# VIBRATIONAL SPECTRA IN CYCLOPROPANE SERIES II. SYMMETRY AND CONFORMATION IN THE GAS PHASE OF THE MONOMER AND DIMER OF CYCLOPROPANECARBOXYLIC ACID\*

### JACQUES MAILLOLS

Laboratoire de Physique Industrielle Pharmaceutique, Faculté de Pharmacie, Montpellier (France)

#### VLADO TABACIK

Laboratoire de Synthèse et d'Etude Physicochimique d'Hétérocycles Azotés, Université des Sciences et Techniques du Languedoc, Montpellier (France)

and

#### SERGE SPORTOUCH

Laboratoire de Spectroscopie Moléculaire, Université des Sciences et Techniques du Languedoc, Montpellier (France)

#### ABSTRACT

Infrared and Raman spectra of gaseous cyclopropanecarboxylic acid ( $C_3H_5COOH$  and  $C_3H_5COOD$ ) were measured from 250 to 4000 cm<sup>-1</sup>. The bands were assigned respectively to the monomer and to an associate. The depolarization ratio measurement, the vib—rot envelope study and the detailed analysis of the  $\nu(C=O)$  and  $\nu(CH)$  regions enabled the symmetry and the conformation of the molecular entities in equilibrium to be determined. The monomer belongs to the  $C_s$  symmetry group and the conformation of its predominant fraction is *trans/trans*. The associate is a centrosymmetrical dimer ( $C_i$  symmetry) having (*trans/cis*)<sub>2</sub> conformation. Some features of the geometry of the pseudocycle are discussed.

### INTRODUCTION

Extending our structural studies of the carboxylic acids, we have lately taken an interest in the cyclanic series. Particularly, we have been able to show that in the liquid state, the molecules of the cyclobutanecarboxylic [1] and cyclopropanecarboxylic [2] acids existed essentially as  $C_i$  (and not  $C_{2h}$ ) dimers. It seemed interesting to try to reach the monomer by means of vibrational spectroscopy (IR and Raman) in the gas phase. Therefore, we chose the cyclopropanecarboxylic acid  $C_3H_5$ —COOH ( $d_0$ -) and its deuterated species  $C_3H_5$ —COOD ( $d_1$ -). Some preliminary results were recently published [3]. The conformational aspect of this molecule was examined by means of an a priori calculation of the NMR spectra [4]. Unfortunately the

<sup>\*</sup>The principal results of this study were presented at the meeting of the Mediterranean Section of the Societé de Chimie Physique in Barcelona (Spain), May 1975.

calculated spectra for the three conformations considered differ appreciably from the observed spectrum, thus preventing the formal determination of the conformation.

The study of this compound was interesting for several reasons: on the one hand the molecule is pharmacologically active. Particularly the hypoglycaemic action of this acid and of its sodium salt have been demonstrated, and their effects on lipid metabolism have recently been proved [5-7]. On the other hand, the fundamental problem that preoccupies the physical chemist is the degradation of the cyclopropane symmetry due to the "substitution", formally speaking, of a -COOH group for a hydrogen atom. Indeed the symmetry group (to be determined) of the acid will contain only one  $(C_1)$  or two  $(C_s)$  symmetry operations whereas there were twelve in the symmetry group  $(D_{3h})$  of cyclopropane.

A preliminary examination of both infra-red and Raman spectra in the gas phase revealed that the monomer could not be completely isolated and remained in equilibrium with associates, even at high temperatures and under low pressure. Therefore the study of the gas phase implies the simultaneous examination of the monomer and of the associates in equilibrium. The shift of the equilibrium by modifying the experimental conditions (p, T) enables us to distinguish the bands of the monomer and those of the associates. We will limit this paper to the study of the symmetry and conformation of the principal molecular species in the gas phase. These results will be used later in the assignment of the bands to the fundamentals, particularly in the a priori calculation of the frequencies [8]. Let us note that if such a calculation is a useful tool for the assignment, it is inefficient in conformational analysis. Hydrocarbons are at present the only exception to this rule [9].

As several conformations are frequently compatible with the same symmetry, the symmetry problem will be solved first. The symmetry and the conformation of the associates cannot be elucidated without previously studying the monomer. We will therefore examine the monomer before the associates.

#### EXPERIMENTAL

## **Products**

Cyclopropanecarboxylic acid (commercial product: Union Carbide Belge, "purissimum") was purified by a vacuum distillation. At room temperature this product is a colourless liquid and its boiling point is 183 °C under 1 atmosphere pressure. Its deuterated homolog ( $d_1$ -) was prepared by us from the "light" species ( $d_0$ -); the acid plus D<sub>2</sub>O mixture was maintained for 2 h at 80 °C under reflux with N<sub>2</sub> bubbling through. D<sub>2</sub>O was then separated by vacuum distillation (D<sub>2</sub>O origin: C.E.A. 99.8 % of D, acid/D<sub>2</sub>O = 1/10). This operation was repeated three times. We have verified, by means of nuclear magnetic resonance, that the deuteration rate of the carboxylic group was higher than 99 %.

### Spectra

### Experimental conditions

The spectra were recorded at constant temperature ( $T = (90 \degree C, 180 \degree C)$ ) under pressures corresponding to those of saturated vapours (pressure lower or near to 760 Torr). At the highest temperatures, the sample underwent only a moderate pyrolysis producing small quantities of CO<sub>2</sub> and cyclopropane. Nevertheless, the only bands were detected in the IR spectra and belonged to CO<sub>2</sub> (at 667.8 and 2349.1 cm<sup>-1</sup> [10]). The Raman active Fermi-doublet (1388.2 and 1285.4 cm<sup>-1</sup> [11]) was not observed.

