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THE CONFORMATION OF 2-CYCLOPROPYLPROPENE AND 1,1-DICYCLOPROPYL ETHYLENE BY MEANS OF AB INITIO SCF CALCULATIONS

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ABSTRACT

The geometrical structure of 2-cyclopropylpropene and 1,1-dicyclopropyl ethylene has been determined by means of the ab initio SCF gradient method. The most stable conformation of 2-cyclopropylpropene has a *gauche* structure and the internal rotation angle between the cyclopropyl ring and the vinyl group is calculated to be 62°. The most stable conformation of 1,1-dicyclopropyl ethylene also has a *gauche* structure and the internal rotation angles between one of two cyclopropyl rings and the vinylidene group are 64°.

INTRODUCTION

Vinylcyclopropane has a form where a hydrogen of ethylene is substituted by a cyclopropyl ring as shown in Fig. 1. It is established that the most stable conformation is *s-trans* (ϕ_a = 180°) by electron diffraction [1]. Raman spectroscopy [2], and ab initio calculations [3—5]. The *gauche* conformation ($\phi_a = 60° \approx 70°$) is calculated to be the second most stable conformation by ab initio calculations [3—5]. Skancke and Boggs [5] have shown that there is no evidence for any minima on the *s-cis* form (ϕ_a = 0°) or near the *s-cis* form. Conjugative interaction between the pi orbital of the vinyl group and a sigma orbital of the ring take a role in stabilizing the conformation [5].

The 2-cyclopropylpropene and 1,1-dicyclopropyl ethylene are obtained by substituting a hydrogen of the vinyl group of vinylcyclopropane by a methyl group and a cyclopropyl ring, respectively. The formula and the rotational angles are shown in Fig. 1. In these molecules, mutual repulsion between nonbonding atoms or groups seems to be more enhanced than in vinylcyclopropane. Therefore, it is interesting to investigate the relative stability of conformations of these molecules. The structure of 2-cyclopropylpropene has been studied by Konaka et al. [6] by means of gas-phase electron diffraction. They have proposed that $\phi_a = 65° \pm 4°$ is the most stable conformation with the aid of the results of our ab initio calculations. The structure of 1,1-dicyclopropyl ethylene has been also studied by Konaka et al. [7] by means of gas-phase electron diffraction, but the conformation of this molecule has not been established. The main aim of this investigation is to calcu-

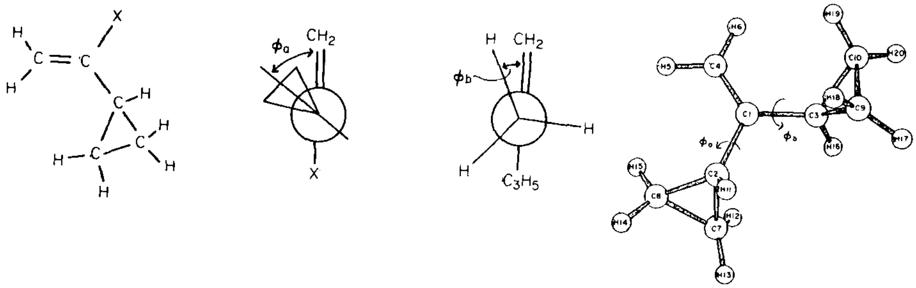

Fig. 1. Constitutional formula and the definition of the internal rotation angles. (a) X = H, vinylcyclopropane; X = CH_3, 2-cyclopropylpropene; X = C_3H_5, 1,1-dicyclopropyl ethylene. (b) The definition of the internal rotation angle ϕ_a. (c) The definition of the internal rotation angle ϕ_b of 2-cyclopropylpropene. (d) The definition of the internal rotation angle ϕ_a and ϕ_b of 1,1-dicyclopropyl ethylene.

late the potential surface versus the rotational angles and to discuss the relative stability among conformations.

CALCULATIONS

We have performed an LCAO-SCF-MO calculation with the 4-21G basis set [8]. This basis set is nearly equivalent to the 4-31G set [9] but requires less computational time and has been recommended by Pulay et al. [8]. Skancke and Boggs [5] have used this basis set for geometry optimization of vinylcyclopropane and obtained reasonable agreement with experiment. Full geometry optimization has been made by means of the gradient method. We have used the computer program TEXAS [10] which is a gradient LCAO-SCF-MO program written by Pulay.

