Molecular Packing Modes. Part VI.[1] Crystal and Molecular Structures of Two Modifications of Tetrolic Acid

By V. Benghiat and L. Leiserowitz,* Department of Chemistry, Weizmann Institute of Science, Rehovot, Israel

The crystal structures of the α- and β-forms of tetrolic acid have been determined from X-ray diffractometer data. Crystals of the α-form are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 7\cdot320$, $b = 5\cdot099$. $c = 7\cdot226$ Å. $\alpha = 83\cdot97$, $\beta = 117\cdot46$, $\gamma = 112\cdot00°$. The structure was refined to R 0·07 for 985 reflections. The molecules form hydrogen-bonded cyclic dimers (O · · · O 2·649 Å) in which the C–O bond lengths are almost equal (1·252, 1·265 Å). 'Half hydrogens' were attached to each oxygen. their parameters refined. and their presence substantiated by a difference-Fourier synthesis. The methyl hydrogen atoms were located.

The structure of the monoclinic β-modification [$a = 7\cdot887$, $b = 7\cdot121$, $c = 3\cdot937$ Å. $\beta = 100\cdot18°$, $Z = 2$. $P2_1$] was refined from counter data to R 0·04 (687 reflections). The methyl hydrogen atoms were located. The bond lengths within the carboxylic group are distinct: C=O 1·204, C–O 1·310 Å; the hydroxy-hydrogen was clearly evident. The molecules form a continuous array of O–H · · · O= hydrogen bonds (O · · · O 2·655 Å) between molecules related by a two-fold screw axis similar to the arrangement in the structure of formic and acetic acids.

The carbon–carbon bond lengths of the α- and β-forms are: H_3C–C 1·458, 1·455, C≡C 1·182. 1·178, and C–CO_2H 1·441, 1·441 Å.

THE structure analyses of two crystal modifications of tetrolic acid were undertaken as part of a programme on the packing modes of carboxylic acids. The existence of two forms, one crystallising in a centrosymmetric, the other in an acentric space group, seemed *a priori* to suggest the existence of two basically different packing arrangements of the same molecule; their parallel investigation might throw light on the effects of packing geometry on the apparent bond lengths in the carboxy-group, more particularly as the investigation of two crystal forms of the same molecule would also provide an

external estimate of the accuracy of bond-length measurements.

EXPERIMENTAL

Tetrolic acid (I) crystallised by slow evaporation from n-pentane solution, yielded a triclinic (α) and a monoclinic (β) form. The α-crystals are rhombic in shape and bounded by {100}, {10$\bar{1}$}, and {120}; the β-dimorph grows in thin plates showing {100} and {010}. The latter is converted at 56—58 °C into the triclinic modification m.p. 77—78 °C. The reverse change α→β, could not be observed when the α-form was cooled to room temperature. The crystals of both forms are soft, easily deformable, and deliquescent;

[1] Part V, V. Benghiat, H. W. Kaufman, L. Leiserowitz, and G. M. J. Schmidt, preceding paper.

specimens for intensity measurements were enclosed in sealed capillaries of Lindemann glass.
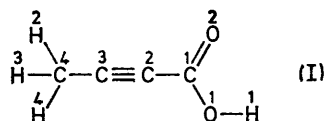
Labelling of atoms employed in this structure analysis

The cell parameters of the two forms were determined by a least-squares analysis of high-angle spectra ($2\theta > 120$, Cu-K_α radiation) measured on a General Electric goniostat.

Crystal Data.—(i) α-*Tetrolic acid.* $C_4H_4O_2$, $M = 84\cdot4$. Triclinic, $a = 7\cdot320(1)$, $b = 5\cdot099(1)$, $c = 7\cdot226(1)$ Å, $\alpha = 83\cdot97(1)$, $\beta = 117\cdot46(1)$, $\gamma = 112\cdot00(1)°$, $U = 221\cdot1$ Å³, $Z = 2$, $D_c = 1\cdot266$, $F(000) = 88$. Space group $P1$ or $P\bar{1}$. The latter space group established as correct by the present analysis. Cu-K_α radiation, $\lambda = 1\cdot5405$ Å; μ(Cu-K_α) = $9\cdot0$ cm⁻¹.

