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Itaconic Acid

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Abstract. Orthorhombic, *Pbca*, $a=11\cdot561$ (3), $b=18\cdot487$ (5), $c=5\cdot441$ (1) Å, 25°C, $C_5H_6O_4$, $Z=8$, $D_x=1\cdot486$ g cm^{-3}. The structure consists of molecules which are hydrogen-bonded in a head-to-tail fashion to form infinite chains in the direction of the *a* axis.

Introduction. The unit-cell dimensions given above were determined from the least-squares refinement of observed 2θ values for 20 high-angle reflections (Cu $K\alpha_1$, $\lambda=1\cdot5405$ Å) and are found to be in agreement with those reported by Goldstein, Mandel & Pindzola (1961). It appears however that their space group assignment ($Pca2_1$ or *Pcam*) was incorrect as we have clearly established it to be *Pbca*.

Intensity data (Cu $K\alpha$ radiation) were collected for 1258 reflections on a Canberra Industries automated G.E. XRD-6 diffractometer using θ–2θ scans of 1° per min. 30 s background counts were taken at both ends of the scan range. Two reference reflections were monitored periodically and showed no systematic changes in intensity. The intensities were corrected for Lorentz and polarization effects; correction for absorption was considered unnecessary ($\mu=11\cdot6$ cm^{-1}).

Symbolic addition methods were used to locate the heavy atoms. The structure was refined using full-matrix least-squares methods (*ORFLS*; Busing, Martin & Levy, 1962) with weights based on experimental counting statistics. Isotropic refinement led to a conventional *R* of 0·153. The hydrogen atoms, located on a difference map, were now included in the refinement ($R=0\cdot134$); each hydrogen atom was assigned the isotropic thermal parameter of the heavy atom to which it was attached. Subsequent refinement of all positional parameters and anisotropic thermal parameters for the non-hydrogen atoms yielded a conventional *R* of 0·054 and a weighted *R* of 0·047. The 040 reflection (with the largest observed structure factor) was omitted from the refinement when it appeared to be suffering severely from extinction effects. The final positional and thermal parameters are given in Table 1. Atomic scattering factors for carbon and oxygen were obtained from *International Tables for X-ray Crystallography* (1962); for hydrogen, those of Stewart, Davidson & Simpson (1965) were used.*

Table 1. *Final structure parameters* (*with standard deviations in parentheses*)

(*a*) Heavy atoms (anisotropic thermal parameters × 10^4)

The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times10^{-4}]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·8406 (2)	0·3758 (1)	−0·0056 (4)	40 (1)	24 (1)	273 (8)	1 (1)	−9 (3)	10 (2)
C(2)	0·7587 (2)	0·3842 (1)	0·2009 (4)	43 (1)	24 (1)	231 (8)	4 (1)	−8 (3)	5 (2)
C(3)	0·6592 (2)	0·3322 (1)	0·2060 (4)	47 (2)	26 (1)	252 (9)	2 (1)	2 (3)	13 (2)
C(4)	0·5711 (2)	0·3458 (1)	0·0095 (4)	42 (1)	24 (1)	270 (8)	1 (1)	14 (3)	0 (2)
C(5)	0·7747 (2)	0·4342 (1)	0·3718 (5)	67 (2)	34 (1)	290 (9)	1 (1)	0 (4)	−3 (3)
O(1)	0·8309 (1)	0·3273 (1)	−0·1553 (3)	56 (1)	30 (1)	315 (6)	−3 (1)	21 (3)	−17 (2)
O(2)	0·9241 (1)	0·4242 (1)	−0·0118 (4)	64 (1)	36 (1)	405 (8)	−16 (1)	51 (3)	−27 (2)
O(3)	0·5737 (1)	0·3976 (1)	−0·1287 (3)	57 (1)	34 (1)	398 (7)	−11 (1)	−43 (3)	42 (2)
O(4)	0·4899 (1)	0·2968 (1)	0·0033 (4)	62 (1)	29 (1)	405 (7)	−13 (1)	−41 (3)	24 (2)

Table 1 (*cont.*)

(*b*) Hydrogen atoms (isotropic thermal parameters assigned from heavy atoms)

	x	y	z	B
H(1)	0·969 (2)	0·415 (1)	−0·150 (5)	4·02
H(2)	0·434 (2)	0·311 (1)	−0·117 (5)	3·89
H(3)	0·687 (2)	0·288 (1)	0·181 (4)	2·96
H(4)	0·617 (2)	0·339 (1)	0·370 (4)	2·96
H(5)	0·841 (2)	0·469 (1)	0·372 (5)	3·81
H(6)	0·717 (2)	0·444 (1)	0·511 (5)	3·81

Discussion. The crystal structure is composed of molecules which are hydrogen-bonded in a head-to-tail fashion to form infinite chains in the direction of the *a* axis (which is also the direction of crystal elongation). This is illustrated in Fig. 1, which gives the intra- and intermolecular bond distances and angles for the molecule, and in Fig. 2, which is a stereographic drawing of a pair of molecules representing one link in the hydrogen-bonded chain.