RESULTS AND DISCUSSION

2-Cyclopropylpropene

The potential curve versus internal rotation angle ϕ_a is illustrated in Fig. 2. It shows that there are two local energy minima, ($\phi_a = 62°$, $\phi_b = 0°$) and ($\phi_a = 180°$, $\phi_b = 0°$), which are designated as the conformer *G*(*gauche* conformation) and the conformer *T*(*s-trans* conformation), respectively. The molecular structures of these conformers are shown in Fig. 3. The potential curve reveals that the conformer *G* is the most stable and the conformer *T* is the second minimum. The feature is just contrary to vinylcyclopropane, in which the conformation of $\phi_a = 180°$ is the most stable. In order to check the most possible stable conformation at $\phi_a = 180°$, we calculated a potential curve against internal rotation angle ϕ_b. The potential curve versus ϕ_b is shown in Fig. 4. It shows that the eclipsed conformer ($\phi_b = 0°$) is the most stable and the staggered conformer ($\phi_b = 60°$) is unstable.

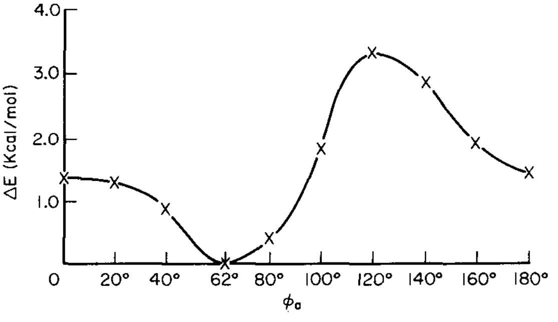

Fig. 2. Potential curve vs. ϕ_a of 2-cyclopropylpropene. In calculation of the potential curve for each point of ϕ_a from 0° to 80°, we have fixed the other internal coordinates to those which have been optimized at $\phi_a = 62°$. The energy maximum has been found around $\phi_a = 120°$. We have performed geometry optimization at $\phi_a = 120°$ in order to get a better potential barrier. Fixing these optimized parameters except for ϕ_a, we have a potential curve versus ϕ_a from 100 to 180°.

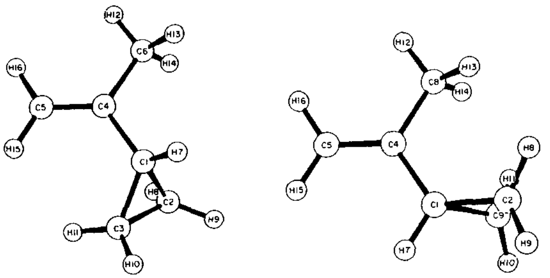

Fig. 3. Optimized molecular structure of 2-cyclopropylpropene. (a) Shows the conformer *G* ($\phi_a = 62°$). (b) Shows the conformer *T* ($\phi_a = 180°$). These diagrams are drawn by the use of the program ORTEP2 [11].

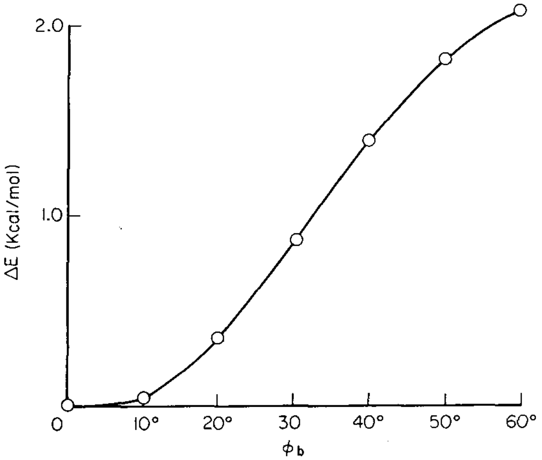

Fig. 4. Potential curve vs. ϕ_b of 2-cyclopropylpropene.

