leurs un rôle identique dans la structure de $Li_{1,5}V_3O_8$, dans laquelle les chaînes V–O s'allongent suivant un plan.

Dans cette structure de type nouveau, le vanadium a nettement la coordinence 5, coordinence qui se manifeste d'une façon plus ou moins marquée dans d'autres composés du vanadium: $V_2O_5$, $Li_xV_2O_5\alpha$, $Li_xV_2O_5\beta$, $Li_{1+x}V_3O_8 \cdots$; les polyèdres d'oxygène ont l'enchaînement rencontré habituellement dans les structures où le vanadium se trouve à des valences élevées.

Le lithium, participant à la cohésion tridimensionnelle de la structure, permettrait d'expliquer un point de fusion et une dureté plus élevés pour $LiV_2O_5$ que pour $V_2O_5$.

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# The Crystal Structure of Tartronic Acid

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Tartronic acid (COOH–CHOH–COOH) crystallizes in space group $P2_12_12_1$ with 4 molecules in the unit cell of dimensions $a$=4·485, $b$=8·813, $c$=10·895 Å. The structure has been solved from two-dimensional photographic data and has been refined by least-squares with 534 three-dimensional diffractometer data. The structure consists of parallel infinite chains of molecules, each chain generated by a twofold screw axis and held together by hydrogen bonds between pairs of carboxyl groups. The molecules have no mirror symmetry.

## Introduction

The structure determination of $\alpha$-hydroxycarboxylic acids has revealed that in the crystalline state the atoms of the part of the molecule that may be designated as the hydroxyacetic acid group are coplanar in the undissociated acids and ions (Jeffrey & Parry, 1952). The same situation is met with in unsubstituted carboxylic acids as for the atoms of the propionic acid group; sometimes, however, the packing in the crystal seems to hamper this coplanarity (MacGillavry, Hoogschagen & Sixma, 1948). It is to be noted that in unsubstituted acids the carbonyl oxygen atom of the carboxyl group is situated at the side of the $\alpha$–$\beta$ carbon–carbon bond, whereas in $\alpha$-hydroxy acids this carbonyl group is found at the side of the carbon–oxygen bond.*

In malonic acid each of the two carboxyl groups may in principle be coplanar with the $\beta$-carbon atom, but the structure analysis has revealed (Goedkoop & Mac Gillavry, 1957) that only one of the carboxyl groups is coplanar with the $\beta$-carbon atom, the other carboxyl group being rotated 90° with respect to the former; apparently steric hindrance excludes the simultaneous coplanarity.

It seemed of interest to investigate the structure of $\alpha$-hydroxymalonic acid (tartronic acid) in order to see to what degree the carboxyl groups in this molecule are coplanar with the hydroxyl oxygen atom.

## Experimental

Orthorhombic crystals of tartronic acid are readily obtained from a butanol solution at room temperature. The unit-cell dimensions deduced from measurements (Cu $K\alpha$ radiation, $\lambda(\alpha_1\alpha_2)=1{\cdot}5418$ Å) on a General Electric single-crystal orienter equipped with a scintillation counter are $a=4{\cdot}485\pm0{\cdot}001$, $b=8{\cdot}813\pm0{\cdot}002$, $c=10{\cdot}895\pm0{\cdot}003$ Å. From systematic absences the space group is uniquely determined as $P2_12_12_1$. With four molecules in the unit cell the calculated density (1.84 g.cm$^{-3}$) agrees with the density as determined by flotation (1.83 g.cm$^{-3}$). The crystals are elongated along the shorter crystallographic axis and can be easily cleaved along (100) and (010).

The structure analysis was started by taking integrated equi-inclination Weissenberg photographs around the $a$ axis. Three-dimensional data were next collected with the General Electric diffractometer. Integrated intensities were measured with $\theta$–$2\theta$ scan over 3°; the background was measured at 1·5° on either side of the peak with the crystal stationary. The spect-

* Recently the opposite situation has been found in one of the modifications of mesotartaric acid (Bootsma, 1964).

rum measured was narrowed down by nickel filters and a discriminator. The non-linearity of the counting apparatus was corrected for experimentally. The crystal had dimensions $0.25 \times 0.20 \times 0.10$ mm; no correction for absorption was made.

### Determination of structure

It was decided to attempt a solution of the structure by making use of the sign correlation method of de Vries (1965), based on a systematic use of correlations between sign relations as given by the Sayre equation. For this purpose unitary structure factors for the [100] projection were calculated after determining the scaling factor by Wilson's method (1942). From 30 unitary structure factors with $U \geq 0.19$ three possible sets of signs were obtained (ZEBRA program Utr. 45, Schoone 1963), apart from the trivial set with all signs positive. A trial model as shown in Fig. 1 could be refined (ZEBRA least-squares program ZK 22, Schoone 1961; atomic scattering factors from Hoerni & Ibers, 1954) with 100 $0kl$ reflexions to $R=0.18$; inspection of the structure factors at this stage revealed a large discrepancy for the 053 reflexion: $F_{obs}=16$, $F_{calc}=+1$. Continued refinement with temporary omission of only this structure factor quickly lowered $R$ to 0·08, $F_{calc}(053)$ now being $-15$. The electron density projection along [100] is presented in Fig. 2.

