We thank the Fonds der Chemischen Industrie for financial support and Dr A. L. Bednowitz for making unpublished information about the *trans* isomer available to us.

References

ALLEN, F. H. (1980). *Acta Cryst.* **B36**, 81–96.

BEDNOWITZ, A. L. (1969). *Acta Cryst.* **A25**, S129.

CHESNUT, D. B. & MARSH, R. E. (1958). *Acta Cryst.* **11**, 413–419.

CLEGG, W. (1981). *Acta Cryst.* **A37**, 22–28.

DEKAPRILEVIČ, M. O. & VORONTSOVA, L. G. (1975). *Zh. Strukt. Khim.* **16**, 826–831.

HOFFMANN, R. & STOHRER, W. D. (1971). *J. Am. Chem. Soc.* **93**, 6941–6948.

HOFMANN, K., OROCHENA, S. F., SAX, S. M. & JEFFREY, G. A. (1959). *J. Am. Chem. Soc.* **81**, 992–997.

JONES, P. G. & SCHRUMPF, G. (1987*a*). *Acta Cryst.* **C43**, 1179–1182.

JONES, P. G. & SCHRUMPF, G. (1987*b*). *Acta Cryst.* **C43**, 1576–1579.

JONES, P. G. & SCHRUMPF, G. (1987*c*). *Acta Cryst.* **C43**, 1579–1582.

LONG, R. E., MADDOX, H. & TRUEBLOOD, K. N. (1969). *Acta Cryst.* **B25**, 2083–2094.

LUHAN, P. A. & MCPHAIL, A. T. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 2372–2375.

MCCOY, L. L. (1958). *J. Am. Chem. Soc.* **80**, 6568–6572.

MEESTER, M. A. M., SCHENK, H. & MACGILLAVRY, C. H. (1971). *Acta Cryst.* **B27**, 630–634.

ROQUES, R., CRASNIER, F., DECLERCQ, J.-P., GERMAIN, G., COUSSE, H. & MOUZIN, G. (1982). *Acta Cryst.* **B38**, 1375–1377.

SCHRUMPF, G. & JONES, P. G. (1987*a*). *Acta Cryst.* **C43**, 1182–1185.

SCHRUMPF, G. & JONES, P. G. (1987*b*). *Acta Cryst.* **C43**, 1185–1187.

SCHRUMPF, G. & JONES, P. G. (1987*c*). *Acta Cryst.* **C43**, 1188–1192.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

TRÆTTEBERG, M., ALMENNINGEN, A., SCHRUMPF, G. & MARTIN, S. (1987). *J. Mol. Struct.* Submitted.

Acta Cryst. (1987). C43, 1752–1755

Substituted Cyclopropanes. 8. 2,2,3,3-Tetramethylcyclopropanecarboxylic Acid*

BY PETER G. JONES

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen,*
Federal Republic of Germany

AND GERD SCHRUMPF

Institut für Organische Chemie der Universität, Tammannstrasse 2, *D*-3400 *Göttingen,*
Federal Republic of Germany

(*Received* 11 *February* 1987; *accepted* 8 *April* 1987)

Abstract. $C_8H_{14}O_2$, $M_r = 142{\cdot}20$, monoclinic, $P2_1/n$, $a = 6{\cdot}3457\ (10)$, $b = 11{\cdot}7207\ (14)$, $c = 11{\cdot}758\ (2)$ Å, $\beta = 104{\cdot}27\ (2)^\circ$, $V = 847{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}11$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}05$ mm^{-1}, $F(000) = 312$, $T = 293$ K, $R = 0{\cdot}059$ for 1313 unique observed reflections. The molecule adopts a slightly distorted *cis*-bisected conformation, with the carbonyl oxygen eclipsing the ring. The cyclopropane ring is asymmetric, with one short and two longer bonds, in accordance with theoretical expectations. The absolute values of the bond lengths and several bond angles indicate substantial steric interactions between the carboxyl and the two *cis* methyl groups. The molecules are linked in pairs across centres of symmetry by the usual carboxylic acid hydrogen bonding.