No unusual bond distances or angles were found (Fig. 1). The estimated standard deviation for bond

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* A table of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30195 (18 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

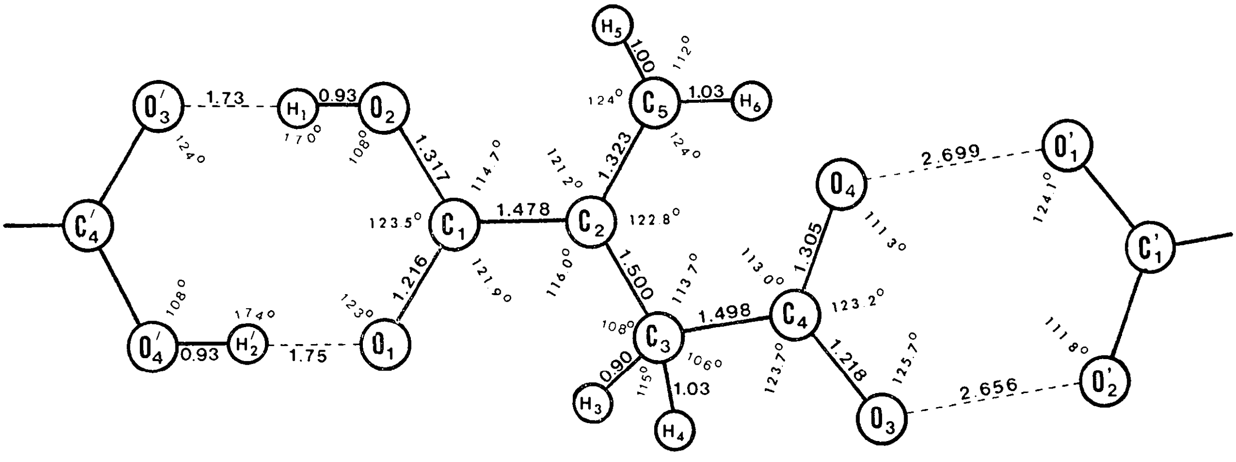

Fig. 1. Intra- and intermolecular bond distances and angles for itaconic acid. Hydrogen atoms H(1′) and H(2) have been omitted from the drawing in order to show the oxygen–oxygen intermolecular distances and angles.

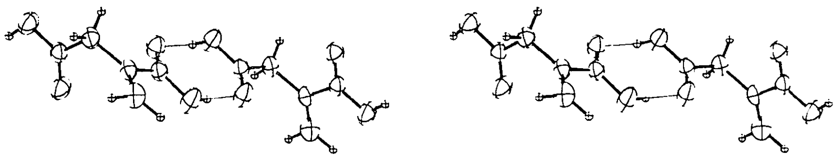

Fig. 2. Stereographic drawing of a pair of hydrogen-bonded molecules, one link in the infinite chain.

distances involving only heavy atoms is 0·003 Å; for bonds to hydrogen atoms, 0·02 Å. The e.s.d.'s for bond angles are approximately as follows: where only non-hydrogen atoms are involved, 0·2°; where one hydrogen is involved, 1·5°; where two hydrogens are involved, 2°.

Several least-squares mean-plane calculations were carried out for the atoms in the molecule and its hydrogen-bonded neighbors. Atoms C(1), C(2), O(1), and O(2) form almost a perfect plane with an average deviation from the plane of only 0·002 Å. Assuming conjugation between the two double bonds, C(1)=O(1) and C(2)=C(5), atoms C(3) and C(5) should also lie in this plane, but these are however found to be slightly out of the plane [0·073 (2) and −0·088 (3) Å, respectively] indicating that a small twist about the C(1)–C(2) single bond has occurred.

The atoms around the second acid group, C(3), C(4), O(3), and O(4), also form a plane with an average deviation of 0·002 Å. Atoms C(1′), O(1′) and O(2′) (across the hydrogen bond) deviate from this plane by 0·036 (2), −0·075 (2) and 0·064 (2) Å respectively, showing that the two hydrogen-bonded acid groups are very nearly coplanar.

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