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Structure and conformational dynamics of the dicyclopropyl ketone in the ground electronic state

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ABSTRACT

Geometric parameters, harmonic and anharmonic vibrational frequencies, conformer energy differences and barriers to internal rotation were obtained for dicyclopropyl ketone (DCPK) in the ground electronic state through MP2, DFT, CCSD and CCSD(T) calculations. VFPA was used to improve the estimations of conformer energy differences and heights of barriers to internal rotation. The *ab initio* calculations demonstrated that there are three stable conformations of DCPK: the *cis–cis*, the *cis–trans* and the *gauche–gauche*. The energy of the *gauche–gauche* conformer is noticeably higher than the energy of the two other conformers, so this conformer was not found experimentally. To study the conformational dynamics of the DCPK molecule, one- and two-dimensional sections of the potential energy surface corresponding to the rotations of the cyclopropyl groups were calculated. These sections were used to calculate torsion transition energies and vibrational wave functions in anharmonic approach. It was found that there is a strong coupling of large-amplitude torsion motions in the area of the *cis–cis* and *gauche–gauche* conformers.

1. Introduction

Studies of cyclopropane derivatives are of great interest because these compounds can react as though they were either saturated or unsaturated [1–3]. Some properties of cyclopropane derivatives are related to the ability of the cyclopropyl group to conjugate with unsaturated substituents and can be explained by the Walsh–Hoffmann [4,5] and Förster–Coulson–Moffitt [6,7] models.

In previous studies, we used *ab initio* methods to study cyclopropane carboxaldehyde [8] and cyclopropyl methyl ketone [9] molecules. In this paper we have applied *ab initio* methods to calculate geometric parameters, potential energy surface (PES) sections and vibrational frequencies in both harmonic and anharmonic approaches for the dicyclopropyl ketone (DCPK) molecule in the ground electronic state, Fig. 1.

2. Computational methods

The restricted Hartree–Fock (RHF) method, the density functional method (B3LYP), the Møller–Plesset perturbation theory (MP2) and the coupled-cluster methods CCSD and CCSD(T) were used to solve the electron problem. Calculations were performed with Pople basis sets (up to 6-311+G(2*d*,2*p*)) and Dunning basis sets (including cc-pV5Z). All calculations were performed under the frozen-core approximation unless stated otherwise. Gaussian-*n* [10–13] methods and the VFPA (valence focal-point analysis) extrapolation procedure were also applied to obtain the values of the conformer energy differences and heights of barriers to internal rotation. For some molecules VFPA estimations of these values are very accurate [14–16].

The computations were performed using the GAMESS US [17], Gaussian 03 [18], MOLPRO [19] and ACES II [20] programs.

3. Geometric parameters

Previously, the structure of DCPK has been studied using vibrational spectroscopy [21–26] and electron-diffraction method [27]. It was found that the symmetric (C_{2V}) *cis–cis* conformer ($\varphi_1 = \angle H_6C_3C_1C_{11} = \varphi_2 = \angle H_{14}C_{11}C_1C_3 = 0°$, Fig. 1) predominates in the gas and liquid phases. The authors of [24–26] found IR and Raman spectral bands, which were assigned to a second conformer, but the structure of this conformer was not exactly determined.

In previously published work [24] the authors proposed that the *cis–cis* and *gauche–gauche* (C_2 symmetry) conformers of DCPK are the two most stable ones. Later, Diallo et al. reassigned several bands in the IR and Raman spectra and came to the conclusion that the *cis–trans* conformer ($\varphi_1 = 0°$, $\varphi_2 = 180°$, C_S symmetry, Fig. 1) exists in liquid along with the *cis–cis* conformer [25]. They made this conclusion on the basis of the Walsh–Hoffmann [4,5] model.