### Infra-red absorption

Perkin Elmer spectrophotometer model 225. The spectral slit widths used: 1 to 1.6 cm<sup>-1</sup> for  $\nu$ (OH), 0.8 to 1.3 cm<sup>-1</sup> for  $\nu$ (CH), 0.7 to 1.1 cm<sup>-1</sup> for  $\nu$ (C=O). The standard deviations of the absolute value of the wavenumbers have been indicated in the tables and depend on the shape of the band (± 1 cm<sup>-1</sup>). We used a laboratory built, heatable vacuum cell [12], optical path 9 cm, equipped with two KBr windows. The product was introduced into the previously evacuated cell.

### Raman scattering

We have used two spectrometers:

(a) Coderg PHO equipped with an argon ion laser Coherent Radiation model 52, providing power of 800 mW for the exciting line at 4880 Å. The spectral slit-widths used were 1 and 2 cm<sup>-1</sup>. The measurement of the degree of depolarisation was made by means of two crossed polaroid films. The vapour cell used [13] was that built in one of our laboratories.

(b) Spex 1401 equipped with a Coherent Radiation model 52 argon ion laser. The power available with the 4880 Å exciting line was 1.6 W. The scattered radiation was collected at 90° space angle and focused by a f/0.95 lens into the entrance slit of the monochromator after having passed through a polarisation scrambler. The f = 0.75 m Czerny—Turner monochromator employed two Bausch and Lomb gratings blazed at 5000 Å and used in the first order. The detector was a photon counting one in conjunction with an R.C.A. C 31034 phototube (linear display). The spectral slit-widths used were 2 and 4 cm<sup>-1</sup>. The spectra of d<sub>0</sub> - and d<sub>1</sub> - were recorded in an l = 1 cm cell and calibrated against the emission lines of neon [14].

## MONOMER

### Symmetry

## Degree of depolarization ( $\rho_{\rm p}$ )

The measurement of this quantity from the Raman bands is essential for obtaining the symmetry of the molecules studied. Excepting for a total lack of symmetry ( $C_1$  group: in such a case all the bands are more or less polarized), the detection of some depolarized bands unambiguously belonging to the monomer implies the  $C_s$  group.

It was possible to identify eight depolarized ( $\rho_p = 3/4 \pm 15$ %) Raman bands in the spectra of the two isotopic species: 3115, 915, 820 and 266 cm<sup>-1</sup> for d<sub>0</sub> - and 3115, 914, 820 and 272 cm<sup>-1</sup> for d<sub>1</sub> - species. This result is in favour of the C<sub>s</sub> symmetry for the monomer.

#### Selection rules

Taking into account the uncertainty of the measurement of  $\rho_p$ , it seemed useful to consider whether the  $C_s$  group selection rules were verified. In order to do this we chose the  $\nu$  (CH) stretching region.

The Raman spectra showed three bands situated at 3038, 3086 and 3115  $cm^{-1}$ , the last of these being the only depolarized one.

In the infra-red spectra we found only two bands situated at 3110 and  $3027 \text{ cm}^{-1}$ . The former presents a typical *B* envelope discernable at high temperatures. The later is the more intense and has a characteristic *C*-type envelope: this is the lowest frequency band in the v (CH) region.

Thus the set of spectra (IR absorption and Raman scattering) includes five bands, three having the characteristics of the a' vibrations and two those of the a'' vibrations. They will be assigned to the five expected  $\nu$ (CH) fundamentals (3  $a' + 2 \bar{a}''$ ) according to the  $C_s$  symmetry of the monomer. Correlation of these spectra with those of cyclopropane ( $D_{3h}$ symmetry), in which the six  $\nu(CH)$  modes are distributed into four classes (see Table 1), enables us to confirm this assignment and thereby our conclusion on the symmetry  $(C_s)$ . It is easy to draw up the predictions of intensity for the two a' bands arising from the non-degenerate modes (Table 1). On the contrary, concerning the degenerate modes, the consequence of the "breaking" of degeneracy (into a' + a'') is more difficult to foresee. Although the a' and a'' vibrations so issued are both Raman and infra-red active, we can expect differences between those arising from the e' mode (both Raman and infra-red active) and those arising from the e'' mode (Raman active only). In the former case, they will probably appear both in scattering and in absorption spectra whereas in the latter they should rather be found in the Raman spectrum.

The substitution of one hydrogen atom of the cyclopropane by the COOH group immediately involves the breaking of degeneracy of the e' and e'' modes as a consequence. Moreover one of the cyclopropane

| D <sub>3h</sub> (C | yclopropane)        |                   | $C_{\rm s}$ (Cyclopropanecarboxylic acid) |  |                                       |  |
|--------------------|---------------------|-------------------|---|--|---------------------------------------|--|
|                    | Active              |                   |   | Active                                       | · · · · · · · · · · · · · · · · · · · |  |
| Class              | IR                  | Raman             | Class                                     | IR   | Raman                                 |  |
| a',<br>a",         | no<br>yes (m; (//)) | yes (vs; p)<br>no | a'<br>a'                                  | yes (w; hybr., (//))<br>yes (m; hybr., (//)) | yes (vs; p)<br>yes (w; p)             |  |
| e'                 | yes (vs; (⊥))       | yes (m; dp) {     | a'<br>a"                                  | yes (?; hybr., (//))<br>yes (vs; C (⊥))      | yes (m; p)<br>yes (?;dp)              |  |
| e"                 | no                  | yes (m; dp) {     | a'<br>a"                                  | yes (w; hybr., (//))<br>yes (w; C (1))       | yes (m; p)<br>yes (m; dp)             |  |

Correlation between the vibrational spectra in the  $\nu$ (CH) region of cyclopropane ( $D_{3h}$ ) and of cyclopropanecarboxylic acid ( $C_{s}$ )

p = polarized band, dp = depolarized band, vs = very strong intensity band, m = middle intensity band, w = weak intensity band, (//) = parallel type band, (1) = perpendicular type band, ? = no provision.