β-*Tetrolic acid*, $C_4H_4O_2$. Monoclinic, $a = 7\cdot887(1)$, $b = 7\cdot121(1)$, $c = 3\cdot937(1)$ Å, $\beta = 100\cdot18(1)°$, $U = 217\cdot6$ Å³, $Z = 2$, $D_c = 1\cdot287$, $F(000) = 88$. Space group $P2_1$ from systematic absences $0k0$ for k odd. Mo-K_α radiation, $\lambda = 0\cdot70926$ Å; μ(Mo-K_α) = $1\cdot1$ cm⁻¹.

Data Collection.—(i) α. A crystal of dimensions $0\cdot28 \times 0\cdot46 \times 0\cdot56$ mm (bounded by faces 001, 00$\bar{1}$, 10$\bar{1}$, $\bar{1}$01, 120, and $\bar{1}$20) was mounted along b^* on a General Electric goniostat; the intensities within a hemisphere of reciprocal space were recorded by means of an ω–2θ scan with Ni-filtered Cu-K_α radiation. The intensity scanning range included the $K_{\alpha,1}$ and $K_{\alpha,2}$ peaks. The background was measured over the same 2θ range, but with the crystal offset by $1\cdot0°$ in the ω-direction.

(ii) β. A crystal of dimensions $0\cdot68 \times 0\cdot26 \times 0\cdot89$ mm (bounded by faces 010, 0$\bar{1}$0, 100, $\bar{1}$00, 001, and 00$\bar{1}$) was mounted along c^* on a paper-tape controlled Siemens diffractometer; the $I(hkl)$ and $I(h\bar{k}l)$ were recorded for $\sin\theta/\lambda \leq 0\cdot71$ with Mo-K radiation filtered with a set of balanced zirconium and yttrium metal foils. Intensities were measured by means of the ω–2θ technique. The mode of intensity measurement and treatment of the data have been described elsewhere.[2,3]

Absorption corrections[4] were applied to both forms in the data-reduction programme. 985 (including 76 unobserved) and 687 (including 116 unobserved) independent reflections were measured for the α- and β-forms respectively.

Structure Determination.—The centrosymmetric space group $P\bar{1}$ of the α-form was indicated by the statistical $N(z)$ test[5]. A planar centrosymmetric hydrogen-bonded system (II) was then assumed as the molecular model and

(II)
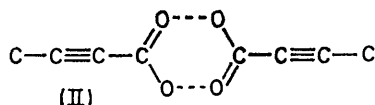
the structure solved by means of SEARCH.[6] As the methyl hydrogens had been excluded from the model the programme yielded 34 trial structures; the R of one of these converged to $0\cdot20$ when tested in a rigid-body least-squares

[2] H. Irngartinger, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc. (B)*, 1970, 497.

[3] H. Irngartinger, L. Leiserowitz, and G. M. J. Schmidt, *Chem. Ber.*, 1970, **103**, 1119.

[4] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

programme on the 30 lowest-order reflections. Individual atomic parameters of this model were refined, first with isotropic and then anisotropic thermal parameters, from all the reflections.

The methyl hydrogen atoms were located on an electron-density difference synthesis (Figure 1). Although the
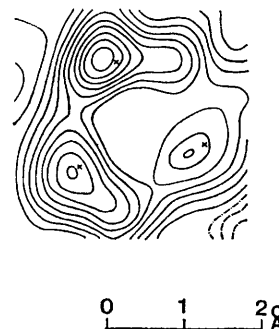

FIGURE 1 α-Tetrolic acid. Electron-density difference-Fourier map showing the methyl hydrogen atom positions. The refined positions are marked with a cross. Contour intervals are $0\cdot03$ eÅ⁻³

hydrogen atoms appeared to show pronounced libratory motion about the methyl bond axis, their positional and isotropic thermal parameters were refined.

At this stage the two C–O bonds were equal in length ($1\cdot255$ and $1\cdot267$ Å). As we could not assign hydrogens to either oxygen on the basis of their C–O bond lengths two
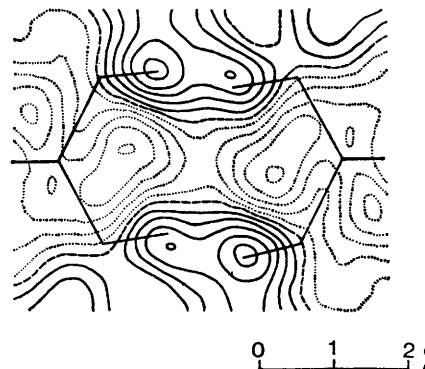

FIGURE 2 α-Tetrolic acid. Electron-density difference-Fourier synthesis in the plane of the carboxylic acid dimer. Full, dashed, and dotted lines correspond to positive, zero, and negative contours respectively at intervals of $0\cdot05$ eÅ⁻³

' half-hydrogens ' [$\frac{1}{2}$H(1) and $\frac{1}{2}$H(1')] were inserted along the O ⋯ O line 1 Å from each oxygen, and their positional and thermal parameters refined. The two ' half-hydrogens ' were located $0\cdot87$ and $0\cdot76$ Å from their nearest oxygen atoms, with temperature factors of $0\cdot094$ and $0\cdot065$ Å². The two C–O bond lengths were then $1\cdot252$ and $1\cdot265$ Å.

