

The Structure of Gaseous Cyclopropanecarboxylic Acid as Studied by Microwave Spectroscopy, Electron Diffraction and *Ab Initio* Calculations

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Cyclopropanecarboxylic acid has been studied by microwave spectroscopy, electron diffraction and *ab initio* computations at the 4-21G level. The molecule is found to prefer a conformation that has the carbonyl group *syn* to the cyclopropyl ring. A second conformer is also present with an energy 3–5 kJ mol⁻¹ less stable. This rotamer is found to have the carbonyl group *anti* to the ring. An accurate structure has been derived making use of electron diffraction and microwave data in a joint analysis.

The aim of this work has been to investigate the structural and conformational properties of cyclopropanecarboxylic acid. This compound may exhibit a variety of conformations which are produced by rotation around the C3–C4 and C4–O7 bond (Fig. 1). The four conformations shown in this figure all possess a symmetry plane formed by the H5C3C4O6O7H8 atoms, as well as the bisector of the cyclopropyl ring ending at C3. In addition to these four conformations, various other forms are of course theoretically possible.

The structural and conformational properties of free, monomeric cyclopropanecarboxylic acid have been subject to several studies by various methods in recent years. IR studies have been made by Tabacik and Maillols¹ and Powell and Klæboe.² The French workers¹ concluded from their gas-phase IR studies that only one conformation is present in the free state, and that this is the *anti-anti* rotamer of Fig. 1. In a theoretical study, Huang and Pan³ used MNDO calculations to optimize the geometrical parameters of monomeric cyclopropanecarboxylic acid. These optimized geometries were then used in *ab initio* computations employing the 3-21G basis set. In this manner, the *syn-syn* conformer was found to be the more stable. The energy difference between *syn-syn* and *anti-syn* was calculated to be 3.41 kJ mol⁻¹.³ Very incomplete results of a microwave (MW) study of the title compound have been reported, and it was concluded that the *syn-syn* form had been assigned.⁴ Owing to the rather conflicting results obtained in the IR¹ study on the one hand, and the theoretical³ and incomplete MW⁴ on the other, it was decided to carry through a new, combined MW, electron-diffraction (ED) and *ab initio* study of cyclopropanecarboxylic acid.

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Experimental

Microwave experiment. The sample used in this work was purchased from Fluka A. G., Buchs, Switzerland. The sample, which was stated to be more than 98 % pure, was used as received. The MW spectrum was studied in the 26.5–38.0 GHz spectral region at room temperature. The pressure was about 1 Pa during the recording of the spectra. The spectrometer is an improved version of the one described briefly in Ref. 5, employing klystrons as radiation sources. The radiofrequency – microwave frequency double-resonance technique (RFMWDR) was used as described in Ref. 6, employing the equipment mentioned in Ref. 7.

Electron-diffraction experiment. The ED data were recorded on a Balzer Eldigraph KD-G2 apparatus⁸ using Kodak Electron Image photographic plates. The experiment was carried out using nozzle-to-plate distances of 498.50 and 248.93 mm, respectively. The nozzle temperatures were approximately 52 °C for the long camera distance and 48 °C for the middle camera distance. The electron wavelength was 5.978 pm in all experiments. Six plates for both camera distances were used in the structure analysis. The optical density (*D*) was recorded on the Snoopy densitometer and processed in the usual way employing a blackness correction of $1 + 0.03D + 0.09D^2 + 0.03D^3$ (Ref. 9). The molecular scattering intensities were modified⁹ with $s/|f_e|/|f_o|$, and the backgrounds were subtracted from the modified form utilizing polynomials of the ninth degree for both camera distances. The intensity data used in the background subtraction cover the $25.00 \leq s \leq 145.00 \text{ nm}^{-1}$ range with data intervals $\Delta s = 1.25 \text{ nm}^{-1}$ for the long camera distance, and $45.00 \leq s \leq 280.00 \text{ nm}^{-1}$ for the

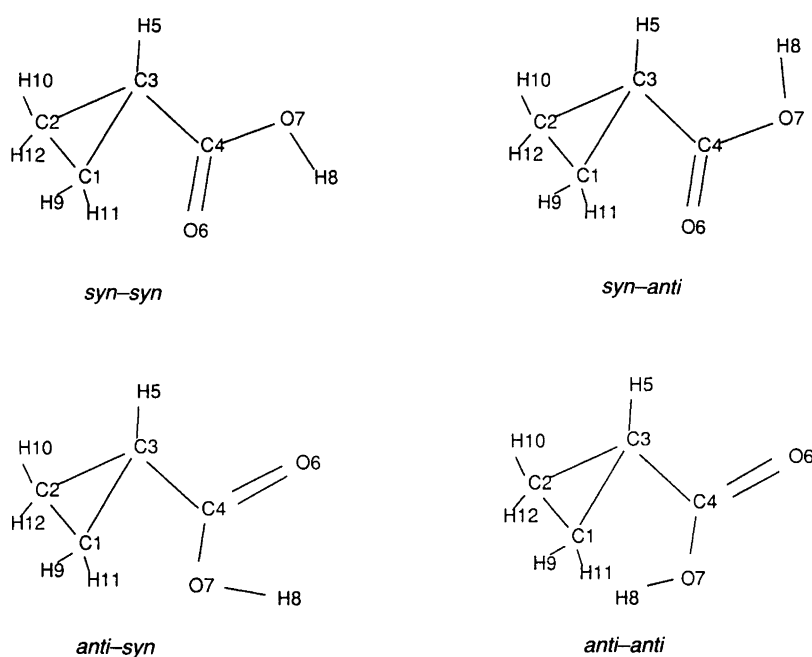


Fig. 1. Four conformations of cyclopropanecarboxylic acid. Atom numbering is indicated.