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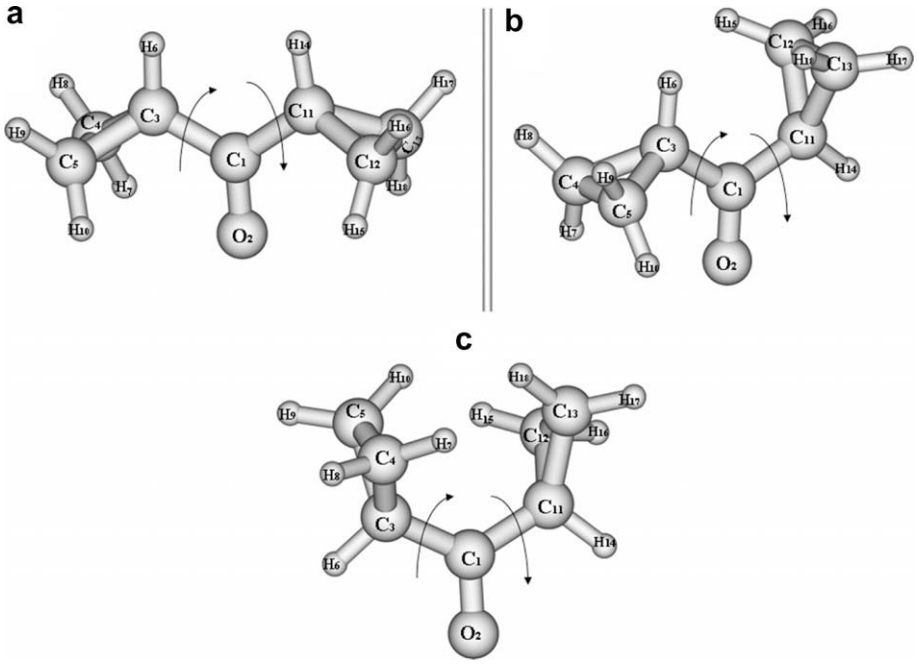

Fig. 1. The structure of the *cis–cis* (a), *cis–trans* (b), *gauche–gauche* (c) conformations of DCPK. Arrows demonstrate the positive directions of change in the $\varphi_1 = \angle H_6C_3C_1C_{11}$ and $\varphi_2 = \angle H_{14}C_{11}C_1C_3$ angles.

According to this model, the maximum overlap of the carbonyl p-orbitals and the p-orbitals of the ring carbons should be observed for the symmetric *cis–cis* (C_{2V}), *cis–trans* (C_S) and *trans–trans* (C_{2V}) conformations. However, the *trans–trans* conformation should have higher energy because it is sterically strained, so in [25] the authors concluded that the second stable conformation of DCPK is *cis–trans*. Analysis of the vibrational spectra of liquid DCPK and its xenon solution, performed in [26], also demonstrates that the most stable are the *cis–cis* and *cis–trans* conformations. DCPK was also studied using the electron-diffraction method [27]. The best agreement of the calculated and experimental radial distribution curves was achieved when the (*cis–cis*):(*cis–trans*) ratio was equal to 93:7. Some internuclear distances and valence angles for the *cis–cis* conformer were determined in work [27] (see Table 1).

Ab initio MP2/6-31G(*d*) calculations have demonstrated that there are minima on the PES of DCPK, corresponding to the *cis–cis* and *cis–trans* conformations [27]. Calculations by the RHF, MP2 and B3LYP methods with Pople basis sets (up to 6-311+G(2*df*,2*pd*)) performed in work [26] agree with the results of [27].

We performed *ab initio* calculations of the structure and of PES sections using RHF, MP2, B3LYP, CCSD methods with Pople (up to the 6-311+G(2*d*,2*p*) and Dunning (up to the cc-pVTZ) basis sets. According to our calculations, the most stable conformers are the *cis–cis* and the *cis–trans* conformations. This result agrees with previous experimental and theoretical investigations of DCPK (Fig. 1). However, the detailed analysis of the PES sections (Fig. 2) obtained by various methods (including MP2/6-31G(*d*)) demonstrated that the *gauche–gauche* conformation of DCPK is also stable (two minima M3, Fig. 2, on the PES correspond to this conformation). According to the CCSD/aug-cc-pVDZ method, the angles for the first minimum are $\varphi_1 = \varphi_2 = 166°$. For the second minimum, these angles are $\varphi_1 = \varphi_2 = 194°$ (Fig. 2). The *gauche–gauche* conformer is sterically strained, and the energy of this conformer is 2700–3500 cm^{-1} higher (according to the results of a variety of computational methods (see below)) than the energy of the *cis–cis* conformer. As a result, experimental study of this conformer is rather complicated. The structure

Table 1
Theoretical and experimental geometric parameters of the DCPK molecule (values of the bond lengths are given in Å, angles are in degrees and rotational constants are in MHz).