A difference-Fourier synthesis $\delta(xyz)$ in the plane of the carboxy-group based on all atoms except the two ' half-hydrogens ' (Figure 2) showed two resolved peaks of heights $0\cdot20$ and $0\cdot26$ eÅ⁻³ in the O ⋯ O region. The final agreement factors were R $0\cdot07$ and R' $0\cdot029$ for all 958 reflections [$R' = \Sigma w(k^2F_o^2 - |F_c|^2)^2/\Sigma\omega k^4F_o^4$].

[5] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

[6] D. Rabinovich and G. M. J. Schmidt, *Nature*, 1966, **211**, 1391.

The structure of the β-form was solved by direct phase determination *via* a modification of a multi-solution method outlined by Germain and Woolfson.[7] The details of the phase determination of β-tetrolic acid have already been described.[8]

The structure was refined in a manner similar to that for α-tetrolic acid. The methyl hydrogen atoms were located on a difference-Fourier synthesis (Figure 3); the hydroxy-
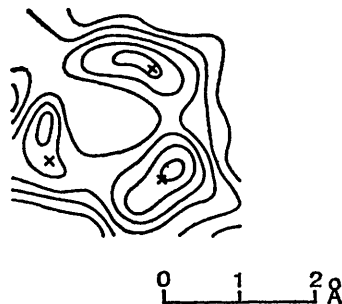

FIGURE 3 β-Tetrolic acid. Electron-density difference-Fourier map showing the methyl hydrogen atom positions. The refined positions are marked with a cross. Contour intervals are 0·03 eÅ⁻³

hydrogen was attached to the oxygen with the longer C–O bond (1·310 *vs.* 1·204 Å). After refinement with anisotropic temperature parameters for all but the hydrogen atoms, a difference-Fourier synthesis $\delta(xyz)$, based on all atoms except H(1) and computed in the plane of the carboxy-group, clearly revealed the position of the hydroxy-hydrogen 0·9 Å from O(1) (Figure 4).
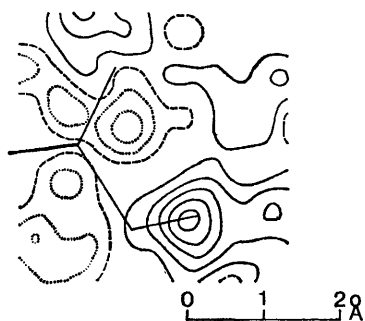

FIGURE 4 β-Tetrolic acid. Electron-density difference-Fourier synthesis in the plane of the carboxy-group. Full, dashed, and dotted lines correspond to positive, zero, and negative contours respectively at intervals of 0·05 eÅ⁻³

The final agreement factors were R 0·040 and R' 0·006. The scattering factor curves for carbon and oxygen were taken from ref. 9 and for hydrogen from ref. 10. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20326 (4 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Tables 1 and 2 list the experimental positional and thermal parameters of α- and β-tetrolic acids, together with their estimated standard deviations.

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full-size copies).

⁷ G. Germain and M. M. Woolfson, *Acta Cryst.*, 1968, *B*, **24**, 91.

Molecular Shape.—Table 3 lists the deviations from the best planes through all heavy atoms, the carboxy-group, and the hydrogen-bonded carboxylic acid pairs. The mean deviations from these planes are, for α-tetrolic acid, 0·003, 0·003, and 0·02 Å, and, for the β-acid, 0·002, 0·002, and 0·07 Å.