middle camera distance with data intervals $\Delta s = 2.50 \text{ nm}^{-1}$. The elastic scattering factors were calculated by the partial wave method¹⁰ based on analytical Hartree-Fock potentials in the case of carbon and oxygen.¹¹ For hydrogen, the electron density for bonded hydrogen was used.¹² The inelastic scattering factors were those of Tevard *et al.*¹³

Method of calculation. The *ab initio* quantum-chemical computations were performed using the GAMESS program package.¹⁴ The program utilized in the present calculations is a revised version prepared by M. W. Schmidt of North Dakota State University and S. Ebert of Iowa State University. The program was slightly modified to run on a Prime 750 computer. The 4-21G basis set¹⁵ was used. This basis set was chosen because it is economical and is presumed to describe the conformational and structural properties of the title compound rather well. In addition, an empirical relationship between the bond distances obtained using this basis and the r_g distances has been worked out.¹⁶ The complete equilibrium geometries for the four selected conformations shown in Fig. 1 were optimized by calculating the analytical energy gradients. The potential function for rotation around the C3-C4 bond was calculated by optimizing all structure parameters for each fixed torsional angle from 0 to 180° in steps of 30°.

Results

Theoretical computations. Not unexpectedly, the *syn-syn* and *anti-syn* (Fig. 1) come out as the low-energy forms of cyclopropanecarboxylic acid, with *syn-syn* predicted to be 2.0 kJ mol⁻¹ more stable. The total energy of *syn-syn* was calculated to be -303.977036 hartree. The *syn-anti* and *anti-anti* are predicted to be rather high-energy forms of the

molecule. These *ab initio* computations find them to be 34.0 and 49.4 kJ mol⁻¹, respectively, less stable than *syn-syn*. These predictions parallel those of Huang and Pan,³ but are in conflict with the conclusion of Tabacik and Maillois that *anti-anti* is the preferred form of cyclopropanecarboxylic acid.¹

The computed potential function for rotation around the C3-C4 bond is shown in Fig. 2, together with the experimental potential function obtained from the present ED work (see below). The present theoretical computations find the maximum to be approximately 33 kJ mol⁻¹ above the *syn-syn* minimum-energy conformation. The optimized structure of *syn-syn* is shown later in Table 8, together with the experimentally determined structures obtained using a static as well as a dynamic model. Moreover, it was found in the computations that several of the structural parameters varied with the torsion around the C3-C4 bond. The variations of some selected parameters are summarized in Table 1.

Microwave spectrum and assignment of the ground vibrational state. Survey spectra revealed a relatively weak and very dense MW spectrum for cyclopropanecarboxylic acid. The strongest lines of the spectrum have peak absorption coefficients of roughly $2.5 \times 10^{-7} \text{ cm}^{-1}$ at room temperature. It turned out that these transitions are the high-*J* *b*-type *Q*-branch transitions.

Based on the above theoretical computations and other accurate, structural studies of carboxylic acids¹⁷ it was presumed that the *syn-syn* and *anti-syn* rotamers of Fig. 1 were the two most probable low-energy forms of cyclopropanecarboxylic acid. A preliminary set of rotational constants was predicted for both the *syn-syn* and *anti-syn* conformers using a preliminary set of structural parameters

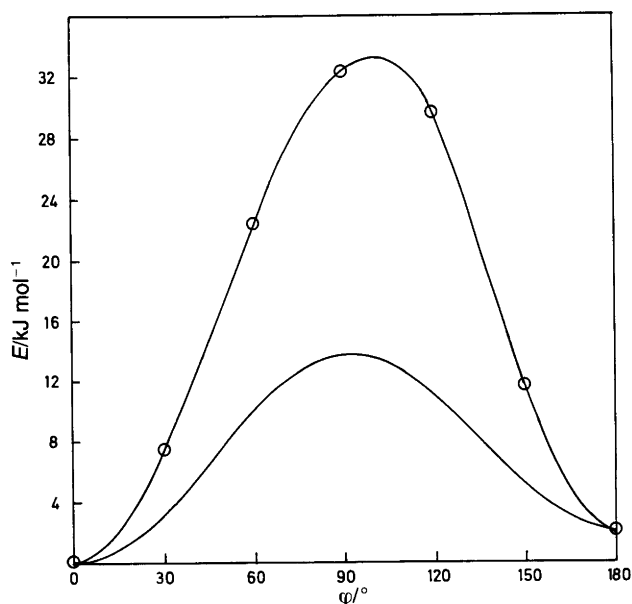


Fig. 2. Potential energy function for torsion about the C3–C4 bond calculated by *ab initio* methods (upper graph) and determined from the dynamic model discussed in the text (lower graph).

which were rather close to those shown later in Table 8. The dipole moment component (in units of 10^{-30} C m) were predicted using the bond-moment method¹⁸ in addition to the *ab initio* computations. The results obtained using the bond-moment method for *syn-syn* were $\mu_a = 0.6$, $\mu_b = 4.4$ and $\mu_c = 0.0$ (for symmetry reasons), respectively. The same three components were computed by the *ab initio* method to be 2.1, 4.6 and 0.0, respectively. The bond-moment predictions for *anti-syn* read $\mu_a = 3.1$, $\mu_b = 3.1$ and $\mu_c = 0.0$ (for symmetry reasons), respectively, compared to 6.0, 3.9 and 0.0, respectively, obtained using the *ab initio* method.

