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Acta Cryst. (1992). C**48**, 106–109

Structures of Two Cyclopropane Derivatives: *cis*- and *trans*-Caronic Acid

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(*Received* 17 *April* 1991; *accepted* 14 *June* 1991)

Abstract. 3,3-Dimethylcyclopropane-1,2-dicarboxylic acid, $C_7H_{10}O_4$, $M_r = 158{\cdot}2$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}12$ mm^{-1}, $T = 295$ K. *cis* isomer (I): monoclinic, $P2_1/c$, $a = 10{\cdot}855$ (3), $b = 6{\cdot}881$ (1), $c = 11{\cdot}054$ (2) Å, $\beta = 109{\cdot}23$ (1)°, $V = 779{\cdot}6$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}347$ Mg m^{-3}, $F(000) = 336$, $wR = 0{\cdot}042$, $R = 0{\cdot}051$ for 1455 observed reflections. *trans* isomer (II): monoclinic, $C2/c$, $a = 12{\cdot}516$ (6), $b = 6{\cdot}122$ (2), $c = 10{\cdot}950$ (2) Å, $\beta = 107{\cdot}43$ (2)°, $V = 800{\cdot}5$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}312$ Mg m^{-3}, $F(000) = 336$, $wR = 0{\cdot}043$, $R = 0{\cdot}050$ for 741 observed reflections. The intermolecular hydrogen bonds between the carboxylic groups form infinite layers in (I) and infinite chains in (II). Compound (II) has C_2 symmetry.

Introduction. As part of hydrogen-bond studies, the title compound (I) is of special interest as a potential precursor for compounds with intramolecular hydrogen bonds. An analysis of the dissociation constants of (I) suggests intramolecular hydrogen bonding to be present in the monodeprotonated anion in solution (Eberson & Wadsö, 1963; McCoy & Nachtigall, 1963; Haslam, Eyring, Epstein, Christiansen & Miles, 1965; Eyring & Haslam, 1966). Furthermore, a recent X-ray structure determination showed that *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid exhibits intramolecular hydrogen bonding (Weber, Hecker, Csöregh & Czugler, 1989), whereas the unsubstituted *cis*-cyclopropane-1,2-dicarboxylic acid does not (Schrumpf & Jones, 1987). In order to study the hydrogen bonding in the 3,3-dimethyl derivatives this X-ray structure analysis was undertaken.

Experimental. Compounds (I) and (II) were synthesized according to Fredga & Sikström (1955) and checked by IR spectroscopy.

(I): The crystal used for this study (mean diameter 0·3 mm) was obtained by evaporation of an aqueous solution at room temperature. Lattice parameters were refined using 30 diffractometer-measured reflections in the range $25 < 2\theta < 50°$. The intensities of 2567 reflections were collected on a Siemens–Stoe AED-2 diffractometer at 295 K by $\theta/2\theta$ scans in the 'learnt-profile' mode (Clegg, 1981). The range of 2θ was 4–60°; ranges of h, k, l were −15/15, 0/10, 0/16. Standard reflections 423, 131 and 308, monitored every hour, showed no significant variation over the data-collection period. The orientation matrix was also checked every 6 h. 1455 unique reflections with $I > 2\sigma(I)$ were used in the refinement ($R_{int} = 0{\cdot}012$). No absorption correction was applied due to the small absorption coefficient in this compound. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986), which located the positions of all non-H atoms, and was refined (based on F) by *SHELX*76 (Sheldrick, 1976). All H atoms were located in a difference Fourier synthesis. Final refinement yielded $wR = 0{\cdot}042$, $R = 0{\cdot}051$ (H atoms having isotropic, all other atoms having anisotropic displacement parameters; isotropic extinction correction; 142 parameters varied). Weights were calculated according to $w = 1/\sigma^2(F_o)$, maximum Δ/σ was 0·006. The isotropic extinction parameter g was $7{\cdot}1\ (4) \times 10^{-7}$ [$F' = F(1 - gF^2/\sin\theta)$]. Maximum and minimum heights in the final difference Fourier synthesis map were 0·20 and −0·19 e Å^{-3}, respectively. Scattering factors for neutral atoms were taken from Cromer & Mann (1968). In addition, the programs *ORFFE* (Busing, Martin & Levy, 1964), *XANADU* (Roberts & Sheldrick, 1975) and *ORTEP*II (Johnson, 1976) were used. All calculations were carried out on a MicroVAX and on a PDP 10 at the