 $\nu$ (CH) modes will be transformed into a new lower frequency mode. This "new" mode must necessarily be an a' mode. However this mode can a priori arise from any class of cyclopropane; we will try to define its origin.

The correlation diagram illustrating the selected filiations has been sketched in Fig. 1. The Raman band detected at  $3038 \text{ cm}^{-1}$  on account of its degree of depolarization and its intensity can only arise from the totally symmetric stretching vibration  $\nu_1(a'_1)$  of cyclopropane [15a] appearing at the same wavenumber. Considering the type of its envelope, the strongest absorption band (3027 cm<sup>-1</sup>) corresponds to an a'' mode and therefore can only arise from the e' or e'' vibrations of cyclopropane. However the infra-red forbidden e'' mode cannot generate the strongest a'' infra-red band. Therefore the 3027 cm<sup>-1</sup> band corresponds to the a'' component arising from the e' mode of cyclopropane ( $\nu_8$  band situated at 3024 cm<sup>-1</sup> both in Raman and IR) [15b]. The a' component, having the same origin, can produce only a band situated at a frequency equal to or lower than  $3038 \text{ cm}^{-1}$  according to the "non-crossing rule" [16]. This component is the new a' mode and its origin (e') is therefore established. The second absorption band  $(3110 \text{ cm}^{-1})$  having a *B*-type envelope corresponds unambiguously to the vibration a' deriving from the mode  $v_6$   $(a''_2)$  of cyclopropane IR active only (3101.7 cm<sup>-1</sup>). The two remaining bands observed in the Raman spectra at  $3115 \text{ cm}^{-1}$  (dp) and  $3086 \text{ cm}^{-1}$  (p) correspond to the a' and a'' modes respectively arising from  $v_{12}$  (e''), Raman active only, of cyclopropane  $(3082 \text{ cm}^{-1})$ . The fact that the assignment proposed again obeys the "non-crossing rule" is in favour of the  $C_s$ symmetry of the monomer.



Fig. 1. Correlation diagram in the  $\nu$ (CH) region between infrared and Raman spectra of cyclopropanecarboxylic acid  $C_s$  monomer and those of cyclopropane  $(D_{3h})$ .

### Conformation

The molecule studied possesses a flexible skeleton particularly due to two internal rotation possibilities. This leads, in the case of a symmetry  $C_s$  to four conformations that we will refer to: *cis/cis* (*C/C*), *cis/trans* (*C/T*), *trans/cis* (*T/C*), *trans/trans* (*T/T*). These prefixes respectively indicate the position of the ring and that of the hydroxyl with respect to the carbonyl group.

No conformational information could be drawn from the study of Ram band contours (Q branch) because of the absence of lateral branches. On the contrary, we should be able to observe, in infra-red absorption, the rotational envelopes of the vibrational bands possessing lateral branches (a eventually even a central branch). This may lead to the specifying of the conformation of the predominant fraction of the monomer molecules tha to a comparison between the measured band envelope characteristics and those calculated for each of the four conformations by a usual approxima [17-22]. For this calculation, the necessary geometrical parameters were those transferred from the X-ray diffraction analysis of cyclopropane-1,1dicarboxylic acid [23] (Table 2). The principal moments of inertia and th asymmetry parameters calculated [21] for the four conformations and th two isotopic species show that each conformation is a non-planar prolate

Geometrical parameters of cyclopropanecarboxylic acid  $C_s$  monomer (conformations (C/C), (C/T), (T/C) and (T/T))

| Interatomic distance ±  | 0.02 (A)   | Angle ± 1 (Deg.)  |   |
|---|--|---|---|
| C (α)-C (carboxylic)<br>C (α)-C (ring)<br>C (ring)-C (ring)<br>C=O<br>C-O<br>O-H<br>C-H (all equal)   | 1.484<br>1.53425<br>1.461808 <sup>a</sup><br>1.21675<br>1.31025<br>0.94<br>0.98125   | C (ring)-C ( $\alpha$ )-C (ring)<br>C ( $\alpha$ )-C (ring)-C (ring)<br>C ( $\alpha$ )-C (carboxyl) = 0<br>C ( $\alpha$ )-C (carboxyl)-O<br>O = C (carboxyl)-O<br>C (carboxyl)-O-H<br>H-C ( $\alpha$ )-C (carboxyl)<br>H-C (ring)-H | 56.9<br>61.55<br>122.4<br>116.15<br>121.45<br>108.5<br>120<br>120 |
| Dihedral angle (Deg.)   |  | $H - C (\alpha) - C (ring)$<br>$H - C (ring) - C (\alpha)$  | 115.441646 <sup>a</sup>   |
| $H - C(\alpha) - C = O \begin{cases} 0 (t) \\ or \\ 180 \\ 0 = C - O - H \\ 0 (t) $ | rans) <sup>b</sup><br>(cis) <sup>b</sup><br>is) <sup>c</sup><br>(trans) <sup>b</sup> | C (carboxyl)—C (α)—C (ring)   | 116.079421ª   |

<sup>a</sup>Calculated value verifying a redundancy. The number of physically significant decimals is given by the standard error; the other decimals are necessary to assure the internal consistency of the data set.

