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)···O(2^{i}) 2·68 (1) Å (symmetry operator 1−*x*, −*y*, −*z*). See Fig. 2.

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

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Abstract. $C_5H_4O_3$, $M_r = 112·09$, monoclinic, $P2_1/m$, $a = 5·324$ (2), $b = 8·369$ (3), $c = 6·057$ (2) Å, $\beta = 114·74$ (3)°, $V = 245·1$ Å^3, $Z = 2$, $D_x = 1·52$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·12 mm^{-1}, $F(000) = 116$, $T = 293$ K, $R = 0·050$ 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).

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the ring geometry, because the overlap that is responsible for the ring asymmetry, between appropriate orbitals of the cyclopropane ring and the carboxyl group, is reduced in non-bisected conformations. For cyclopropanecarboxaldehyde, this has been shown theoretically by geometry-optimized *ab initio* calculations at the 6–31G* level using the gradient method (De Mare & Peterson, 1983). The calculated average ring bond lengths at the *cb*, *trans*-bisected (*tb*) and perpendicular (*p*) conformations are the same.

In order to test this prediction experimentally, we examined the structure of the anhydride of *cis*-1,2-cyclopropanedicarboxylic acid. According to molecular models, the carbonyl groups in this molecule should adopt the anticlinal conformation, *i.e.* rotated from the *tb* conformation by at most 30°, and other degrees of freedom are restricted because of the five-membered ring and the probable C_s (*m*) symmetry.

Experimental. The title compound was synthesized according to the literature (McCoy, 1958). Crystals in the form of long colourless needles were obtained by recrystallization from diethyl ether.

Crystal 0·7 × 0·25 × 0·1 mm; 1336 profile-fitted intensities (Clegg, 1981) recorded on a Stoe–Siemens four-circle diffractometer. Monochromated Mo *Kα* radiation, $2\theta_{\max}$ 55°, $+h\pm k\pm l$. Three check reflections, no significant intensity change. $R_{\rm int}$ 0·018 for 599 unique reflections, 469 with $F > 4\sigma(F)$ used for all calculations [program systems *SHELX76* (Sheldrick, 1976) and *SHELX86* (Sheldrick, 1986)]. Index ranges after merging $|h| \le 6$, $|k| \le 10$, $|l| \le 7$. Cell constants refined from 2θ values of 48 reflections in the range 20–23°.

Structure solution by routine direct methods. Full-matrix refinement on *F* to *R* 0·050, *wR* 0·052 [H atoms refined freely; 50 parameters; weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00025F^2$; $S = 2{\cdot}13$]. Max. Δ/σ 0·01, max. features in final $\Delta\rho$ map ±0·23 e Å^{-3}. Atomic scattering factors those of *SHELX*.

A rigid-body libration correction was applied; $R_{\rm lib} = 0{\cdot}052$.

Discussion. The cell constants determined here are consistent with those reported previously (Hofmann, Orochena, Sax & Jeffrey, 1959). The final atomic coordinates, derived parameters and libration-corrected bond lengths are given in Table 1 and 2.† The discussion here is however based on uncorrected bond lengths (for comparison with other uncorrected data).

The molecule (Fig. 1) has the anticipated C_s (*m*) symmetry, which is crystallographically imposed; C(2) and O(1) lie in the mirror plane *x*, 0·25, *z*. The carbonyl groups are rotated by 25·6° from the *tb* position [torsion angle O(2)—C(3)—C(1)—midpoint C(1$^{\rm i}$), C(2) = −155·4°]. The unusual *tg* conformation is forced on the molecule by the anhydride ring. The ring bond lengths C(1)C(2) (1·497 Å) and C(1)C(1$^{\rm i}$) (1·505 Å) are very similar. The direction of the scarcely significant ring asymmetry is of the correct sign for 1,2-dicarbonylcyclopropanes, with a marginally longer bond between the substituted carbon atoms, from which we may infer a very small π-type interaction, if any, between the carbonyl groups and the ring. The mean ring bond distance is 1·500 Å, a little smaller than the average (1·505 Å) of many carbonyl-substituted cyclopropanes reviewed by Allen (1980).

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 ×10^3)

	x	*y*	*z*	$U/U_{\rm eq}$
C(1)	8138 (3)	1601 (2)	3131 (3)	43 (1)*
C(2)	9510 (5)	2500	5472 (5)	48 (1)*
C(3)	5279 (4)	1130 (2)	2586 (3)	50 (1)*
O(1)	3762 (3)	2500	2520 (3)	58 (1)*
O(2)	4205 (3)	−148 (2)	2218 (2)	70 (1)*
H(1)	9120 (35)	998 (19)	2491 (25)	43 (5)
H(2*A*)	8692 (57)	2500	6601 (47)	57 (8)
H(2*B*)	11512 (55)	2500	6188 (41)	51 (7)

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

Table 2. *Bond lengths* (Å) *and angles* (°)

		Corrected
C(1)—C(2)	1·497 (3)	1·507
C(3)—O(1)	1·394 (2)	1·402
C(1)—C(1$^{\rm i}$)	1·505 (3)	1·512
C(1)—C(3)	1·470 (2)	1·482
C(3)—O(2)	1·189 (2)	1·196

C(3)—C(1)—C(2)	113·4 (2)	C(3)—C(1)—C(1$^{\rm i}$)	105·6 (2)
C(2)—C(1)—C(1$^{\rm i}$)	59·8 (2)	C(1)—C(2)—C(1$^{\rm i}$)	60·3 (2)
O(1)—C(3)—C(1)	108·6 (2)	O(2)—C(3)—C(1)	130·9 (2)
O(2)—C(3)—O(1)	120·4 (2)	C(3)—O(1)—C(3$^{\rm i}$)	110·7 (2)

Symmetry operator (i): *x*, 0·5 −*y*, *z*.