Assuming standard bond lengths and bond angles approximate $x$ parameters could be calculated. Refinement with 298 photometrically measured $0kl$, $1kl$ and $2kl$ reflexions gave $R=0.09$. Coordinates thus obtained were used as the starting point of a fully three-dimensional refinement with diffractometer intensities. In order to weaken the influence of the hydrogen atoms not yet located, this refinement was first carried out using reflexions with $\theta > 30°$ only, giving $R=0.105$. A three-dimensional difference synthesis of reflexions with $\theta < 30°$, taking the phases of the structure factors equal to those of the contribution of carbon and oxygen atoms only, yielded positions of the four hydrogen atoms (Table 1, column 1), for which an isotropic $B$ value of 3·00 Å$^2$ was assumed. Now the phases of the structure factors could be calculated inclusive of hydrogen atoms (scattering factors for hydrogen from McWeeny, 1951), and a new difference synthesis was computed. With hydrogen atoms kept fixed in the positions found from this synthesis, least-squares refinement was continued to $R=0.08$ all reflexions included, after which new coordinates of the hydrogen atoms were found from another difference synthesis.

Table 1. *Fractional coordinates of hydrogen atoms in three different stages of structure analysis*

| | | | | |
|---|---|---|---|---|
| H(1) | $x$ | −0·28 | −0·31 | −0·319 |
| | $y$ | −0·12 | −0·12 | −0·122 |
| | $z$ | 0·50 | 0·51 | 0·498 |
| H(2) | $x$ | −0·30 | −0·36 | −0·348 |
| | $y$ | 0·21 | 0·17 | 0·180 |
| | $z$ | 0·47 | 0·47 | 0·446 |
| H(3) | $x$ | 0·19 | 0·18 | 0·195 |
| | $y$ | −0·13 | −0·14 | −0·141 |
| | $z$ | 0·30 | 0·32 | 0·292 |
| H(4) | $x$ | 0·18 | 0·19 | 0·221 |
| | $y$ | −0·13 | −0·12 | −0·115 |
| | $z$ | 0·68 | 0·67 | 0·698 |

At this stage of the analysis allowance for anisotropic vibration was thought to be desirable. For this purpose a new least-squares program (X1, OX9m, Rutten-Keulemans, 1963) was applied. After one cycle, which reduced $R$ to 0·054, a difference synthesis was made that yielded the H coordinates shown in Table 1, column 2. Further refinement with 534 reflexions, including the hydrogen atoms too, diminished the $R$ value to 0·037; the reflexions 020 and 113 which apparently suffered from extinction were omitted. Final parameters are given in Table 1, column 3 and Table 2; structure factors observed and calculated in Table 3.

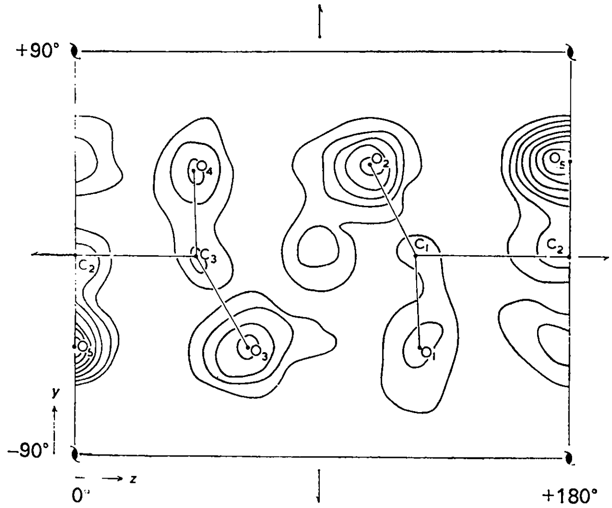


Fig. 1. Electron-density projection along [100]; signs obtained by the correlation method.

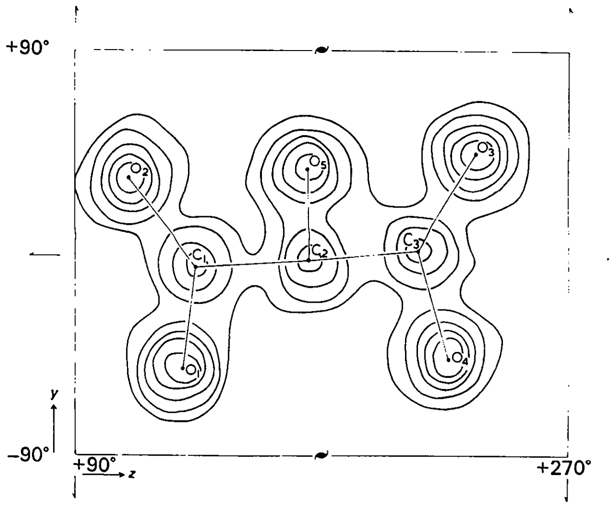


Fig. 2. Electron-density projection along the $a$ axis; contours at intervals of 2e.Å$^{-2}$ with the lowest contour at 2e.Å$^{-2}$ ($R=0.080$).

Table 2. *Fractional atomic coordinates and U-values appearing in the thermal factor* $\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2a^*b^*hkU_{12}+2b^*c^*klU_{23}+2c^*a^*hlU_{31})\right]$ *as used in the least-squares program*

| | $x$ | $y$ | $z$ | 1000 $U_{11}$ | 1000 $U_{22}$ | 1000 $U_{33}$ | 2000 $U_{12}$ | 2000 $U_{23}$ | 2000 $U_{31}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | +0·1305 | −0·1396 | +0·3601 | +32 | +28 | +30 | +12 | +0 | +17 |
| O(2) | −0·0271 | +0·0927 | +0·3069 | +29 | +31 | +29 | +12 | +16 | +10 |
| O(3) | +0·0153 | +0·1156 | +0·6625 | +28 | +27 | +30 | +5 | −11 | −5 |
| O(4) | +0·1314 | −0·1279 | +0·6278 | +30 | +26 | +29 | +6 | −2 | −15 |
| O(5) | −0·4277 | +0·0993 | +0·4889 | +19 | +34 | +39 | +21 | +12 | +9 |
| C(1) | −0·0229 | −0·0152 | +0·3753 | +16 | +23 | +23 | −2 | −4 | −9 |
| C(2) | −0·2129 | −0·0155 | +0·4921 | +18 | +22 | +26 | +4 | +2 | −1 |
| C(3) | −0·0066 | −0·0010 | +0·6043 | +16 | +23 | +23 | −3 | +4 | +7 |