 $^{b}(trans)$  and (cis) indicate the position of the ring with respect to the carbonyl group.  $^{c}(cis)$  and (trans) indicate the position of the hydroxyl group with respect to the carbonyl group.

asymmetric top. The plane of symmetry  $(\sigma_h)$  contains the principal axes A and B (Fig. 2).

Besides the atomic principal coordinates, the INERTIE Computer Program [24] enabled us to determine the orientation of the electric vector induced for three modes, to appreciate the type of rotational envelope and to calculate the separation of the lateral branches. The conformation was studied through the envelopes of the bands  $\nu(OH)$ ,  $\nu(C=O)$  and  $\nu(\alpha$ -CH). These three modes represent reasonably "pure" stretching vibrations with characteristic frequencies allowing the unambiguous identification of the bands, (Tables 3 and 4). Among the recorded spectra we have selected those showing the most characteristic envelopes permitting the best measurement of the separation  $\Delta \nu$  (PR) of the lateral branches (Figs. 3-5).

The experimental results (i.e. envelope type and corresponding  $\Delta \nu$  (PR)) have been gathered in Table 4 (column six). This table also contains the theoretical provisions for each of the four conformations examined. A comparison between the expected forms of the envelopes and the experimental form makes it definitely possible to rule out the conformational hypotheses (C/C) and (C/T). Among the two remaining conformations, the



Fig. 2. Conformation of cyclopropanecarboxylic acid  $C_s$  monomer. Projection on the AB principal plane. (The units for the two axes are A.)

(T/T) one presents the  $\Delta \nu$  (PR) separation nearest to our measurements. It is also to be noted that the calculated  $\Delta \nu$  (PR) for (C/C) and (C/T) are the farthest from the experimental values, an additional argument consistent with the conclusion based on the band type. Consequently, the predominant fraction of the monomer molecules seems to possess the (T/T)conformation.

#### ASSOCIATES

#### Symmetry

Just as the  $\nu$  (CH) region was crucial for the study of the symmetry of the monomer, so the  $\nu$  (C=O) stretching vibration region enabled us to specify the symmetry of the associates. Indeed the  $\nu$  (C=O) vibration being particular affected by the hydrogen bond, this spectral range contains the required information.

In the liquid state, the structure of the associates is known [2]; in the vapour state we must examine all the a priori admissible hypotheses such as closed or open dimers, pseudo-cyclic or linear oligomers and so on.

However a comparison of the Raman and IR spectra in the carbonyl

| ŝ      |
|--------|
| E      |
| 1      |
| 9      |
| $\leq$ |
| F      |

Calculated characteristics of the vib-rot envelopes of the cyclopropanecarboxylic acid  $C_{\rm s}$  monomer bands