TABLE 1

Atomic co-ordinates (fractional) and standard deviations referred to axes *a*, *b*, *c*

(*a*) α-Tetrolic acid

Atom	*x*	*y*	*z*
O(1)	0·10354(21)	−0·18298(30)	−0·08840(17)
O(2)	0·20729(25)	−0·03837(31)	0·23758(19)
C(1)	0·22650(22)	−0·15506(29)	0·10491(22)
C(2)	0·40114(25)	−0·26578(33)	0·18690(24)
C(3)	0·54811(24)	−0·35030(34)	0·26073(24)
C(4)	0·72987(33)	−0·45366(50)	0·35451(31)
½H(1)	−0·0092(89)	−0·1378(110)	−0·1185(83)
½H(1′)	0·1085(70)	0·0049(89)	0·2041(66)
H(2)	0·7470(46)	−0·4939(69)	0·2467(55)
H(3)	0·6815(36)	−0·6372(52)	0·4242(48)
H(4)	0·8584(43)	−0·3126(55)	0·4429(39)

(*b*) β-Tetrolic acid

Atom	*x*	*y*	*z*
O(1)	0·82242(23)	0·45385(41)	0·15657(62)
O(2)	1·01637(19)	0·25317(42)	0·03280(54)
C(1)	0·88422(25)	0·28421(50)	0·13615(59)
C(2)	0·77684(27)	0·14045(0)	0·24486(60)
C(3)	0·69543(26)	0·01597(48)	0·33056(57)
C(4)	0·59562(41)	−0·13882(61)	0·43455(88)
H(1)	0·893(5)	0·540(6)	0·093(9)
H(2)	0·522(7)	−0·078(8)	0·639(14)
H(3)	0·555(6)	−0·219(10)	0·269(14)
H(4)	0·657(5)	−0·224(10)	0·617(12)

The 'half-hydrogens' of α-tetrolic acid each lie 0·14 and 0·10 Å from the plane of the carboxy-group; in the β-acid, the deviation of the hydroxylic hydrogen H(1) is 0·02 Å.

Bond Lengths and Angles.—Bond lengths and angles of the α- and β-forms are shown in Figures 5 and 6 respectively. The means of their σ values are 0·003 Å and 0·2°, and 0·004 Å and 0·3° respectively. The corresponding values where one hydrogen is involved are 0·06 Å and 3°, and 0·05 Å and 4° respectively.

A comparison of the chemically equivalent carbon-carbon bond lengths of the α- and β-molecules leads to an average deviation from the mean of 0·001 Å; the two sets of data are satisfactorily consistent. On the other hand, this average value is misleading as a measure of the precision in bond-length determination, for the lengths of the C≡C triple bond (1·182, 1·178 Å) are 0·02 Å shorter than the commonly accepted value of 1·206 Å.[11] This shortening of the C≡C bond is probably an artefact, for it has been correlated with the neglect

⁸ H. W. Kaufman and L. Leiserowitz, *Acta Cryst.*, 1970, *B*, **26**, 422.
⁹ J. Berghius, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
¹⁰ R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.
¹¹ *Chem. Soc. Special Publ.*, No. 11, 1958.

TABLE 2

Observed thermal parameters u^{ij} and U and standard deviations (Å^2) referred to axes a, b, c

(a) α-Tetrolic acid

Atom	u^{11}	u^{22}	u^{33}	u^{12}	u^{23}	u^{13}
O(1)	0·0884(8)	0·1211(10)	0·0721(7)	0·0678(7)	0·0144(5)	0·0295(5)
O(2)	0·1005(9)	0·1156(9)	0·0774(6)	0·0719(7)	0·0092(6)	0·0053(6)
C(1)	0·0632(6)	0·0717(7)	0·0726(7)	0·0354(5)	0·0136(5)	0·0283(5)
C(2)	0·0701(7)	0·0823(8)	0·0780(7)	0·0412(6)	0·0136(6)	0·0304(6)
C(3)	0·0689(7)	0·0879(9)	0·0710(7)	0·0431(6)	0·0134(6)	0·0288(5)
C(4)	0·0794(9)	0·1189(14)	0·0832(9)	0·0639(10)	0·0185(9)	0·0311(8)

Atom	U	Atom	U	Atom	U	Atom	U	Atom	U
½H(1)	0·094(15)	½H(1′)	0·065(11)	H(2)	0·116(9)	H(3)	0·095(7)	H(4)	0·097(8)

