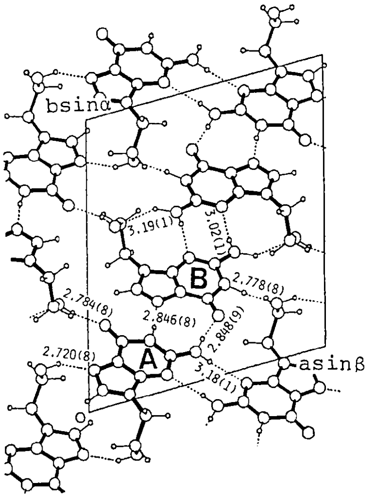

Fig. 2. The crystal structure projected along **c**. Broken lines indicate the hydrogen bonds. Distances (Å) for N···N, N···O, O···N or O···O are given with e.s.d.'s in parentheses.

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Structure of Tetramethylammonium Hydrogen Maleate

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Abstract. $N(CH_3)_4^+.C_4H_3O_4^-$, $M_r = 189{\cdot}2$, monoclinic, $P2_1/c$, $a = 5{\cdot}789\,(1)$, $b = 9{\cdot}718\,(1)$, $c = 18{\cdot}362\,(2)$ Å, $\beta = 90{\cdot}83\,(1)°$, $V = 1032{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}20\,(5)$, $D_x = 1{\cdot}217$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}091$ mm^{-1}, $F(000) = 408$, $T = 293\,(1)$ K, final $R = 0{\cdot}047$ for 1109 unique observed reflexions. There is an intramolecular hydrogen bond O···H···O of 2·403 (4) Å in the hydrogen maleate residue. The skeletal C atoms are planar, but the carboxyl groups are twisted out of the plane by 6·0 (4) and 5·4 (4)°. The tetramethylammonium ion has the usual tetrahedral shape.

Introduction. The structural investigation reported here is a part of the research programme dealing with the acid salts of carboxylic acids. The main purpose of this work is to obtain additional data about the intramolecular hydrogen bond in the hydrogen maleate residue and to make a comparison with known structures which contain this structural unit [see Olovsson, Olovsson & Lehmann (1984) for a concise list].

Experimental. Single crystals grown from the equimolar aqueous solutions of tetramethylammonium hydroxide and maleic acid; density measurement by flotation in chlorobenzene/CCl_4; colourless prisms, 0·34 × 0·38 ×

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0·40 mm; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation (graphite monochromator), cell dimensions by least squares on θ values of 60 accurately centred reflexions; $\omega/2\theta$ scans, variable scan rate (min. 2·5, max. 20·1° min^{-1}), max. scan time 40 s, scan width (2θ) $(0{\cdot}8 + 0{\cdot}3\tan\theta)°$, aperture $(2{\cdot}5 + 0{\cdot}9\tan\theta)$ mm, background measured for $\frac{1}{4}$ of scan time at each of scan limits, $(\sin\theta/\lambda)_{\max}$ in intensity measurements: 0·7035 Å^{-1}. Three reference reflexions monitored at intervals of 240 reflexions, no significant decline; data corrected for intensity variation and Lp effects, but absorption ignored. 11932 measured reflexions ($\pm h$, $\pm k$, $\pm l$), 2934 unique reflexions ($R_{\rm int} = 0{\cdot}112$), 1109 unique observed reflexions [$I > 4\sigma(I)$, index range h −7/7, k 0/12, l 0/22], $\sigma(I)$ based on counting statistics. Monoclinic system derived from preliminary oscillation and Weissenberg photographs; space group $P2_1/c$ chosen after examination of systematic absences and distribution of $|E|$ values. Structure determination by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Structure refined anisotropically by full-matrix least squares minimizing $\sum w(\Delta F)^2$ with *SHELX*76 (Sheldrick, 1976); final R and wR values: 0·047 and 0·072 with $w = [\sigma^2(F_o) + 0{\cdot}004F_o^2]^{-1}$; all H-atom positions found from a difference synthesis and included in refinement at calculated positions [d(C–H) = 1·09 Å] with a common isotropic temperature factor, $U = 0{\cdot}101\,(3)$ Å^2, acidic H refined separately. No features greater than ±0·15 e Å^{-3} in final difference map. At convergence max. and mean values of Δ/σ: 0·337 and 0·062. Scattering and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations performed on the DEC 1091 computer at RCU Ljubljana. Besides *SHELX*76, *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for data reduction and interpretation.