Table 3. *Observed and calculated structure factors* (*scaling factor* $c=10$)

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 2 | 0 | 0 | 546 | 547 |
| 4 | | | 102 | 102 |
| 1 | 1 | 0 | 62 | 58 |
| 2 | | | 189 | 185 |
| 3 | | | 27 | 19 |
| 4 | | | 54 | 53 |
| 5 | | | 139 | 140 |
| 0 | 2 | 0 | 615 | 718 |
| 1 | | | 110 | 124 |
| 2 | | | 252 | 235 |
| 3 | | | 321 | 323 |
| 4 | | | 167 | 167 |
| 5 | | | 113 | 118 |
| 1 | 3 | 0 | 350 | 364 |
| 2 | | | 73 | 77 |
| 3 | | | 69 | 62 |
| 4 | | | 60 | 58 |
| 5 | | | 6 | 5 |
| 0 | 4 | 0 | 516 | 515 |
| 1 | | | 73 | 75 |
| 2 | | | 134 | 134 |
| 3 | | | 17 | 15 |
| 4 | | | 144 | 144 |
| 5 | | | 6 | 3 |
| 1 | 5 | 0 | 131 | 125 |
| 2 | | | 164 | 168 |
| 3 | | | 57 | 63 |
| 4 | | | 35 | 33 |
| 0 | 6 | 0 | 37 | 41 |
| 1 | | | 13 | 3 |
| 2 | | | 71 | 78 |
| 3 | | | 167 | 173 |
| 4 | | | 17 | 20 |
| 1 | 7 | 0 | 75 | 76 |
| 2 | | | 32 | 27 |
| 3 | | | 98 | 101 |
| 4 | | | 54 | 53 |
| 0 | 8 | 0 | 323 | 313 |
| 1 | | | 121 | 117 |
| 2 | | | 81 | 81 |
| 3 | | | 10 | 30 |
| 1 | 9 | 0 | 21 | 22 |
| 2 | | | 58 | 58 |
| 3 | | | 16 | 15 |
| 0 | 10 | 0 | 132 | 127 |
| 1 | | | 60 | 57 |
| 2 | | | 97 | 96 |
| 1 | 0 | 1 | 31 | 30 |
| 2 | | | 352 | 331 |
| 3 | | | 14 | 6 |
| 4 | | | 72 | 70 |
| 5 | | | 6 | 6 |
| 0 | 1 | 1 | 4 | 6 |
| 1 | | | 426 | 441 |
| 2 | | | 216 | 198 |
| 3 | | | 67 | 64 |
| 4 | | | 92 | 92 |
| 5 | | | 122 | 124 |
| 0 | 2 | 1 | 3 | 9 |
| 1 | | | 295 | 303 |
| 2 | | | 88 | 75 |
| 3 | | | 202 | 193 |
| 4 | | | 31 | 33 |
| 5 | | | 17 | 15 |
| 0 | 3 | 1 | 109 | 106 |
| 1 | | | 63 | 63 |
| 2 | | | 230 | 223 |
| 3 | | | 104 | 104 |

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 4 | 3 | 1 | 47 | 50 |
| 5 | | | 86 | 87 |
| 0 | 4 | 1 | 107 | 107 |
| 1 | | | 57 | 59 |
| 2 | | | 303 | 305 |
| 3 | | | 51 | 55 |
| 4 | | | 24 | 25 |
| 5 | | | 22 | 24 |
| 0 | 5 | 1 | 64 | 68 |
| 1 | | | 97 | 91 |
| 2 | | | 48 | 52 |
| 3 | | | 43 | 46 |
| 4 | | | 79 | 80 |
| 0 | 6 | 1 | 18 | 17 |
| 1 | | | 153 | 156 |
| 2 | | | 51 | 47 |
| 3 | | | 69 | 69 |
| 4 | | | 23 | 24 |
| 0 | 7 | 1 | 151 | 153 |
| 1 | | | 176 | 176 |
| 2 | | | 93 | 89 |
| 3 | | | 22 | 23 |
| 4 | | | 57 | 58 |
| 0 | 8 | 1 | 91 | 89 |
| 1 | | | 69 | 72 |
| 2 | | | 68 | 72 |
| 3 | | | 32 | 33 |
| 0 | 9 | 1 | 160 | 155 |
| 1 | | | 72 | 72 |
| 2 | | | 37 | 35 |
| 3 | | | 54 | 38 |
| 0 | 10 | 1 | 58 | 55 |
| 1 | | | 10 | 11 |
| 2 | | | 52 | 52 |
| 0 | 0 | 2 | 132 | 134 |
| 1 | | | 115 | 117 |
| 2 | | | 181 | 163 |
| 3 | | | 100 | 94 |
| 4 | | | 31 | 28 |
| 5 | | | 59 | 61 |
| 0 | 1 | 2 | 10 | 9 |
| 1 | | | 299 | 313 |
| 2 | | | 136 | 138 |
| 3 | | | 39 | 37 |
| 4 | | | 53 | 50 |
| 5 | | | 36 | 36 |
| 0 | 2 | 2 | 196 | 196 |
| 1 | | | 384 | 397 |
| 2 | | | 84 | 81 |
| 3 | | | 133 | 39 |
| 4 | | | 36 | 38 |
| 5 | | | 29 | 32 |
| 0 | 3 | 2 | 58 | 52 |
| 1 | | | 56 | 54 |
| 2 | | | 154 | 159 |
| 3 | | | 96 | 99 |
| 4 | | | 76 | 76 |
| 5 | | | 21 | 23 |
| 0 | 4 | 2 | 202 | 199 |
| 1 | | | 198 | 201 |
| 2 | | | 33 | 27 |
| 3 | | | 59 | 62 |
| 4 | | | 86 | 85 |
| 5 | | | 14 | 15 |
| 0 | 5 | 2 | 54 | 56 |
| 1 | | | 45 | 47 |
| 2 | | | 11 | 7 |
| 3 | | | 81 | 86 |