Searches were first made for the high-*J* *b*-type *Q*-branch transitions of *syn-syn*. These lines were soon identified. The strongest low-*J* *b**R*-transitions were found next. The assignments were then gradually extended to include the rather weak high-*J* *b*-type *P*- and *R*-branch transitions. The

Table 1. Variation of important structural parameters^a as a function of rotation around the C3–C4 bond.

Dihedral angle ^b /°	0	30	60	90	120	150	180
<i>r</i> (C1–C2)	149.6	150.0	151.0	151.6	151.1	150.1	149.7
<i>r</i> (C1–C3)	152.3	152.6	151.7	150.4	150.4	151.4	152.2
<i>r</i> (C2–C3)	152.3	151.2	150.5	150.7	151.8	152.4	152.2
\angle C1C3C4	115.3	116.4	118.1	118.4	119.5	119.3	118.1
\angle C2C3C4	115.3	115.7	116.8	117.5	117.9	116.9	118.1
\angle C3C4O6	125.8	126.5	127.1	126.9	126.0	126.3	126.6
\angle C3C4O7	112.2	111.6	111.0	111.4	112.7	112.2	111.9

^aBond distances in pm; angles in degrees. ^b0° corresponds to *syn-syn*; 180° corresponds to *anti-syn*.

Table 2. Selected transitions of the ground-state MW spectrum of the *syn-syn* conformer of cyclopropanecarboxylic acid.

Transition	Obs. freq./MHz	Obs. – calc. freq./MHz	Centrifugal dist./MHz	
			Total	Sextic
a-Type				
6 _{1,5} ← 5 _{1,4}	31513.89	0.00	–0.47	
6 _{1,6} ← 5 _{1,5}	29488.01	–0.04	–0.62	
6 _{2,4} ← 5 _{2,3}	31125.62	–0.05	–0.41	
6 _{2,5} ← 5 _{2,4}	30562.23	–0.04	–0.68	
7 _{1,6} ← 6 _{1,5}	36683.19	–0.02	–0.81	
7 _{1,7} ← 6 _{1,6}	34352.01	–0.06	–0.91	
7 _{2,5} ← 6 _{2,4}	36464.18	0.00	–0.66	
7 _{3,4} ← 6 _{3,3}	35926.22	–0.02	–0.95	
7 _{3,5} ← 6 _{3,4}	35858.40	0.02	–1.05	
7 _{5,2} ← 6 _{5,1}	35807.88	–0.03	–1.47	
7 _{5,3} ← 6 _{5,2}	35807.88	–0.01	–1.47	
b-Type				
7 _{4,3} ← 7 _{3,4}	35295.40	0.00	–0.98	
9 _{3,7} ← 9 _{2,8}	26751.69	–0.05	–0.17	
11 _{2,10} ← 11 _{1,11}	26986.38	–0.03	–2.35	
14 _{1,13} ← 14 _{0,14}	30929.87	0.05	–5.70	
17 _{4,13} ← 17 _{3,14}	27817.90	–0.06	–5.82	
20 _{3,17} ← 20 _{2,18}	26825.36	0.00	13.52	
23 _{5,18} ← 23 _{4,19}	34604.78	–0.05	–15.29	
26 _{5,21} ← 26 _{4,22}	31571.17	0.05	–1.91	
29 _{5,24} ← 29 _{4,25}	32637.78	–0.04	28.04	
32 _{6,26} ← 32 _{5,27}	37484.93	0.09	–7.33	
34 _{6,28} ← 34 _{5,29}	37386.46	–0.02	27.17	
3 _{2,2} ← 2 _{1,1}	30020.86	–0.10	–0.23	
6 _{1,6} ← 5 _{0,5}	32466.85	–0.04	–0.86	
9 _{1,8} ← 8 _{2,7}	37340.42	0.13	–0.66	
12 _{3,9} ← 11 _{4,8}	28451.93	–0.12	–0.44	0.01
15 _{4,11} ← 14 _{5,10}	33041.29	0.03	–2.68	0.02
18 _{6,13} ← 17 _{7,10}	27077.68	0.05	–7.31	0.05
20 _{7,14} ← 19 _{8,11}	27154.43	0.03	–9.86	0.09
20 _{7,13} ← 19 _{8,12}	27157.63	0.01	–9.81	0.09
Coalescing b-type transitions^b				
22 ₁₅ ← 23 ₁₄	29197.82	0.05	12.11	–0.18
25 ₁₇ ← 26 ₁₆	34118.51	0.18	17.66	–0.34
26 ₁₇ ← 27 ₁₆	28964.21	0.06	20.17	–0.41
29 ₁₉ ← 30 ₁₈	33887.45	0.06	27.90	–0.69
32 ₂₀ ← 33 ₁₉	28614.77	–0.03	38.19	–1.12
35 ₂₂ ← 36 ₂₁	33542.87	–0.02	50.01	–1.37
38 ₂₃ ← 39 ₂₂	28269.62	–0.14	65.07	–2.58
43 ₂₆ ← 44 ₂₅	33092.07	0.13	95.37	–4.71
49 ₂₉ ← 50 ₂₈	32763.31	–0.04	144.32	–8.39
24 ₉ ← 23 ₁₀	27335.35	0.04	–16.79	0.23
28 ₁₀ ← 27 ₁₁	37974.56	0.07	–27.37	0.49
32 ₁₃ ← 31 ₁₄	27756.14	0.05	–39.16	0.96
36 ₁₅ ← 35 ₁₆	27975.98	–0.02	–55.55	1.73
40 ₁₇ ← 39 ₁₈	28196.74	–0.05	–76.10	2.93
44 ₁₉ ← 43 ₂₀	28416.51	0.06	–101.37	4.71
48 ₂₁ ← 47 ₂₂	28633.63	0.00	–131.93	7.28
52 ₂₃ ← 51 ₂₄	28847.39	0.06	–168.43	10.86
55 ₂₄ ← 54 ₂₅	34159.17	–0.13	–200.58	14.37
59 ₂₆ ← 58 ₂₇	34362.54	–0.03	–248.87	20.42
62 ₂₈ ← 61 ₂₉	29361.50	0.14	–290.11	26.17
65 ₂₉ ← 64 ₃₀	34657.83	–0.09	–336.15	33.14
69 ₃₁ ← 68 ₃₂	34847.58	0.05	–405.41	44.67

^a±0.10 MHz. ^bThe K_{-1} -energy doublets coalesce for high values of K_{-1} . Subscripts on the *J* quantum number refer to K_{-1} .

