
$\angle CCH(\text{methyl})$	112.1 (0.4)

<sup>a</sup>See footnote a of Table 3. <sup>b</sup>See text and Fig. 4 for definitions. <sup>c</sup>These errors refer to the resolution of the R-factors as described in the text.

error and least squares method was applied. Several least squares refinements were carried out, each time using a slightly different value of  $\phi$  which was kept constant in each refinement run. The R-factor showed a distinct minimum at  $\phi = 56.7^\circ$ . The same procedure for  $\alpha$ , the angle of inclination of the  $C_1H_8$  bond against the plane of the cyclopropane ring, yielded  $\alpha = 60.0^\circ$ . These angles are essentially identical with those of the dimethyl compound within the error limits.

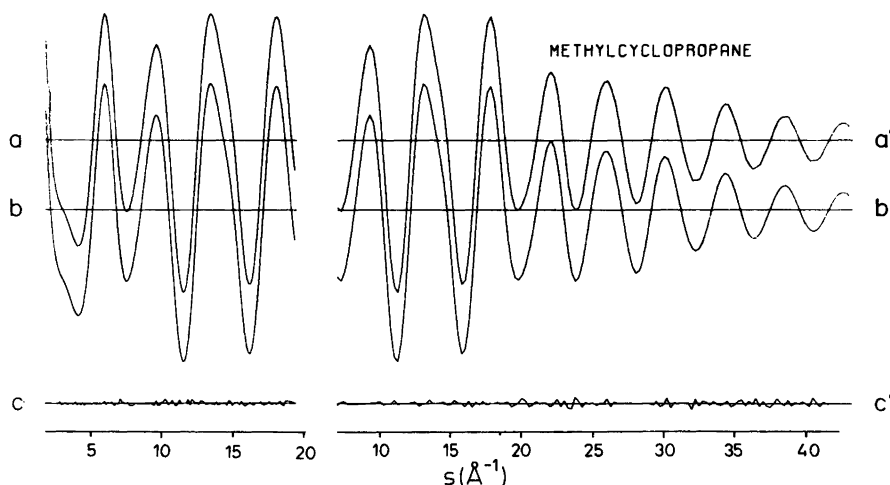


Fig. 5. (a) Experimental and (b) calculated molecular intensity curve for nozzle to photographic plate distance of 48 cm; (c) difference curve (a) - (b) multiplied by a factor of 2. (a'), (b') and (c') are the corresponding curves for the 20 cm distance.

The least squares refinement yielded an  $R$ -factor of 1.4%. The final theoretical molecular intensity curve is shown in Fig. 5 and its Fourier transformed form in Fig. 6. The structural parameters are listed in Table 4 together with the standard deviation values resulting from least squares refinements with the weighting scheme given in Table 2.

## DISCUSSION

The exocyclic CC bond distances of methylcyclopropane and *trans*-1,2-dimethylcyclopropane of 1.519 and 1.520 Å, respectively, are identical within the limits of experimental error.

In Table 5, a series of CC bond distances ( $r_g$ ) between methyl carbon and differently hybridized carbon atoms are compared with each other. The literature values are grouped as  $sp^3-sp^3$  and  $sp^3-sp^2$  bonds. Clearly, the exocyclic CC bonds determined in this study are significantly shorter than the CC bonds in propane<sup>22</sup> and isobutane,<sup>23</sup> and they fall into the region between saturated and olefinic molecules. The results suggest that the cyclopropane orbital pointing towards the methyl group is hybridized intermediately between  $sp^3$  and  $sp^2$ .

This is in agreement with theoretical studies using the INDO method.<sup>24</sup> The calculated molecular orbitals for isobutane, methylcyclopropane, and propene were transformed into localized bond orbitals.<sup>25</sup> The percentage of s-character of the orbital pointing towards the neighbouring methyl group was calculated to be 26, 33.6 and 36.1%, for isobutane, methylcyclopropane, and propene, respectively.

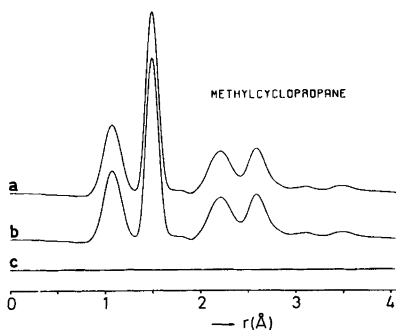


Fig. 6. (a) Experimental and (b) calculated radial distribution curve with an artificial damping factor  $k = 0.0015 \text{ \AA}^{-2}$ ; (c) difference curve (a) - (b) multiplied by a factor of 2.

Table 5. Comparison of CC bond lengths between methyl carbon and carbon atoms of varying hybridization.

	$r_g$ (Å)	Ref.
Ethane	1.534	29
Propane	1.532	22
Isobutane	1.535	23
Methylcyclopropane	1.519	This work
Dimethylcyclopropane	1.520	This work
Propene	1.506	30
Isobutene	1.508	31

Thus, the electron diffraction results support the Walsh model for cyclopropane. This appears to be contrary to the microwave results. By assuming the ring geometry to be an equilateral triangle with a CC bond length of 1.514 Å, the rotational constants from the microwave spectrum were fit with an exocyclic CC bond length of 1.522 Å.<sup>6</sup> In comparison, the CC bond length in propane was determined to be  $r_s = 1.525 \text{ \AA}$  by microwave spectroscopy.<sup>7</sup> The same value was found for the CC bond in isobutane.<sup>26</sup>

The average CC bond distances in the rings found in the present study appear shorter than the exocyclic bonds being 1.510 Å for both compounds. They are identical with those of the parent molecule cyclopropane for which 1.510 Å was determined,<sup>15</sup> suggesting insignificant substitution effects on the ring.

Recently, *ab initio* calculations of methylcyclopropane have been published by Skancke and Boggs<sup>27</sup> with the aim of a partial geometry optimization. At variance with our results and the uncertain microwave results, they predict the exocyclic CC bond length ( $r_e = 1.500 \text{ \AA}$ ) to be shorter than the ring CC bond distances of  $r_e(C_1C_2) = 1.517 \text{ \AA}$  and  $r_e(C_2C_3) = 1.519 \text{ \AA}$ . Based on charge distributions the short exocyclic bond is interpreted as being largely a result of hyperconjugative flow of electron density from the methyl group to the ring, which also accounts for the slight asymmetry of the ring geometry of about 0.002 Å. The predicted asymmetry is beyond the detectability of the electron diffraction method.

Penn and Boggs analyzed the planar moments of a number of cyclopropyl derivatives<sup>28</sup> and arrived at a  $C_2C_3$  bond length in methylcyclopropane of  $r_s$

= 1.510 Å. No value could, however, be given for the  $C_1-C_2$  and  $C_1-C_3$  bond lengths but their considerations were suggestive of ring asymmetry.

In order to clarify these points, it seems highly desirable to investigate the microwave spectra of some isotopic species of methylcyclopropane. Vibrational spectroscopic studies of the methylcyclopropanes are in progress in our laboratory with the aim of further analysis of the electron diffraction data with calculated  $u$ -values and including the reported rotational constants.

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