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C-C Bond Lengths and Hybridization in some Cyclopropane Derivatives. GED Structure Studies of 1-Methyl-1-*tert*-butyl-cyclopropane and 1-Methyl-1-*iso*-propyl-cyclopropane*

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The molecular structures of 1-methyl-1-*tert*-butyl-cyclopropane and 1-methyl-1-*iso*-propyl-cyclopropane have been studied by gas-phase electron diffraction. The effects of hybridization and sterical overcrowding on the central C-C bond are discussed. Theoretical calculations (*ab initio* HF/6-31G*; AM1;MM3) of the geometry of a series of molecules of relevance for the problems treated, have been carried out.

INTRODUCTION

As a result of systematic investigations of the structure of numerous molecules, Linus Pauling[1] ascribed different covalent radii to the elements, their size depending upon the nature of the element and the respective bond order. The sum of two covalent radii should ideally be equal to the equilibrium distance between the atoms in question.

Coulson[2] has shown that the covalent radius of carbon is determined by the electron distribution in the bonding σ-orbital, as characterized by its hybridization.[3] In the case of multiple bonds, the π-bond order must also be taken into account. The strength and the local arrangement of the carbon atom bonds also depend upon the s-character of the carbon hybrid orbitals. In agreement with this concept, the lengths of C-C bonds in normal alkanes are generally observed to be nearly the same (*ca* 1.534 Å) and the

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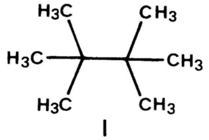
* Dedicated to Professor Linus Pauling on the occasion of his 90'th birthday.

C-C-C valence angles approximately constant (*ca* 112°), independent of the length of the carbon chain. In moderately branched alkanes, as for example *iso*-butane or *neo*-pentane, the sum of the carbon covalent radii is in relatively good agreement with the observed C-C bond lengths (*iso*-butane: 1.535[4], *neo*-pentane: 1.537 Å[5]).

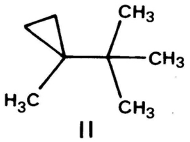
In highly branched alkanes with adjacent quarternary carbon atoms the sterical overcrowding is, however, sufficiently severe to cause significant structural deformations, including stretching of C-C bonds and bending of C-C-C valence angles. Also, the equilibrium between conformers may be shifted in favour of those with the weakest steric interactions. An example of a molecule with structural deformations caused by sterical overcrowding is hexamethyl-ethane (HME; 2,2,3,3-tetramethyl-*n*-butane), where the central C-C bond is observed to be stretched by 0.045 Å (C-C : 1.583) and the $C-CH_3$ bonds by a smaller amount ($C-CH_3$: 1.542 , Δ: +0.005 Å).[6] As a result of severe methyl methyl repulsions across the central C-C bond, the CH_3 groups at both ends of the HME molecule are bent back, resulting in a $C-C-CH_3$ angle increase to 111.0°, as compared to the tetrahedral C-C-C angle in *neo*-pentane and to the sterically undisturbed situation in *iso*-butane[4] ($H-C-CH_3$: 108.1°). As a consequence of these steric interactions, HME appears to prefer a somewhat distorted conformation of D_3 symmetry, with dihedral angles of either 46° or 74°, separated by an energy barrier of *ca* 5 kcal/mol, instead of the D_{3d} dihedral angle of $60^{\circ 6-8}$ in these cases.

A similar behaviour, particularly by elongation of the central C-C bond up to 1.64 Å, was found by Rüchardt and Beckhaus[8] in several hexaalkyl-ethanes. Even though the valence angle bending is generally substantial less costly energetically than covalent bond stretching, repulsions between vicinal substituents can be minimized only to a minor extent by angle bending.

A remarkable change in the steric situation of hexamethyl-ethane is to be expected by a quite small structural intervention, namely by interconnecting two (or four) of its geminal methyl groups to form cyclopropyl group(s), as shown in the following sequence of molecules:



I



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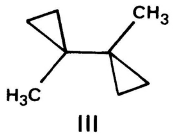

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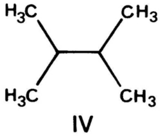

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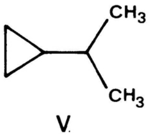

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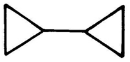


VI

There is supportive evidence from synthetic chemistry for the view that replacement of a gem-dimethyl substituted carbon with a cyclopropyl group will result in reduced sterical overcrowding. No one has, for example, succeeded so far in synthesizing tetra-*tert*-butyl-ethene, while tetra (1-methyl-cyclopropyl)-ethene has been prepared.[9,10] A decrease in steric requirements is, therefore, to be expected in the series I → II → III and the set IV → V → VI chosen for comparison.

In addition to the reduced sterical strain on going from a -C(CH$_3$)$_2$ to a cyclopropyl group, hybridization of the carbon atoms changes from sp^3 to approximately sp^2, and the carbon covalent radius is accordingly reduced. Both effects should diminish the central C-C bond length, and this was in fact observed for compound III, where the central C-C bond was found to be 1.508 Å.[11]

In the present work, we want to contribute to the elucidation of the combined influence of hybridization and sterical strain on the central C-C bond length in hexaalkyl-, pentaalkyl- and tetraalkyl-substituted C-C groups. We will do this by reporting the results from experimental gas-phase electron diffraction studies of the molecules 1-methyl-1-*tert*-butyl-cyclopropane (MTC) and 1-methyl-1-*iso*-propyl-cyclopropane (MIC). We will also report the results obtained by theoretical calculations (*ab initio*, AM1 and MM3) of structural parameters for series of related molecules.