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Rechenzentrum der Universität Kiel. Atomic coordinates and equivalent isotropic displacement parameters for all non-H atoms are listed in Table 1.*

(II): Initially, crystallization by cooling a hot saturated aqueous solution yielded orthorhombic crystals with unit-cell dimensions $a = 10{\cdot}02\ (2)$, $b = 12{\cdot}21\ (1)$, $c = 13{\cdot}71\ (2)$ Å. However, all crystals were twinned and therefore no further investigations were carried out. The monoclinic phase, which is investigated in this study, was obtained by evaporation at room temperature. The specimen used for structure determination had a mean diameter of 0·4 mm. Experimental conditions, structure solution and refinement conditions were the same as for (I). Lattice parameters were refined using 20 reflections in the range $24 < 2\theta < 50°$. The intensities of 1355 reflections were collected at 295 K. The range of 2θ was 4–60°; the ranges of h, k, l were $-18/18$, 0/9, 0/15. Standard reflections were $\bar{1}1\bar{2}$, $31\bar{6}$ and $\bar{3}1\bar{3}$. 741 unique reflections with $I > 2\sigma(I)$ were used in the refinement ($R_{int} = 0{\cdot}029$). Final refinement yielded $wR = 0{\cdot}043$, $R = 0{\cdot}050$ with 73 parameters varied. Maximum Δ/σ was 0·001. The isotropic extinction parameter g was $3{\cdot}3\ (4) \times 10^{-7}$. Maximum and minimum heights in the final difference Fourier synthesis map were 0·21 and $-0{\cdot}17$ e Å^{-3}, respectively. Atomic coordinates and equivalent isotropic displacement parameters for all non-H atoms are listed in Table 2.

Discussion. The molecular geometries of (I) and (II) (Figs. 1 and 2) are similar to those of the unsubstituted *cis*- and *trans*-1,2-cyclopropanedicarboxylic acids (Schrumpf & Jones, 1987). Bond lengths and angles for both compounds are given in Tables 3 and 4.

(I) *cis-Caronic acid.* The molecule is in a general position. The deviation from mirror symmetry is considerable. One carboxylic group, O(1)—C(4)—O(2), is rotated 75° out of the plane through C(1), C(4) and the midpoint of C(2)—C(3) [synclinal (*sc*) conformation]. The other carboxylic group, O(3)—C(5)—C(4), is only 9° off the respective plane through C(2), C(5) and the midpoint of C(1)—C(3) [*cis*-bisected (*cb*) conformation]. The carbonyl group C(5)—O(3) is oriented towards the ring. The asymmetry is also reflected in the ring bond lengths. The bond C(1)—C(3) opposite the *cb* group is significantly shorter (1·491 Å) than the bond C(2)—C(3) opposite the *sc* group (1·539 Å). Since the C(2)—C(5) bond is also shorter than the C(1)—C(4) bond, this effect may be attributed to conjugative interaction of the *cb* carboxylic group with the cyclopropane ring which shortens the participating bonds.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* U_{eq} (Å$^2 \times 10^4$) *for cis-caronic acid* (I)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	1494 (2)	1834 (3)	10063 (2)	321 (4)
C(2)	2896 (2)	2158 (3)	10918 (2)	337 (4)
C(3)	2430 (2)	181 (3)	10280 (2)	347 (4)
C(4)	928 (2)	2928 (3)	8835 (2)	334 (4)
C(5)	3764 (2)	3414 (3)	10486 (2)	349 (4)
C(6)	2908 (3)	−557 (4)	9227 (2)	490 (7)
C(7)	2313 (2)	−1381 (4)	11198 (2)	464 (6)
O(1)	594 (1)	2214 (2)	7775 (1)	497 (4)
O(2)	762 (2)	4769 (2)	9033 (1)	479 (4)
O(3)	3645 (1)	3738 (2)	9368 (1)	457 (4)
O(4)	4710 (1)	4166 (2)	11454 (1)	493 (4)