Discussion. The final atomic parameters are in Table 1.[*] A view of the crystal packing with the atomic numbering is in Fig. 1. The hydrogen maleate anion is shown in Fig. 2. Interatomic distances and angles are listed in Table 2.

There are discrete tetramethylammonium ions, $N(CH_3)_4^+$, and hydrogen maleate residues, $C_4H_3O_4^-$, in the structure. The skeletal chain of C atoms in the hydrogen maleate residue is planar to within 0·005 (3) Å. The end carboxyl groups are rotated out of the C-atom plane by 6·0 (4) and 5·4 (4)°. The

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^4) (*Hamilton,* 1959) *for non*-H *and isotropic* U_{iso} (Å^2 ×10^3) *for refined acidic* H *atom*

	x	y	z	$U_{\rm eq}$ or $U_{\rm iso}$
O(1)	750 (4)	6309 (2)	2984 (1)	783 (14)
O(2)	3310 (3)	5014 (3)	3553 (2)	866 (15)
O(3)	3329 (3)	3119 (3)	4394 (1)	870 (16)
O(4)	823 (4)	1889 (2)	4984 (2)	939 (17)
C(1)	1225 (5)	5415 (3)	3434 (2)	545 (15)
C(2)	−672 (4)	4788 (3)	3850 (1)	515 (14)
C(3)	−660 (4)	3755 (3)	4325 (2)	529 (14)
C(4)	1267 (4)	2850 (3)	4591 (2)	583 (16)
N	5012 (3)	4357 (2)	1469 (1)	490 (12)
C(5)	6273 (5)	3907 (4)	804 (2)	670 (18)
C(6)	6731 (5)	4863 (4)	2017 (2)	815 (22)
C(7)	3695 (6)	3177 (3)	1762 (2)	814 (22)
C(8)	3365 (5)	5477 (3)	1279 (2)	713 (19)
H	3429 (61)	3982 (44)	4018 (22)	101 (3)

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

$C_4H_3O_3^-$ moiety			
C(1)–O(1)	1·227 (4)	O(1)–C(1)–O(2)	122·0 (3)
C(1)–O(2)	1·284 (4)	O(1)–C(1)–C(2)	118·6 (3)
C(4)–O(3)	1·279 (3)	O(2)–C(1)–C(2)	119·4 (3)
C(4)–O(4)	1·210 (4)	C(1)–C(2)–C(3)	130·8 (2)
C(1)–C(2)	1·478 (4)	C(2)–C(3)–C(4)	130·9 (2)
C(2)–C(3)	1·330 (4)	O(4)–C(4)–O(3)	122·2 (3)
C(3)–C(4)	1·497 (4)	O(4)–C(4)–C(3)	119·0 (2)
		O(3)–C(4)–C(3)	118·8 (3)
O(2)···H	1·32 (4)		
O(3)···H	1·09 (4)	O(2)···H···O(3)	174 (3)
O(2)···O(3)	2·403 (4)		
$N(CH_3)_4^+$ ion			
N–C(5)	1·497 (4)	C(5)–N–C(6)	108·6 (2)
N–C(6)	1·489 (4)	C(5)–N–C(7)	109·2 (2)
N–C(7)	1·483 (4)	C(5)–N–C(8)	110·0 (2)
N–C(8)	1·485 (4)	C(6)–N–C(7)	110·7 (2)
		C(6)–N–C(8)	109·7 (2)
		C(7)–N–C(8)	108·7 (2)

