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Five-membered cyclic ketones: microwave spectra of isotopic substituted cyclopentenones[1]

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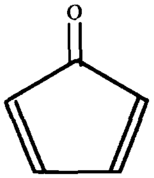
Abstract

The rotational spectra of cyclopentene-2-one-1 in the ground state and the first excited vibrational state of the ring puckering mode ν_{30} have been re-measured with improved accuracy in the range from 11–40 GHz. One hundred and eleven and sixty nine rotational transitions with J quantum numbers up to fifty eight and forty eight, respectively, could be assigned. The isotopomer 3-d-cyclopentene-2-one-1 has been prepared and its microwave spectra in the ground state and in the first and second excited vibrational states of the ring puckering mode ν_{30} have been measured. We were able to assign 117 rotational transitions up to $J = 69$ in the ground state and 63 and 44 transitions with J quantum numbers up to 40 and 18, respectively, for the excited states. We also prepared 4-d-cyclopentene-2-one-1 and 5-d-cyclopentene-2-one-1 in an isotopomeric mixture together with the parent molecule. For each of these D isotopomers, respectively, 87 and 119 rotational transitions of the ground state with J quantum numbers up to 65 were measured and assigned. The molecule appears to be very rigid—in all cases the quartic centrifugal distortion constants could be determined with remarkable accuracy, whereas only for two fits were one and two sextic constants needed, despite the high J and K values. The C_s symmetry of the molecule is definitively confirmed. © 1997 Elsevier Science B.V.

Keywords: Cyclopentene-2-one-1; Deuteration; Microwave Spectra; Molecular Structure

1. Introduction

In the course of our work on the structure of cross-conjugated compounds [1–4] we also measured the rotational spectra of some isotopomers of the unstable cyclopentadienone (**I**). To obtain the appropriate precursors we had to carry out the isotopic substitutions at the level of cyclopentenone (**II**). Since the isotopomers of (**II**) were therefore partly at hand it seemed interesting to measure their microwave spectra also and to gain at least an approximate knowledge of their molecular structure. The compound has also been object of extensive studies by vibrational and electronic spectroscopy [5–7], so our data may be considered a worthwhile supplement to these investigations.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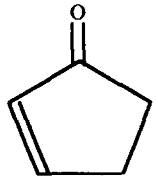
II

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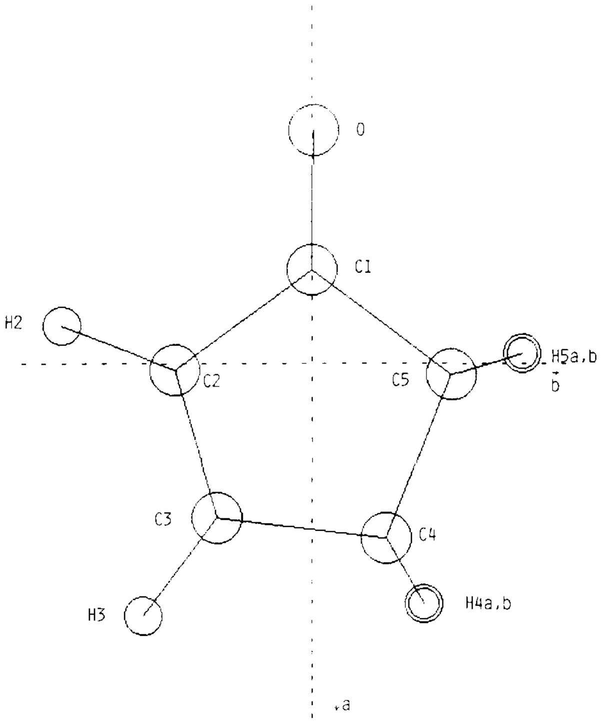


Fig. 1. Projection of the cyclopentene-2-one-1 molecule on the a,b plane with numbering of the atoms as used in the text; approximate geometry from AM1 calculation.

In contrast to I (life-time 15 s under microwave measuring conditions) II is a stable molecule from the viewpoint of spectroscopy. The microwave spectrum of its main isotopic abundance and of the ^{18}O isotopomer had already been measured by Chadwick et al. [8] but their analysis of the few transitions was not very accurate and resulted in poor constants, unsuitable for predicting the rich spectrum. But for measurements on isotopomeric mixtures, which in addition still contain some unsubstituted molecules, much more detailed information is needed to avoid incorrect assignments. Therefore we had at first to reinvestigate the spectra of the parent molecule in its vibrational ground state and in the first excited state of the ring puckering mode ν_{30} at 94.4 cm^{-1} [6]. Fig. 1 shows a projection of the molecule on the a,b plane as calculated by MOPAC-AM1 [9] and gives the numbering of the atoms; the structural parameters are listed in Table 1.