Introduction. The interaction between a cyclopropane ring and a π-acceptor substituent induces a shortening of the connecting bond and a ring-bond asymmetry, with a short bond opposite the substituent and two longer adjacent bonds. This is documented by many structures of appropriate cyclopropane derivatives determined by X-ray diffraction in the crystalline state and by electron diffraction and rotational spectroscopy in the vapour phase (Allen, 1980). Cyclopropane derivatives of chemical interest are for the most part polysubstituted molecules, and the question arises as to the additivity of these substituent effects. Moreover, since the simple monosubstituted cyclopropanes are mostly liquids at ambient temperatures, crystal structures of those compounds are only feasible at low temperatures, for example cyano- and aminocyclopropane (Kiers, de Boer, Heijdenrijk, Stam & Schenk,

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* Part 7: Schrumpf & Jones (1987).

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1985; de Boer, Schenk & Stam, 1986). In order to gain information on the geometry of these molecules in the crystalline state at ambient temperatures, one has to study appropriate model molecules carrying additional substituents with known or presumed small effects on the structure, *e.g.* methyl groups.

We were interested in the influence of the carboxyl group on the cyclopropane ring geometry and the dependence of the effect on the conformation of the acid group. Cyclopropanecarboxylic acid melts at 292 K. In the literature, the structure of *trans,trans*-2,3-dimethylcyclopropanecarboxylic acid has been reported (Luhan & McPhail, 1972). Since methyl groups do not significantly affect the cyclopropane geometry (Klein & Schrumpf, 1981), the geometry of this molecule might be considered to be close to the hitherto unknown structure of the unsubstituted acid. However, in the crystal, the dimethyl-substituted acid deviates from the anticipated molecular C_s symmetry. The deviation from C_s symmetry might be induced by crystal packing effects. The dihedral angle of the carboxyl group with respect to the bisector plane of the adjacent intra-annular angle is 5°, and the lengths of the ring bonds adjacent to the substituent differ by 0·012 Å. However, this is insignificant in view of the rather large standard deviations (0·007 Å) of that study.

We have therefore investigated the structure of 2,2,3,3-tetramethylcyclopropanecarboxylic acid.

Experimental. The title compound was synthesized according to the literature (Meshcheryakov & Dolgii, 1960). Suitable crystals were grown from acetic acid–water as colourless prisms. Since the compound sublimes readily, they were sealed in glass capillaries.

Crystal 0·6 × 0·4 × 0·4 mm; 2523 profile-fitted intensities (Clegg, 1981) recorded on a Stoe–Siemens four-circle diffractometer. Monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 55°, $-h+k\pm l$ and some $+h$ equivalents. Three check reflections, no intensity change. R_{int} 0·019 for 1949 reflections, 1313 with $F > 4\sigma(F)$ used for all calculations [program systems *SHELX*76 (Sheldrick, 1976) and *SHELX*86 (Sheldrick, 1986)]. Index ranges after merging $|h| < 8$, $|k|$, $|l| < 15$. Cell constants refined from 2θ values of 58 reflections in the range 20–23°.

Structure solution by routine direct methods. Full-matrix refinement on F to R 0·059, wR 0·058 [rigid methyl groups with C—H 0·96 Å, H—C—H 109·5°, $U(\text{H}) = 0{\cdot}1$ Å^2; other H refined freely; 111 parameters; weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00025F^2$; $S = 2{\cdot}07$]. Max. Δ/σ 0·024, max. and min. features in final $\Delta\rho$ map +0·15, −0·21 e Å^{-3}. Atomic scattering factors those of *SHELX*.