Full geometry optimization are performed at the two conformers *G* and *T*. The energy difference between them is 1.14 kcal mol^{-1}. Assuming the Boltzman distribution law for the two conformers and using the calculated energy difference, we obtain the result that the relative abundance of the conformer *G* is 93.5% and the conformer *T* is 6.5% at 18°C. This agrees quite well with experimental results by Konaka et al. [6] who reported that the conformation with $\phi_a = 65° \pm 4°$ is the most stable conformation and its relative abundance is 93.5 ± 4%.

The calculated and observed bond lengths and bond angles are shown in Tables 1 and 2, respectively. The experimental values by Konaka et al. [6] are also shown in the Tables.

Because the relative abundance of the conformer *T* is a few percent, it is not easy to get information about the molecular structure from experiment. It may be useful to obtain structural information from the ab initio calculations. The calculated molecular structure for conformer *T* is already given in Tables 1 and 2. In comparison with the structure of the conformer *G*, the following two differences are to be noted. The cyclopropyl ring of the conformer *G* has no symmetry, but the ring becomes an isosceles triangle for the conformer *T*. Secondly, the bond angles between the methyl and cyclopropyl groups ($\angle C_6$—C_4—C_1) in the two conformers differ by 2° whereas other bond angles agree within 1°. The angles are 113° and 115° for the two conformers *G* and *T*, respectively. For the conformer *T*, the repulsion

TABLE 1

Bond lengths of 2-cyclopropylpropene (A)

	$\phi_a = 62°$	$\phi_a = 180°$	Exp.
ring			
C_1—C_2	1.523	1.525	
C_2—C_3	1.515	1.509	1.519(6)
C_3—C_1	1.508	1.524	
C_4—C_1 (*ring*)	1.495	1.494	1.485(11)
C_4=C_5	1.317	1.320	1.346(5)
C_4—C_6 (*methyl*)	1.514	1.513	1.508
ring			
C_1—H_7	1.074	1.070	
C_2—H_8	1.072	1.069	
C_2—H_9	1.072	1.070	
C_3—H_{10}	1.070	1.071	1.105(5)
C_3—H_{11}	1.071	1.070	
vinyl			
C_5—H_{15}	1.072	1.074	1.105(5)
C_5—H_{16}	1.074	1.074	
methyl			
C_6—H_{12}	1.081	1.079	
C_6—H_{13}	1.087	1.082	1.113
C_6—H_{14}	1.086	1.083	

TABLE 2

Bond angles of 2-cyclopropylpropene (deg.)

	$\phi_a = 62°$	$\phi_a = 180°$	Exp.
ring			
$\angle C_1—C_2—H_8$	118	118	114.5(1.8)
$\angle C_1—C_3—H_{11}$	117	118	
$\angle C_1—C_2—H_9$	117	118	
$\angle C_1—C_3—H_{10}$	117	118	
$\angle C_2—C_1—H_7$	115	115	
vinyl			
$\angle C_4=C_5—H_{16}$	122	122	
$\angle C_4=C_5—H_{15}$	122	122	121.3
$\angle H_{15}—C_5—H_{16}$	116	116	
methyl			
$\angle C_4—C_6—H_{12}$	111	112	109.5(3.6)
$\angle C_4—C_6—H_{13}$	110	109	
$\angle C_4—C_6—H_{14}$	110	110	
$\angle C_6—C_4—C_1$	113	115	
$\angle C_5=C_4—C_1$	123	122	123.2(1.6)
$\angle C_5=C_4—C_6$	123	123	121.2(2.5)
$\angle C_2—C_1—C_4$	121	120	122.0(0.8)

between the methyl group and the cyclopropyl ring seems to be more enhanced than the conformer *G*. As the bond length between the methyl and vinyl groups and that between the cyclopropyl and vinyl groups is not changed very much, energy stabilization from $\phi_a = 62°$ to $\phi_a = 180°$ almost resulted by adjusting the angle $\angle C_6—C_4—C_1$.