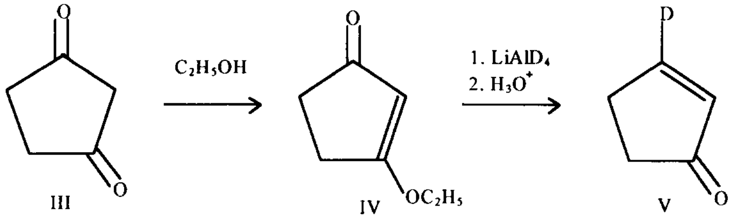
Table 1
Structural parameters of cyclopentene-2-one-1 as calculated by MOPAC-AM1

r	(Å)	$\sphericalangle$	(°)
O-C1	1.229	C2-C1-C5	107.2
C1-C2	1.486	C1-C2-C3	110.3
C2-C3	1.347	C2-C3-C4	117.3
C3-C4	1.501	C3-C4-C5	99.9
C4-C5	1.534	C4-C5-C1	105.3
C1-C5	1.520	O-C1-C2	126.6
C2-H2	1.091	C1-C2-H2	121.4
C3-H3	1.092	C4-C3-H3	115.4
C4-H4	1.119	C1-C5-H5 (a,b)	110.0
C5-H5	1.117	C5-C4-H4 (a,b)	111.3
		H5a-C5-H5b	108.2
		H4a-C4-H4b	107.9

2. Preparation of deuterated cyclopentenones

2.1. 3-Deuterocyclopentene-2-one-1

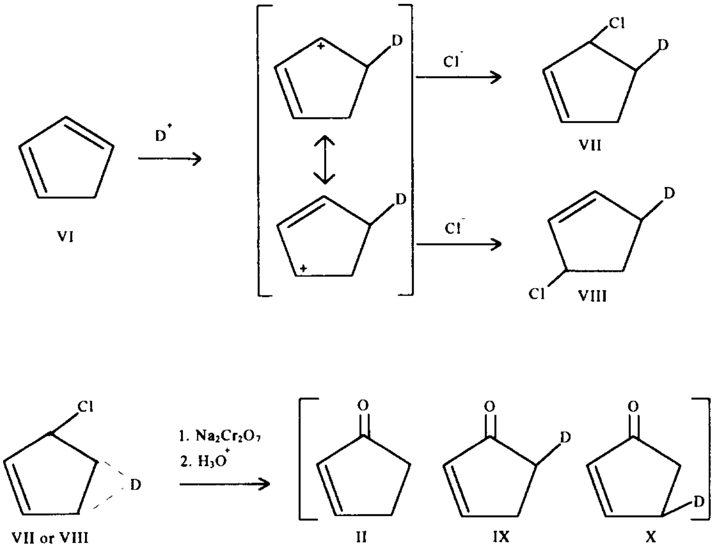
3-d-Cyclopentene-2-one-1 (**V**) was prepared in a two-step reaction according to the reaction scheme given below:



In a first step 1,3-cyclopentanedione (**III**) was converted to the corresponding enol ether 3-ethoxycyclopentene-2-one-1 (**IV**) using ethanol [10]. In the second step 3-ethoxycyclopentene-2-one-1 was converted with lithium aluminum deuteride to an aluminum complex yielding 3-d-cyclopentene-2-one-1 [11] after hydrolysis. The sample was almost isotopomerically pure, so that transitions of the parent molecule could hardly be detected (Fig. 2).

2.2. *4-Deuterocyclopentene-2-one-1 and 5-deuterocyclopentene-2-one-1*

An isotopomeric mixture of 4-d- (IX) and 5-d-cyclopentene-2-one-1 (X)—also containing the parent molecule—was prepared in a two-step reaction following the reaction scheme below:



In accordance with [12] gaseous DCl was added to freshly distilled cold cyclopentadiene (**VI**). The resulting crude isotopomeric mixture of 4- (**VII**) and 5-deutero-3-chlorocyclopentene (**VIII**) was purified by distillation (T = 30°C, p = 25 mbar). In the following step the chlorocyclopentenes were added dropwise to a cooled solution of sodium dichromate and the resulting complex was hydrolyzed with dilute sulfuric acid. The reaction mixture was then saturated with NaCl and the products were extracted with ether. Finally the ether was removed by distillation, and the remaining crude isotopomeric mixture of 4- and 5-deuterocyclopentene-2-one-1 was purified by distillation (T = 42°C, p = 15 mbar). Due to the fact that H_2O and H_2SO_4 instead of the deuterated compounds had to be used in this step to avoid multiple substitution, the resulting mixture also contained the parent molecule cyclopentene-2-one-1 as shown in Fig. 3.