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* U_{eq} (Å$^2 \times 10^4$) *for trans-caronic acid* (II)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	4396 (1)	53 (3)	2521 (2)	304 (4)
C(2)	5000	−2081 (4)	2500	315 (6)
C(3)	5298 (2)	−3434 (4)	3710 (2)	462 (7)
C(4)	3539 (2)	978 (3)	1409 (2)	338 (5)
O(1)	3601 (1)	970 (2)	316 (1)	465 (4)
O(2)	2703 (1)	1891 (3)	1715 (2)	490 (5)

Table 3. *Bond lengths* (Å) *and angles* (°) *for cis-caronic acid* (I)

C(1)—C(2)	1·502 (2)	C(1)—C(3)	1·491 (3)
C(1)—C(4)	1·496 (3)	C(2)—C(3)	1·539 (3)
C(2)—C(5)	1·469 (3)	C(3)—C(6)	1·511 (4)
C(3)—C(7)	1·512 (3)	C(4)—O(1)	1·211 (2)
C(4)—O(2)	1·308 (3)	C(5)—O(3)	1·220 (2)
C(5)—O(4)	1·320 (2)		

C(2)—C(1)—C(3)	61·5 (1)	C(2)—C(1)—C(4)	121·2 (2)
C(3)—C(1)—C(4)	125·8 (2)	C(1)—C(2)—C(3)	58·3 (1)
C(1)—C(2)—C(5)	120·1 (2)	C(3)—C(2)—C(5)	121·4 (2)
C(1)—C(3)—C(2)	60·2 (1)	C(1)—C(3)—C(6)	121·4 (2)
C(1)—C(3)—C(7)	116·6 (2)	C(2)—C(3)—C(6)	120·4 (2)
C(2)—C(3)—C(7)	114·2 (2)	C(6)—C(3)—C(7)	113·8 (2)
C(1)—C(4)—O(1)	125·2 (2)	C(1)—C(4)—O(2)	111·9 (2)
O(1)—C(4)—O(2)	122·8 (2)	C(2)—C(5)—O(3)	124·9 (1)
C(2)—C(5)—O(4)	112·2 (2)	O(3)—C(5)—O(4)	122·9 (2)

Table 4. *Bond lengths* (Å) *and angles* (°) *for trans-caronic acid* (II)

C(1)—C(1^i)	1·528 (4)	C(1)—C(2)	1·514 (3)
C(1)—C(4)	1·474 (2)	C(2)—C(3)	1·512 (3)
C(4)—O(1)	1·223 (3)	C(4)—O(2)	1·315 (3)

C(1^i)—C(1)—C(2)	59·7 (1)	C(1^i)—C(1)—C(4)	117·2 (2)
C(2)—C(1)—C(4)	124·2 (2)	C(1)—C(2)—C(1^i)	60·6 (2)
C(1)—C(2)—C(3)	117·0 (1)	C(1)—C(2)—C(3^i)	120·0 (1)
C(3)—C(2)—C(3^i)	113·5 (2)	C(1)—C(4)—O(1)	124·3 (2)
C(1)—C(4)—O(2)	112·9 (2)	O(1)—C(4)—O(2)	122·7 (2)

Symmetry code: (i) $1 - x$, y, $0{\cdot}5 - z$.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54345 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(II) *trans-Caronic acid.* The molecule has C_2 symmetry, lying on a twofold axis at 0·5, *y*, 0·25 through C(2). The carboxylic groups are very close to *cb* conformation [4° out of the plane through C(1), C(4) and the midpoint of C(1^i)—C(2)] with the carbonyl group directed towards the ring. The conjugative effect on the bond lengths is not as pronounced as in (I) [C(1)—C(1^i) 1·528, C(1)—C(2) 1·514 Å]. This may be caused by the competition of two *cb* carbonyl groups for ring electrons.