Table 3. Spectroscopic constants^{a,b} for the *syn-syn* conformer of cyclopropanecarboxylic acid in the ground vibrational state.

Species	Parent	Deuterated
No. of transitions	210	56
R.m.s. dev./MHz	0.078	0.063
A_0 /MHz	7625.0001(27)	7619.8344(38)
B_0 /MHz	2724.75298(96)	2629.4620(22)
C_0 /MHz	2382.06299(84)	2308.5222(21)
Δ_J /kHz	0.37938(70)	0.37938 ^c
Δ_{JK} /kHz	3.178(10)	3.094(11)
Δ_{KJ} /kHz	-0.5827(19)	-0.5827 ^c
δ_J /kHz	0.04581(51)	0.04042(50)
δ_K /kHz	-11.317(25)	-11.892(25)
φ_J ^d /Hz	0.004760(25)	0.0 ^c
$(I_a + I_b - I_c)/10^{-20} \text{ m}^2 \text{ u}$	39.595758(48)	39.603706(71)

^aUncertainties represent one standard deviation. ^bA-reduction, *I*-representation.¹⁹ ^cHeld fixed at this value in least-squares fit; see text. ^dFurther sextic centrifugal distortion constants preset at zero. ^eConversion factor $505376 \times 10^{-20} \text{ MHz m}^2 \text{ u}$.

maximum value for *J* was 69 for the *R*-branch lines and 50 for the *P*-branch transitions. The frequencies of the very weak low-*J* *R*-branch *a*-type transitions could now be predicted very accurately. They were identified using ordinary Stark effect spectroscopy, or the RFMWDR technique.⁷ A total of about 230 transitions were ultimately assigned for the ground vibrational state; a portion of which are shown in Table 2. 210 of these transitions were used to determine the spectroscopic constants (*A*-reduction, *I*-representation)¹⁹ shown in Table 3.* Inclusion of one sextic centrifugal distortion constant had to be made in order to get the best fit. It is seen in Table 3 that the value of $I_a + I_b + I_c = 39.595758(48) \times 10^{-20} \text{ m}^2 \text{ u}$, which is typical for cyclopro-

* The complete spectra are available from the authors upon request, or from the Molecular Spectra Data Center, Bldg. 221, Room B 268, National Institute of Standards and Technology, Gaithersburg, MA 20899, USA, where they have been deposited.

Table 4. Spectroscopic constants^{a,b} of the *syn-syn* conformer of cyclopropanecarboxylic acid in vibrationally excited states of the C1-C2 torsional vibration.

Excited state	First	Second	Third	Fourth
No. of transitions	117	54	42	31
R.m.s. dev./MHz	0.065	0.071	0.076	0.119
A_v /MHz	7597.9444(35)	7572.0765(48)	7547.2952(62)	7523.561(11)
B_v /MHz	2725.7145(12)	2726.5714(26)	2727.3151(28)	2727.9538(61)
C_v /MHz	2385.3840(10)	2388.6003(25)	2391.7122(27)	2394.7326(60)
Δ_J /kHz	0.3845(13)	0.3794 ^c	0.3794 ^c	0.3794 ^c
Δ_{JK} /kHz	3.087(11)	3.072(15)	3.045(19)	3.132(33)
Δ_{KJ} /kHz	-0.447(15)	-0.5827 ^c	-0.5827 ^c	-0.5827 ^c
δ_J /kHz	0.04375(52)	0.04427(67)	0.04478(84)	0.0482(14)
δ_K /kHz	-11.972(25)	-12.763(33)	-13.553(42)	-14.512(71)
φ_J ^d /Hz	0.005092(87)	0.0	0.0	0.0
$(I_a + I_b - I_c)$ ^e	40.061722(52)	40.515959(83)	40.95985(11)	41.39421(19)

^{a-e}Comments as for Table 3.

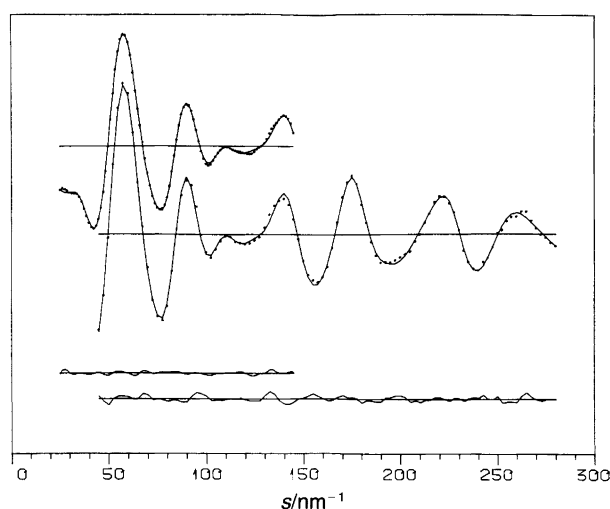


Fig. 3. Experimental (dots) and theoretical (full line) intensity curves for cyclopropanecarboxylic acid, and the corresponding difference curves.

pane derivatives that possess a symmetry plane of the kind found for the *syn-syn* conformer.⁴

Unfortunately, the dipole moment could not be determined because the low-*J* transitions generally used for this purpose were too weak to allow quantitative measurements to be made.

