Further *ab initio* Calculations on the Molecular Structure of Methylcyclopropane

ANNE SKANCKE

Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, Box 953, N-9001 Tromsø, Norway

The molecular structure of methylcyclopropane has been investigated *ab initio* calculations. The results are compared with earlier theoretical calculations, a microwave study and a recent electron diffraction work.

Fig. 1. Numbering of atoms in methyl cyclopropane.

In a series of articles we have studied the effect of various substituents on the structure of the cyclopropane ring.[1] These studies were carried out within the Hartree-Fock approximation. In the first articles in the series, only the key structure parameters were optimized; the optimizations being carried out consecutively. When the computer programme TEXAS[2] became available to us, these calculations were carried out more efficiently and also more accurately, since the program calculates the forces on all atoms leading to a simultaneous optimization of all internal parameters. Also, we were now able to carry out complete geometry calculations including, for instance, deformations from local C_{2v} symmetry of methylene groups. In this way, more insight into the fine details of molecular structure is given. As for the accuracy of our calculations on these specific compounds, we have in several cases shown them to be at least as reliable as experimental works.[3-6]

In a recent paper by Klein and Schrumpf,[7] an electron diffraction study of methylcyclopropane and *trans*-1,2-dimethylcyclopropane is carried out, the former being compared to the results of our previous calculations.[3] Although the two works may be construed to be in essential agreement when the experimental errors are taken into account, the authors of the ex-
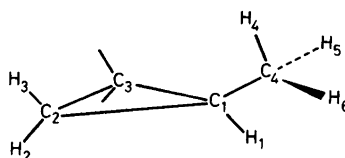
perimental work point out the difference in relative magnitude of the ring and exocyclic CC bonds between the two works. We have therefore recalculated the structure of methylcyclopropane using the computer programme TEXAS.

We have, in the present calculation, carried out complete geometry optimizations for both the eclipsed and staggered forms. In our previous articles in this series, optimizations were carried out at the 4−21 level,[8] but since in the present work we are looking for very small variations in bond distances, we have carried out complete optimizations also with the 4−31G basis set which contains one extra primitive function at each of the heavy atoms, the number of contracted basis functions being the same as for the 4−21 set. A typical run with the latter basis set used about 20 % more computer time. The results of the calculations are given in Table 1.

RESULTS AND DISCUSSION

As is seen from Table 1, all C−C bonds are predicted to be larger in the 4−21 calculations compared to the slightly larger 4−31G basis set.

Table 1. Calculated geometric parameters (in Å and degrees), dipole moments (in debyes) and barriers to internal rotation for methyl cyclopropane (in kJ/mol). See Fig. 1 for numbering of atoms).

Bond/angle	Eclipsed form		Staggered form	
	4−31G	4−21	4−31G	4−21
C_1-C_2	1.503	1.517	1.502	1.515
C_2-C_3	1.501	1.515	1.504	1.518
C_1-C_4	1.519	1.529	1.506	1.516
C_2-H_3	1.071	1.072	1.070	1.072
C_2-H_2	1.070	1.071	1.070	1.071
C_1-H_1	1.071	1.072	1.072	1.073
C_4-H_4	1.081	1.083	1.082	1.083
C_4-H_5	1.081	1.082	1.083	1.083
$\angle C_1C_4H_4$	110.7	110.8	111.3	110.8
$\angle C_1C_4H_5$	111.5	111.4	111.1	111.0
$\angle H_4C_4H_5$	107.3	107.5	107.5	107.9
$\angle H_5C_4H_6$	108.4	108.1	108.1	108.1
$\angle C_4-$ring plane	54.3	54.6	54.0	54.8
$\angle C_4C_1H_1$	114.4	114.9	114.3	114.8
$\angle H_2C_2H_3$	114.0	114.6	114.0	114.5
θ_{wag} [a]	0.0	0.0	0.0	0.1
θ_{rock} [b]	−0.5	−0.4	−0.2	−0.2
θ_{twist} [c]	0.2	0.6	0.0	0.5
$|\mu|$	0.15	0.13	0.14	0.10
V_3	11.29	11.23		

[a] $\theta_{wag}=(\alpha_{12}+\alpha_{13})-(\alpha_{32}+\alpha_{33})$;
[b] $\theta_{rock}=(\alpha_{12}+\alpha_{32})-(\alpha_{13}+\alpha_{33})$;
[c] $\theta_{twist}=(\alpha_{12}-\alpha_{32})-(\alpha_{13}-\alpha_{33})$; where $\alpha_{ik}=\angle C_iC_2H_k$.