3. Calculation of approximate rotational constants

As already pointed out, the spectra are very rich

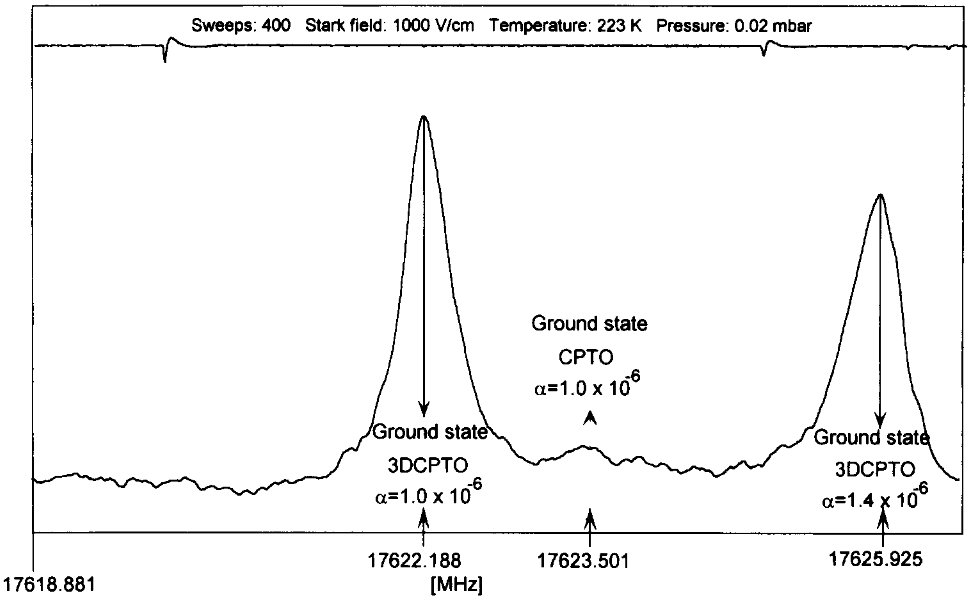


Fig. 2. Rotational transitions $45_{15,30} \leftarrow 45_{15,31}$ and $3_{2,2} \leftarrow 2_{2,1}$ of the 3-d isotopomer and $21_{7,14} \leftarrow 21_{7,15}$ of the parent molecule of cyclopentene-2-one-1. Theoretical absorption coefficients α are given in cm^{-1}.

due to the numerous low-lying vibrational states. Therefore it was essential, for correct assignments, to use all information so far available to predict the rotational constants of the deuterated compounds as closely as possible:

4. Expected structure and rotational constants for the deuterated isotopomers in the vibrational ground state

Assuming a planar arrangement of the heavy-atom skeleton as stated in [6,8] and in addition C_s symmetry (heavy-atom plane is symmetry plane) cyclopentene-2-one-1 has 19 independent structural parameters. The semiempirical program MOPAC (model AM1) was used to obtain preliminary information about their values, independent of estimates deduced from related compounds. MOPAC also yielded a structure with C_s symmetry. The parameters calculated in this manner were used as a starting data set and fitted to the experimentally determined rotational constants of the parent molecule (three constants) and the ^{18}O isotopomer (only one additional quantity due to the O position in

Table 2
Comparison of consecutively calculated and experimentally determined rotational constants

	Calculated rotational constants (MHz) of the					
	3-d Isotopomer	Exp. – calc. (/MHz)	5-d Isotopomer	Exp. – calc. (/MHz)	4-d Isotopomer	Exp. – calc. (/MHz)
MOPAC-Model AM1						
A	7224	–41	7011	20	7257	– 20
B	3433	33	3537	30	3431	27
C	2400	8	2444	7	2421	7
Fitted to the experimental data						
A	7194(37)	–12	6980(9)	11	7234(180)	3
B	3461(13)	5	3567(1)	1	3453(220)	5
C	2408(5)	1	2451(1)	1	2426(91)	2