Vibrationally excited states. The ground-state transitions were accompanied by a rich satellite spectrum, presumably belonging to vibrationally excited states of *syn-syn*. Six such states were assigned, as shown in Tables 4 and 5. The strongest of these satellite spectra had approximately 67% of the intensity of the ground-state spectrum at room temperature. About 130 transitions were measured for this spectrum, 117 of which were used to determine the spectroscopic constants shown in Table 4. The maximum value of *J* was 52 in this case. Only the relatively weak high-*J* *b*-type *R*-branch transitions were assigned. None of the even

Table 5. Spectroscopic constants^{a,b} for the *syn-syn* conformer of cyclopropanecarboxylic acid in vibrationally excited bending states.

Vib. exc. state	Lowest bend	Second lowest bend
No. of transitions	40	26
R.m.s. dev./MHz	0.085	0.121
<hr/>		
A_v /MHz	7637.8806(79)	7625.325(17)
B_v /MHz	2725.6348(47)	2724.9911(73)
C_v /MHz	2382.6952(46)	2381.8640(71)
Δ_J /kHz	0.3794 ^c	0.3794 ^c
Δ_{JK} /kHz	3.085(23)	2.962(46)
Δ_K /kHz	-0.5827 ^c	-0.5827 ^c
δ_J /kHz	0.05024(92)	0.0380(19)
δ_K /kHz	-10.937(46)	-10.958(86)
$(I_a + I_b - I_c)^d/10^{-20} \text{ m}^2 \text{ u}$	39.48027(12)	39.55900(29)

^{a-c}Comments as for Table 3. ^dSame conversion factor as used in Table 3.

weaker high- J P -type transitions could be identified with certainty.

Relative intensity measurements made largely as described in Ref. 20 yielded $82(15) \text{ cm}^{-1}$ for this vibration, which is assumed to be the first excited state of the torsion around the C3–C4 bond. This value is rather close to $63.3(4) \text{ cm}^{-1}$ found for the corresponding vibration in the isoelectronic *syn* conformer of cyclopropanecarboxylic acid fluoride.²¹ It is seen from Tables 2 and 3 that $I_a + I_b - I_c$ increases by $0.465964 \cdot 10^{-20} \text{ m}^2 \text{ u}$, slightly less than the $0.4808 \cdot 10^{-20} \text{ m}^2 \text{ u}$ found in cyclopropanecarboxylic acid fluoride.²¹ The slight increase seen in the latter molecule may reflect the fact that the C3–C4 torsional vibration is lower in the fluoride [$63.3(4) \text{ cm}^{-1}$]²¹ than in the acid [$82(15) \text{ cm}^{-1}$]. Tabacik and Maillols¹ calculated this frequency to be 98.1 cm^{-1} .

Three more successively excited states of the C3–C4 torsional vibration were also assigned, as shown in Table 4. It is seen from Tables 3 and 4 that the rotational constants change rather linearly upon excitation of the torsional mode. This is characteristic of a harmonic vibration.²² In these three cases, as well as for the two other vibrationally excited states shown in Table 5, the spectroscopic constants were determined from low- J b -type R -branch transitions and bQ -branch lines with maximum value of $J = 35$ in most cases. Accurate values for the Δ_J and the Δ_K centrifugal distortion constants could not be determined from these transitions. Δ_J and Δ_K were therefore preset to the values found for the ground state (Table 3) in the final fits.

Table 5 lists the spectroscopic constants of two additional excited states, which are believed to be the first excited states of the two lowest bending vibrations. The reason for assigning these two excited states as bending vibrations is that the value of $I_a + I_b - I_c$ decreases upon excitation,²² as can be seen from Tables 3 and 5. Relative intensity measurements yielded a frequency of $183(30) \text{ cm}^{-1}$ for the lowest bending vibration and $209(40) \text{ cm}^{-1}$ for the second lowest bending vibration. Tabacik and Maillols¹ calculated

these two frequencies to appear at 217.7 and 268.3 cm^{-1} , respectively.

Structure determination. The rotational constants of the ground vibrational state (Table 3) were used in a modified form (described below), together with the ED intensity data, to determine the geometrical structure of cyclopropanecarboxylic acid in the following manner. The *syn-syn* conformer was assumed to have C_s symmetry, in accordance with the MW results above. The molecular geometry (Fig. 1) was described by twenty independent parameters: $r(\text{C1-C2})$, $\Delta[r(\text{C1-C3}) - r(\text{C1-C2})]$, $\Delta[r(\text{C3-C4}) - r(\text{C1-C2})]$, $r(\text{C3-H5})$, $\Delta[r(\text{C1-H9}) - r(\text{C3-H5})]$, $\Delta[r(\text{C1-H11}) - r(\text{C3-H5})]$, $r(\text{C4-O6})$, $r(\text{C4-O7})$, $r(\text{O7-H8})$, $\angle\text{C1C3C4}$, $\angle\text{C3C1H9}$, $\Delta(\angle\text{C3C1H11} - \angle\text{C3C1H9})$, $\Delta(\angle\text{C2C1H9} - \angle\text{C3C1H9})$, $\Delta(\angle\text{C2C1H11} - \angle\text{C3C1H9})$, $\angle\text{C3C4O6}$, $\angle\text{C3C4O7}$, $\angle\text{C4C3H5}$, $\angle\text{C4O7H8}$, $\tau(\text{O6C4O7H8})$ and $\tau(\text{H5C3C4O6})$. The torsional angle $\tau(\text{O6C4O7H8})$ is equal to 0° when O6–C4 bond is *syn* to the O7–H8 bond. $\tau(\text{H5C3C4O6})$ is equal to 0° when the C3–H5 bond is *syn* to the C4–O7 bond.