1,1-Dicyclopropyl ethylene

There are three local minima in a conformational potential surface. We draw a wide potential surface against ϕ_a and ϕ_b where the other structural parameters are fixed as those optimized at $\phi_a = 64°$ and $\phi_b = 64°$. The potential surface is shown in Fig. 5. The conformer of ($\phi_a = 64°$ and $\phi_b = 64°$) is the most stable and it is also *gauche*. Let us designate it as the conformer G^+G^+(*gauche-gauche* conformation). Other than this conformer, two local minima are found around ($\phi_a = 60°$ and $\phi_b = -60°$) and ($\phi_a = 60°$ and $\phi_b = 180°$).

Full optimization of geometry parameters are carried out around these minima. The one minimum is located at ($\phi_a = 65°$ and $\phi_b = -176°$) and it is higher in energy by 0.71 kcal mol^{-1} than the conformer G^+G^+. Let us designate it as the conformer *TG*(*s-trans-gauche* conformation). The other minimum is found at ($\phi_a = 59°$ and $\phi_b = -59°$) and its energy is 0.91 kcal mol^{-1} relative to the conformer G^+G^+. This conformer is named as the conformer G^+G^-(*gauche-gauche* conformation). The structures of the conformer G^+G^+,

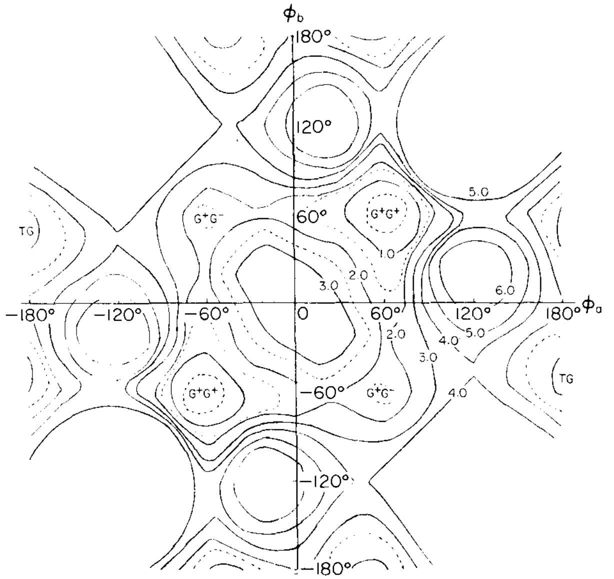

Fig. 5. Potential surface vs. ϕ_a and ϕ_b of 1,1-dicyclopropyl ethylene.

TG and G^+G^- are illustrated in Fig. 6a, 6b, and 6c, respectively. If we assume the Boltzman distribution law for the three conformations, we have found that relative abundance of the conformer G^+G^+ is 67%, the conformer *TG* is 19% and the conformer G^+G^- is 14% at 18°C. Using Fig. 5, we have estimated that the potential barrier height from the conformer G^+G^+ to the conformer G^+G^- is almost 1.7 kcal mol^{-1}. So the transition from the conformer G^+G^+ to the conformer G^+G^- has probably taken place at room temperature. In such a case, the experimentalist should be careful in analyzing experimental data, as experimental data could carry information about internal structures. Other conformations of (ϕ_a = 0° and ϕ_b = 0°, *s-cis-s-cis* conformation) and (ϕ_a = 180° and ϕ_b = 180°, *s-trans-s-trans* conformation) are the maximum point

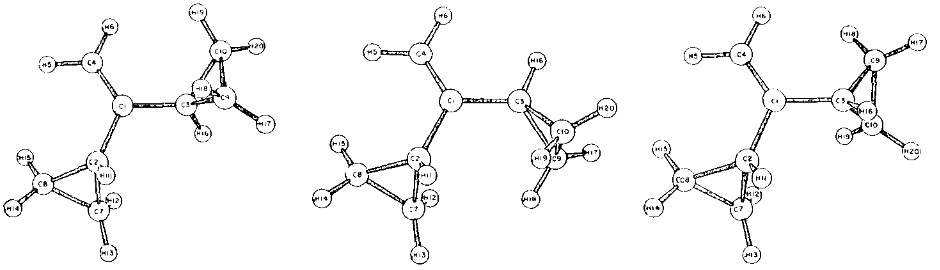

Fig. 6. Optimized molecular structure of 1,1-dicyclopropyl ethylene. (a) Shows the conformer G^+G^+ of ϕ_a = 64° and ϕ_b = 64°. (b) Shows the conformer G^+G^- of ϕ_a = 59° and ϕ_b = −59°. (c) Shows the conformer *TG* of ϕ_a = 65° and ϕ_b = −176°. These diagrams are drawn by the use of the program ORTEP2 [11].

and each energy is higher than the conformer G^+G^+ by about 3.5 kcal mol^{-1} and 112 kcal mol^{-1}, respectively.