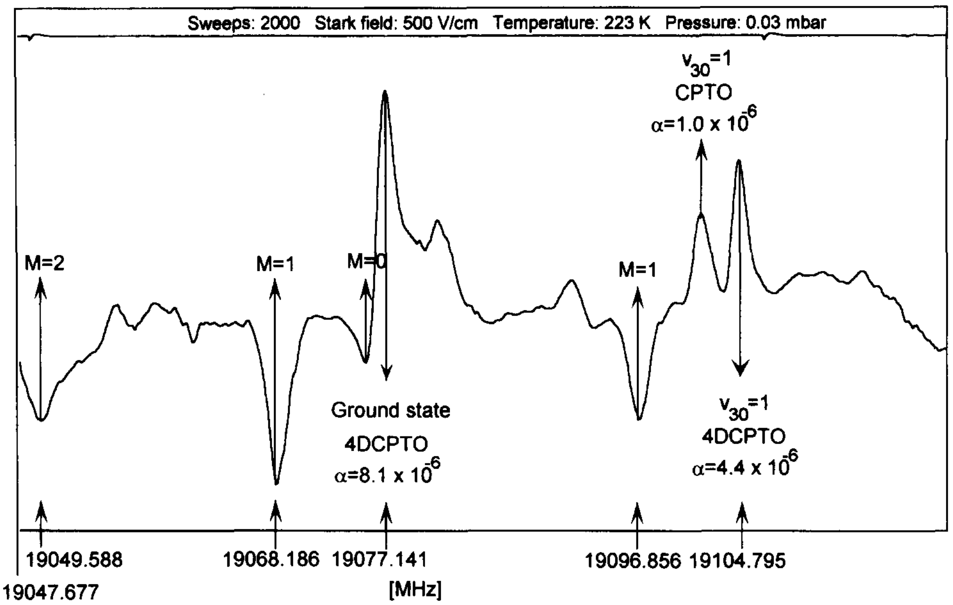


Fig. 3. Rotational transition $3_{1,2} \leftarrow 2_{1,1}$ of 4-d-cyclopentene-2-one-1: ground state and 1st excited state of ν_{30} with Stark components. The third, weaker line is assigned to the transition $27_{9,18} \leftarrow 27_{9,19}$ of $\nu_{30} = 1$ of the parent molecule. Theoretical absorption coefficients α are given in cm^{-1}.

the plane and very close to the a axis); 15 of the 19 parameters were kept fixed. A set of structural parameters resulted for calculating the rotational constants of the 3d isotopomer. With these fast assignment of the rotational transitions and the determination of the spectroscopic constants was possible. Then these additional rotational constants (again only two are independent due to the position of H3 in the plane) together with those of the parent molecule and the ^{18}O isotopomer were used for fitting 6 of the 19 parameters and calculating the rotational constants of the 5-d isotopomer. The whole procedure of fitting structural parameters and calculating approximate rotational constants was repeated for the 4-d isotopomer using, in addition, the now determined rotational constants of the 5-d isotopomer (variation of 8 structural parameters possible). These calculated rotational constants for the deuterated isotopomers are listed in Table 2 and show clearly how the predictions improve steadily.

5. Expected frequencies for the rotational transitions in the excited vibrational states of ν_{30}

Some rotational transitions of the parent molecule in excited vibrational states had already been measured and assigned [8], so a complete set of approximate rotational constants was available, as therefore, were the α constants. Since isotopic effects are negligible in this context, the spectra of the excited states of ν_{30} for the D isotopomers could easily be assigned if the degree of substitution was sufficient to detect these weaker transitions (Fig. 4). The assignments could also be verified by means of the Stark effect, as is well illustrated by Fig. 3.

6. Microwave spectra

The spectra were recorded using a conventional Stark spectrometer with a 3-m cell that allows measurements at temperatures between + 40° and − 70°C. Digital data collection was used, the frequency standard was checked against DCF77, Mainflingen, Germany. The frequency range from 8 to 40 GHz was studied. All observed transitions were a-type, since the a axis lies almost parallel to this dipole component [8]. The line widths of the low J transitions of the D-containing isotopomers were larger due to the nuclear quadrupole interaction of deuterium. This explains the