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 4 | 5 | 2 | 13 | 11 |
| 0 | 6 | 2 | 81 | 77 |
| 1 | | | 83 | 87 |
| 2 | | | 13 | 13 |
| 3 | | | 71 | 68 |
| 4 | | | 66 | 66 |
| 0 | 7 | 2 | 51 | 53 |
| 1 | | | 69 | 67 |
| 2 | | | 68 | 72 |
| 3 | | | 15 | 17 |
| 4 | | | 65 | 65 |
| 0 | 8 | 2 | 27 | 28 |
| 1 | | | 104 | 103 |
| 2 | | | 31 | 32 |
| 3 | | | 62 | 61 |
| 0 | 9 | 2 | 68 | 65 |
| 1 | | | 80 | 76 |
| 2 | | | 32 | 33 |
| 3 | | | 35 | 36 |
| 0 | 10 | 2 | 37 | 33 |
| 1 | | | 28 | 26 |
| 2 | | | 27 | 27 |
| 1 | 0 | 3 | 230 | 234 |
| 2 | | | 136 | 132 |
| 3 | | | 65 | 62 |
| 4 | | | 153 | 147 |
| 5 | | | 11 | 15 |
| 0 | 1 | 3 | 164 | 170 |
| 1 | | | 665 | 767 |
| 2 | | | 119 | 117 |
| 3 | | | 188 | 181 |
| 4 | | | 149 | 146 |
| 5 | | | 7 | 1 |
| 0 | 2 | 3 | 38 | 37 |
| 1 | | | 221 | 224 |
| 2 | | | 79 | 80 |
| 3 | | | 44 | 42 |
| 4 | | | 105 | 102 |
| 5 | | | 71 | 71 |
| 0 | 3 | 3 | 19 | 21 |
| 1 | | | 243 | 246 |
| 2 | | | 103 | 106 |
| 3 | | | 133 | 129 |
| 4 | | | 134 | 138 |
| 5 | | | 17 | 21 |
| 0 | 4 | 3 | 56 | 57 |
| 1 | | | 74 | 76 |
| 2 | | | 84 | 89 |
| 3 | | | 68 | 66 |
| 4 | | | 26 | 27 |
| 5 | | | 10 | 10 |
| 0 | 5 | 3 | 159 | 154 |
| 1 | | | 289 | 292 |
| 2 | | | 84 | 87 |
| 3 | | | 12 | 10 |
| 4 | | | 85 | 87 |
| 0 | 6 | 3 | 43 | 41 |
| 1 | | | 68 | 65 |
| 2 | | | 108 | 111 |
| 3 | | | 26 | 30 |
| 4 | | | 18 | 19 |
| 0 | 7 | 3 | 3 | 6 |
| 1 | | | 83 | 86 |
| 2 | | | 118 | 122 |
| 3 | | | 10 | 7 |
| 4 | | | 77 | 80 |
| 0 | 8 | 3 | 21 | 23 |
| 1 | | | 71 | 75 |

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 2 | 8 | 3 | 76 | 73 |
| 3 | | | 22 | 21 |
| 0 | 9 | 3 | 62 | 56 |
| 1 | | | 128 | 129 |
| 2 | | | 38 | 43 |
| 0 | 10 | 3 | 5 | 4 |
| 1 | | | 68 | 65 |
| 0 | 0 | 4 | 401 | 406 |
| 1 | | | 46 | 48 |
| 2 | | | 229 | 215 |
| 3 | | | 33 | 32 |
| 4 | | | 12 | 5 |
| 5 | | | 36 | 38 |
| 0 | 1 | 4 | 65 | 68 |
| 1 | | | 348 | 353 |
| 2 | | | 252 | 244 |
| 3 | | | 82 | 82 |
| 4 | | | 17 | 14 |
| 5 | | | 16 | 15 |
| 0 | 2 | 4 | 2 | 13 |
| 1 | | | 26 | 23 |
| 2 | | | 222 | 227 |
| 3 | | | 168 | 165 |
| 4 | | | 85 | 88 |
| 5 | | | 21 | 24 |
| 0 | 3 | 4 | 48 | 51 |
| 1 | | | 141 | 146 |
| 2 | | | 197 | 203 |
| 3 | | | 180 | 181 |
| 4 | | | 38 | 41 |
| 5 | | | 16 | 12 |
| 0 | 4 | 4 | 143 | 137 |
| 1 | | | 69 | 72 |
| 2 | | | 168 | 177 |
| 3 | | | 34 | 32 |
| 4 | | | 96 | 98 |
| 0 | 5 | 4 | 21 | 18 |
| 1 | | | 117 | 116 |
| 2 | | | 129 | 136 |
| 3 | | | 151 | 156 |
| 4 | | | 16 | 19 |
| 0 | 6 | 4 | 168 | 171 |
| 1 | | | 30 | 32 |
| 2 | | | 155 | 163 |
| 3 | | | 139 | 139 |
| 4 | | | 20 | 22 |
| 0 | 7 | 4 | 9 | 7 |
| 1 | | | 106 | 109 |
| 2 | | | 65 | 68 |
| 3 | | | 7 | 9 |
| 0 | 8 | 4 | 156 | 156 |
| 1 | | | 102 | 100 |
| 2 | | | 100 | 104 |
| 3 | | | 35 | 34 |
| 0 | 9 | 4 | 8 | 9 |
| 1 | | | 82 | 79 |
| 2 | | | 59 | 57 |
| 0 | 10 | 4 | 33 | 26 |
| 1 | | | 38 | 35 |
| 1 | 0 | 5 | 15 | 12 |
| 2 | | | 60 | 56 |
| 3 | | | 20 | 17 |
| 4 | | | 106 | 105 |
| 5 | | | 22 | 22 |
| 0 | 1 | 5 | 328 | 325 |
| 1 | | | 142 | 145 |
| 2 | | | 142 | 142 |
| 3 | | | 19 | 23 |