EXPERIMENTAL

Preparation of 1-methyl-1-tert-butyl-cyclopropane (MTC)

By converting triphenyl-methyl-phosphonium iodide with potassium *tert*-butanolate in anhydrous diethyl ether under a nitrogen atmosphere by the method of Fitjer and Quabeck[12], the corresponding Wittig reagent was obtained. The reaction of this ylide with pinacolone, in the same solvent and protecting gas system, gave 1-methyl-1-*tert*-butyl-ethene. After separation of the solvent the olefine was purified by vacuum sublimation and condensation in a trap cooled by liquid nitrogen (yield: 79%). From this olefine, MTC was formed by a cyclopropanation reaction of the Simmons-Smith type[13], using methylene iodide and a freshly prepared Zn/Ag catalyst. After hydrolysis and separation of the solvent, diethyl ether, the colourless product was purified by preparative GLC and characterized by its ^{1}H-, ^{13}C-NMR and its mass spectrum. Yield: 69%.

1-Methyl-1-isopropyl-cyclopropane (MIC) was obtained by an analogous cyclopropanation reaction of commercial 1-methyl-1-*iso*propyl-ethene (yield: 58%).

Electron diffraction experiments.

Electron diffraction diagrams of MIC and MTC were recorded with the Balzer's Eldigraph KD-G2 unit[14,15], and the experimental details are summarized in Table I.

TABLE I

Experimental conditions for the GED data of 2-cyclopropyl-3-methyl-butane (1-methyl-1-iso-propyl--cyclopropane; MIC) and 2-cyclopropyl-3,3-dimethyl-butane (1-methyl-1-tert-butylcyclopropane; MTC)

	MIC		MTC	
Nozzle-to-plate distance (mm)	498.64	248.83	498.57	248.61
Nozzle temperature (K)	299	296	297	293
Electron wavelength (Å)	0.05869	0.05869	0.05978	0.05978
Wavelength calibrated against	Benzene		Benzene	
No. of plates	5	4	6	6
Sector number	3	3	3	3
Type of plates[a]	KEI	KEI	KEI	KEI
Blackness correction	$-\ln(1.00-0.35*D)/(0.35*D)$		$1.00+0.03D+0.09D^2+0.03D^3$	
Data range				
$S_{\min}$(Å^{-1})	2.00	3.50	2.00	2.75
$S_{\max}$(Å^{-1})	15.00	29.00	14.75	28.00
ΔS(Å^{-1})	0.25	0.25	0.25	0.25

[a] KEI: Kodak Electron Image

The calculation of the scattering amplitudes and phases, the data reduction and the correction to the $s/|f_c'|^2$ modified molecular intensities were carried out as described elsewhere.[16,17] A diagonal weighting scheme was applied, and the standard deviations in the structural parameters (σ_{LS}) should be augmented by a factor of two to account for data correlation. The experimental molecular intensity curves and the corresponding radial distribution curves (RD-curves) are shown in Figures 1–4.

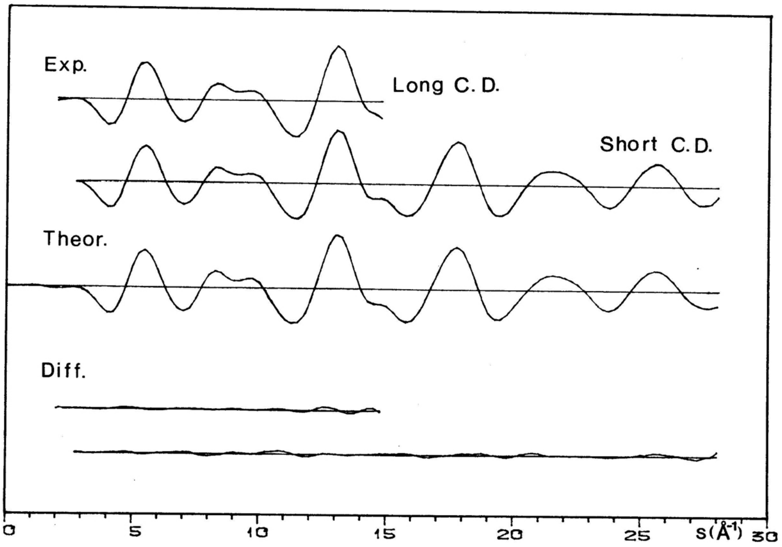


Figure 1. Experimental and theoretical molecular intensities for MTC. The theoretical curve is calculated from the parameters in Table II.