Table 3
Spectroscopic constants and standard deviations of the fits

Vibrational ground state of	Cyclopentene-2-one-1	3-d-CPTO	4-d-CPTO	5-d-CPTO	^{18}O-CPTO[a]
Rotational constants (MHz)					
A	7410.2192(14)	7182.9816(16)	7237.4728(30)	6990.6410(20)	7409.962(39)
B	3586.35009(60)	3466.34422(89)	3458.2164(20)	3567.8405(11)	3392.7464(57)
C	2492.56044(47)	2408.99096(74)	2428.0017(20)	2451.8179(10)	2397.4671(51)
Quartic centrifugal distortion constants (kHz)					
Δ_J	0.27072(92)	0.2429(15)	0.304(28)	0.2692(72)	0.27072[a]
Δ_{JK}	0.9919(49)	0.9698(94)	1.008(45)	1.051(34)	0.9919[b]
Δ_K	1.1779(97)	0.984(26)	0.96(16)	0.77(11)	1.1779[b]
δ_J	0.07645(26)	0.06943(35)	0.0725(20)	0.0788(17)	0.07645[b]
δ_K	0.6174(21)	0.5698(41)	0.470(30)	0.557(24)	0.6174[b]
Sextic centrifugal distortion constants (mHz)					
Φ_K	− 38(13)	–	–	–	–
ϕ_{JK}	− 2.40(68)	–	–	–	–
Planar moment (amu Å^2)					
P_c	3.182	3.183	3.911	3.909	3.183
No. of lines/Standard deviations (kHz) of the fits					
	111/31	117/40	87/39	119/39	20/187
First excited vibrational state of ν_{30}					
Rotational constants (MHz)					
A	7392.9998(39)	7167.5450(35)	not measured due to low yield		
B	3590.2198(17)	3469.8746(27)			
C	2498.9205(13)	2414.9737(27)			
Quartic centr. distortion constants (kHz)					
Δ_J	0.2159(67)	0.355(42)			
Δ_{JK}	0.706(44)	0.986(46)			
Δ_K	2.02(12)	0.85(17)			
δ_J	0.0803(24)	0.0728(15)			
δ_K	0.340(32)	0.562(22)			
Sextic centr. distortion constants (mHz)					
ϕ_{JK}	12.9(31)	–			
Planar moment (amu Å^2)					
P_c	3.443	3.444			
No. of lines/Standard deviations (kHz) of the fits					
	69/56	63/34			
Second excited vibrational state of ν_{30}					
Rotational constants (MHz)					
A	7375.1(1)[c]	7151.5075(51)	not measured due to low yield		
B	3593.992(8)[c]	3473.2962(26)			
C	2504.810(8)[c]	2420.4857(25)			
Quartic centr. distortion constants (kHz)					
Δ_J	–	0.206(34)			
Δ_{JK}	–	1.046(70)			
Δ_K	–	0.85(32)			
δ_J	–	0.0763(20)			
δ_K	–	0.588(30)			
Planar moment (amu Å^2)					
P_c	3.689	3.690			
No. of lines/Standard deviations (kHz) of the fits					
	17/230	44/33			

[a] Recalculated from the measurements in Ref. [8]. [b] Fixed to the value of the parent molecule. [c] According to Ref. [8].

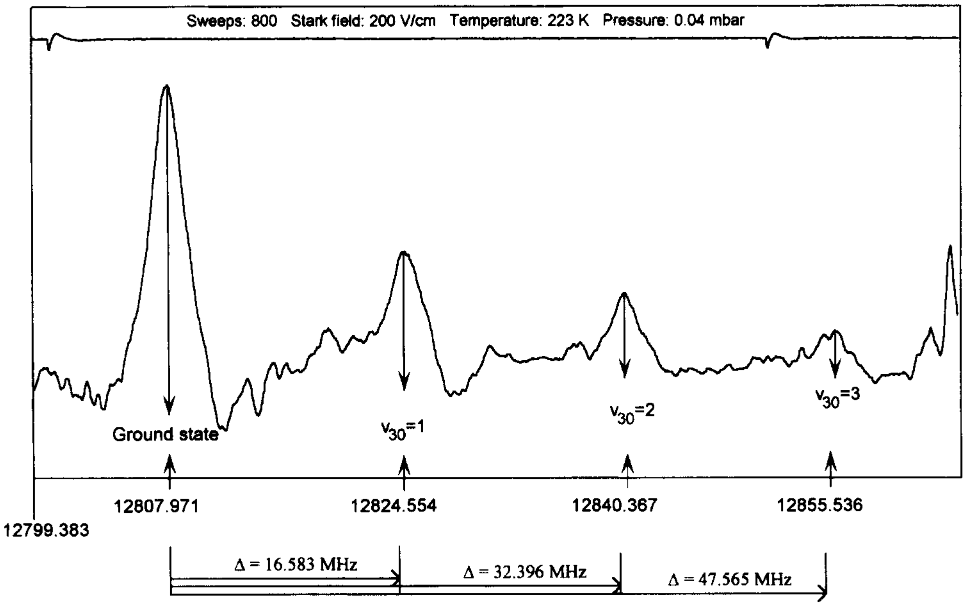


Fig. 4. The rotational transition $2_{1,1} \leftarrow 1_{1,0}$ of 3-d-cyclopentene-2-one-1 in different states of ν_{30}.