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 4 | 1 | 5 | 64 | 62 |
| 5 | | | 30 | 31 |
| 0 | 2 | 5 | 203 | 204 |
| 1 | | | 55 | 55 |
| 2 | | | 110 | 111 |
| 3 | | | 83 | 86 |
| 4 | | | 67 | 69 |
| 5 | | | 76 | 73 |
| 0 | 3 | 5 | 366 | 367 |
| 1 | | | 72 | 75 |
| 2 | | | 197 | 204 |
| 3 | | | 185 | 189 |
| 4 | | | 13 | 16 |
| 0 | 4 | 5 | 12 | 12 |
| 1 | | | 79 | 85 |
| 2 | | | 51 | 51 |
| 3 | | | 111 | 113 |
| 4 | | | 27 | 30 |
| 0 | 5 | 5 | 55 | 64 |
| 1 | | | 99 | 105 |
| 2 | | | 65 | 71 |
| 3 | | | 175 | 179 |
| 4 | | | 38 | 39 |
| 0 | 6 | 5 | 57 | 55 |
| 1 | | | 35 | 35 |
| 2 | | | 36 | 39 |
| 3 | | | 25 | 20 |
| 4 | | | 34 | 35 |
| 0 | 7 | 5 | 150 | 156 |
| 1 | | | 106 | 110 |
| 2 | | | 37 | 35 |
| 3 | | | 51 | 51 |
| 0 | 8 | 5 | 17 | 14 |
| 1 | | | 60 | 64 |
| 2 | | | 19 | 20 |
| 3 | | | 29 | 27 |
| 0 | 9 | 5 | 22 | 24 |
| 1 | | | 48 | 47 |
| 2 | | | 32 | 32 |
| 0 | 10 | 5 | 26 | 26 |
| 0 | 0 | 6 | 481 | 481 |
| 1 | | | 41 | 43 |
| 2 | | | 103 | 108 |
| 3 | | | 15 | 13 |
| 4 | | | 22 | 18 |
| 0 | 1 | 6 | 192 | 190 |
| 1 | | | 87 | 89 |
| 2 | | | 63 | 67 |
| 3 | | | 47 | 47 |
| 4 | | | 31 | 30 |
| 0 | 2 | 6 | 81 | 83 |
| 1 | | | 40 | 39 |
| 2 | | | 59 | 57 |
| 3 | | | 109 | 115 |
| 4 | | | 15 | 13 |
| 0 | 3 | 6 | 46 | 44 |
| 1 | | | 104 | 107 |
| 2 | | | 58 | 61 |
| 3 | | | 69 | 71 |
| 4 | | | 28 | 28 |
| 0 | 4 | 6 | 280 | 268 |
| 1 | | | 27 | 25 |
| 2 | | | 211 | 221 |
| 3 | | | 48 | 49 |
| 4 | | | 25 | 25 |
| 0 | 5 | 6 | 135 | 133 |
| 1 | | | 35 | 36 |

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 2 | 5 | 6 | 96 | 99 |
| 3 | | | 71 | 72 |
| 4 | | | 18 | 17 |
| 0 | 6 | 6 | 84 | 80 |
| 1 | | | 22 | 26 |
| 2 | | | 126 | 129 |
| 3 | | | 62 | 66 |
| 0 | 7 | 6 | 29 | 29 |
| 1 | | | 20 | 19 |
| 2 | | | 36 | 37 |
| 3 | | | 66 | 64 |
| 0 | 8 | 6 | 88 | 83 |
| 1 | | | 29 | 31 |
| 2 | | | 14 | 13 |
| 0 | 9 | 6 | 59 | 55 |
| 1 | | | 29 | 30 |
| 2 | | | 24 | 22 |
| 1 | 0 | 7 | 19 | 21 |
| 2 | | | 209 | 212 |
| 3 | | | 23 | 25 |
| 4 | | | 82 | 86 |
| 0 | 1 | 7 | 97 | 97 |
| 1 | | | 85 | 88 |
| 2 | | | 48 | 49 |
| 3 | | | 74 | 80 |
| 4 | | | 51 | 52 |
| 0 | 2 | 7 | 3 | 1 |
| 1 | | | 115 | 123 |
| 2 | | | 34 | 38 |
| 3 | | | 90 | 93 |
| 4 | | | 38 | 42 |
| 0 | 3 | 7 | 64 | 59 |
| 1 | | | 72 | 74 |
| 2 | | | 46 | 48 |
| 3 | | | 74 | 80 |
| 4 | | | 27 | 31 |
| 0 | 4 | 7 | 60 | 59 |
| 1 | | | 42 | 47 |
| 2 | | | 189 | 200 |
| 3 | | | 37 | 39 |
| 4 | | | 23 | 25 |
| 0 | 5 | 7 | 37 | 32 |
| 1 | | | 48 | 53 |
| 2 | | | 29 | 30 |
| 3 | | | 28 | 30 |
| 4 | | | 78 | 78 |
| 0 | 6 | 7 | 51 | 51 |
| 1 | | | 98 | 102 |
| 2 | | | 40 | 43 |
| 3 | | | 42 | 42 |
| 0 | 7 | 7 | 52 | 56 |
| 1 | | | 128 | 130 |
| 2 | | | 30 | 28 |
| 3 | | | 26 | 24 |
| 0 | 8 | 7 | 24 | 23 |
| 1 | | | 13 | 15 |
| 2 | | | 53 | 52 |
| 0 | 9 | 7 | 81 | 79 |
| 1 | | | 17 | 22 |
| 0 | 0 | 8 | 270 | 269 |
| 1 | | | 7 | 10 |
| 2 | | | 34 | 32 |
| 3 | | | 0 | 4 |
| 4 | | | 40 | 42 |
| 0 | 1 | 8 | 59 | 57 |
| 1 | | | 109 | 114 |
| 2 | | | 53 | 54 |