A rigid-body libration correction was applied; $R_{\text{lib}} = 0{\cdot}066$.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}
C(3)	4833 (3)	3022 (2)	2277 (2)	44 (1)
C(2)	4693 (3)	2113 (2)	3139 (1)	46 (1)
C(1)	3551 (4)	1926 (2)	1844 (2)	44 (1)
C(31)	6952 (4)	3244 (2)	1957 (2)	67 (1)
C(32)	3500 (5)	4103 (2)	2223 (2)	73 (1)
C(21)	6693 (5)	1423 (2)	3699 (2)	70 (1)
C(22)	3222 (5)	2277 (2)	3958 (2)	75 (1)
C(11)	4236 (4)	1094 (2)	1075 (2)	42 (1)
O(1)	6103 (3)	790 (1)	1141 (1)	61 (1)
O(2)	2573 (3)	697 (1)	267 (1)	59 (1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°) *in the title compound*

		Corrected
C(3)–C(2)	1·488 (3)	1·504
C(3)–C(31)	1·506 (3)	1·522
C(2)–C(1)	1·532 (2)	1·541
C(2)–C(22)	1·510 (3)	1·523
C(11)–O(1)	1·221 (2)	1·234
C(1)–C(3)	1·539 (3)	1·548
C(3)–C(32)	1·516 (3)	1·529
C(2)–C(21)	1·512 (3)	1·527
C(1)–C(11)	1·467 (3)	1·474
C(11)–O(2)	1·318 (2)	1·327

C(1)–C(3)–C(2)	60·8 (1)	C(31)–C(3)–C(2)	120·1 (2)
C(31)–C(3)–C(1)	119·6 (2)	C(32)–C(3)–C(2)	120·1 (2)
C(32)–C(3)–C(1)	116·1 (2)	C(32)–C(3)–C(31)	111·6 (2)
C(3)–C(2)–C(1)	61·2 (1)	C(21)–C(2)–C(3)	119·7 (2)
C(21)–C(2)–C(1)	119·8 (2)	C(22)–C(2)–C(3)	119·6 (2)
C(22)–C(2)–C(1)	115·9 (2)	C(22)–C(2)–C(21)	112·0 (2)
C(2)–C(1)–C(3)	58·0 (1)	C(11)–C(1)–C(3)	123·1 (2)
C(11)–C(1)–C(2)	124·7 (2)	O(1)–C(11)–C(1)	125·8 (2)
O(2)–C(11)–C(1)	111·9 (2)	O(2)–C(11)–O(1)	122·3 (2)

Discussion. Final atomic coordinates, derived parameters and libration-corrected bond lengths are given in Tables 1 and 2.*

In the following discussion, we shall use the uncorrected bond lengths, because the data for the molecules taken for comparison are also uncorrected. The carboxyl group (see Fig. 1) adopts the *cis* bisected (*cb*) conformation with a small deviation of 5° from the ideal dihedral angle. This is a typical result for cyclopropanes substituted by carboxyl groups and their derivatives; however, here we expected an ideal *cb* conformation, because the symmetric steric interactions with the two *cis* methyl groups should prevent the acid group from leaving the *cb* potential-energy well.

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* 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 43949 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The ring asymmetry is as expected, with a short C(3)—C(2) bond (1·488 Å) and two larger lateral bonds C(1)—C(3) (1·539 Å) and C(2)—C(1) (1·532 Å). The difference between the latter of about two e.s.d.'s is probably insignificant. The most interesting result is that the average ring bond length is 1·520 Å, which is about 0·016 Å longer than the average of many structures with carbonyl and carboxyl substituents (1·504 Å; Allen, 1980). In the 2,3-dimethyl-substituted acid (Luhan & McPhail, 1972), the average is 1·503 Å. The difference between the average adjacent and the opposite ring bonds is 0·037 Å in the dimethyl, but 0·048 Å in the tetramethyl derivative. Allen (1980) gives an average difference of 0·035 Å for carbonyl derivatives with *cb* conformations. Thus, substantial steric pressure in the present molecule between the two methyl groups and the carboxyl group is indicated, which tends to lengthen the lateral bonds preferentially. There are two more pieces of evidence for this interaction. The bond C(1)—C(11) between the ring and the carboxyl group (1·467 Å) is 0·011 Å longer than the same bond in the dimethyl derivative (1·456 Å). Second, the angle of inclination of the carboxyl group towards the ring as measured in terms of the average of bond angles C(3)C(1)C(11) and C(2)C(1)C(11) (123·9°) is larger than in the dimethyl analogue (121·1°) or in the *trans* diacid (Schrumpf & Jones, 1987) with sterically essentially unperturbed carboxyl groups (117·9°). Concomitantly, the *cis* methyl groups are bent backwards away from the cyclopropane threefold axis. Their average CCC bond angle is 119·7°, compared with 116·0° for the *trans* methyl groups.