Parameter	CCSD/aug-cc-pVDZ[a]			ED[b] [27]
	cis–cis	*cis–trans*	*gauche–gauche*	*cis–cis*
$R(C_1O_2)$	1.229 (+2)	1.228 (+1)	1.229 (+1)	1.2171 (11)
$R(C_1C_3)$	1.500 (+6)	1.504 (+7)	1.508 (+7)	1.4945 (26)
$R(C_1C_{11})$	1.500 (+6)	1.499 (+6)	1.508 (+7)	1.4945 (26)
$R(C_3C_4)$	1.531 (+4)	1.530 (+4)	1.532 (+5)	1.4872 (11)
$R(C_3C_5)$	1.531 (+4)	1.530 (+4)	1.527 (+6)	1.4872 (11)
$R(C_4C_5)$	1.505 (+3)	1.506 (+3)	1.512 (+5)	1.448
$R(C_{11}C_{12})$	1.531 (+4)	1.530 (+5)	1.532 (+5)	1.4872 (11)
$R(C_{11}C_{13})$	1.531 (+4)	1.530 (+5)	1.527 (+6)	1.4872 (11)
$R(C_{12}C_{13})$	1.505 (+3)	1.510 (+4)	1.512 (+5)	1.448
$\angle C_3C_1O_2$	121.4 (+1)	120.7 (−1)	117.6 (−2)	121.59 (13)
$\angle C_{11}C_1O_2$	121.4 (+1)	120.3 (−1)	117.6 (−2)	121.59 (13)
$\angle C_3C_1C_{11}$	117.3 (−2)	119.0 (+2)	124.8 (+4)	—
$\angle C_1C_3H_6$	116.7 (−1)	117.9 (0)	109.9 (−3)	115.75 (2.79)
$\angle C_1C_{11}H_{14}$	116.7 (−1)	112.8 (−4)	109.9 (−3)	115.75 (2.79)
$\angle C_1C_3C_4$	116.9 (+1)	116.5 (+1)	121.1 (0)	—
$\angle C_1C_3C_5$	116.9 (+1)	116.5 (+1)	127.3 (+2)	—
$\angle C_1C_{11}C_{12}$	116.9 (+1)	120.4 (+2)	121.1 (0)	—
$\angle C_1C_{11}C_{13}$	116.9 (+1)	120.4 (+2)	127.3 (+2)	—
$\angle C_3C_5C_4$	60.6 (0)	60.5 (+1)	60.6 (0)	—
$\angle C_3C_4C_5$	60.6 (0)	60.5 (+1)	60.2 (0)	—
$\angle C_4C_3C_5$	58.9 (0)	59.0 (0)	59.3 (0)	—
$\angle C_{11}C_{12}C_{13}$	60.6 (0)	60.4 (+1)	60.2 (0)	—
$\angle C_{11}C_{13}C_{12}$	60.6 (0)	60.4 (+1)	60.6 (0)	—
$\angle C_{12}C_{11}C_{13}$	58.9 (0)	59.1 (0)	59.3 (0)	—
φ_1	0.0 (0)	0.0 (0)	165.6 (−1)	0.0
φ_2	0.0 (0)	180.0 (0)	165.6 (−1)	0.0
A	5522	3847	2648	—
B	1165	1411	1942	—
C	1348	1235	1347	—

Notes: $\varphi_1 = \angle H_6C_3C_1C_{11}$ and $\varphi_2 = \angle H_{14}C_{11}C_1C_3$ angles were taken as the coordinates of the internal rotations.

[a] Differences ($r_z - r_e$) of the vibrationally averaged geometric parameters calculated using perturbation theory and equilibrium geometric parameters calculated using the MP2/6-31G(*d*) method are presented in brackets (10^{-3} Å for the internuclear distances, and 10^{-1} deg for angles for the angles).

[b] r_α-structure. Standard deviations are presented in the brackets.