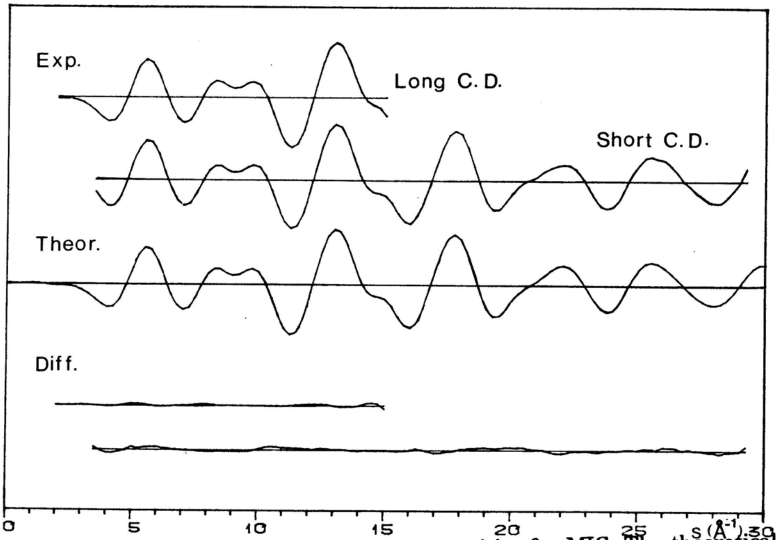


Figure 2. Experimental and theoretical molecular intensities for MIC. The theoretical curve is calculated from the parameters in Table III.

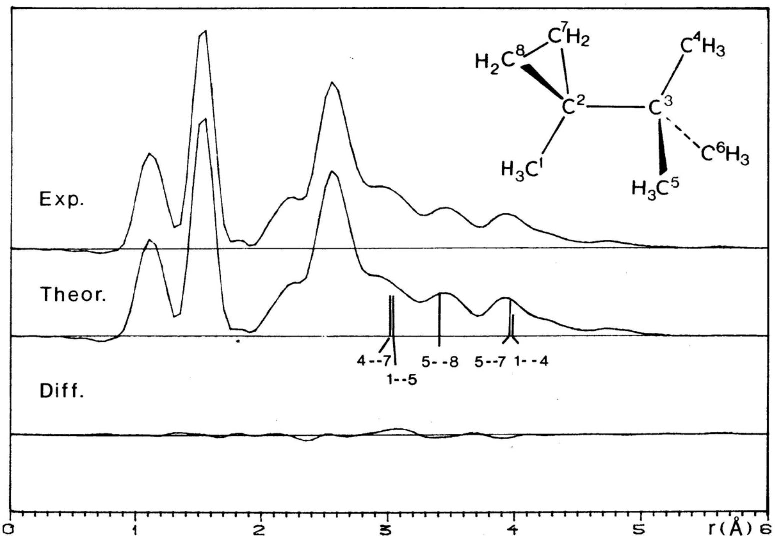


Figure 3. Experimental and theoretical radial distribution curves for MTC. The theoretical curve is calculated from the parameters in Table II. The molecular model shows the numbering of the atoms as used in the present study.

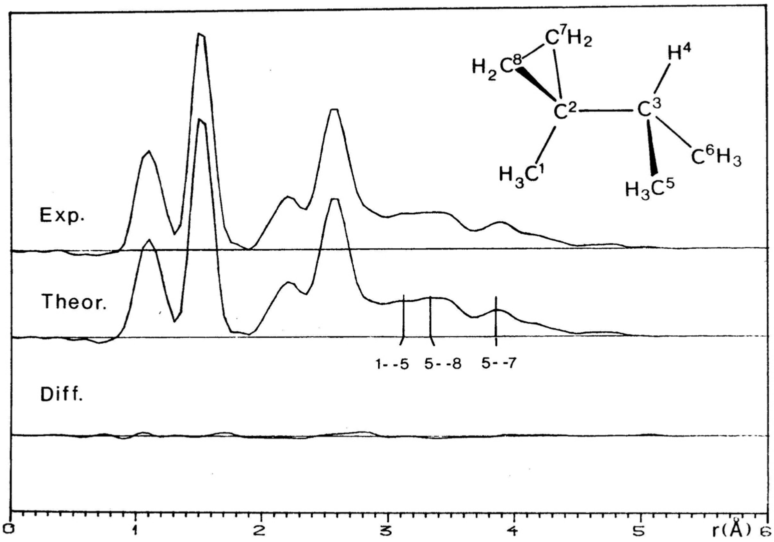


Figure 4. Experimental and theoretical radial distribution curves for MIC. The theoretical curve is calculated from the parameters in Table III. The molecular model shows the numbering of the atoms as used in the present study.

STRUCTURE REFINEMENTS AND RESULTS

The molecular structures of MTC and MIC were studied by least-squares refinements on the molecular intensity data. Vibrational amplitudes (u) and perpendicular correction coefficients (K) for all interatomic distances in the two molecules were calculated[18], based on a valence force field transferred from other similar molecules.[11] The geometries of the two molecules were based on r_a molecular models, that include corrections for shrinkage effects.[19]

Molecular models of the two molecules under study are shown in Figures 3 and 4, where also the numbering of the atoms, as used in the present study, is shown. The somewhat unusual numbering of the secondary hydrogen atom in MIC (H^4) has been chosen because it is an advantage to have similar numbering systems of the MIC and MTC models when the results obtained for the two compounds are to be compared.