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 3 | 1 | 8 | 42 | 38 |
| 4 | | | 38 | 39 |
| 0 | 2 | 8 | 114 | 114 |
| 1 | | | 254 | 257 |
| 2 | | | 24 | 22 |
| 3 | | | 7 | 4 |
| 4 | | | 66 | 62 |
| 0 | 3 | 8 | 67 | 66 |
| 1 | | | 169 | 173 |
| 2 | | | 56 | 57 |
| 3 | | | 43 | 44 |
| 4 | | | 91 | 91 |
| 0 | 4 | 8 | 22 | 25 |
| 1 | | | 93 | 92 |
| 2 | | | 80 | 82 |
| 3 | | | 54 | 56 |
| 4 | | | 150 | 148 |
| 0 | 5 | 8 | 89 | 86 |
| 1 | | | 72 | 72 |
| 2 | | | 107 | 108 |
| 3 | | | 11 | 8 |
| 0 | 6 | 8 | 139 | 142 |
| 1 | | | 78 | 78 |
| 2 | | | 56 | 57 |
| 3 | | | 40 | 40 |
| 0 | 7 | 8 | 55 | 53 |
| 1 | | | 57 | 55 |
| 2 | | | 15 | 14 |
| 0 | 8 | 8 | 125 | 123 |
| 1 | | | 19 | 22 |
| 1 | 0 | 9 | 53 | 54 |
| 2 | | | 27 | 22 |
| 3 | | | 32 | 35 |
| 4 | | | 3 | 1 |
| 0 | 1 | 9 | 65 | 66 |
| 1 | | | 22 | 23 |
| 2 | | | 25 | 22 |
| 3 | | | 15 | 20 |
| 4 | | | 31 | 32 |
| 0 | 2 | 9 | 75 | 74 |
| 1 | | | 49 | 51 |
| 2 | | | 46 | 48 |
| 3 | | | 56 | 54 |
| 4 | | | 34 | 35 |
| 0 | 3 | 9 | 65 | 65 |
| 1 | | | 127 | 127 |
| 2 | | | 36 | 38 |
| 3 | | | 82 | 82 |
| 0 | 4 | 9 | 27 | 26 |
| 1 | | | 119 | 119 |
| 2 | | | 69 | 73 |
| 3 | | | 71 | 72 |
| 0 | 5 | 9 | 16 | 18 |
| 1 | | | 145 | 144 |
| 2 | | | 35 | 37 |
| 3 | | | 82 | 83 |
| 0 | 6 | 9 | 8 | 6 |
| 1 | | | 119 | 121 |
| 2 | | | 36 | 34 |
| 0 | 7 | 9 | 8 | 4 |
| 1 | | | 51 | 53 |
| 2 | | | 22 | 26 |
| 0 | 8 | 9 | 28 | 27 |
| 0 | 0 | 10 | 86 | 84 |
| 1 | | | 50 | 51 |
| 2 | | | 26 | 28 |
| 3 | | | 28 | 30 |