Intramolecular steric interactions are apparent from the inclination of the carboxyl groups towards the ring. In (II) the average of the bond angles C(2)—C(1)—C(4) and C(1^i)—C(1)—C(4) is 120·7°. The corresponding values in (I) are 120·8° (*cb* group) and 123·5° (*sc* group). These are appreciably higher than the corresponding angles in the 1,2-cyclopropanedicarboxlic acids (117·9, 119·7 and 122·3°, respectively), apparently as a result of repulsion from the additional methyl substituents. The repulsion of an unconjugated *sc* group appears to be easier than that of a conjugated *cb* group.

Molecular packing. The unit cells are shown in Figs. 3 and 4. The molecular packing of carboxylic acids has been studied by Leiserowitz (1976). The *trans*-caronic acid (II) shows the usual pairwise hydrogen bonding ('dimer' type). Infinite chains are formed along the [101] direction, the distance of the hydrogen-bonded O atoms O(2)—O(1′) (at 0·5 − *x*, 0·5 − *y*, − *z*) is 2·674 (2) Å, the angle O(2)—H(2)—O(1′) is 175 (2)°.

In the *cis*-caronic acid (I), only the *cb* carboxylic groups of two neighbouring molecules, related by an inversion centre, form such hydrogen-bond pairs [distance O(4)—O(3′) (at 1 − *x*, 1 − *y*, 2 − *z*) is 2·677 (2) Å, angle O(4)—H(4)—O(3′) is 174 (2)°]. The *sc* carboxylic group, however, is connected with two different neighbouring molecules at − *x*, − 0·5 + *y*, 1·5 − *z* and − *x*, 0·5 + *y*, 1·5 − *z*, respectively; distance O(2)—O(1′) is 2·656 (2) Å, angle O(2)—H(3)—O(1′) is 161 (2)°. This motif ('catamer' type) is rare among carboxylic acids. Layers are made instead of chains by a combination of these two hydrogen-bond types.

The different packing accounts for the remarkably different densities [(I) 1·347, (II) 1·312 g cm^{-3}]. (I) is closer packed because hydrogen bonds extend in two dimensions in (I) and in one dimension in (II), whereas weaker van der Waals bonds are present in the other dimensions.

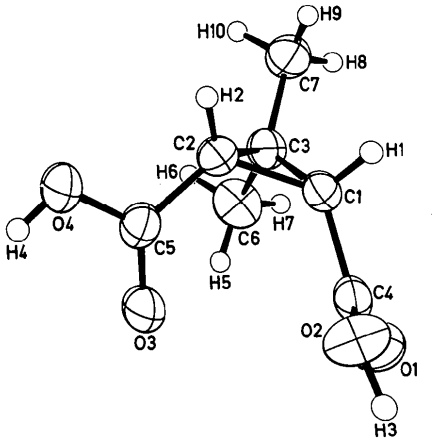

Fig. 1. Thermal ellipsoid plot (50% level) of (I), showing the atom-numbering scheme.

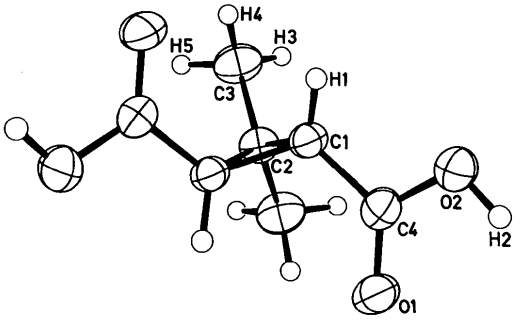

Fig. 2. Thermal ellipsoid plot (50% level) of (II), showing the atom-numbering scheme.

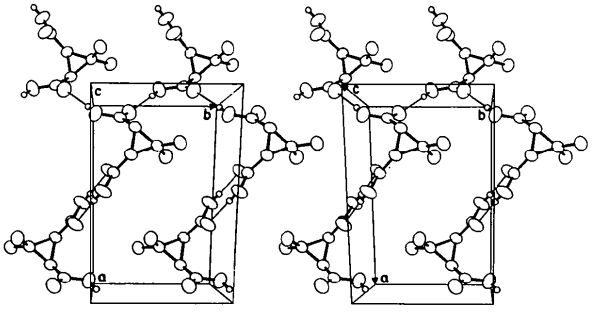

Fig. 3. Stereoscopic view of the crystal structure of (I). Thermal ellipsoids are drawn at 50% probability level. Only the H atoms involved in hydrogen bonds (thin lines) are drawn (with fixed radius), the others are omitted for clarity.