| woode       Species $v(OH)$ $(a')$ $d_0$ - $(C/C)$ $(T/T)$ $(T/T)$ $(T/T)$ $(T/T)$ $(T/T)$ $v(OH)$ $(a')$ $d_0$ - $36.3$ $74.4$ $17.6$ $18.0$ $AB$ $B$ $A$ $A$ $v(OH)$ $(a')$ $d_0$ - $36.5$ $74.4$ $17.6$ $18.0$ $AB$ $B$ $A$ $A$ $v(OH)$ $(a')$ $d_0$ - $36.5$ $75.6$ $16.3$ $17.9$ $AB$ $B$ $A$ $A$ $v(C=O)$ $(a')$ $d_0$ - $86.2$ $87.3$ $32.3$ $30.9$ $B$ $B$ $AB$ $AB$ $v(C=O)$ $(a')$ $d_0$ - $88.6$ $33.6$ $30.9$ $B$ $A$ <t< th=""><th></th><th>-</th><th>Vector<br/>(with re<br/>axis)</th><th>angle (Despect to</th><th>g.)<br/>the A pri</th><th>incipal</th><th>Envelo</th><th>pe type</th><th></th><th></th><th>Lateral<br/>(cm<sup>-1</sup> )</th><th>branche<br/>at 92 ° C</th><th>s separati</th><th>u u</th></t<> |                  | -                | Vector<br>(with re<br>axis) | angle (Despect to | g.)<br>the A pri | incipal | Envelo | pe type |       |       | Lateral<br>(cm <sup>-1</sup> ) | branche<br>at 92 ° C | s separati | u u   |
|---|------------------|------------------|-----------------------------|-------------------|------------------|---------|--------|---------|-------|-------|--------------------------------|----------------------|------------|-------|
| $\nu(OH)$ $(a')$ $d_0$ - $36.3$ $74.4$ $17.6$ $18.0$ $AB$ $B$ $A$ $A$ $(AB$ plane) $d_1$ - $36.5$ $75.6$ $16.3$ $17.9$ $AB$ $B$ $A$ $A$ $(AEO)$ $(a')$ $d_0$ - $36.5$ $75.6$ $16.3$ $17.9$ $AB$ $B$ $A$ $A$ $\nu(C=O)$ $(a')$ $d_0$ - $86.2$ $87.3$ $32.3$ $30.9$ $B$ $B$ $AB$ $AB$ $\nu(C=O)$ $(a')$ $d_0$ - $88.6$ $33.6$ $30.9$ $B$ $B$ $AB$ $AB$ $\nu(C=O)$ $(a')$ $d_0$ - $88.6$ $89.7$ $85.3$ $86.7$ $B$  | Mode             | Species          | (c/c)                       | (C/T)             | (T/C)            | (T/T)   | (c/c)  | (C/T)   | (T/C) | (T/T) | ( <i>C</i> / <i>C</i> )        | (C/T)                | (T/C)      | (T/T) |
| (AB plane) $d_1$ - $36.5$ $75.6$ $16.3$ $17.9$ $AB$ $B$ $A$ $A$ $\nu$ (C=O) $(a')$ $d_o$ - $86.2$ $87.3$ $32.3$ $30.9$ $B$ $B$ $AB$ $AB$ $\nu$ (C=O) $(a')$ $d_o$ - $86.2$ $87.3$ $32.3$ $30.9$ $B$ $B$ $AB$ $AB$ $(AB plane)$ $d_1$ - $86.4$ $88.6$ $33.6$ $30.9$ $B$ $B$ $AB$ $AB$ $\nu$ ( $\alpha$ -CH) $(a')$ $d_0$ - $88.6$ $89.7$ $85.3$ $86.7$ $B$   | ν(OH) (a')       | d <sub>0</sub> - | 36.3                        | 74.4              | 17.6             | 18.0    | AB     | B       | A     | A     | 14.9                           | 14.0                 | 15.9       | 16.0  |
| u(C=O) (a') d <sub>0</sub> - 86.2 87.3 32.3 30.9 B B AB AB<br>(AB plane) d <sub>1</sub> - 86.4 88.6 33.6 30.9 B B AB AB<br>$ u(\alpha$ -CH) (a') d <sub>0</sub> - 88.6 89.7 85.3 86.7 B B B B<br>(AB plane) d <sub>1</sub> - 88.8 89.0 83.9 86.7 R R R R  | (AB plane)       | d                | 36.5                        | 75.6              | 16,3             | 17.9    | AB     | B       | Ą     | A     | 14.7                           | 13.8                 | 15.8       | 16.0  |
| (AB plane) $d_1$ - 86.4 88.6 33.6 30.9 B B AB AB $\nu(\alpha \cdot CH)$ (a') $d_0$ - 88.6 89.7 85.3 86.7 B B B (AB plane) $d_1$ - 88.8 89.0 83.9 86.7 P R R R R   | $\nu$ (C=O) (a') | d₀-              | 86.2                        | 87.3              | 32.3             | 30.9    | B      | B       | AB    | AB    | 13.3                           | 13.4                 | 15.4       | 15.6  |
| ν(α-CH) (α') d <sub>0</sub> - 88.6 89.7 85.3 86.7 <i>B B B</i> ( <i>AB</i> blane) d <sub>1</sub> - 88.8 89.0 83.9 86.7 <i>B R R R R R R</i>   | (AB plane)       | d                | 86.4                        | 88.6              | 33.6             | 30.9    | a,     | £       | AB    | AB    | 13.1                           | 13.2                 | 15.2       | 15.6  |
| (AB plane) d 88.8 89.0 83.9 86.7 R R R R  | ν(α-CH) (a')     | d₀-              | 88.6                        | 89.7              | 85.3             | 86.7    | ą      | 8       | B     | В     | 13,2                           | 13.3                 | 13.6       | 13.7  |
|   | (AB plane)       | d <sub>1</sub> - | 88.8                        | 89.0              | 83.9             | 86.7    | B      | B       | B     | В     | 13.0                           | 13.2                 | 13.6       | 13.6  |

|          | Separation | Temperature |          |            |                |      |
|----------|------------|-------------|----------|------------|----------------|------|
| Mode     | Theoretica | 1           |          |            | Experimental   | (*C) |
|          | C/C        | C/T         | T/C      | <i>T/T</i> |                |      |
| ν(OH)    | 15.2(AB)   | 14.2(B)     | 16.1(A)  | 16.3(A)    | $17 \pm 1(A)$  | 104  |
| ν(C=Ó)   | 13.7(B)    | 13.7(B)     | 15.8(AB) | 16.0(AB)   | $16 \pm 1(AB)$ | 110  |
| ν (α-CH) | 14.7(B)    | 14.8(B)     | 15.2(B)  | 15.2(B)    | $14 \pm 2(B)$  | 180  |

Comparison of the calculated and measured  $\Delta v$  (PR) values for three monomer bands

The error  $(\pm 1, \pm 2)$  represents here the  $3\sigma$  interval.

stretching vibration range (Fig. 6), where the strongest bands are expected, made it possible to detect only four distinct bands. Two appearing at the same frequency (Table 5) in Raman and infra-red belong to the monomer. Two others belong to the associates, the former appearing only in Raman scattering, the latter in infra-red absorption. These latter two bands in agreement with the mutual exclusion rule prove that the associates are centrosymmetrical dimers. The symmetry group must be  $C_i$  or  $C_{2h}$ 



Fig. 3.  $\nu$  (OH) infra-red band of the cyclopropanecarboxylic acid monomer.  $A(\parallel)$  type vib—rot envelope.



Fig. 4. Cyclopropanecarboxylic acid infra-red bands: v(C=0) of the monomer and  $v_{as}(C=0)$  of the dimer. AB hybrid type vib—rot envelope for each band.



Fig. 5.  $\nu$  (CH) infra-red bands of the cyclopropanecarboxylic acid monomer. The types of the vib—rot envelopes are  $B(\perp)$  and  $C(\perp)$  for the bands 3110 and 3025 cm<sup>-1</sup> respectively.