MTC: The geometry of MTC was described by thirteen independent parameters: six bond distances (r_a) and six valence angles ($\angle_a$), in addition to one dihedral angle. The following geometrical parameters were chosen: $r(C^2\text{-}C^3)$, $r(C^3\text{-}CH_3)$, $r(\text{C-C})_{cpr}$, $r(C^1\text{-}C^2)$, $r(C_{sp}3\text{-H})$, $r(C_{sp}2\text{-H})$, $\angle C^2\text{-}C^3\text{-}C^{5(6)}$, $\angle C^1\text{-}C^2\text{-}C^3$, $\angle M\text{-}C^2\text{-}C^3$, $\Delta C^2\text{-}C^3\text{-}C^4 = \angle C^2\text{-}C^3\text{-}C^4 - \angle C^2\text{-}C^3\text{-}C^{5(6)}$, $\angle$C-C-H (in CH_3), $\angle$H-C-H (in CH_2), $\theta(C^1\text{-}C^2\text{-}C^3\text{-}C^5) = -\theta(C^1\text{-}C^2\text{-}C^3\text{-}C^6)$. Inherent in this model are several assumptions, the most important ones being those of C_s molecular symmetry, of equal CCH angles in the methyl groups and of an equilateral cyclopropyl group.

Due to similarity of many of the geometrical parameters, a high degree of correlation between several of these is expected. In such cases, it is often difficult to deter-

TABLE II

Final structure parameters obtained for MTC (1-methyl-1-tert-butyl-cyclopropane). GED: gas electron diffraction, AM1: Austin Model 1 semiempirical calculation[21], MM3: Molecular mechanics calculation[22], 6-31G: Ab initio calculation.[21] Distances (r_a) in Å, angles in degrees, standard deviations in brackets.*

	GED	AM1	MM3	6-31G*
$r(C^2\text{-}C^3)$	1.540(5)	1.518	1.546	1.552
$r(C^3\text{-}CH_3)$	1.551(2)	1.526	1.547	1.540
$r(C^2\text{-}CH_3)$	1.516(10)	1.501	1.527	1.526
$r(\text{C-C})_{cpr}$	1.506(3)	$1.508_{Av.}$	$1.514_{Av.}$	$1.503_{Av.}$
$r(C_{sp}3\text{-H})$	1.121(2)	1.116	1.113	1.085
$r(C_{sp}2\text{-H})$	(1.094)[a]	1.104	1.087	1.075
$\angle C^1\text{-}C^2\text{-}C^3$	114.7(1.3)	115.0	120.9	115.8
$\angle M\text{-}C^2\text{-}C^3$	126.6[b]	125.6	121.5	126.0
$\angle C^2\text{-}C^3\text{-}C^4$	112.5[b]	112.9	117.2	113.4
$\angle C^2\text{-}C^3\text{-}C^{5(6)}$	109.4(6)	109.9	108.8	109.8
$\angle$C-C-H (CH_3)	110.7(4)	110.5	111.8	111.3
$\angle$H-C-H (CH_2)	(114.5)[a]	111.5	113.9	113.4
$\theta(C^1\text{-}C^2\text{-}C^3\text{-}C^5)$	59.5[b]	59.9	58.8	59.9
R_1(%)	6.092			
R_2(%)	7.266			
R (%)	6.871			

[a] Transferred from cyclopropane
[b] Studied separately; see text.

TABLE III

Final structure parameters obtained for MIC (1-methyl-1-iso-propyl-cyclopropane). GED: gas electron diffraction, AM1: Austin Model 1 semiempirical calculation.[21] *MM3: Molecular mechanics calculation*[22]*, 6-31G*:* Ab initio *calculation.*[21] *Distances (r_a) in Å, angles in degrees, standard deviations in brackets.*

	GED(I)	GED(II)[d]	AM1	MM3	6-31G*
$r(C^2\text{-}C^3)$	1.535(14)	1.535(61)	1.510	1.532	1.532
$r(C^3\text{-}CH_3)$	1.541(3)	1.541(12)	1.516	1.539	1.534
$r(C^2\text{-}CH_3)$	1.519(18)	1.520(66)	1.494	1.523	1.520
$r(C\text{-}C)_{cpr}$	1.502(4)	1.502(10)	$1.498_{Av.}$	$1.513_{Av.}$	1.501_{Av}
$r(C_{sp}3\text{-}H)$	1.105(2)	1.105(2)	1.116	1.113	1.085
$r(C_{sp}2\text{-}H)$	(1.094)[a]	(1.094)[a]	1.104	1.087	1.077
$\angle C^1\text{-}C^2\text{-}C^3$	116.9[b]	116.9(1.8)	116.1	121.4	117.4
$\angle M\text{-}C^2\text{-}C^3$	121.2[b]	121.3(5.3)	121.8	119.5	121.3
$\angle C^2\text{-}C^3\text{-}H^4$	(108.2)[c]	(108.2)[c]	107.8	108.3	106.8
$\angle C^2\text{-}C^3\text{-}C^{5(6)}$	110.8(6)	110.8(1.3)	111.6	111.8	112.2
$\angle C\text{-}C\text{-}H\ (CH_3)$	112.2(6)	112.3(1.0)	110.6	111.6	111.3
$\angle H\text{-}C\text{-}H\ (CH_2)$	(114.5)[a]	(114.4)[a]	112.0	114.8	113.8
$\theta(C^1\text{-}C^2\text{-}C^3\text{-}C^5)$	61.9(7)	61.9(2.6)	62.0	61.9	62.8
$R_1(\%)$	4.673	4.667			
$R_2(\%)$	7.549	7.551			
R (%)	6.704	6.703			

[a] Transferred from cyclopropane.

