Fig. 2. Spatial distribution of Br^- ions with respect to N^+R_4. Br' and Br'' are related to Br by $(x, y, z + 1)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ respectively. Distances are in Å, e.s.d.'s are 0·003 Å.

Crogyroidine is an example of a non-ester type PA. It lacks the structural features common to most diester and monoester alkaloids, such as the double bond between atoms C(1) and C(2), the ester linkages and associated macrocycles. The present structure also differs from other known PA's in having exocyclic substitution at N(4). In most PA molecules referred to above, the N atom is unsubstituted and invariably forms a hydrogen bond with a neighboring hydroxyl group.

Fig. 2 shows the association of the N^+R_4 system with the Br ions. It is seen that the positively charged N is associated with three Br^- ions. Association of more than one halide ion to tetracovalent N^+R_4 ions has been reported in the case of thelepogine methiodide (Fridrichsons & Mathieson, 1963). In the present structure, the closest approach of the negative ion [Br—N(4) = 4·303 (3) Å] is through the approximate center of a triad formed by the atoms C(3), C(8) and C(1'). The other two approach distances are somewhat longer, Br'—N(4) = 4·494 (3) and Br''—N(4) = 4·635 (3) Å. Compared to Br, both Br' and Br'' assume less symmetric positions with respect to the N^+R_4 system (see Fig. 2). Such orientations of the Br^- ions with respect to the N^+R_4 ions are likely to cause uneven charge distribution among the four C atoms attached to the N atoms, and may very well explain the asymmetry in the four N—C bonds.

The nearest neighbors of the Br^- ion are two water molecules. The Br—O(1) distance of 3·420 (4) Å and Br—O(1)$(\frac{1}{4} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ distance of 3·468 (4) Å are somewhat longer than the normally accepted distance (3·28 Å) for a Br···O hydrogen bond (Kuleshova & Zorkii, 1981).

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Structure of 2-Furoic Acid, $C_5H_4O_3$: a Redetermination

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Abstract. $M_r = 112·1$, triclinic, $P\bar{1}$, $a = 10·221$ (2), $b = 6·762$ (1), $c = 3·781$ (2) Å, $\alpha = 83·59$ (2), $\beta = 96·75$ (2), $\gamma = 106·76$ (2)°, $V = 247·6$ Å³, $Z = 2$, $D_m = 1·483$ [Goodwin & Thomson (1954). *Acta Cryst.* **7**, 166–173], $D_x = 1·503$ Mg m⁻³, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·137$ mm⁻¹, $F(000) = 116$, $T = 293$ K. Final $R = 0·035$ based on 901 independent observed reflections. The structure determined from

projections by Goodwin & Thomson has been confirmed. The acidic H atoms, involved in the formation of the centrosymmetric carboxylic dimer, are disordered.

Introduction. The structure of 2-furoic acid (2-furancarboxylic acid) (formula I, where the asterisk shows a centre of symmetry) was determined, so far as the C and O atoms were concerned, by Goodwin & Thomson (1954) (see also Hudson, 1962). Precise positions have now been found for all the atoms. They are of interest in connection with microwave work on furan itself, C_4H_4O (Mata, Martin & Sørensen, 1978), with theoretical work on furan and its derivatives (John & Radom, 1978), and with general ideas on the dimerized carboxyl group (*e.g.* Dieterich, Paul & Curtin, 1974).

(I)
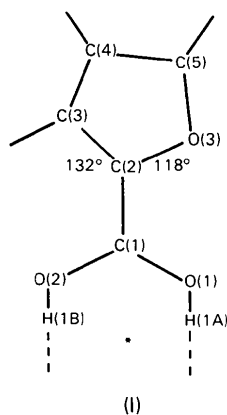
Experimental. Title compound, derived from a commercial sample, crystallizes from water as plates, often twinned; single crystal (dimensions $1.00 \times 0.50 \times 0.16$ mm) mounted in a Lindemann capillary. CAD-4 diffractometer, $\omega/2\theta$ scan to $\theta = 27°$, Mo radiation. Cell dimensions calculated from diffractometer angles for 25 strong reflections. Domain of reciprocal space covered ranged in $h -13/13$, in $k -8/8$, and in $l -4/4$. Neither of two standard reflections drifted significantly. All accessible reflections recorded at least once, and half of them twice, amounting to 3138 data, which merged to yield 901 with $I > 3\sigma(I)$. Internal consistency indicated by $R(F) = 0.016$. Absorption factors, for F^2, ranged from 0.980 to 0.931; absorption corrections not made. Refinement by full-matrix anisotropic least squares started from coordinates of Goodwin & Thomson (1954). H atoms, located from difference density maps, were allowed isotropic vibrations. Convergence at $R = 0.035$, $R_w = 0.050$, $S = 4.6$. Of 14 significant peaks in final difference map, 11 could be attributed to deformation density (Coppens & Vos, 1971; Hirshfeld & Hope, 1980); highest of such peaks 0.25 e Å^{-3}. Least-squares weighting $w = 1/\sigma^2(F)$ where $\sigma(F)$ is based on counting statistics. At convergence ratio of shift to e.s.d. for 93 parameters up to 0.03 for C atoms and O(3), up to 0.06 for O(1), O(2) and H atoms connected to C, but as high as 0.26 for disordered H(1A) and H(1B). No evidence for extinction – not