It was found in the course of the analysis that insufficient experimental data were available to allow independent determination of the structure the two methylene groups. It was therefore assumed that the differences between some of the parameters are equal to the differences computed above by the *ab initio* method; *i.e.* $\Delta[r(\text{C1-H9}) - r(\text{C3-H5})] = 0.41 \text{ pm}$, $\Delta[r(\text{C1-H11}) - r(\text{C3-H5})] = 0.41 \text{ pm}$, $\Delta(\angle\text{C3C1H11} - \angle\text{C3C1H9}) = -0.98^\circ$, $\Delta(\angle\text{C2C1H9} - \angle\text{C3C1H9}) = 1.69^\circ$ and $\Delta(\angle\text{C2C1H11} - \angle\text{C3C1H9}) = 0.50^\circ$.

As mentioned above, and also shown in Table 8, the *ab initio* results indicate that some of the structural parameters change somewhat with the torsional angle. Allowance for

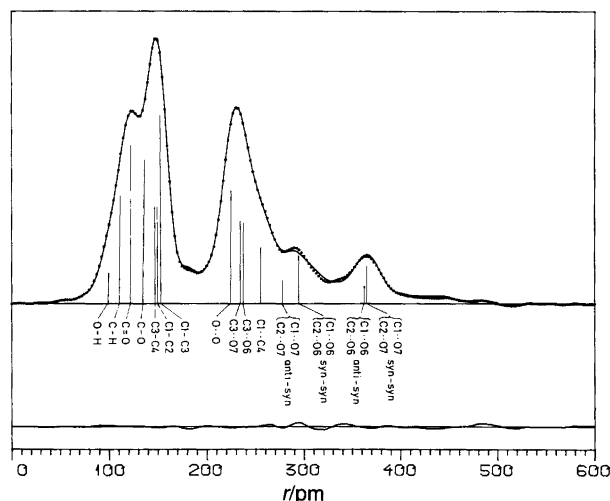


Fig. 4. Experimental (dots) and theoretical (full line) radial distribution functions with an artificial damping constants $B = 2.5 \text{ pm}^2$. The position and approximate area (length of the bar) of the peaks corresponding to the most important distances are shown, together with the difference curve. Theoretical intensities have been used below $s = 25.00 \text{ nm}^{-1}$.

Table 6. Zero-point rotational constants.^a

	$\Delta\beta_{\text{vib}}$	β_z^b/MHz	β_z^c/MHz
Parent molecule			
A	8.472	7633.47(169) ^d	7633.83(200) ^e
B	-0.917	2723.84(18)	2723.98(25)
C	-0.827	2381.24(17)	2381.32(23)
O-D isotopomer			
A	8.828	7628.66(176)	7629.35(202)
B	-0.766	2628.70(15)	2628.61(22)
C	-0.760	2307.76(15)	2307.69(21)

^aSee text. ^bCalculated from β_0 rotational constants shown in Table 3 in the manner described in the text. ^cCalculated from r_{α} -structure. This structure was derived from the r_g -structure in Table 8 using the relationship between r_g and r_{α} given in the text. ^dUncertainties estimated as 20 % of the $\Delta\beta_{\text{vib}}$ correction. ^eUncertainties are two standard deviations from least-squares refinements using a diagonal weight matrix.

such a variation is not incorporated in the structure analysis. The structure derived from the combined MW and ED analysis therefore must be considered as an average structure.

Both a static and a dynamic model have been used. The static model refined the composition of the *syn-syn* and *anti-syn* conformations. *Syn-syn* was found to make up 65 % and *anti-syn* 35 % at 323 K.

In the dynamic model, twelve rotamers were included

between 0° (*syn-syn*) and 180° (*anti-syn*) rotation about the C3–C4 bond. Each rotamer was weighted according to its population calculated from potential energy function (lower graph shown in Fig. 2) and the Boltzmann distribution law. The procedure employed is described in more detail elsewhere.²³ In the present case the potential function (V) was presumed to be adequately represented by

$$V(\varphi) = \frac{1}{2}V_1(1.0 - \cos \varphi) + \frac{1}{2}V_2(1.0 - \cos 2\varphi) \quad (1)$$

eqn. (1) for the dynamic model. φ is equal to 0° for *syn-syn* and 180° for *anti-syn*. V_1 and V_2 were fitted to the intensity data and found to be 2.1(9) and 13(2) kJ mol⁻¹, respectively. This translates into an energy difference between *syn-syn* and *anti-syn* of 2.1(9) kJ mol⁻¹, with *syn-syn* the more stable. This energy difference is the same as that found above (2 kJ mol⁻¹) by *ab initio* methods. However, the microwave data indicate a somewhat larger energy difference, and below arguments are given that 3 kJ mol⁻¹ is the minimum energy difference between *syn-syn* and *anti-syn*.