[b] Studied separately; see text.

[c] Fixed (see text).

[d] Angle parameters marked [b] in GED(I) included in refinement.

mine all geometrical parameters with high precision. In order to reduce these problems, some of the parameters were kept constant during the refinements.

In the final part of the present study, the C-H bond and the H-C-H angle of the cyclopropyl group were fixed at the values obtained for these parameters in cyclopropane.[20] The final structural results are presented in Table II. These results were obtained keeping $\angle M\text{-}C^2\text{-}C^3$, $\Delta C^2\text{-}C^3\text{-}C^4$ and $\theta(C^1\text{-}C^2\text{-}C^3\text{-}C^5)$ constant. The values for these parameters were, however, carefully studied by including them in the refinements, as well as by varying them continuously over assumed parameter ranges, but keeping them fixed. All studies of the parameters were in agreement with the results given in Table II but the standard deviations of most parameters were of course considerably larger when these parameters were included in the refinements. (See columns GEDI and GEDII of Table III). It should also be mentioned that it was possible to include the discussed parameters in the refinements only when the calculated parameter shifts were multiplied by a reducement factor in the region 0.1 – 0.25.

MIC: The MIC molecule might exist in different conformations, and the structural problems associated with this molecule are therefore in principle more complicated than those of MTC. Preliminary semiempirical[21] and molecular mechanics[22] calculations (see below) indicated clearly that the symmetrical *anti* (H^4 *anti* relative to C^1) conformer is energetically favoured. The geometry of this conformer may be described by nearly the same geometric parameters as those applied in the study of MTC, the only difference being that instead of the parameter $\Delta C^2\text{-}C^3\text{-}C^4$ in MTC, the angle $C^2\text{-}C^3\text{-}H^4$ is introduced in MIC.

In order to get an insight into the conformational problem of MIC, semiempirical AM1 calculations[21] with full geometry optimization were carried out for conformers where the torsion angle parameter $\theta(C^1\text{-}C^2\text{-}C^3\text{-}H^4)$ was varied in steps of 15° in the region 0–180°.

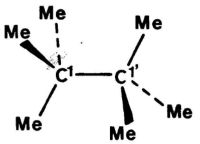
The calculated energies showed two minima, at $\theta(C^1\text{-}C^2\text{-}C^3\text{-}H^4)$ equal to *ca* 30° and at 180°, and with an energy difference of 1.54 kcal/mole in favour of the latter conformer. When the more favourable entropy of the high-energy conformer is accounted for, these calculations indicate that the MIC molecules might exist as a conformational mixture consisting of *ca* 70% *anti* ($\theta(C^1\text{-}C^2\text{-}C^3\text{-}H^4) = 180°$) and 30% *gauche* (30°). A two-conformer model of MIT was accordingly studied. In this model, the second conformer had to be described by more parameters than those necessary to describe the symmetric *anti* conformer, and special attention was given to the differences in angle parameters calculated for the two conformers.

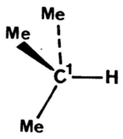
In the GED study of MIC it was not possible to detect any contribution from other conformers than the symmetric *anti* one. The parameter details of a possible second conformer of a conformational mixture are therefore not discussed further. MM3 calculations[22], carried out at a later stage than the AM1 calculations, gave an energy difference between the two energy minima (at 44.5° and 180°) of 2.42 kcal/mole, in agreement with an eventual high-energy conformer being present in a very low concentration at the temperature of the GED recordings.

The final results obtained for the structural parameters of MIC in the GED study are presented in Table III. As in the case of the MTC study, the C-H bond lengths and the H-C-H angles of the cyclopropyl groups were kept constant at the values obtained for cyclopropane.[20] Additionally, the $C^2\text{-}C^3\text{-}H^4$ angle was fixed at 108.2°, in agreement with the results from AM1 and MM3 calculations. The MIC structural results presented in column GED(I) of Table III are based on refinements where the angles $C^1\text{-}C^2\text{-}C^3$ and $M\text{-}C^1\text{-}C^2$ were fixed at the reported values, but the given quantities for these parameters are, however, based on careful studies, similarly to those described for the MTC parameters $\angle M\text{-}C^2\text{-}C^3$, $\Delta C^2\text{-}C^3\text{-}C^4$ and $\theta(C^1\text{-}C^2\text{-}C^3\text{-}C^5)$. Column GED(II) show the results obtained when the discussed parameters are included in the refine-

TABLE IV

Results from ab initio *calculations of the structure of hexamethyl-ethane and of iso-butane, using 6-31G* basis sets. Results of experimental GED studies (hexamethyl-ethane, Ref. 6; iso-butane, Ref. 4) are given in brackets. Distances in Å, angles in degrees.*





$\angle C^{1'}(H)\text{-}C^1\text{-}CH_3$	111.85(111.0)	107.85(108.1)	+4.00
$\angle H_3C\text{-}C^1\text{-}CH_3$	107.0	111.0(110.9)	–4.00
$r(C^1\text{-}CH_3)$	1.5431(1.542)	1.5310(1.534)	+0.012
$r(C^1\text{-}C^{1'}(H))$	1.5844(1.583)	1.0886(1.119)	

ment scheme. The resulting parameter values are hardly influenced, but the standard deviations are drastically increased.