(b) β-Tetrolic acid

Atom	u^{11}	u^{22}	u^{33}	u^{12}	u^{23}	u^{13}
O(1)	0·0642(9)	0·0441(8)	0·1161(15)	0·0005(7)	0·0005(9)	0·0420(10)
O(2)	0·0548(7)	0·0463(8)	0·0984(12)	−0·0044(7)	−0·0061(8)	0·0363(7)
C(1)	0·0478(9)	0·0438(11)	0·0600(12)	−0·0066(8)	−0·0034(9)	0·0138(8)
C(2)	0·0497(9)	0·0474(10)	0·0609(11)	−0·0027(8)	−0·0030(9)	0·0170(8)
C(3)	0·0474(9)	0·0474(10)	0·0560(10)	−0·0017(7)	−0·0026(9)	0·0145(8)
C(4)	0·0716(16)	0·0600(14)	0·0745(17)	−0·0209(12)	0·0039(13)	0·0214(14)

Atom	U	Atom	U	Atom	U	Atom	U
H(1)	0·088(13)	H(2)	0·120(17)	H(3)	0·130(18)	H(4)	0·109(14)

TABLE 3

Equations of planes in the form $Ax + By + Cz + D = 0$
where x,y,z are fractional atomic co-ordinates; distances (10^3 Å) of relevant atoms form the planes, are given in square brackets

(a) α-Tetrolic acid

Plane (I):

O(1), O(2), $-3·2487x - 3·3670y + 2·5287z - 0·0564 = 0$
C(1)—(4)

[O(1) 0, O(2) 0, C(1) −5, C(2) 8, C(3) 2, C(4) −4, ½H(1) 138, ½H(1′) 91, H(2) −196, H(3) 948, H(4) −673]

Plane (II):
O(1), O(2), $-3·2739x - 3·3530y + 2·5292z - 0·0488 = 0$
C(1), C(2)

[O(1) 2, O(2) 2, C(1) −5, C(2) 2, C(3) −10, C(4) −21, H(1) 144, H(2) 96]

Plane (III): *
O(1), O(2), $-3·4049x - 3·2786y + 2·5379z = 0$
C(Ī), C(2̄),
O(Ī), O(2̄),
C(1), C(2)

[O(1) 23, O(2) 23, C(1) 3, C(2) −20, ½H(1) 183, ½H(1′) 133]

(b) β-Tetrolic acid

Plane (I):
O(1), O(2), $2·7231x + 0·5454y + 3·3846z - 3·0194 = 0$
C(1)—(4)

[O(1) −2, O(2) −3, C(1) 4, C(2) 1, C(3) 2, C(4) −2, H(1) 22, H(2) 520, H(3) −718, H(4) 737]

Plane (II):
O(1), O(2), $2·7312x + 0·5552y + 3·3820z - 3·0291 = 0$
C(1), C(2)

[O(1) −1, O(2) −2, C(1) 4, C(2) −1, C(3) −3, C(4) −10, H(1) 24]

Plane (III): †
O(1), O(2), $2·9956x + 0·3278y + 3·3162z - 3·1703 = 0$
C(1), C(2),
O(1′), O(2′),
C(1′), C(2′)

[O(1) −39, O(2) 66, C(1) 23, C(2) 15, C(3) 14, C(4) 10, H(1) −10, O(1′) 151, O(2′) −86, C(1′) −22, C(2′) −108, C(3′) −189, C(4′) −286, H(1′) 178]

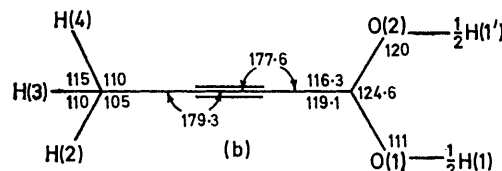* Hydrogen bonded carboxy-dimer.   † Hydrogen-bonded open dimer.

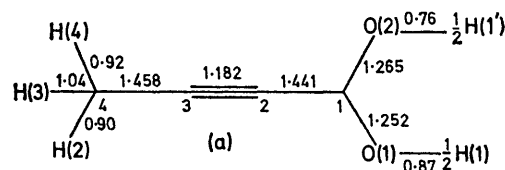

FIGURE 5 α-Tetrolic acid: (a) bond lengths (Å) and (b) angles (°) [H(4)–C(4)–H(2) and C(3)–C(4)–H(3) 108°]

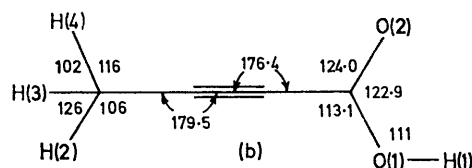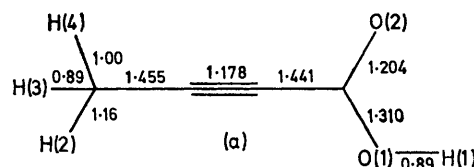FIGURE 6 β-Tetrolic acid: (a) bond lengths (Å) and (b) angles (°) [C(3)–C(4)–H(3) 115, H(4)–C(4)–H(2) 88°]

of the triple-bond charge-density in the least-squares refinement.[2]

The carbon chains of the α- and β-forms are approximately collinear: H_3C–$C\equiv C$ 179·3 and 179·5°, $C\equiv C$–CO_2H 177·6 and 176·4°.