In *cis*-1,2-cyclopropanedicarboxylic acid, with considerable steric strain between the two acid groups, one group adopts the *cb* and the other the *sc* conformation (Schrumpf & Jones, 1987). The average CCC bond angles defining the inclination of the carboxyl group towards the ring plane are also opened to 122·3° (*sc*) and 119·6° (*cb*). The CC bond length between the *cb* carboxyl group in the *cis* diacid, which is sterically similar to the carboxyl group in the title molecule, and the ring (1·465 Å) is very close to the one found in the present study.

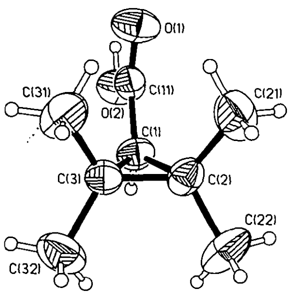

Fig. 1. Thermal-ellipsoid plot (50% level) of the title compound, showing the atom-numbering scheme.

For methylcyclopropane and *trans*-1,2-dimethylcyclopropane in the vapour phase, we found 118·3 and 118·4°, respectively, for the CCC bond angles involving the methyl carbon atoms (Klein & Schrumpf, 1981). This is about midway between the corresponding CCC bond angles found in the title molecule. The distortion of each of the two geminal dimethyl groups is thus a bending of the whole CMe_2 moiety away from the carboxyl group. The average CCC(methyl) angle of the dimethyl acid (120·7°; Luhan & McPhail, 1972) is somewhat larger than expected. This is probably associated with the *cis* position of the two vicinal methyl groups, but may also be a consequence of crystal packing. Interestingly, the average length of the bond between the methyl groups and the ring in the tetramethyl acid (1·511 Å) is slightly larger than that of the corresponding bonds in the dimethyl acid (1·501 Å), which may be taken as additional evidence for steric crowding in the tetramethyl acid.

Finally, the relaxation of steric pressure is obvious from the angles about the trigonal carboxylic carbon C(11). In unstrained molecules, the angle corresponding to C(1)C(11)O(1) would be 121–122°, rising to 122·8 (3)° for the *sc* carboxyl group in *cis*-1,2-cyclopropanedicarboxylic acid. In the tetramethyl acid, this angle opens to 125·8°, mainly at the expense of C(1)C(11)O(2) (111·9°). This corresponds to a tilt of the O—C=O moiety away from the *cis* methyl groups relative to the unstrained dimethyl acid (122·0 and 116·0°).

The conformation of each methyl group is staggered with respect to the neighbouring ring atoms, *i.e.* the relative position of the H atoms at geminal methyl groups in the tetramethyl acid resembles that in propane. This means that the methyl hydrogens are not substantially (> 1°) rotated from their normal positions with one H atom pointing towards the threefold axis of the cyclopropane ring. If the steric strain at the carboxylic face of the ring were solely due to the

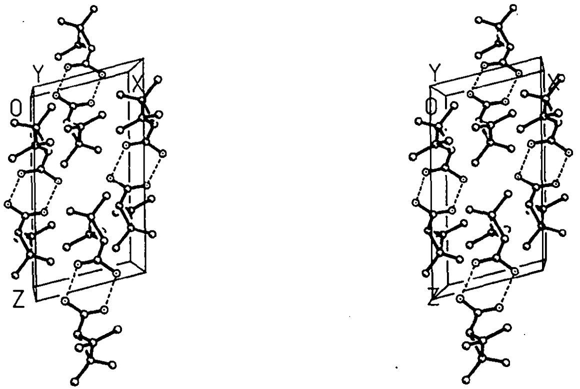

Fig. 2. Stereo packing plot of the title compound. H atoms omitted. Hydrogen bonds are indicated by dashed lines.

repulsion between the methyl hydrogens and the carbonyl oxygen, a rotation of the *cis* methyl groups at C(21) and C(31) would be expected to relax a great deal of the strain, unless the whole methyl group must be regarded as spherically symmetrical with respect to its repulsive non-bonded potential. But this is not found in the present study, even if the relatively large errors of the hydrogen positions are taken into account. Thus, the structure determined here reflects the delicate balance of all the forces between bonded and non-bonded atoms in the molecule.