Fig. 6. Raman and infra-red spectra in the v (C=O) region of the cyclopropanecarboxylic acid vapour, showing the simultaneous presence of monomer and centrosymmetrical dimensional dimensionad dimensional dimensionad dim

#### TABLE 5

|                  | ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | Wavenumb                | er (cm <sup>-1</sup> ) |                         |           |
|------------------|--|-------------------------|------------------------|-------------------------|-----------|
| Molecule         | Mode                                   | d <sub>o</sub> -species |                        | d <sub>1</sub> -species |           |
|                  |  | Raman                   | Infra-red              | Raman                   | Infra-ree |
| Monomer<br>Dimer | $\nu$ (C=O)<br>$\nu_{-}$ (C=O)         | 1782<br>1688            | 1780                   | 1764<br>1664            | 1765      |
|                  | $v_{as}^{s}(C=0)$                      |                         | 1717                   |                         | 1710      |

Band positions in the  $\nu$  (C=O) region of the gaseous cyclopropanecarboxylic acid vibrational spectra

Contrary to what had been observed for the monomer, we were unable to find any depolarized band strictly assignable to the dimer; such bands  $(b_g)$  must be present in the case of  $C_{2h}$  symmetry. This is not surprising since, in the liquid state, the cyclopropanecarboxylic acid exists as dimers having  $C_i$  symmetry (i.e. complete lack of depolarized lines). Therefore, we will again select the  $C_i$  group for the dimers in the vapour state.

184

### Conformation

The cyclic dimer cannot be formed from monomer molecules having the trans (OH vs. C=O) conformation (i.e. (C/T) and (T/T)). In comparison with the results reported above for the monomer, it appears that only the associates  $(T/C)_2$  can arise from the association of two monomer units. To make the calculation of the principal moments of inertia easier for the dimer, we assumed the  $C_{2h}$  symmetry. We can make two remarks about this approximation. On the one hand, the lack of direct measurements (neutron or electron diffraction) deprives us of information on the localization of the atoms and consequently on the dihedral angle between the  $C_3$  ring plane and the  $CO_2$  plane. On the other hand, in the liquid state Raman spectra of the compound, the modes similar to the  $b_g$  class vibrations in the  $C_{2h}$  hypothesis correspond to the bands having the greatest  $\rho_p$ . This feature shows that the cyclic dimer has a "nearly  $C_{2h}$ " symmetry. Consequently, the calculations made on account of this last hypothesis are a good approach.

Among the structural parameters of the dimer, the set of values concerning each of two linked units is that of the monomer (T/C). The pseudo-cycle  $-(COOH)_2$  —is considered as planar and centrosymmetrical, each of the two  $O \cdots H$ —O motifs being linear.

## $r (O \cdots O)$ distance

In order to appreciate the  $r(0 \cdots 0)$  distance between the two oxygen atoms linked by a hydrogen bond, we have used the stretching frequencies  $\nu(OH)$  of the dimer and of the monomer. It is a fact that several authors [25-28] have proposed (graphically) functions (f) connecting these three parameters

$$r(\mathbf{O}\cdots\mathbf{O})=f(\Delta v)$$

where

 $\Delta v = v (OH)_{monomer} - v (OH)_{associate}$ 

For  $\nu$  (OH)<sub>associate</sub> we will take the average value

 $v(OH)_{associate} = \frac{1}{2}(v_s(OH)_{dumer} + v_{as}(OH)_{dimer})$ 

The values (in cm<sup>-1</sup>) corresponding to our compound have been gathered in Table 6. Proceeding from this shift  $\Delta \nu$  (OH) = 633 ± 20 cm<sup>-1</sup> it has been possible to estimate the distance  $r(O \cdots O)$  by means of the different curves proposed. Our choice was mainly influenced by the comparison between the  $\Delta \nu$  (OH) and on the one hand the observations in the vapour phase spectra of the acetic [29] and formic [30] acids (for which  $r(O \cdots O)$ were measured by Karle and Brockway [31]), and on the other hand the results concerning malonic acid [32]. It is finally to be noted that the proposed  $r(O \cdots O)$  inserts itself equally well into the validity interval given by Sokolov [33].

As previously for the monomer, we have obtained [24] the atomic

Estimation of the  $r(O \cdots O)$  distance corresponding to the  $\Delta v(OH) = 633 \pm 20 \text{ cm}^{-1}$  value

| v(OH) <sub>monomer</sub>                    | v <sub>s</sub> (OH) <sub>dimer</sub> | $\nu_{\rm as}({\rm OH})_{\rm dimer}$ | v (OH) <sub>associate</sub> |
|---|--------------------------------------|--------------------------------------|-----------------------------|
| 3583 ± 1                                    | 2930 ± 30                            | 2970 ± 30                            | 2950 ± 30                   |
| $\Delta \nu = 633 \pm 20$                   |                                      |                                      |                             |
| $r(\mathbf{O}\cdots\mathbf{O})=f(633\pm20)$ | estimated after differ               | ent authors                          |                             |
| Nakamoto et al. [25]                        | Lippincott and<br>Schroeder [26]     | Pimentel and<br>McClellan [27]       | Blinc et al. [28]           |
| 2.71 ± 0.05                                 | 2.71 ± 0.05                          | 2.69 ± 0.05                          | 2.65 ± 0.06                 |
| Our estimation = $2.68 \pm 6$               | 0.05                                 |                                      |                             |

The units are  $cm^{-1}$  for wavenumbers, A for  $r(0 \cdots 0)$  distances.

principal coordinates (Fig. 7) and determined for three  $b_u$  fundamental modes the angle between the electric vector and the principal axes. Again this calculation shows that the plane of symmetry  $(\sigma_h)$  contains the Aand B principal axes. Consequently, in infra-red absorption the  $b_u$  and  $a_\mu$  vibrational modes respectively produce bands of the same type as the a' and a'' vibrations of the monomer. As in this latter case and for the same reasons, the conformation was studied by means of the band envelopes  $\nu_{as}$  (OH),  $\nu_{as}$  (C=O) and  $\nu_{as}$  ( $\alpha$ -CH), the characteristics being collected in Table 7.