larger standard errors of the least squares fits of 3-d-, 4-d- and 5-d-cyclopentene-2-one-1 compared with the fit of the parent molecule.

The most suitable parameters for the measurements were: sample pressure ≤ 0.04 mbar, cell temperature ≈ -50°C. The deuterium content of the substituted species could independently be checked with an on-line quadrupole mass spectrometer.

7. Results

Table 3 shows all the spectroscopic constants and the standard deviations of the fits. These could be improved for the re-measured ground state and the first excited state of ν_{30} to 31 and 56 kHz as compared with 190 and 180 kHz, respectively, in [8]. In addition, the measurements of [8] on the ^{18}O isotopomer have been re-evaluated using the centrifugal distortion constants of the parent molecule, thereby improving the quality of the fit from 248 to 187 kHz standard deviation. The results are also given in Table 3. It can be seen that—in contrast to the argument in [8]—the distortion constants undergo less change between different isotopomers in their ground states than between different vibrational states of the same isotopomer, thus justifying the procedure described above. The line listings with frequencies, assignments, errors, and centrifugal distortion contributions (quartic and sextic) have been deposited with the British Library Document Supply Centre and are available as supplementary data (reference no. SUP26579). All calculations were done with Watson's A reduction in I^r representation.

The small quartic and sextic centrifugal distortion constants indicate that the molecule is rather rigid, like other five-membered cyclic ketones. It is remarkable that even their numerical values are close to those of cyclopentanone and cyclopentadienone as shown in Table 4.

8. Structure

The fact that the spectra of only one isomer of each of the isotopomers 4-d-cyclopentenone and 5-d-cyclopentenone could be observed establishes unambiguously two structural features: the planarity of the ring skeleton including the two vinyl H atoms and the untwisted arrangement of the two methylene groups, making the overall symmetry of the molecule C_s, the ring plane being the symmetry plane. This is further confirmed by the planar moments P_c and the pseudo-inertial defects of the C_s isotopomers: the planar

Table 4
Quartic centrifugal distortion constants of five-membered cyclic ketones (kHz)

	Cyclopentanone[a]	Cyclopentadienone[b]	Cyclopentene-2-one-1[c]
Δ_J	0.291(12)	0.3163(35)	0.27072(92)
Δ_{JK}	1.171(37)	1.397(22)	0.9919(41)
Δ_K	0.533(57)	1.146(69)	1.1779(97)
δ_J	0.0540(25)	0.0983(11)	0.07645(25)
δ_K	0.494(54)	1.094(16)	0.6174(20)

[a] Ref. [13]. [b] Ref. [14]. [c] This work.

moments are practically identical, the pseudoinertial defects can be calculated using the c coordinates of the methylene H atoms as

$$\Delta = 2[m_H \times (cH_4^2 + cH_5^2) - P_c] = -0.1520 \text{ amu Å}^2 \quad (1)$$

which is consistent with the value − 0.1435 amu $Å^2$ for 3-methylene-1,4-cyclohexadiene [3]. Also the contribution of one pair of out-of-plane hydrogens to the planar moment P_c of 1.5907 amu $Å^2$ fits well with the numbers from Table 3 in [3]. This result is also in very good agreement with the potential energy function determined by Cheatham and Laane [6].

The ground state spectra of the five isotopomers yielded 15 rotational constants and moments of inertia. Since these are not all independent there is at present no chance of calculating even an r_0 structure for the 19 parameters, but work on the 2-d and several ^{13}C isotopomers is in progress.

9. Supplementary material available

The British Library Document Supply Centre document reference no. SUP26579 contains seven tables listing the rotational transitions of cyclopentene-2-one-1 (CPT2O1) and 3-d-cyclopentene-2-one-1 (3-d-CPT2O1) in the vibrational ground state and in the first excited vibrational state of ν_{30} (16 pages of table).

Acknowledgements

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