even in $01\bar{1}$ which had E as high as 4.3; no corrections made. Scattering factors from *International Tables for X-ray Crystallography* (1974). All crystallographic calculations performed with *GX* (the Glasgow suite of programs).

Discussion. Coordinates are in Table 1, and the more important geometrical details in Table 2.*

A feature of this structure, shown in formula (I), is the 14° difference between the take-off angles C(3)–C(2)–C(1) and O(3)–C(2)–C(1). A similar difference, 17°, was found at the corresponding C—H bonds in furan (Mata *et al.*, 1978). A consequence of this difference is an abnormal non-bonded contact between O(1) and O(3), and this may explain an anomaly in the C(2)–C(1)–O angles.

Apart from this detail, the dimensions of the carboxyl group imply (Dieterich *et al.*, 1974; Berkovitch-Yellin & Leiserowitz, 1982) that the H atom is disordered, as in benzoic acid (Feld, Lehmann, Muir & Speakman, 1981). Confirmation came from the location of 'partial' H atoms, designated H(1A) and H(1B) in (I), with site-occupancy factors close to 0.5.

The five atoms of the ring are coplanar. From this plane, C(1), O(1) and O(2) deviate, all in the same direction, by 0.057 (1), 0.155 and 0.016 Å, respectively. Analysis of the anisotropic vibrational parameters of the C_5O_3 atoms indicates rigid-body libration, with a maximum r.m.s. amplitude of 8.0 (4)° about an axis nearly parallel to C(1)—C(2).

Cell parameters

Groth (1919) reports the crystal system of 2-furoic acid as 'monoklin (?)'; his parameters are not easily reconciled with the X-ray results. Goodwin & Thomson (1954) give $\alpha = 92° 57'$, which must be an error, as we have evidently used the same lattice.

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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 38570 (16 pp.). Copies may be obtained through The Executive Secretary, Intenational Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* $(\times 10^5, \times 10^4 \text{ for } H)$ *and isotropic thermal parameters* $(\text{Å}^2 \times 10^4, \times 10^3 \text{ for } H)$

$$U_{eq} = (U_{11}.U_{22}.U_{33})^{1/3}.$$

	x	y	z	U_{eq}/U_{iso}
C(1)	36731 (12)	12095 (17)	12867 (29)	430 (6)
C(2)	26998 (12)	22537 (17)	21285 (28)	425 (6)
C(3)	28767 (13)	41363 (20)	32633 (31)	492 (7)
C(4)	15507 (14)	43397 (21)	34416 (36)	569 (8)
C(5)	6624 (15)	25770 (23)	24155 (40)	594 (8)
O(1)	32006 (10)	−5381 (13)	−396 (26)	566 (6)
O(2)	49252 (10)	21083 (15)	18952 (28)	583 (6)
O(3)	13355 (9)	12524 (14)	15769 (25)	530 (5)
H(1A)*	3817 (32)	−1031 (42)	−619 (70)	24 (6)
H(1B)†	5505 (37)	1512 (37)	1438 (88)	28 (8)
H(2)	3715 (19)	5052 (26)	3828 (46)	44 (4)
H(3)	1369 (17)	5519 (26)	4198 (40)	37 (4)
H(4)	−326 (20)	2143 (28)	2052 (48)	47 (5)

* S.o.f. = 0.55.