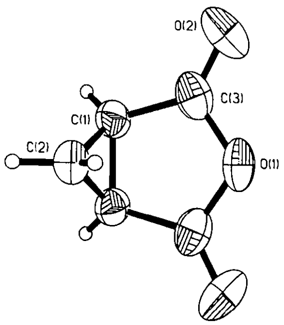

Fig. 1. Thermal-ellipsoid plot of the title molecule (50% level), showing the numbering scheme of the asymmetric unit.

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† Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43950 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The length of the bond C(1)C(3) joining the carbonyl groups to the cyclopropane ring (1·470 Å) is similar to the corresponding value in phthalic anhydride (1·469 Å av.; Bates & Cutler, 1977) and maleic anhydride (1·470 Å av.; Marsh, Ubell & Wilcox, 1962), where some conjugative interaction between the carbonyl groups and the adjacent coplanar aromatic and olefinic π bonds can be expected. Interestingly, the analogous bond in crystalline succinic anhydride, with no conjugation, is of the same order (1·475 Å; Ehrenberg, 1965). This has been challenged by Seip (Brendhaugen, Kolderup Fikke & Seip, 1973), who determined the structure of succinic anhydride in the vapour phase by electron diffraction and found 1·510 Å for that bond. The unusually large discrepancy of 0·035 Å between a bond length in the crystal and the vapour is unexpected and a redetermination of the crystal structure of succinic anhydride is therefore under way in our laboratories. At present, we cannot decide whether the bond length between carbonyl groups and the adjacent carbon skeleton in anhydrides is susceptible to conjugative shortening at all. In aldehydes and ketones, there is a definite difference in the lengths of the CC bonds between the carbonyl group and a saturated or unsaturated carbon atom. For example, in propanal, the length of the bond adjacent to the carbonyl group is 1·513 Å (r_g, *cis* conformer; van Nuffel, van den Enden, van Alsenoy & Geise, 1984), whereas in acrolein, the corresponding bond length is contracted to 1·478 Å (r_s, *cis* conformer; Blom, Grassi & Bauder, 1984).

The angles within the five-membered ring are obviously influenced by ring closure, with substantial deviations from a hypothetical open-chain 1,2-dicarbonylcyclopropane. Thus, the angle C(1)C(3)-O(1) is unusually small at the expense of C(1)-C(3)O(2). C(3)O(1)C(3^i) is also smaller than in open-chain anhydrides, which admittedly also exist in a different conformation. However, the bond angles about the carboxyl atom C(3) are normal compared with other cyclic anhydrides, which exhibit similar deviations from the data of open-chain anhydrides (Vledder, Mijlhoff, Leyte & Romers, 1971).

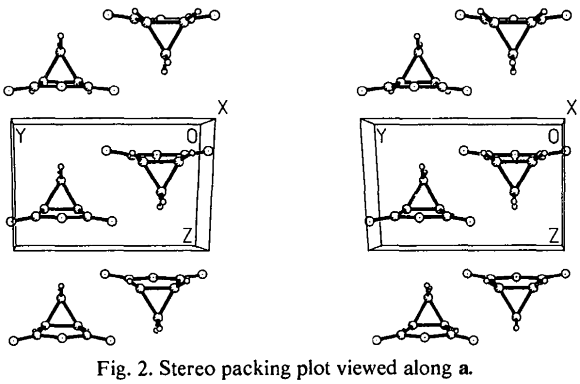

Fig. 2. Stereo packing plot viewed along **a**.

Another consequence of the formation of a five-membered ring is that the C(1)C(3) bond does not lie in the intra-annular bisector plane through C(1), *i.e.* the plane including the bisector of C(1^i)—C(1)—C(2) and perpendicular to the three-membered ring. The deviation is about 4°. This is expected to weaken further the overlap between the carbonyl and the Walsh-type orbitals responsible for conjugative interaction.

Finally, the five-membered ring is not planar, but O(1) lies slightly (0·13 Å) out of the plane defined by C(3), C(1), C(1^i) and C(3^i) in the direction of the cyclopropane ring. This brings the carbonyl groups closer to the *tb* conformation relative to the cyclopropane ring than would a displacement of O(1) in the opposite sense. For comparison, maleic anhydride in the crystalline phase is marginally non-planar (Marsh *et al.*, 1962). However, the electron diffraction data of succinic anhydride were interpreted on the basis of a planar ring (Brendhaugen *et al.*, 1973). Crystalline phthalic anhydride is planar (Bates & Cutler, 1977).

In summary, the structure of the five-membered ring of the title compound is very similar to that in other cyclic anhydrides except for the CC bond not involving the carbonyl C atoms. The three-membered ring shows no marked ring-bond asymmetry, as expected for 1,2-disubstituted cyclopropanes with unconjugated substituents (carbonyls in *tg* conformation) lacking substantial inductive properties.

The molecular packing (Fig. 2). shows no unusual features.

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