| h | k | l | c.Fo | c.Fc |
|---|---|---|---|---|
| 0 | 1 | 10 | 81 | 79 |
| 1 | | | 91 | 91 |
| 2 | | | 51 | 53 |
| 3 | | | 48 | 52 |
| 0 | 2 | 10 | 127 | 125 |
| 1 | | | 35 | 36 |
| 2 | | | 57 | 59 |
| 3 | | | 21 | 23 |
| 0 | 3 | 10 | 44 | 44 |
| 1 | | | 17 | 15 |
| 2 | | | 27 | 29 |
| 3 | | | 55 | 56 |
| 0 | 4 | 10 | 98 | 95 |
| 1 | | | 7 | 7 |
| 2 | | | 28 | 28 |
| 3 | | | 28 | 25 |
| 0 | 5 | 10 | 23 | 26 |
| 1 | | | 41 | 40 |
| 2 | | | 33 | 33 |
| 0 | 6 | 10 | 15 | 6 |
| 1 | | | 5 | 6 |
| 2 | | | 28 | 31 |
| 0 | 7 | 10 | 20 | 19 |
| 1 | | | 48 | 48 |
| 1 | 0 | 11 | 29 | 30 |
| 2 | | | 70 | 73 |
| 3 | | | 47 | 46 |
| 0 | 1 | 11 | 113 | 111 |
| 1 | | | 26 | 25 |
| 2 | | | 42 | 44 |
| 3 | | | 34 | 33 |
| 0 | 2 | 11 | 135 | 130 |
| 1 | | | 50 | 52 |
| 2 | | | 72 | 72 |
| 3 | | | 0 | 9 |
| 0 | 3 | 11 | 112 | 109 |
| 1 | | | 46 | 45 |
| 2 | | | 53 | 56 |
| 0 | 4 | 11 | 28 | 27 |
| 1 | | | 22 | 21 |
| 2 | | | 50 | 49 |
| 0 | 5 | 11 | 63 | 63 |
| 1 | | | 19 | 14 |
| 2 | | | 21 | 22 |
| 0 | 6 | 11 | 92 | 89 |
| 1 | | | 32 | 31 |
| 0 | 0 | 12 | 23 | 25 |
| 1 | | | 54 | 52 |
| 2 | | | 17 | 16 |
| 0 | 1 | 12 | 26 | 25 |
| 1 | | | 64 | 63 |
| 2 | | | 52 | 53 |
| 0 | 2 | 12 | 5 | 3 |
| 1 | | | 49 | 49 |
| 2 | | | 64 | 63 |
| 0 | 3 | 12 | 15 | 14 |
| 1 | | | 27 | 28 |
| 2 | | | 84 | 82 |
| 0 | 4 | 12 | 0 | 0 |
| 1 | | | 14 | 12 |
| 0 | 5 | 12 | 64 | 64 |
| 1 | 0 | 13 | 86 | 83 |
| 0 | 1 | 13 | 12 | 10 |
| 1 | | | 58 | 56 |
| 0 | 2 | 13 | 2 | 2 |
| 1 | | | 54 | 53 |
| 0 | 3 | 13 | 8 | 6 |

Table 4. *Vibrational ellipsoids*

Coordinates (in Å, relative to the mean atomic positions) determine points on the axes of vibration. $B$ values correspond to the r.m.s. displacements ($B=8\pi^2\overline{u^2}$).

| | I | | | | II | | | | III | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $B_{\text{I}}$ | $x$ | $y$ | $z$ | $B_{\text{II}}$ | $x$ | $y$ | $z$ | $B_{\text{III}}$ |
| O(1) | +0·15 | +0·07 | +0·11 | 3·25 | +0·01 | +0·13 | −0·10 | 2·25 | +0·09 | −0·07 | −0·08 | 1·59 |
| O(4) | +0·14 | +0·05 | −0·12 | 3·01 | +0·01 | +0·15 | +0·07 | 2·05 | +0·10 | −0·05 | +0·10 | 1·72 |
| O(2) | +0·10 | +0·14 | +0·12 | 3·37 | +0·14 | −0·04 | −0·06 | 1·92 | +0·02 | −0·10 | +0·11 | 1·72 |
| O(3) | +0·08 | +0·11 | −0·13 | 2·80 | +0·14 | −0·03 | +0·07 | 2·07 | +0·02 | −0·12 | −0·09 | 1·80 |
| O(5) | +0·07 | +0·13 | +0·16 | 3·68 | +0·05 | +0·12 | −0·12 | 2·51 | +0·10 | −0·05 | −0·01 | 1·06 |
| C(1) | +0·05 | +0·07 | −0·13 | 2·01 | +0·06 | −0·13 | −0·05 | 1·77 | +0·10 | +0·02 | +0·06 | 1·10 |
| C(3) | +0·04 | +0·09 | +0·13 | 2·00 | +0·06 | −0·12 | +0·06 | 1·83 | +0·10 | +0·03 | −0·05 | 1·13 |
| C(2) | +0·00 | +0·04 | +0·16 | 2·05 | +0·06 | +0·13 | −0·04 | 1·80 | +0·12 | −0·05 | +0·01 | 1·37 |

Standard deviations in coordinates are 0·002 Å for O, 0·003 Å for C and 0·04 Å for H; standard deviations in all $U$ values are 0·001 Å$^2$.

### Discussion of the structure

The structure consists of parallel infinite chains of molecules, each chain generated by a twofold screw axis and held together by hydrogen bonds between pairs of carboxyl groups. The molecules have no mirror symmetry. The atoms in the group C(1)C(2)O(1)O(2) as well as in the group C(2)C(3)O(3)O(4) are coplanar within experimental error.

Bond lengths and bond angles (Fig. 3) were calculated without correction for anisotropic motion; the standard deviations are 0·005 Å and 0·2° respectively, except for bonds involving hydrogen atoms, in which case these values are 0·05 Å and 2° respectively.

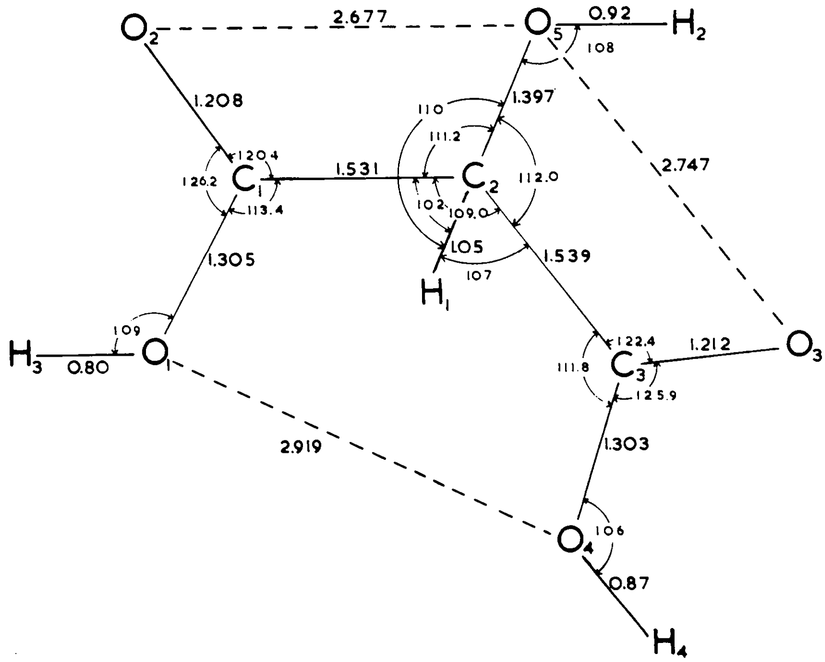


Fig. 3. Bond lengths and valency angles in the tartronic acid molecule.

