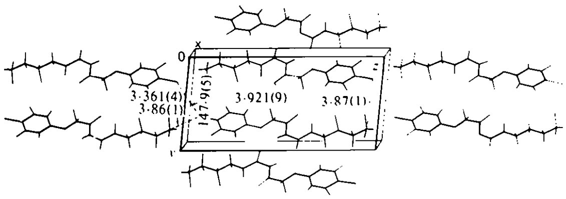

Fig. 3. The packing of the molecules when viewed perpendicular to the *bc* plane, along with some intermolecular distances (Å) and an angle (°).

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Reinvestigation of the Structure of Feist's Acid 3-Methylene-*trans*-1,2-cyclopropanedicarboxylic Acid

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Abstract. $C_6H_6O_4$, M_r = 142, triclinic, $P\bar{1}$, a = 4·842 (1), b = 7·607 (1), c = 9·168 (3) Å, α = 98·41 (2), β = 99·89 (2), γ = 77·74 (1)°, V = 320·9 Å^3, Z = 2, D_m = 1·45 (flotation), D_x = 1·470 g cm^{-3}, μ(Mo $K\alpha$, λ = 0·7107 Å) = 0·63 cm^{-1}, $F(000)$ = 148. The structure was solved by direct methods and refined to an R value of 0·038 for 723 intensity measurements. The geometrical changes in the cyclopropane ring are discussed in the light of substituent effects. In the crystal structure the carboxylic groups are disordered.

Introduction. Feist's acid (Feist, 1893) (see Fig. 1), initially thought to embody a methylcyclopropylene system, is now known to be a methylenecyclopropane. The latter structure, suggested by NMR (Ettlinger & Kennedy, 1956; Kende, 1956; Lloyd, 1969), was confirmed by simple X-ray work (Lloyd, Downie & Speakman, 1954*a*,*b*; Petersen, 1956). We now report a more precise X-ray study as a part of a programme of investigations of substituent effects on three-membered rings. Our results are of particular relevance to a theoretical interest in such rings (Deakyne, Allen & Laurie, 1976).

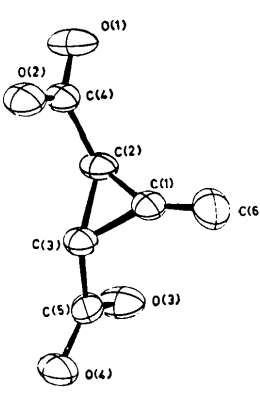

Fig. 1. Perspective view of the molecule viewed down **a**. The H atoms were given numbers corresponding to the bonded C atoms.

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The compound was prepared by the method used by Feist (1893) [see also Goss, Ingold & Thorpe (1923)] and suitable crystals (m.p. 415 K) were grown from ethyl acetate. Intensity data were collected with a crystal of dimensions 0·6 × 0·5 × 0·2 mm on a CAD-4 diffractometer using monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) by the $\omega/2\theta$ technique to a limit of $2\theta = 45°$. The analysis was based on 723 terms with $|F_o| \geq 2\sigma(|F_o|)$.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Block-diagonal least-squares refinement with anisotropic thermal parameters for C and O atoms converged at $R = 0{\cdot}088$. The four H atoms bonded to C were located by a difference synthesis. The acidic H atoms appeared only as residual density extended along the O···O directions. Other evidence suggested that the acid H atoms are disordered; two half-hydrogen atoms were therefore placed, along each hydrogen bond, in calculated positions, which were not refined. The final cycles of full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961) with H atoms isotropic and other atoms anisotropic converged at $R = 0{\cdot}038$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where w is of the form $[5{\cdot}0 + |F_o| + 0{\cdot}075\,|F_o|^2]^{-1}$ (Cruickshank, 1961). Coordinates are given in Table 1, geometric details are in Table 2.*

Table 1. *Fractional coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and equivalent isotropic temperature factors* (*isotropic for* H)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}/B_{\rm iso}$ (Å^2)
C(1)	1588 (5)	7632 (3)	1581 (3)	2·8 (1)
C(2)	4174 (6)	6768 (3)	2480 (3)	3·0 (1)
C(3)	2183 (5)	8473 (3)	3113 (3)	2·8 (1)
C(4)	4128 (5)	4982 (3)	2953 (3)	2·9 (1)
O(1)	5988 (4)	3674 (2)	2550 (3)	4·7 (1)
O(2)	2158 (4)	4869 (2)	3664 (2)	4·0 (1)
C(5)	3125 (5)	10247 (3)	3302 (3)	2·8 (1)
O(3)	5127 (4)	10387 (2)	2629 (2)	4·1 (1)
O(4)	1781 (4)	11532 (2)	4080 (2)	4·2 (1)
C(6)	−114 (8)	7653 (5)	301 (3)	4·6 (1)
H(2)	601 (7)	687 (4)	217 (3)	2·6 (5)
H(3)	101 (6)	833 (4)	384 (3)	1·9 (5)
H(61)	37 (7)	673 (5)	−58 (4)	3·5 (7)
H(62)	−209 (8)	871 (5)	16 (4)	4·2 (7)
H(O1)	563	257	289	5·0
H(O2)	239	358	383	5·0
H(O3)	563	1167	284	5·0
H(O4)	249	1263	407	5·0