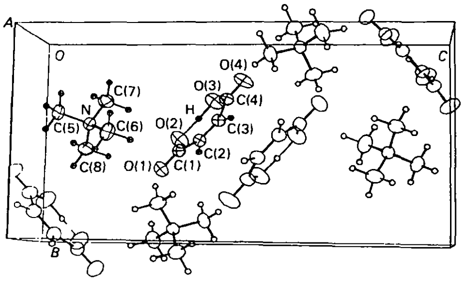

Fig. 1. *ORTEP* (Johnson, 1965) view of the unit cell. The atoms are represented by thermal ellipsoids at the 50% probability level.

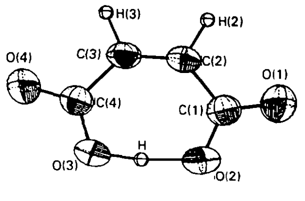

Fig. 2. Hydrogen maleate residue.

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42329 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

carboxyl groups are twisted in such a way that O(2) and O(3) are on the same side of the plane of the C atoms at distances of 0·122 (3) and 0·099 (3) Å respectively. This distortion from planarity is probably caused by a rather strong intramolecular hydrogen bond O(2)···O(3) of 2·403 (4) Å. A similar situation has been observed in other compounds containing hydrogen maleate residues, for example in manganese(II) hydrogen maleate tetrahydrate (Lis, 1983) and in imidazolium hydrogen maleate (Sakhawat Hussain, Schlemper & Fair, 1980; James & Matsushima, 1976).

The arrangement of C atoms around N in $N(CH_3)_4^+$ is almost ideally tetrahedral. The N—C lengths range from 1·483 (4) to 1·497 (4) Å, and the C—N—C angles from 108·6 (2) to 110·7 (2)° with average values of 1·489 (2) Å and 109·5 (1)° respectively.

There are no unusually close contacts between the $N(CH_3)_4^+$ ions and $C_4H_3O_4^-$ ions in the structure.

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2,6-Dimethyl-4*H*-1-thiapyran-4-one*

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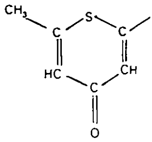
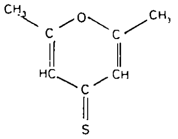
Abstract. C_7H_8OS, $M_r = 140{\cdot}20$, monoclinic, $I2/a$, $a = 9{\cdot}036$ (4), $b = 11{\cdot}348$ (5), $c = 7{\cdot}360$ (4) Å, $\beta = 104{\cdot}4$ (1)°, $V = 730{\cdot}99$ Å^3, $Z = 4$, $D_m = 1{\cdot}275$ (10), $D_x = 1{\cdot}274$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}35$ mm^{-1}, $F(000) = 296$, $T = 294$ K, $R = 0{\cdot}028$ for 456 observed diffractometer reflexions. Molecules are effectively planar and stack in the unit cell in a close-packed arrangement in layers perpendicular to **c**, with the S, O and one C atom lying on twofold axes of symmetry. The S to C distance [1·737 (2) Å] represents a bond order of 1·5. There is no intermolecular bonding other than van der Waals with shortest distance 3·594 (4) Å.

Introduction. Research into the effectiveness of derivatives of γ-pyrones as corrosion inhibitors for steel led to the synthesis of the title compound (I) as a new intermediate. The crystal-structure determination was undertaken to afford a comparison with the corresponding homologous thiopyrone (II) (Toussaint, 1956).



(I)



(II)

Experimental. Material prepared by Drs E. M. Briggs and A. E. Hill of the Chemistry Department of this polytechnic (Hill, 1971). Sample recrystallized by vacuum sublimation to give white acicular crystals elongated along **c** (≈ 0·2 × 0·2 × 1·0 mm), m.p. 377 K. Density by flotation in NaI solution. Lattice parameters initially from Stoe Reciprocal Lattice Explorer and subsequently refined by least squares

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