The root mean-square amplitudes of vibration, l , and the perpendicular correction coefficients, K , used in the analysis were calculated employing a normal coordinate program written by Hilderbrandt and Wieser.²⁴ The modified force field used in this work was based on force constants of related molecules^{25–29} and adjusted to fit the observed vibrational frequencies.¹ Framework values for l and K were used for the dynamic model, i.e. the contribution from the torsional motion about the C3–C4 bond was sub-

Table 7. The root mean-square amplitude of vibration, l , and perpendicular correction coefficient, K , at 323 and 0 K, respectively, for the parent species of cyclopropanecarboxylic acid for the *syn-syn* conformer.^a

Atom pair ^b	$l(323 \text{ K})/\text{pm}$		$l(0 \text{ K})/\text{pm}$ (Calc.)	$K(323 \text{ K})/\text{pm}$ (Calc.)	$K(0 \text{ K})/\text{pm}$ (Calc.)
	Calc.	Obs. ^c			
C1–C2	4.92	4.92	4.86	1.45	0.49
C1–C3	5.04	5.04	4.97	1.15	0.49
C3–C4	4.99	4.99	4.87	0.31	0.20
C4=O6	4.04	4.04	4.01	0.50	0.27
C4–O7	4.41	4.41	4.35	0.90	0.33
C1–H9	7.70	7.70	7.70	2.50	1.21
C1–H11	7.70	7.70	7.70	2.40	1.17
C3–H5	7.70	7.70	7.70	2.34	1.76
O7–H8	7.03	7.03	7.03	2.80	2.37
C1...C4	8.04	7.6(5)			
C3...O6	5.96	6.4			
C3...O7	6.34	6.8 (8)			
O6...O7	5.60	6.1			
C1...H5	10.71	10.71			
C1...H10	10.78	10.78			
C1...H12	10.72	10.72			
C3...H8	9.71	9.71			
C4...H5	10.37	10.37			
O6...H8	13.30	13.30			

^aOnly l and K values for torsion-independent distances are given. They are equal to the framework values. ^bSee Fig. 1 for numbering of atoms. ^cValues with uncertainties given were refined. The remaining l -values were fixed to the calculated values given in the previous column.

tracted. Separate framework values for l and K were calculated for all 12 conformations between $\varphi = 0$ and $\varphi = 180^\circ$.

The asymmetry parameters,³⁰ κ , for bonded atomic pairs were estimated from the diatomic approximation as $\kappa = a/l^2/6$, where a is the constant in the Morse potential, and are assumed to be 0.020 pm^{-1} for C–C, C–O and C=O bonds,³¹ and 0.026 pm^{-1} for C–H bonds.^{32,33} The asymmetry parameters for all non-bonded atom pairs were ignored. Correction for shrinkage was incorporated by refining a geometrically consistent r_α -structure.³⁴

The rotational constants were used in the analysis after transforming the ground vibrational state constants β_0 (where $\beta_0 = A_0, B_0$ or C_0) into the zero-point rotational constants β_z using eqn. (2),³⁴ where $\Delta\beta_{\text{vib}}$ is the harmonic

$$\beta_z \approx \beta_0 + \Delta\beta_{\text{vib}} \quad (2)$$

correction to the ground-state rotational constants. These corrections were calculated from the force field, employing the program of Hilderbrandt and Wieser.²⁴ The results are shown in Table 6.

The weights of the ED and MW data were chosen so that the standard deviation calculated from the r_α -structure (defined below) are approximately the same as the standard deviations of the β_z rotational constants, which are estimated to be 20% of $\Delta\beta_{\text{vib}}$.

The conversion from r_a to r_α is given by³⁴ eqn. (3), where

$$r_\alpha = r_g - 1.5a(l_T^2 - l_0^2) - K_0 \quad (3)$$

$r_g = r_a - l_T/r$ and l_T and l_0 are the root mean-square amplitudes of vibration at temperatures T and 0 K, respectively. The zero-point isotopic change in the C–H bond distance, defined by eqn. (4), was accounted for using eqn. (5),³⁴

$$\delta r_z = r_z(\text{C–D}) - r_z(\text{C–H}) \quad (4)$$

$$\delta r_z(\text{C–D}) = 1.5a[l_0^2(\text{C–D}) - l_0^2(\text{C–H})] - [K_0(\text{C–D}) - K_0(\text{C–H})] \quad (5)$$

which gives the same equilibrium geometry as when the equilibrium bond distance is estimated from the diatomic approximation as in eqn. (6). In Table 7 the root-mean-

$$r_c = r_\alpha + 1.5al^2 - K_0 \quad (6)$$

square amplitudes, l , and the perpendicular correction coefficients, K , are shown.

MW searches for anti-syn. The ED data and the *ab initio* results strongly imply that another high-energy conformer, the *anti-syn*, coexists with the *syn-syn*. A total of about 600 transitions were assigned for the *syn-syn* conformer. These include all the strongest lines of the spectrum, practically all lines of intermediate intensities and a large number of

weak absorptions. The Stark effects of the strongest of the unassigned transitions were investigated, and RFWDR studies⁶ were also made in attempts aimed at finding further conformations. In particular, the *anti-syn* conformation was looked for. The rotational constants for this form were predicted to be approximately $A = 7.47, B = 2.86$ and $C = 2.47 \text{ GHz}$, with sizable components of the dipole moment along the a and b inertial axes, as predicted above using both the bond-moment method¹⁸ and *ab initio* computations. The high- K_{-1} lines of the a -type $J = 6 \leftarrow 5$ and $J = 7 \leftarrow 6$ transitions should be easy to identify using the RFWDR technique.⁶ This search was made, however, with a negative result. It is thus concluded that the *syn-syn* conformer is more stable than any other rotameric form of cyclopropanecarboxylic acid by at least 3 kJ mol^{-1} . In the ED refinement the energy difference was found to be $2.1(9) \text{ kJ mol}^{-1}$. The MW data strongly indicate that 3 kJ mol^{-1} is the minimum energy difference between *syn-syn* and *anti-syn*. It is suggested that the latter conformer is $3\text{--}5 \text{ kJ mol}^{-1}$ less stable than *syn-syn*.