The differences between the angles of H_3C–$C\equiv C$ and $C\equiv C$–CO_2H are significant in terms of σ, and may be correlated with the higher degree of cylindrical symmetry, about the chain axis, of the methyl as compared to the carboxy-group. The latter contains two oxygen atoms of different valence states, and most probably of different force fields acting on the carbon chain C(1)–C(2)≡C(3). We suggest that the system H_3C·C∶C is less subject to non-cylindrical intramolecular forces than the system C∶C·CO_2H which includes the carboxy-group, and so the former system is the less deformed from linearity.

The methyl hydrogens of both α- and β-tetrolic acid exhibit noticeable libratory motion as shown by the difference-Fourier electron-density sections (Figures 1 and 3). The refined methyl hydrogen positions of the α-form incorporate a fair measure of tetrahedral symmetry; the mean bond angle at C(4) is 109 with a scatter of 3°, and the mean C–H bond length is 0·95 with a scatter of 0·1 Å. The hydrogen atoms of the β-modification are less well determined; the mean bond angle at the methyl carbon is 109 with a scatter of 12°, and the corresponding values for the C–H bond are 1·0 and 0·15 Å. As expected, (Figures 1 and 3) the peak heights of the methyl hydrogens of the β-form (0·15, 0·15, and 0·18 e$Å^{-3}$) are lower than those of the α-form (0·21, 0·30, and 0·33 e$Å^{-3}$).

In β-tetrolic acid, the molecules of which are linked by a set of continuous hydrogen bonds, the lengths of the carboxylic bonds are 1·204 (C=O), and 1·310 Å (C–OH). The corresponding bond lengths in crystalline acetic acid,[12] with a hydrogen-bonded network similar to that of β-tetrolic acid, are 1·228 and 1·319 Å. Further comparison is provided by the bond lengths of the formic acid fragment (1·202 and 1·320 Å) of the formamide-formic acid crystalline complex,[13] in which the hydrogen-bonded environment of the formic acid molecule is similar to that of β-tetrolic acid.

In α-tetrolic acid, on the other hand, the structure of which consists of hydrogen-bonded cyclic pairs, the C–O bonds are almost equal in length (1·252 and 1·265 Å) suggesting either considerable proton tautomerism within the cyclic dimer, or orientational disorder whereby the
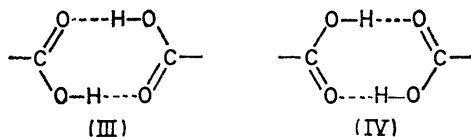
carboxy-dimer is incorporated into the crystal structure in either of the two (equivalent) orientations (III) and (IV). A tautomeric state would require a symmetrical O · · · H · · · O hydrogen bond, which is imcompatible with the O · · · H · · · O distance of the α-form (2·649 Å),

being only 0·005 Å shorter than that of the unsymmetric (O–H · · · O) hydrogen bond of the β-form. We therefore consider that the carboxy-dimer of the α-form is orientationally disordered in the lattice.

Packing.—The packing modes of the α- and β-forms are different (Figures 7, 8); the β-modification is the more stable and has, as expected, the denser structure.