In summary, the title molecule is found to adopt a slightly distorted *cb* conformation, as found in all sterically unperturbed carboxyl-substituted cyclopropanes studied so far. The ring-bond asymmetry predicted by simple molecular-orbital considerations is observed with the expected sign and approximate magnitude. However, the absolute values of several bond lengths and angles exceed those of similar molecules with carboxyl groups lacking steric interference. This limits the suitability of the tetramethyl-substituted acid as a model for cyclopropanecarboxylic acid.

The molecules are linked in pairs by hydrogen bonding across a centre of symmetry in the manner typical of carboxylic acids, with $O(1)\cdots O(2^i)$ 2·68 (1) Å (symmetry operator $1-x, -y, -z$). See Fig. 2.

We thank the Verband der Chemischen Industrie for financial assistance.

References

ALLEN, F. H. (1980). *Acta Cryst.* B**36**, 81–96.

BOER, J. S. A. M. DE, SCHENK, H. & STAM, C. H. (1986). *Recl Trav. Chim. Pays-Bas*, **105**, 434–435.

CLEGG, W. (1981). *Acta Cryst.* A**37**, 22–28.

KIERS, C. T., DE BOER, J. S. A. M., HEIJDENRIJK, D., STAM, C. H. & SCHENK, H. (1985). *Recl Trav. Chim. Pays-Bas*, **104**, 7–9.

KLEIN, A. W. & SCHRUMPF, G. (1981). *Acta Chem. Scand. Ser. A*, **35**, 425–430.

LUHAN, P. A. & MCPHAIL, A. T. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 2372–2375.

MESHCHERYAKOV, A. P. & DOLGII, I. E. (1960). *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, pp. 931–934.

SCHRUMPF, G. & JONES, P. G. (1987). *Acta Cryst.* C**43**, 1748–1752.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELX86*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1987). C**43**, 1755–1757

Substituted Cyclopropanes. 9. *cis*-1,2-Cyclopropanedicarboxylic Anhydride*

BY PETER G. JONES

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen,*
Federal Republic of Germany

AND GERD SCHRUMPF

Institut für Organische Chemie der Universität, Tammannstrasse 2, *D*-3400 *Göttingen,*
Federal Republic of Germany

(*Received* 11 *February* 1987; *accepted* 8 *April* 1987)

Abstract. $C_5H_4O_3$, $M_r = 112{\cdot}09$, monoclinic, $P2_1/m$, $a = 5{\cdot}324\ (2)$, $b = 8{\cdot}369\ (3)$, $c = 6{\cdot}057\ (2)$ Å, $\beta = 114{\cdot}74\ (3)^\circ$, $V = 245{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}52$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}12$ mm^{-1}, $F(000) = 116$, $T = 293$ K, $R = 0{\cdot}050$ for 469 reflections. The molecule possesses crystallographic mirror symmetry. The cyclopropane ring is symmetric with a libration-corrected average CC bond length of 1·509 Å, close to that of cyclopropane. The bond angles in the slightly non-planar anhydride ring correspond to some Bayer ring strain. The anhydride ring structure is similar to that of other five-membered cyclic anhydrides.

Introduction. In our previous communications, we studied the effect of substituents on the geometry of the cyclopropane ring. In part 7 of this series (Schrumpf & Jones, 1987), the additivity of substituent influences in *cis*- and *trans*-1,2-cyclopropanedicarboxylic acids was investigated. We interpreted our results in terms of the simple Hoffmann model (Hoffmann, 1970), treating the carboxyl group in the *cis*-bisected (*cb*) conformation as a π-electron acceptor. In other conformations, carboxyl groups were assumed to have no π-electronic effect on

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* Part 8: Jones & Schrumpf (1987).