For both molecules, the vibrational amplitudes were kept fixed at the values calculated from the normal coordinate analyses. Attempts of including the various vibrational amplitudes in groups in the refinement scheme did not present special calculation problems. However, they did not generally give results differing significantly from those observed using fixed vibrational amplitudes. This statement applies to the refined geometric parameters, as well as to most vibrational amplitudes. The refined *u*-values for some of the non-bonded CH distances were, however, unrealistic, a fact that is probably primarily connected to the inaccuracy of the assumption of equal C-C-H valence angles. The effect of including the vibrational amplitudes in the refinement scheme will therefore be primarily that of artificially improving the reliability factors.

The *ab initio* structure of MTC and MIC were calculated after the GED studies were completed. Substitution of the fixed parameters for the cyclopropyl hydrogens and the MIC C^2-C^3-H^4 angle parameter referred to above, with the results from the *ab initio* calculations, did not noticeably influence the experimental parameters determined for MTC and MIC. The experimental parameters are, therefore, presented in their original form.

THEORETICAL CALCULATIONS

Theoretical calculations of molecular parameters of MTC, MIC, as well as of structurally related hydrocarbons that are of relevance to the problems discussed in the present study, have been carried out using several different calculation methods. Most of the calculations were carried out using the program GAUSSIAN90.[21] These calculations were done on a CRAY X-MP/28 supercomputer at SINTEF/NTH in Trondheim. They include semiempirical methods (AM1), as well as *ab initio* methods, with 6-31G* basis sets. In addition, molecular mechanics calculations were carried out using Allinger's MM3 program.[23]

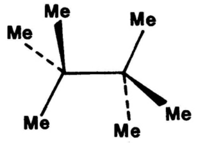
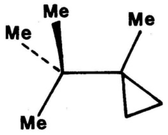
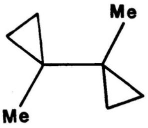
In order to throw light on some of the sterical aspects of HME, *ab initio* 6-31G* calculations have been carried out for this molecule, as well as for isobutane – which may be considered as its building block. The results are presented in Table IV.

Table V presents the results from various calculations of the central C-C bond length of HME, MTC and 1,1'-dimethyl-bicyclopropyl (DMBC). All calculations were carried out with complete geometry optimization. They illustrate the effect on the central C-C bond with successive closing of terminal dimethyl groups to form cyclopropyl groups. The calculated bond lengths for each molecule differ considerably when different calculation methods are being used. The changes in the central C-C bond length with successive formation of cyclopropyl groups, as obtained by the use of the various calculation methods, are, however, in reasonably good agreement.

Table VI shows the results of *ab initio* calculations for a series of molecules that differ in the number of substituted methyl groups, and where one, resp. two terminal dimethyl groups are systematically replaced by dimethylene/cyclopropyl groups. The data for bicyclopropyl were calculated by B. Klahn[23] (SCF-Basis: 7s/3p), while the other calculations were carried out by us, using HF/6-31G* basis sets. The results are discussed below.

TABLE V

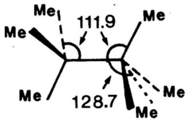
The length of the central C-C bond (in Å) in hexamethyl-ethane, MTC and 1,1'-dimethyl-bicyclopropyl, as calculated by various theoretical methods. Theoretical data are compared to experimental results. Numbers in brackets denote the changes in bond length on going from one compound to the next.

			
AM1[21]	1.548	1.518(–0.030)	1.490(–0.028)
MNDO[21]	1.607	1.566(–0.041)	1.534(–0.032)
MINDO3[21]	1.637	1.598(–0.039)	1.567(–0.031)
MM3[22]	1.577	1.546(–0.031)	1.511(–0.035)
ab initio (6-31G*)[21]	1.584	1.552(–0.032)	1.528(–0.029)
Exp. (GED, r_a)	1.583[6]	1.540(–0.043) P.S.	1.508(–0.032)[a]

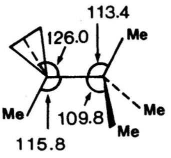
[a] Experimental value for *gauche* conformer.[11] The calculated value refers to *anti* conformer; the corresponding *ab initio* result for *gauche* is 1.521 Å.

TABLE VI

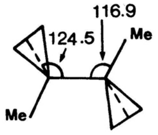
*The central C-C bond length and adjacent valence angles in some molecules, as calculated by the HF/6-31G** ab initio *method.*[21] *Distances in A, angles in degrees. Symbols ↓ and → illustrate the reductions in central C-C bond length when a CH_3 group is replaced by H (↓) or dimethyl replaced by dimethylene (cyclopropyl) (→).*



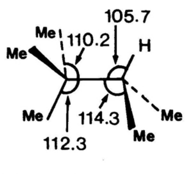
C-C: 1.584



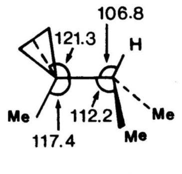
1.552 (→:0.032)



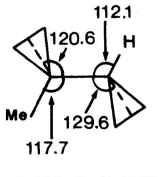
1.528 (→:0.024)