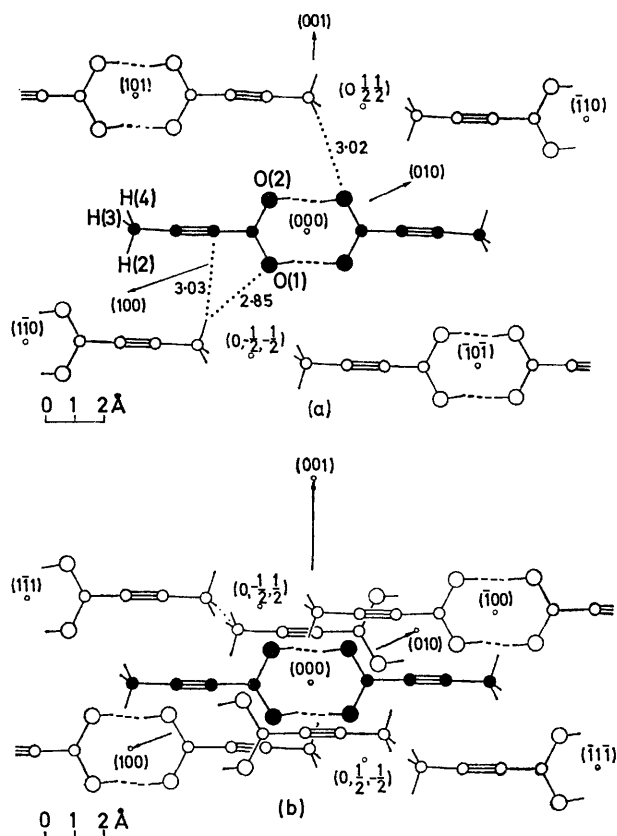
FIGURE 7 α-Tetrolic acid: packing arrangement seen perpendicular to the best plane of the shaded dimer which is close to the (11Ī) plane. (a) Neighbouring molecules which lie almost within the (11Ī) plane and (b) molecules which lie in sheets above and below the shaded dimer

The crystal structure of α-tetrolic acid consists of hydrogen-bonded centrosymmetric pairs which are linked by Me · · · Me contacts (3·81 Å) across centres of inversion at (1, $-\frac{1}{2}$, $\frac{1}{2}$) and so generate approximately linear chains along the [2Ī1] direction (Figure 7a). These chains are interconnected by the vector a–b to form an (approximate) sheetlike structure in the (11Ī) plane (Figure 7a). Within this sheet the molecules, in close contact across the inversion centre ($\frac{1}{2}$, $-\frac{1}{2}$, 0), are coplanar to within 0·01 Å. The C(4)–H(2) bond lies in this plane and straddles the available lone-pair lobe of O(1) [H(2) · · · O(1) 2·85 Å] and the π-electron system of the –C∶C– bond [H(2) · · · C(2) 3·03 Å]. The closest intersheet contact (2·77 Å) is H(3) · · · O(2). Intermolecular contacts are listed in Table 4a.

[12] I. Nahringbauer, *Acta Chem. Scand.*, 1970, **24**, 453.
[13] I. Nahringbauer and G. Larsson, *Arkiv Kemi*, 1968, **30**, 91.

TABLE 4

Interatomic distances (≤ 3.70 Å)

(a) α-Tetrolic acid

$A(000)$ * $A(0\bar{1}0)$	
H(1) · · · C(1)	3·363
H(1) · · · C(2)	3·193
O(1) · · · C(1)	3·309
O(1) · · · C(2)	3·503
C(1) · · · C(1)	3·662

$A(000)$ $A(010)$	
O(2) · · · C(3)	3·427
O(2) · · · H(3)	2·999
C(1) · · · H(3)	3·315
C(2) · · · H(3)	3·226

$A(000)$ $A(1\bar{1}0)$	
O(1) · · · H(2)	2·849
C(1) · · · H(2)	3·371
C(2) · · · H(2)	3·028
C(3) · · · H(2)	3·281

$A(000)$ $A(1\bar{1}1)$	
O(2) · · · H(3)	2·774
C(1) · · · H(3)	3·289
C(2) · · · H(3)	3·092
C(3) · · · H(3)	3·381

$A(000)$ $A(000)$	
O(1) · · · O(2)	2·228
O(1) · · · C(2)	2·323
O(1) · · · C(3)	3·426
O(2) · · · C(1)	1·265
O(2) · · · C(2)	2·301
O(2) · · · C(3)	3·364
C(3) · · · H(2)	1·902
C(3) · · · H(3)	2·033
C(3) · · · H(4)	1·974
H(2) · · · H(3)	1·586
H(2) · · · H(4)	1·474
H(3) · · · H(4)	1·647

$A(000)$ $\bar{A}(000)$	
O(1) · · · O(2)	2·649
O(1) · · · C(1)	3·411
O(2) · · · C(1)	3·430

$A(000)$ $\bar{A}(100)$	
O(1) · · · C(3)	3·531

$A(000)$ $\bar{A}(2\bar{1}1)$	
C(4) · · · H(4)	3·302

(b) β-Tetrolic acid

$A(000)$ * $A(000)$	
H(1) · · · O(2)	2·292
H(1) · · · C(1)	1·831
O(1) · · · O(2)	2·210
O(1) · · · C(2)	2·297
O(1) · · · C(3)	3·382
O(2) · · · C(2)	2·338
O(2) · · · C(3)	3·418
C(3) · · · H(3)	1·998
C(3) · · · H(4)	2·098
C(3) · · · H(2)	2·096
H(3) · · · H(4)	1·463
H(3) · · · H(2)	1·828
H(4) · · · H(2)	1·503