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

C(1)–C(2)	1·461 (4)	C(1)–C(2)–H(2)	115·1 (1·9)
C(1)–C(3)	1·464 (3)	C(3)–C(2)–C(4)	118·8 (2)
C(1)–C(6)	1·313 (4)	C(3)–C(2)–H(2)	120·2 (1·9)
C(2)–C(3)	1·546 (4)	C(4)–C(2)–H(2)	115·3 (1·9)
C(2)–C(4)	1·491 (3)	C(1)–C(3)–C(2)	58·0 (2)
C(3)–C(5)	1·492 (3)	C(1)–C(3)–C(5)	116·4 (2)
C(4)–O(1)	1·251 (3)	C(1)–C(3)–H(3)	118·4 (1·8)
C(4)–O(2)	1·268 (3)	C(2)–C(3)–C(5)	118·4 (2)
C(5)–O(3)	1·265 (3)	C(2)–C(3)–H(3)	117·9 (1·8)
C(5)–O(4)	1·254 (3)	C(5)–C(3)–H(3)	115·6 (1·8)
C(2)–H(2)	1·00 (3)	C(2)–C(4)–O(1)	116·7 (2)
C(3)–H(3)	0·98 (3)	C(2)–C(4)–O(2)	118·6 (2)
C(6)–H(61)	1·01 (4)	O(1)–C(4)–O(2)	124·6 (2)
C(6)–H(62)	1·11 (4)	C(3)–C(5)–O(3)	118·7 (2)
		C(3)–C(5)–O(4)	117·1 (2)
C(2)–C(1)–C(3)	63·8 (2)	O(3)–C(5)–O(4)	124·1 (2)
C(2)–C(1)–C(6)	148·6 (3)	C(1)–C(6)–H(61)	120·7 (2·1)
C(3)–C(1)–C(6)	147·6 (3)	C(1)–C(6)–H(62)	120·2 (2·0)
C(1)–C(2)–C(3)	58·2 (2)	H(61)–C(6)–H(62)	119·1 (2·9)
C(1)–C(2)–C(4)	116·7 (2)		

Discussion. The changes in the geometry of the ring caused by the addition of a methylene group can be seen from the comparison of bond lengths in related compounds in Table 3. The presence of two carboxyl groups seems to have no significant effect on the ring. In other derivatives of cyclopropane, for example 1,1-cyclopropanedicarboxylic acid (Meester, Schenk & MacGillavry, 1971), the interaction between the acid groups and the ring has drastically affected the ring geometry. In the present case, it appears that the ring and $=\mathrm{CH_2}$ group interaction overrides the $-$COOH and ring interaction, thereby reorganizing the molecular orbitals. As a consequence, the adjacent bonds have shortened significantly and the opposite bond has increased significantly.

Both carboxyl groups take the *cg* conformation (Allen, 1980). In the present case, the C–O distances are averaged out. There is also evidence, from difference electron density maps, that the $-$COOH moieties are disordered through interchange of their carboxylic and hydroxyl groups. This phenomenon is not uncommon in carboxylic acids (Dieterich, Paul & Curtin, 1974; Bryan & Freyberg, 1975). A similar

Table 3. *Bond-length distribution in some related compounds*

Compound	Adjacent bond (Å)	Opposite bond (Å)	Reference
Feist's acid	1·461 (4) 1·464 (3)	1·546 (4)	This work
Methylene-cyclopropane	1·457 (1)	1·542 (1)	Laurie & Stigliani (1970)
1,1-Cyclopropane-dicarboxylic acid	1·531 (3) 1·535 (3)	1·456 (4)	Meester, Schenk & MacGillavry (1971)
Cyclopropane	1·510	1·510	Bastiansen, Fritsch & Hedberg (1966)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36411 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

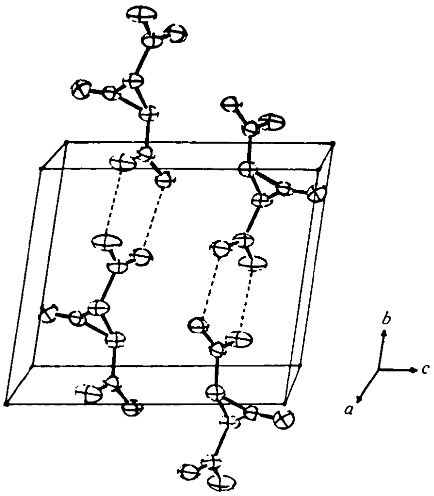

Fig. 2. Packing of the molecules viewed down **a**.

disorder has also been proposed to account for both bond-length anomaly and space-group ambiguity in the structure of 1,1-cyclopropanedicarboxamide (Usha & Venkatesan, 1979). The molecules are arranged in infinite chains with intermolecular hydrogen bonds of length 2·637 (3) Å [O(3)···O(1)′] and 2·675 Å [O(4)···O(2)′] almost parallel to **b** (Fig. 2).

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Structure of Verticinone Hydrochloride

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Abstract. $C_{27}H_{44}NO_3^+.Cl^-$, $M_r = 466{\cdot}1$, $F(000) = 1016$, orthorhombic, space group $P2_12_12_1$, $a = 10{\cdot}311\ (1)$, $b = 10{\cdot}869\ (1)$, $c = 23{\cdot}564\ (6)$ Å, $U = 2640{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}10$, $D_c = 1{\cdot}09$ Mg m^{-3}, Cu $K\alpha(\lambda = 1{\cdot}54178$ Å), $\mu = 0{\cdot}55$ mm^{-1}. The final R is 0·050 for 1231 independent observed reflections. All the six-membered rings in this compound are in the chair conformation and the five-membered ring is in the envelope conformation. Ring fusions are *A*/*B trans*, *B*/*C trans*, *C*/*D cis*, *D*/*E trans* and *E*/*F trans*.

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