The calculated bond lengths and bond angles are shown in Tables 3 and 4, respectively. The numbering of atoms in the table is already shown in Fig. 6. It is noted that the molecular structure of the conformer G^+G^+ and the conformer G^+G^- is almost the same except for the two internal rotation angles. A big difference in molecular structure between the conformer TG and the other conformers is found in the bond angle $\angle C_2—C_1—C_3$.

CONCLUSIONS

The most stable conformers of both 2-cyclopropylpropene and 1,1-dicyclopropyl ethylene have the *gauche* form in contrast to vinylcyclopropane, in which the *s-trans* conformer is the most stable. In 2-cyclopropylpropene, the relative abundance of the *gauche* conformer is about 94% assuming the Boltzman distribution law. In 1,1-dicyclopropyl ethylene, the barrier height between the two *gauche-gauche* conformations is so low that the ring easily rotates between the two conformers. So the experimental information may include the intermediate structure as well as the two conformers.

TABLE 3

Bond lengths of 1,1-dicyclopropyl ethylene (A)

	$\phi_b = 64°$	$\phi_b = -59°$	$\phi_b = -176°$
$C_1—C_2$ (*ring*)	1.500	1.501	1.500
$C_1—C_3$ (*ring*)	1.500	1.501	1.500
ring A			
$C_2—C_7$	1.520	1.520	1.522
$C_2—C_8$	1.512	1.512	1.514
$C_7—C_8$	1.519	1.515	1.513
$C_2—H_{11}$	1.074	1.075	1.074
$C_7—H_{12}$	1.071	1.071	1.071
$C_7—H_{13}$	1.071	1.071	1.071
$C_8—H_{14}$	1.071	1.072	1.071
$C_8—H_{15}$	1.070	1.071	1.070
ring B			
$C_3—C_9$	1.512	1.512	1.520
$C_3—C_{10}$	1.520	1.520	1.521
$C_9—C_{10}$	1.519	1.515	1.513
$C_3—H_{16}$	1.074	1.075	1.072
$C_9—H_{17}$	1.071	1.072	1.071
$C_9—H_{18}$	1.071	1.071	1.069
$C_{10}—H_{19}$	1.070	1.071	1.070
$C_{10}—H_{20}$	1.071	1.071	1.071
vinylidene			
$C_1{=}C_4$	1.316	1.316	1.320
$C_4—H_5$	1.072	1.072	1.071
$C_4—H_6$	1.072	1.072	1.073

TABLE 4

Bond angles of 1,1-dicyclopropyl ethylene (deg.)

	$\phi_b = 64°$	$\phi_b = -59°$	$\phi_b = -176°$
$\angle C_2-C_1-C_3$	114	113	118
$\angle C_2-C_1-C_4$	123	123	122
$\angle C_1-C_4-H_5$	122	122	122
ring A			
$\angle C_7-C_2-C_8$	60	60	60
$\angle H_{11}-C_2-C_7$	115	116	115
$\angle H_{12}-C_7-C_2$	118	118	117
$\angle H_{13}-C_7-C_2$	118	118	118
$\angle H_{14}-C_8-C_2$	118	118	118
$\angle H_{15}-C_8-C_2$	118	118	118
ring B			
$\angle C_7-C_2-C_8$	60	60	60
$\angle H_{16}-C_3-C_9$	115	116	115
$\angle H_{17}-C_9-C_3$	118	118	118
$\angle H_{18}-C_9-C_3$	118	118	118
$\angle H_{19}-C_{10}-C_3$	118	117	118
$\angle H_{20}-C_{10}-C_3$	118	118	117

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