$A(000)$ $B(2\bar{1}0)$	
O(2) · · · C(1)	3·521

$A(000)$ $B(200)$	
H(1) · · · O(2)	1·786
H(1) · · · C(1)	2·738
H(1) · · · C(2)	3·209
O(1) · · · O(2)	2·655
O(2) · · · C(2)	3·477
O(2) · · · C(3)	3·444

$A(000)$ $B(201)$	
O(2) · · · C(3)	3·597
O(2) · · · C(4)	3·477
O(2) · · · H(4)	2·702

$A(000)$ $A(00\bar{1})$	
O(2) · · · C(1)	3·507
O(2) · · · C(2)	3·430
C(1) · · · C(2)	3·610
C(2) · · · C(3)	3·652
C(2) · · · H(2)	3·237
C(3) · · · C(4)	3·647
C(3) · · · H(4)	3·255
C(3) · · · H(2)	2·903
C(4) · · · H(4)	3·393
C(4) · · · H(2)	3·114
H(3) · · · H(2)	2·645

$A(000)$ $B(1\bar{1}1)$	
C(4) · · · H(2)	3·262
H(3) · · · H(2)	2·667

$A(000)$ $B(100)$	
C(2) · · · H(3)	3·174
C(3) · · · H(3)	3·373

$A(000)$ $B(101)$	
O(1) · · · H(2)	2·972
C(2) · · · H(2)	3·184
C(3) · · · C(4)	3·594
C(3) · · · H(3)	3·325
C(3) · · · H(4)	3·378
C(3) · · · H(2)	3·371

* Co-ordinates of equivalents positions:

A x, y, z B $-x, \frac{1}{2} + y, -z$
$\bar{A}$ $-x, -y, -z$
$A(pqr)$ denotes fractional co-ordinates $p + x, q + y, r + z$.

The molecules of the β-form are linked by a coplanar set of continuous O–H · · · O hydrogen bonds (2·655 Å) between carboxy-groups related by a two-fold screw axis (Figure 8).
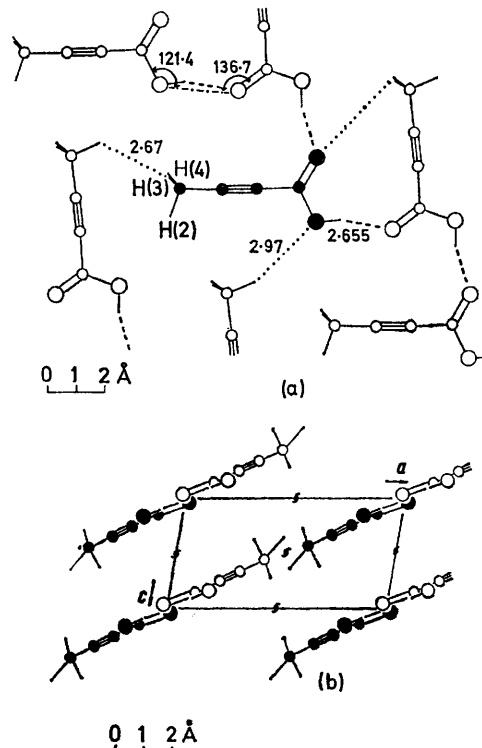

FIGURE 8 β-Tetrolic acid: (a) packing arrangement seen perpendicular to the best plane of the shaded molecule showing some intermolecular contacts (Å) and angles (°) and (b) packing arrangement seen along [010]

These hydrogen-bonded stacks along b form part of a sheet-like structure in the (101) plane (Figure 8b). Close contacts within this sheet are shown in Figure 8a. Interatomic distances are listed in Table 4b.

The hydrogen-bonding pattern exhibited by β-tetrolic acid occurs also in the crystal structure of formic[14] and acetic acids[12] and in the α-form of oxalic acid.[15]

[14] F. Holtzberg, B. Post, and I. Fankuchen, Acta Cryst., 1953, 6, 127.
[15] E. G. Cox, M. W. Dougill, and G. A. Jeffrey, J. Chem. Soc., 1952, 4854.