Fig. 7. Conformation of cyclopropanecarboxylic acid dimer ( $C_{2h}$  approximation). Projection on the AB principal plane (the units for the two axes are A).

| Characteristics                                       | Vibrational mode   |                       |                                  |
|---|--------------------|-----------------------|----------------------------------|
|   | $v_{as}(C=0)(b_u)$ | $\nu_{as}(OH)(b_{u})$ | $\nu_{as}(\alpha$ -CH) $(b_{u})$ |
| Angle (deg.)  | 44.2               | 5.7                   | 73.3                             |
| Envelope  | AB                 | A(//)                 | $B(\perp)$                       |
| $\Delta \nu$ (PR) (110 °C) (cm <sup>-1</sup> )        | 5.2 <sup>a</sup>   | 5.6 <sup>b</sup>      | 4.9 <sup>b</sup>                 |
| $\frac{I(\mathbf{Q})}{I(\mathbf{P}) + I(\mathbf{R})}$ | < 9 %              | 9%                    | 0 %                              |

Calculated characteristics of the vib—rot envelopes for the cyclopropanecarboxylic acid dimer bands ( $C_{2h}$  approximation)

<sup>a</sup>Compare the experimental value  $\simeq 5 \text{ cm}^{-1}$  at 110 °C (see Fig. 5). <sup>b</sup>See discussion in the text.

| Angle<br>A(//) | = angle between the electric vector of the mode and the $A$ principal axis.<br>= $A$ type envelope, corresponding to the parallel band of a symmetric |
|----------------|---|
|                | rotator.  |
| AB             | = Hybrid type envelope.   |
|                |   |

I(P, Q or R) = Integral intensity of the branch (P, Q or R).

It is to be noted that the band  $v_{as}$  (OH)<sub>dimer</sub> cannot give any conformational information on account of its superposition with other bands and its important width. The same remark applies to  $v_{as}$ (OD)<sub>dimer</sub>, the band occurrin in a region that contains many combinations.

The band  $\nu_{as}(\alpha$ -CH)<sub>dimer</sub> is approximately expected at the same wavenumber as  $\nu(\alpha$ -CH)<sub>monomer</sub>. Both bands must present *B*-type envelopes (see Tables 3 and 7). In the case of monomer, the lateral branches have been observed only at high temperatures (~180 °C), the measured separation  $\Delta \nu$  (PR) being *smaller* than the calculated value (Table 7). At temperatures near 100 °C, the lateral branches do not appear. The observed phenomenon can be explained by the superposition of the two *B* bands. The separation of the lateral branches could be distinguished only at 180 °C due to the predominance of the monomer. Even at this temperature, the proportion of dimer is not negligible and the dimer band causes the "diminution" of the measured  $\Delta \nu$  (PR).

The  $\nu_{as}$  (C=O)<sub>dimer</sub> band is the most characteristic feature of the dimer spectrum because of its isolated position, its great intensity and its typically *AB* envelope shape (Fig. 4). The orientation of the  $\nu_{as}$  (C=O)<sub>dimer</sub> induced electric vector is practically intermediate between the *A* and *B* principal axes (Table 7 and Fig. 7). The calculated separation of the lateral branches is near to 5 cm<sup>-1</sup> in complete agreement with the observed value (Fig. 4).

#### DISCUSSION

We have determined the symmetry and the conformation of the molecular entities in equilibrium in the gas phase of cyclopropanecarboxylic acid and we have studied successively the monomer and the associates.

For the monomer, the shape of the envelope of three fundamentals enabled us to determine the position (trans) of the carbonyl group in relation to the normal of the  $C_3$  ring. However the band type as well as  $\Delta v$  (PR) by themselves are not sufficiently sensitive to lead to a conclusion concerning the symmetry. A study of the Raman spectra and the measurement of the depolarization ratio  $\rho_{p}$  of the bands were indispensable. The evaluation of  $\rho_{p}$  always being difficult, it was necessary to verify the conclusion independently. For this purpose we have particularly analyzed the assignment of the infra-red and Raman bands in the  $\nu$  (CH) region. The correlation between our spectra and those of cyclopropane formally confirmed that the monomer belongs to the  $C_{\rm s}$  symmetry group. In IR absorption, the calculation and the measurement of the envelope of the vib—rot bands have led us to select only the (T/C) and (T/T) conformations. However, the (T/T) conformation is most probably the predominant one since it shows a better agreement between theoretical and experimental  $\Delta v$  (PR) values.

These conclusions are consistent with those concerning glyoxylic acid which presents some similarities with cyclopropanecarboxylic acid. The carboxylic carbonyl group is, in both cases, strongly conjugated with either the aldehyde carbonyl or the cyclopropyl ring. The vibrational spectra of glyoxylic acid in the gaseous state established [34] that the conformation of this molecule was planar and *trans*, without giving any precision to the carboxylic proton position. A recent study of this compound, by means of microwave spectroscopy by Marstokk and Mollendal [35] confirmed the previous results, and led to the *trans* conformation of O—H in relation to C=O (carboxylic).

When examining the associates in the gaseous state, the simultaneous analysis of Raman and infra-red spectra and especially the careful exploration of the v (C=O) range led us to establish that they were predominantly centrosymmetrical dimers; as no band assignable to the dimer was depolarized, the center of inversion seems to be, with the identity, the only symmetry element ( $C_i$  group). However, the  $C_{2h}$ symmetry, accepted with a view to calculation facilities, seems to be a reasonable approximation.