† S.o.f. = 0.45.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–O(1)	1·276 (1)	O(1)–H(1A)	0·85 (3)
C(1)–O(2)	1·255 (2)	O(2)–H(1B)	0·85 (4)
C(1)–C(2)	1·456 (2)	C(3)–H(2)	0·92 (2)
C(2)–C(3)	1·345 (2)	C(4)–H(3)	0·95 (2)
C(3)–C(4)	1·411 (2)	C(5)–H(4)	0·97 (2)
C(4)–C(5)	1·339 (2)	O(1)···O(3)	2·691 (1)
C(5)–O(3)	1·359 (2)	O(1)···O(2^i)	2·635 (1)
O(3)–C(2)	1·366 (2)		

O(1)–C(1)–O(2)	124·5 (1)	C(1)–O(1)–H(1A)	114 (2)
C(2)–C(1)–O(1)	118·2 (1)	C(1)–O(2)–H(1B)	118 (2)
C(2)–C(1)–O(2)	117·3 (1)	C(2)–C(3)–H(2)	125 (1)
C(1)–C(2)–C(3)	131·9 (1)	C(4)–C(3)–H(2)	129 (1)
C(1)–C(2)–O(3)	117·6 (1)	C(3)–C(4)–H(3)	124 (1)
C(2)–C(3)–C(4)	106·3 (1)	C(5)–C(4)–H(3)	129 (1)
C(3)–C(4)–C(5)	106·6 (1)	C(4)–C(5)–H(4)	132 (1)
C(4)–C(5)–O(3)	110·8 (1)	O(3)–C(5)–H(4)	117 (1)
C(5)–O(3)–C(2)	105·7 (1)		
O(3)–C(2)–C(3)	110·5 (1)		

Symmetry code: (i) = $1 - x, -y, -z$.

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# A Redetermination of the Structure of 1,1,2,2-Tetracarbomethoxyethane,* C10H14O8, at 145 K

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Abstract. $M_r = 262\cdot2$, monoclinic, $P2_1/n$, $a = 6\cdot679$ (2), $b = 7\cdot648$ (2), $c = 12\cdot115$ (3) Å, $\beta = 104\cdot36$ (2)°, $V = 599\cdot5$ (5) Å^3, $Z = 2$, $F(000) = 276$, $D_x = 1\cdot453$ (2) g cm^{-3}, $\lambda = 0\cdot71073$ Å, $\mu(\text{Mo } K\alpha) = 1\cdot20$ cm^{-1}, $R = 0\cdot046$ for 1283 observations (of 1740 unique data). The previously reported structure [Schaefer & Costin (1968). *J. Org. Chem.* **33**, 1677–1678] is confirmed.

Introduction. The structure of 1,1,2,2-tetracarbomethoxyethane (I) was previously determined (Schaefer & Costin, 1968) using film data, and refined to $R = 0\cdot116$. During our studies of ligands derived from dimethyl malonate, we isolated this tetraester and determined its structure using cryogenic diffractometer data.

MeO₂C ╲   ╱CO₂Me
        ╲CHCH╱
MeO₂C ╱   ╲CO₂Me

(I)
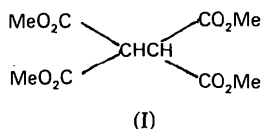
* Tetramethyl ethanetetracarboxylate.
† On leave from University of Delhi, India, 1980–1983.
‡ To whom correspondence should be addressed.

Experimental. 1,1,2,2-Tetracarbomethoxyethane was obtained as a by-product (10–20%) during the synthesis of pyridine- or pyrazine-malonate ligands (Newkome, Gupta & Fronczek, 1982) in the form of colorless crystals:§ m.p. 407–408 K; ¹H NMR (CDCl₃) $\delta 3\cdot77$ (*s*,OCH₃, 12H), 4·18 (*s*, CH, 2H); ¹³C NMR $\delta 51\cdot1$ (CH₃), 53·0 (CH), 167·4 (C=O); MS (70eV) m/e 231 (M^+–OCH₃, 23), 203 (M^+–CO₂CH₃, 28), 171 (M^+–C₃H₇O₃, 100), 159 (M^+–C₄H₇O₃, 48). Other experimental details can be found elsewhere (Newkome, Gupta & Fronczek, 1982; Newkome, Puckett *et al.*, 1982).

Single crystals grown from EtOAc–cyclohexane (1:3). Crystal dimensions 0·24 × 0·32 × 0·48 mm, Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator and a N₂ gas-stream cryostat. Cell dimensions and crystal orientation by least-squares fit of setting angles of 25 reflections with $13° < \theta < 16°$. Space group $P2_1/n$ was chosen because this indexing yields a more nearly orthogonal cell than the $P2_1/c$ of the original study (Schaefer & Costin, 1968).

§ Analytical data are within acceptable limits.