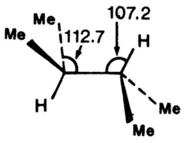
C-C: 1.564 (↓:0.020)



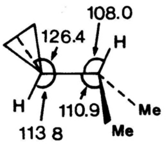
1.532 (→:0.032) (↓:0.020)



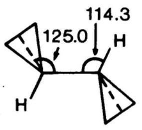
1.510 (→:0.022) (↓:0.018)



C-C: 1.548 (↓:0.016)



1.518 (→:0.030) (↓:0.014)



1.487 (→:0.031) (↓:0.023)

DISCUSSION

MTC

The structure parameters determined for MTC are presented in Table II, while the experimental and theoretical RD curves are shown in Figure 3. The position of the nonbonded CC distances over more than one valence angle are indicated in Figure 3. The contributions to the four unmarked innermost peaks in the RD curve are rather obvious: The peaks centered at *ca* 1.2 Å and 1.5 Å represent the bonding C-H and C-C distances, respectively, while the peaks at *ca* 2.2 Å and 2.6 Å contain contributions from the various nonbonded CH and CC distances over one valence angle (1.3-distances).

The agreement between the experimentally determined parameters and those calculated by the *ab initio* method is generally satisfactory, especially for the bond angles. The calculated MM3 bond distances are also in fairly good agreement with the corresponding experimental parameters, but the MM3 valence angles deviate considerably from the experimental and *an initio* angles.

The central C^2-C^3 bond is observed to be elongated by *ca* 0.025 Å, compared to the corresponding unstrained bond in methyl-cyclopropane (GED: 1.517 Å[24]; *ab initio* (7s/3p): 1.517 Å[23]). The observed bond stretching is interpreted as a result of nonbonded repulsion due to sterical overcrowding. The C-CH_3 bond in the *tert*-butyl group is also found to be somewhat elongated relative to a normal unstrained $C_{sp}3$-$C_{sp}3$ bond. The increase is larger in the experimental (+ 0.017 Å) than in the theoretical *ab initio* (+0.006 Å) results.

The calculated *ab initio* C-C bonds within the cyclopropyl group deviate slightly in the fourth decimal (Å), showing that the assumption in the GED study of an equilateral cyclopropyl ring does not reduce the accuracy of the determined parameters.

MIC

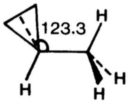
The structure parameters obtained for MIC are listed in Table III, while the experimental and theoretical RD curves are shown in Figure 4. Also, in this case the positions of the nonbonded CC distances over more than one valence angle are indicated in the figure.

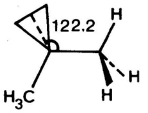
The agreement between experimentally determined parameters and the *ab initio* results is excellent for all types of parameters. Apart from some angle deviations, the correspondence with the MM3 results is fairly good.

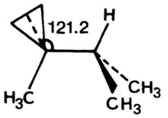
The central C^2-C^3 bond is in this case found to be elongated by 0.020 Å, compared to the C-CH_3 bond in the sterically unstrained compound methyl-cyclopropane.[24] The error limits of the determined C^2-C^3 bonds in MTC and MIC do not justify the conclusion stating that the MTC C^2-C^3 bond is significantly longer than that in MIC. It is, however, satisfactory to note that the observed bond stretching is smaller in MIC than in MTC, in correspondence with the reduced sterical strain in the former molecule.

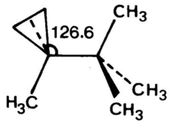
The C^1-C^2-C^3-$C^{5(6)}$ dihedral angle is observed to be slightly larger than corresponding to perfect staggering. Although the deviation from 60° is small, this increase was of importance for the experimental study, since the R-values and the standard deviations clearly increased if the dihedral angle was restrained to 60°. This result may be also interpreted as a result of nonbonded repulsions between the *gauche* methyl groups at C^2 and C^3.

It has been pointed out above that angle bending may be an effective way of reducing sterical strain. This is clearly illustrated by the flexibility of the bending of the cyclopropyl group in the following cases:









The unstrained methyl-cyclopropane molecule has a M-C-C angle of 123.3°. When a second methyl group is substituted in position 1, repulsion between the methyl groups reduces the M-C-C angle to 122.2°. When two hydrogens in one of the methyl groups are replaced by CH_3 groups (MIC), the increased repulsion between the larger substituent groups further reduces the M-C-C angle to 121.2°. When, finally, the third hydrogen in the »original« methyl group is replaced by a CH_3 group (MTC), the additional repulsion between this methyl group and the *syn* cyclopropyl ring causes the M-C-C angle to open up to 126.6°.

In order to elucidate the meaning of the results obtained for MTC and MIC, the structure parameters will be compared to those of related molecules with systematically varied structures, a set of which is presented in Table 6. For all nine compounds in the table, theoretical structures (6-31G* *ab initio* and MM3 force field; the latter data are not shown) were calculated. For six of the molecules, experimental GED results are available (see Table VII).

In the following, we will discuss the characteristic CC bond lengths, some intermolecular angles and the conformational preferences.