Our results enable us to account for the equilibrium between the different forms in the vapour state as

 $2(T/T) \rightleftharpoons 2(T/C) \rightleftharpoons (T/C)_2$ 

the temperature decrease displacing this equilibrium from left to right. Therefore the (T/C) monomer may be considered as a *fugitive* intermediate leading either to the (T/T) monomer (by an internal rotation about C–O and passing over a potential barrier) or to the  $(T/C)_2$  dimer.

The association of two monomer molecules into a cyclic dimer introduces the problem of the conservation or loss of the plane of symmetry of the  $C_s$  monomer. It is well known [36] that the more the O—H axis coincides with that of one of the  $sp_2$  free orbitals of the carbonyl oxygen atom, the stronger the hydrogen bond is. This situation cannot be realized in a plane pseudo-cycle on account of the carboxyl geometry. So the diminution in the internal energy of the dimer requires the non-planarity of the pseudocycle. This accounts for the evolution of the associate system from the  $C_{2h}$  state towards the  $C_i$  symmetry.

#### ACKNOWLEDGEMENTS

The authors wish to thank Professor R. J. H. Clark (University College, London) for the use of the SPEX 1401 Spectrometer and Professor R. Gaufres (Laboratoire de Spectroscopie Moléculaire, Montpellier) for aid in obtaining Raman spectra in the vapour state.

#### REFERENCES

- 1 L. Bardet, J. Maillols, R. Granger and E. Fabregue, J. Mol. Struct., 10 (1971) 343.
- 2 J. Maillols, J. Mol. Struct., 14 (1973) 171.
- 3 J. Maillols, V. Tabacik and S. Sportouch, C. R. Acad. Sci. Ser. B, 279 (1974) 395.
- 4 P. D. Ellis and G. E. Maciel, Mol. Phys., 20 (1971) 433.
- 5 W. G. Duncombe and T. J. Rising, Biochem. Pharmacol., 21 (1972) 1075.
- 6 W. G. Duncombe and T. J. Rising, Biochem. Pharmacol., 21 (1972) 1089.
- 7 R. H. Rynbrandt, F. E. Dutton and F. L. Schmidt, J. Med. Chem., 15 (1972) 424.
- 8 V. Tabacik and J. Maillols, Spectrochim. Acta, (to be published).
- 9 S. Califano, Molecular Spectroscopy IX, General lectures presented at the Ninth European Congress on Molecular Spectroscopy, Madrid, Butterworths, London, 1969, p. 353.
- 10 C. P. Courtoy, Ann. Soc. Sci. Bruxelles, 73 (1959) 5.
- 11 B. P. Stoicheff, Advan. Spectrosc., 1 (1959) 91.
- 12 V. Tabacik and V. Pellegrin, Patent No. 6931581 (1969), A.N.V.A.R. (France).
- 13 R. Gaufres (to be published).
- 14 Commission on molecular structure and spectroscopy, Tables of Wavenumbers for the Calibration of Infra-red Spectrometers, Butterworths, London, 1961.
- 15 a R. J. Butcher and W. J. Jones, J. Mol. Spectrosc., 47 (1973) 64.
   b A. W. Baker and R. C. Lord, J. Chem. Phys., 23 (1955) 1636.
- 16 G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand, New York, Vol. II, 1960, pp. 200 and 319.
- 17 S. L. Gerhard and D. M. Dennison, Phys. Rev., 43 (1933) 397.
- 18 R. M. Badger and L. R. Zumwalt, J. Chem. Phys., 6 (1938) 711.
- 19 W. A. Seth-Paul and G. Dijkstra, Spectrochim. Acta Part A, 23 (1967) 2861.
- 20 W. A. Seth-Paul and H. De Meyer, J. Mol. Struct., 3 (1969) 11.
- 21 V. Tabacik and G. Fleury, J. Mol. Struct., 4 (1969) 117.
- 22 V. Tabacik and G. Fleury, J. Mol. Struct., 14 (1972) 1.
- 23 A. M. Meester, H. Schenk and C. H. McGillavry, Acta Crystallogr. Sect. B 27 (1971) 630.

- 24 V. Tabacik and G. Fleury, INERTIE Program, Program Exchange Library, The Perkin-Elmer Corp., Norwalk, Conn., 1969.
- 25 K. Nakamoto, M. Margoshes and R. E. Rundle, J. Amer. Chem. Soc., 77 (1955) 6480.
- 26 E. R. Lippincott and R. Schroeder, J. Chem. Phys., 23 (1955) 1099.
- 27 G. C. Pimentel and A. L. McClellan, The Hydrogen Bond, Freeman and Co, San Francisco, 1960.
- 28 R. Blinc, D. Hadzi and A. Novak, Z. Elecktrochem., 64 (1960) 567.
- 29 M. Haurie and A. Novak, J. Chim. Phys., 62 (1965) 146.
- 30 R. C. Millikan and K. S. Pitzer, J. Amer. Chem. Soc., 80 (1958) 3515.
- 31 J. Karle and L. O. Brockway, J. Amer. Chem. Soc., 66 (1944) 574.
- 32 J. A. Goedkoop and C. H. McGillavry, Acta Crystallogr., 10 (1955) 125.
- 33 N. D. Sokolov, Ann. Chim., 10 (1965) 497.
- 34 G. Fleury and V. Tabacik, J. Mol. Struct., 10 (1971) 359.
- 35 K. M. Marstokk and H. Mollendal, J. Mol. Struct., 15 (1973) 137.
- 36 J. E. Del Bene, J. Chem. Phys., 62 (1975) 1314.