Table 2. Key bond distances (Å) for methyl cyclopropane. Results from previous work.

Bond	Method		
	M.W.[a]	E.D.[b](r_a)	SCF [c]
C_1-C_2	1.514	1.509(1)	1.517
C_2-C_3			1.519
C_1-C_4	1.513	1.517(2)	1.500

[a] Ref. 9. [b] Ref. 7. [c] Ref. 3.

Comparison with experimental values (see Table 2) gives us reason to believe that the 4−21 basis set may even be superior to the larger set when structure refinements are carried out. We have in this series of articles extensively been using molecular structures as indicators of intramolecular electronic interactions but, as we have pointed

out before, it is especially important to have good quality trends in structures.

The internal consistency in Table 1 gives us reason to believe that trends are indeed well reproduced in the present work, although absolute values in C−C bond lengths may well differ by several thousands of an Ångström compared to experimental data. Our limited basis on hydrogen gives us C−H distances definitely too short, but since there is a systematic trend also in these, we believe their relative magnitudes to be of considerable better quality than their absolute values.

Our earlier calculation of this molecule [3] gave two nearly identical ring distances (1.517 and 1.519 Å for adjacent and opposite bond, respectively) and a C_1-C_4 bond distance of 1.500 Å. See Table 2. Calculations were carried out only for the staggered form. These results deviate from the present where the lowest energy form for both basis sets has an external C−C bond that must be considered as identical in length to the nearly identical ring bonds.

There is a microwave investigation of methyl cyclopropane,[9] but the number of observables did not suffice for a complete structure determination. Based on the assumption of an equilateral ring with distances equal to 1.514 Å, a C_1-C_4 bond of 1.513 Å was in agreement with observed data. A number of structures may be construed to be in agreement with this microwave work, depending on the actual ring size of the molecule. Thus, a lengthening of the C_1-C_2 bond would lead to a shortening of the C_1-C_4 bond and *vice versa,* the experimental moments of inertia giving a high precision determination of the overall size of the molecule. Thus, the results of our previous calculations as well as the electron diffraction results and the results from the present 4−21 calculations are equally well in agreement with the microwave work. Additional support of the latter is, however, given in the calculated, V_3 potential which agrees well with the experimental [9] of 11.95 kJ/mol and the total dipole moment that agrees well with the experimental [9] of 0.14 D.

Our results give nearly identical structures for the eclipsed and staggered forms, the only difference being in the C_1-C_4 which is lengthened in the high energy form.

The calculated value of the angle between the methyl group and the ring is 2 degrees smaller

than the electron diffraction result of 56.7°. The present result gives practically no distortions of the CH_2 groups; this was an assumption in the electron diffraction work. There is, however, a minute distortion from C_{3v} symmetry of the methyl group for the eclipsed form. This was apparently an additional assumption in the experimental work, although not explicitly mentioned therein. We believe that our computed distortions should be considered reliable, the calculated differences between bond angles and bond lengths being determined more reliably than their absolute values.

At this point an interesting comparison may be made to results of calculations on cyclopropylsilane.[10] This has been carried out with the same procedure and with a basis set compatible with the present work. The computed distortion of the methyl group closely parallels the SiH_3 group distortions.

In cyclopropylsilane, there is a lengthened C_1-C_2 bond and a C_2-C_3 bond unchanged from the parent compound. The authors of that work attribute this to the combined effect of pi and sigma donation from the substituent to the ring. From the results of the present work, it appears that any such charge flow must be negligibly small for methyl cyclopropane, a result compatible with the higher electronegativity of carbon as compared to silicon.

As a final comment, we find the present calculations to be in good agreement with both the electron diffraction work and the microwave study. Any disagreement of a few thousands of an Ångström may be attributed to the fact that the electron diffraction data give the r_a structure while our values are r_e values. Also, the slightly longer C_1-C_4 bond length in the electron diffraction work may be attributed to admixture of non-staggered forms, since it is seen from Table 1 that the eclipsed form has indeed a lengthened C_1-C_4 bond.

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