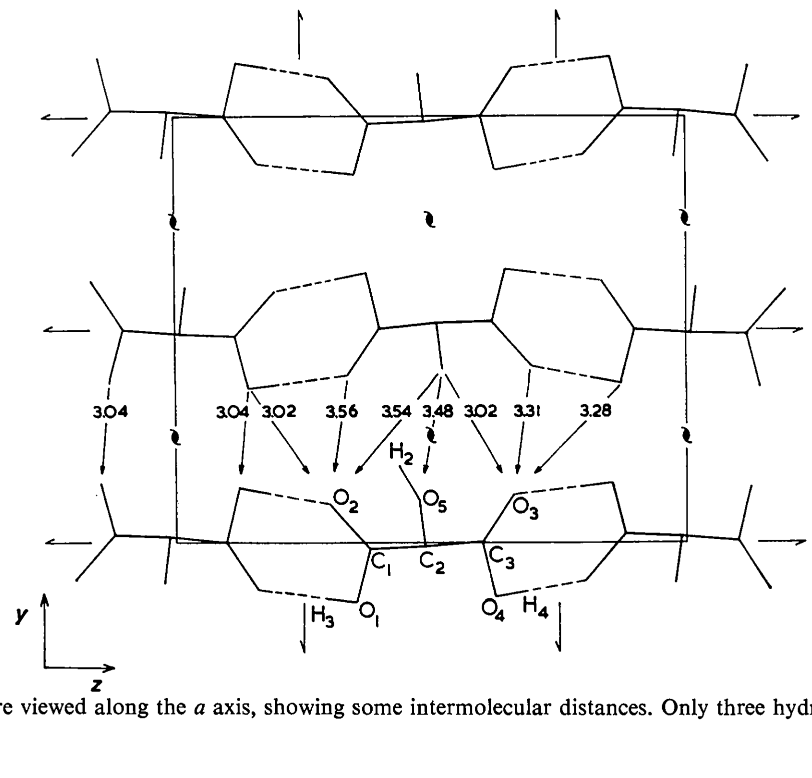


Fig. 4. The structure viewed along the $a$ axis, showing some intermolecular distances. Only three hydrogen atoms are depicted.

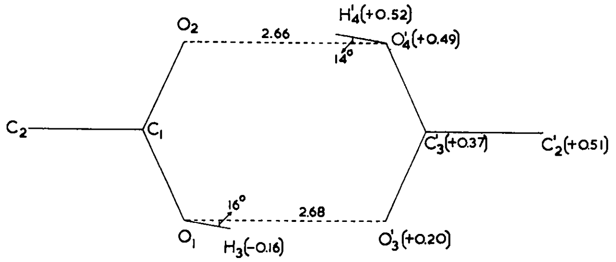


Fig. 5. Carboxylic dimer. Figures in brackets denote distances to the least-squares plane through C(1), C(2), O(1) and O(2).

Deviation of mirror symmetry in the molecule is not due to differences in equivalent bond lengths, but results from significant differences in equivalent bond angles and from asymmetry in the rotational position of the carboxyl groups, the angle between planes C(1)O(1)O(2) and C(1)C(2)O(5) being 15·0° and the angle between planes C(3)O(3)O(4) and C(2)C(3)O(5) being 18·5°. A planar arrangement of atoms of the hydroxyacetic acid groups is impossible because of the short O(1)–O(4) distance (2·53 Å); the actual distance is 2·92 Å, which may be seen as a compromise between steric hindrance and the tendency towards planarity.

The orientations of the principal axes of the vibrational ellipsoids (Algol-program Utr. E1, van Eijck, 1964) are given in Table 4. These data seem compatible with a libration of the carboxyl groups around the carbon–carbon bonds.

Tartronic acid, which may have mirror symmetry, crystallizes in an enantiomorphic space group. As the deviation from mirror symmetry is significant one could speak of the existence of two antipodes in spite of the absence of a carbon atom with four chemically different substituents.

Fig. 4 gives a projection of the structure along the shorter axis, showing chains of molecules connected by hydrogen bonds in the direction of the *c* axis.

In contrast to other structures containing dimers of this type (*e.g.* Jeffrey & Sax, 1963) tartronic acid crystallizes in a non-centrosymmetric space group, which implies that in the eight-membered ring formed by linking two molecules (Fig. 5) the atoms are not related by a center of symmetry.

It can be seen in Table 1 that a discrepancy exists between coordinates of hydrogen atoms as found by difference syntheses and by least-squares refinement, the former method yielding significantly shorter O–H distances than those usually found in the literature. Least-squares procedure gives O–H distances that are more in agreement with the 'expected' bond lengths; however, both methods give nearly identical bond angles.

It is questionable whether hydrogen atom H(2) (Fig. 4) is involved in a hydrogen bond or not; judged from distances and angles the only atom to be considered is O(3′) at $(x-\frac{1}{2}, \frac{1}{2}-y, 1-z)$: distance O(5)–O(3′) is 3·02 Å and angle H(2)–O(5)–O(3′) is 28°.

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