Table 8. Structure of cyclopropanecarboxylic acid.^a

	Static model, ^b $r_g, \angle_\alpha(\text{ED+MW})$	Dynamic model, ^c <i>Ab initio</i> , $r_g, \angle_\alpha(\text{ED+MW})$	r	r_e ^d
Bond distances/pm				
C1–C2	149.7(6)	149.3(7)	149.6	149.2
C1–C3	152.2(3)	152.4(3)	152.3	151.9
C3–C4	147.5(4)	147.8(5)	146.6	147.3
C4=O6	121.4(2)	121.4(2)	120.9	121.9
C4–O7	134.9(3)	134.9(3)	135.8	135.2
C1–H9	110.3] ^e	110.4] ^e	107.1	108.6
C1–H11	110.3](4)	110.4](4)	107.1	108.6
C3–H5	109.9]	110.0]	106.7	108.0
O7–H8	98.5(11)	98.2(12)	96.9	
Bond angles/°				
C1C3C4	116.8(3)	116.6(3)	115.3	
C3C4O6	124.7(4)	124.1(6)	125.8	
C3C4O7	112.5(3)	112.6(3)	112.5	
C3C1H9	116.4] ^e	117.0] ^e	116.9	
C3C1H11	115.4]	116.0]	115.9	
C2C1H9	118.1](9)	118.7](10)	118.6	
C2C1H11	116.9]	117.5]	117.4	
C4C3H5	115.6]	115.6]	115.6	
C4O7H8	105.4(8)	105.4(12)	111.3	
R factor ^f				
R2(LC)	3.41	3.20		
R2(MC)	6.47	6.49		

^aUncertainties are 2σ from least-squares refinements using a diagonal weight matrix. ^b65(5)% *syn-syn* and 35(5)% *anti-syn*. ^c $V_1 = 2.1(9) \text{ kJ mol}^{-1}$ and $V_2 = 13(2) \text{ kJ mol}^{-1}$. ^dEstimated using eqn. (6). ^eCould not be refined and selected differences (see text) were therefore fixed to the values obtained in the *ab initio* computations. ^fDefined in Ref. 9.

Discussion

The present investigation shows beyond doubt that the most stable conformer is the *syn-syn*, contrary to the suggestion of Ref. 1 that *anti-anti* is the preferred rotameric form. Undoubtedly, another conformer in addition to *syn-syn* is present. This is the *anti-syn*, which is 3–5 kJ mol⁻¹ less stable than *syn-syn*.

The preferred form of cyclopropanecarboxylic acid has the carbonyl group in the *syn* position. This is also the case with cyclopropanecarboxaldehyde,³⁵ cyclopropyl methyl ketone,³⁶ and cyclopropanecarboxylic acid fluoride³⁷ and chloride.^{35a} One reason for this conformational choice is presumably a stabilization effect caused by interaction of the carbonyl group electrons with the cyclopropyl group electrons. Steric effects might also be important in some of these molecules.

A notable feature of the structure of cyclopropanecarboxylic acid is the fact that the C1–C2 bond length is slightly shorter (2.5 pm) than the C1–C3 bond length (Table 8). This finding is reproduced in the *ab initio* calculations also shown in Table 8. It has been pointed out that unsaturated substituents have such an effect on the cyclopropyl ring.^{4a} In Table 9 experimental results for

Table 9. Selected structural parameters for cyclopropyl derivatives.

Compound	Type of distance	Bond distances/pm	
		C1–C2	C1–C3
Cyclopropyl cyanide ³⁸	r_s	150.0(3)	152.9(5)
Isocyanocyclopropane ³⁹	r_s	151.3(5)	152.3(7)
Cyclopropylacetylene ^{38,40}	r_s	150.3(7)	152.5(6)
Vinylcyclopropane ^{41,a}	r_a	150.0	152.7(6)
Cyclopropylisothiocyanate ^{42,b}	r_a	151.5(3)	152.0(3)
Cyclopropyl bromide ⁴³	r_g	153.4(12)	150.1(6)
Cyclopropylamine ⁴⁴	r_0	148.6(8)	151.3(3)
Cyclopropane ⁴⁵	r_z	151.57(23)	151.57(23)
Cyclopropanecarboxylic acid ^c	r_g	149.3(6)	152.4(3)

^aTwo rotamers are present in this molecule. Results pertain to *syn*. ^bTwo rotamers are present in this molecule. Results pertain to *trans*. ^cThis work; dynamic model.

Table 10. Carboxylic group structural parameters.^{a,b}

	Cyclopropanecarboxylic acid (ED + MW)	Acetic acid	
		MW ⁴⁶ (r_s)	ED ⁴⁷ (r_a)
C3–C4	147.8(5)	150.3(5)	151.7(15)
C4=O6	121.4(3)	120.5(4)	121.2(9)
C4–O7	134.9(3)	135.2(4)	136.1(9)
∠C3C4O6	124.1(6)	125.4(4)	126.6(18)
∠C3C4O7	112.1(4)	111.7(3)	110.6(2)

^aThis work, dynamic model. ^bBond lengths in pm; angles in degrees.

several cyclopropyl derivatives with electronegative or unsaturated substituents are collected. It is noted that there are no really great differences between the cyclopropyl bond lengths in these compounds. The comparatively small difference between C1–C2 and C1–C3 bond lengths (2.5 pm) found for the title molecule is rather typical.^{4a,48}

There is nothing unusual about the carboxyl group geometry of cyclopropanecarboxylic acid. The structure of this group is close to that of acetic acid (Table 10). The possible conjugation of the carboxyl group electrons into the cyclopropyl ring is thus seen to have practically no effect on the carboxyl group geometry.

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