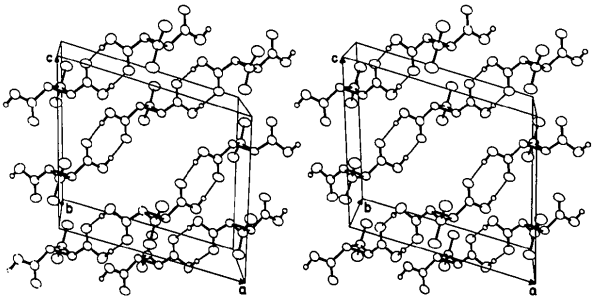

Fig. 4. Stereoscopic view of the crystal structure of (II). Thermal ellipsoids are drawn at 50% probability level. Only the H atoms involved in hydrogen bonds (thin lines) are drawn (with fixed radius), the others are omitted for clarity.

The suggestions about intramolecular hydrogen bonding, which stem from the investigation of dissociation constants, have been confirmed, since X-ray crystal structure analysis showed this type of bond to be present in ammonium hydrogen *cis*-caronate and potassium hydrogen *cis*-caronate hydrate (Jessen & Küppers, 1991).

The author would like to thank Mrs U. Bennewitz for retouching the drawings.

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Acta Cryst. (1992). C**48**, 109–111

Structure and Intramolecular Hydrogen Bonding of 1-Phenazinecarboxylic Acid

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(*Received* 26 *October* 1990; *accepted* 25 *June* 1991)

Abstract. $C_{13}H_8N_2O_2$, $M_r = 224{\cdot}22$, monoclinic, $P2_1/n$, $a = 18{\cdot}149\ (2)$, $b = 14{\cdot}2768\ (9)$, $c = 3{\cdot}8191\ (3)$ Å, $\beta = 92{\cdot}029\ (6)°$, $V = 988{\cdot}95$ Å^3, $Z = 4$, $D_x = 1{\cdot}51$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 7{\cdot}61$ cm^{-1}, $F(000) = 464$, $T = 163\ (1)$ K, $R = 0{\cdot}037$ for 1479 data with $I \geq 2\sigma(I)$. An intramolecular hydrogen bond is observed between the carboxyl hydrogen atom and the nearby nitrogen atom with the N···O distance being 2·67 Å.

Introduction. Previous spectroscopic studies of the fungal antibiotic produced by a fluorescent pseudomonad (*P. fluorescens* 2-79, NRRL B-15132) have shown evidences in favor of both a dimeric (Gurusiddaiah, Weller, Sarkar & Cook, 1986) and a monomeric (Brisbane, Janik, Tate & Warren, 1987) structure. The mass spectrum of our microbially produced material displayed a dimer peak in the gas phase, but vapor-pressure osmometry showed the material to be monomeric in solution (CH_2Cl_2). Melting-point determination, thin-layer chromatography, UV–visible spectroscopy and NMR spectroscopy (^{1}H, ^{13}C) all showed the microbially produced material to be identical to chemically synthesized 1-phenazinecarboxylic acid. The crystal structure of 1-phenazinecarboxylic acid at room temperature reported recently (Jones, Lewis, Tate, Snow & Tiekink, 1988) provided unequivocal evidence that the antibiotic has the monomeric structure. However, in the room-temperature structure, the carboxyl hydrogen was not located. The possible reason for this missing hydrogen atom was pointed out by the authors to be the 'disorder in the absence of hydrogen-bonding effects' (Jones *et al.*, 1988). In our low-temperature structure, the location of this hydrogen atom has been determined and it participates in an intramolecular hydrogen bond.

Experimental. A crystal of dimensions 0·05 × 0·06 × 0·30 mm was used for X-ray diffraction studies. The oscillation picture of this crystal showed that its needle axis was a very short crystallographic axis of

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