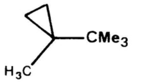
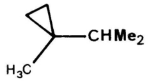
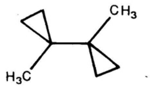
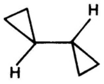
From the data of Table VI two trends may be clearly extracted: Moving horizontally through each row, from left to right in the matrix of molecules, a marked decrease in the central C-C bond length may be noted. The same effect is observed when moving vertically downward in each of the three columns, *i.e.* from hexaalkylated ethanes, combining two quarternary carbons, to tetraalkylated »bisecondary« hydrocarbons.

This decrease in CC bond distances has two different causes: When moving horizontally through a row, the general substitution pattern is maintained, and the sterical congestion is more or less the same. But when comparing the members of the first to those of the second and third columns, the hybridization[26] (and hence the covalent radius) of their central carbon atoms changes from $sp^3 - sp^3$ to $sp^3 - sp^2$ and to $sp^2 - sp^2$. By using Coulson's covalent carbon radii[2], we obtain for $sp^3 - sp^3$: 1.542 Å, $sp^3 - sp^2$: 1.520 Å and $sp^2 - sp^2$: 1.498 Å. These data correspond quite closely, but by no means exactly, to the entries in the third row of Table VI, where the sterical problems are the smallest among the molecules in this table. The calculated decreases in C-C bond length on moving from column 1 to columns 2 and 3 are, average, 0.031 and 0.026 Å, compared to the estimated decreases of 0.022 and 0.022 Å based on Coulson's covalent radii. This reflects quite clearly the influence of the hybridization of the carbon atoms on the C-C bond lengths.

The effect of sterical crowding on the C-C bond length is conspicious when the molecules within a row in Table VI are compared. The difference in C-C bond length

TABLE VII

The length of the central carbon-carbon bond (in Å) in some selected hydrocarbons. Theoretical data are all calculated by ab initio *methods, using 6-31G* basis sets. Experimental data are cited from GED studies. P.S.: present study.*

Molecule	Calc.	Ref.	Exp.	Ref.
H_3C-CH_3	1.529	23	1.532(2)	28
MeH_2C-CH_2Me	1.530	26	1.531(2)	29
Me_2HC-$CHMe_2$	1.548	P.S.	1.544	6
Me_3C-CMe_3	1.584	P.S.	1.583(10)	6
	1.552	P.S.	1.540(5)	P.S.
	1.532	P.S.	1.535(14)	P.S.
	1.528	P.S.	1.508*	11
	1.487	24	1.499	27

between the molecules with maximum and minimum sterical strain within each row is 0.036, 0.034 and 0.041 Å, respectively. This indicates that the influence of sterical strain on the lengths of the three different types of C-C bonds represented in Table VI are of comparable magnitude. Table VII compares C-C bond lengths for molecules of relevance for the present discussion, and where experimental data are available. In cases where the calculated *ab initio* structures were not already known from the literature, they were calculated by us.

Steric interactions between 1,2-substituted alkyl groups have been shown to have a profound influence on the intervening C-C bond length. As valence angle bending requires less energy than covalent bond stretching, it is of interest to examine the effects of sterical strain on the valence angles of the molecules discussed. The symmetrical molecules in Table VI might, for example, be compared with their »building blocks«. In Table IV, the parameters of HME[6] are compared to those of *iso*butane.[4] In the former, the methyl groups are bent back and together (CH_3-C-CH_3:107.0°) compared to the latter (111.0°). The same applies to 1,1'-dimethyl-cyclopropane[25] (CH_3-C-median of cyclopropyl : 122.2°) and 1,1'-dimethyl-bicyclopropyl (DMBC)[11] (Table 6: 124.5°), as compared to the situation in MTC (Table II: 126.6°).

The conformations of the substances in Table VI deviate somewhat from the rather common standard type. In most cases, nevertheless, their dihedral angle differ only slightly from perfect 60° staggering (HME[6]: 65°, MTC: 59.5°, MIC: 61.9°, DMBC[11]: 58°, bicyclopropyl[27]: 48.7°). With respect to their rotamer concentrations, it should be mentioned that rotamers of molecules with an internal rotator group of threefold symmetry appear as identical – they are only indirectly traceable.[7] This applies to HME and to MTC. This does not hold for BCP and DMBC and the determination of the rotamer structure and concentrations showed for BCP 47.5%; *anti* 52.5% *gauche*[27], for DMBC 100% of a sterically interlocked *gauche* conformer.[11] Its predominance might be a consequence of the hybridization-induced shortening of its central CC-bond, which in turn reinforces the steric interactions between the two parts of the molecule.

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The theoretical calculations have been made possible by a generous allocation of computing time on SINTEF's CRAY X-MP/28 for which we want to extend our gratitude to RUNIT/SIMA and to the Norwegian Research Council for Science and the Humanities.

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SAŽETAK

Duljine C-C veza i hibridizacija u nekim derivatima ciklopropana. Istraživanje strukture 1-metil-1-*tert*-butil-ciklopropana i 1-metil-1-*iso*-propil-ciklopropana

M. Trætteberg i W. Lüttke

Molekulska struktura 1-metil-1-*tert*-butil-ciklopropana i 1-metil-1-*iso*-propil-ciklopropana određena je metodom elektronske difrakcije u plinskoj fazi. Razmatrani su utjecaji hibridizacije i prostorne prenapučenosti atoma. Eksperimentalna mjerenja nadopunjena su teorijskim proračunima primjenom *ab initio* i semiempirijskih metoda.