

The Crystal Structure of Mesaconic Acid, C₅H₆O₄

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The crystal structure of mesaconic acid, C₅H₆O₄, has been determined from 491 X-ray intensities, and refined to $R=9.5\%$. The crystals are monoclinic with $a=7.22_5$, $b=11.88$, $c=7.00$ Å, $\beta=98^\circ 40'$, space group $P2_1/c$, $Z=4$. The structure consists of infinite chains parallel to a , adjacent molecules being linked by hydrogen bonds of length 2.63 and 2.74 Å. The longer of these is a bifurcated hydrogen bond, with its partner of length 2.88 Å holding the chains together. The C=O bonds in the molecule are in the *cis* configuration.

As part of a programme of studying hydrogen-bonded systems, we have investigated mesaconic acid, also called methylfumaric acid. The present work describes the crystal and molecular structure and adduces evidence to show that the name methylfumaric acid is to some extent misleading, since the C=O bonds are not in the *trans* configuration.

Experimental

The crystals were grown from ethanol. They were platy in habit with face (010), and show extinction at an angle of about 16° with the long edge [001]. Cell dimensions were obtained from high $\sin \theta$ reflexions on Weissenberg films calibrated with silver lines. The crystal data are

$a=7.22_5$, $b=11.88$, $c=7.00$ Å, $\beta=98^\circ 40'$,
 $d_o=1.44$, $d_c=1.45$ g.cm⁻³, $Z=4$, space group $P2_1/c$,
 $\mu(\text{Cu } K\alpha)=11.5$ cm⁻¹.

491 independent reflexions were collected by Weissenberg photography. The intensities were measured vis-

ually and brought to an approximate absolute scale by statistical methods.

Determination and refinement of the structure

The structure was solved by interpretation of Patterson projections. The c projection had a marked similarity to one projection of fumaric acid on which one of us (M.P.G.) had worked earlier, and the crystal structure of which is now well established (Brown, 1966; Bednowitz & Post, 1966). Assuming similar linkages of molecules in chains, packing considerations gave reasonable trial coordinates. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) with unit weights for the observed reflexions and anisotropic thermal factors for carbon and oxygen reduced R to 12.7%. A three-dimensional difference synthesis served to locate the hydrogen atoms, and a structure factor calculation gave a final R of 9.5%. The positional and thermal parameters are given in Table 1(a) and (b). Observed and calculated structure factors are in Table 2. Bond lengths, bond angles, and intermolecular con-

Table 1. Atomic and thermal parameters

(a) Final atomic coordinates and their e.s.d.'s ($\times 10^4$), (for hydrogen atoms $\times 10^3$)

	x/a	y/b	z/c		x/a	y/b	z/c
C(1)	4418 (12)	3146 (7)	1924 (14)	H(1)	256	210	65
C(2)	6404 (12)	3255 (7)	2902 (13)	H(2)	1110	98	541
C(3)	7359 (11)	2299 (7)	3296 (13)	H(3)	666	151	260
C(4)	9330 (13)	2215 (8)	4272 (14)	H(4)	601	470	234
C(5)	7129 (13)	4452 (7)	3377 (17)	H(5)	650	466	453
O(1)	3818 (9)	2146 (5)	1526 (11)	H(6)	804	471	243
O(2)	3455 (8)	4001 (5)	1502 (11)				
O(3)	10359 (9)	3025 (6)	4758 (11)				
O(4)	9878 (10)	1187 (5)	4574 (12)				

(b) Thermal parameters and their e.s.d.'s ($\times 10^4$ Å²) $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	$B(\text{Å}^2)$
C(1)	109 (19)	54 (8)	144 (34)	22 (10)	-15 (18)	6 (11)	H(1) 4.8
C(2)	145 (20)	42 (7)	165 (32)	3 (9)	-4 (20)	-14 (10)	H(2) 4.3
C(3)	137 (20)	52 (8)	64 (31)	22 (9)	-15 (18)	-3 (10)	H(3) 3.7
C(4)	154 (20)	80 (9)	62 (31)	-4 (11)	-10 (18)	18 (11)	H(4) 5.5
C(5)	177 (22)	50 (6)	269 (41)	-1 (9)	-23 (23)	-8 (12)	H(5) 5.5
O(1)	166 (15)	58 (5)	268 (26)	-7 (7)	-67 (15)	-2 (8)	H(6) 5.5
O(2)	147 (15)	57 (5)	339 (29)	1 (7)	-63 (16)	13 (9)	
O(3)	154 (15)	58 (6)	359 (30)	-2 (8)	-93 (16)	-7 (10)	
O(4)	222 (17)	53 (6)	367 (32)	30 (7)	-115 (17)	10 (5)	

Table 2. Observed calculated structure factors

h k	$ F_o $	$ F_c $	h k	$ F_o $	$ F_c $	h k	$ F_o $	$ F_c $	h k	$ F_o $	$ F_c $	h k	$ F_o $	$ F_c $	h k	$ F_o $	$ F_c $	h k	$ F_o $	$ F_c $
2 0	25.7	24.9	1 2	9.0	7.4	1 11	8.7	11.0	3 4	3.7	3.2	3 4	14.9	14.3	1 10	11.9	11.9	3 6	3.8	3.3
2 0	21.9	22.5	2 2	1.6	1.6	2 2	14.1	13.9	3 5	4.6	5.4	3 7	5.1	6.4	1 3	9.9	9.9	4 1	8.4	9.2
3 0	81.1	82.5	3 2	6.1	5.5	2 2	33.4	33.0	3 6	1.5	0.7	3 9	6.9	7.4	1 4	26.4	25.7	4 2	2.9	2.7
5 0	11.9	10.6	4 2	9.0	7.5	2 2	10.8	10.7	3 7	4.3	4.2	4 3	13.8	12.4	1 5	29.2	28.6	4 3	11.9	13.0
0 0 4	32.1	31.6	4 6	10.2	9.2	2 2	21.7	22.3	3 8	4.0	4.9	4 4	30.0	21.6	1 6	17.5	17.5	4 6	5.7	6.3
0 0 0 4	13.4	11.5	5 2	5.5	4.7	2 2	5.5	41.9	3 9	4.0	3.6	4 4	15.1	13.0	1 7	6.0	5.2	4 7	3.8	2.1
0 0 0 8	13.8	11.6	6 2	5.5	4.5	2 2	6.5	6.3	3 10	2.1	3.6	4 5	27.5	29.3	1 8	10.4	10.1	4 8	2.4	1.7
0 10 10	16.4	16.9	7 2	11.3	9.4	2 2	14.7	14.9	3 11	2.1	1.6	4 6	6.3	8.0	1 9	19.1	20.9	5 1	2.1	1.8
0 12 9	9.7	8.2	8 2	4.9	7.0	2 2	2.4	2.0	3 12	2.8	3.9	4 7	13.1	13.9	1 10	13.3	13.6	5 2	3.1	2.5
1 1	4.8	4.7	9 2	5.6	5.4	3 3	1.4	2.6	3 13	2.1	2.5	4 8	4.5	4.7	1 11	6.5	7.1	5 3	3.1	3.9
1 2	6.4	5.9	10 2	5.6	5.1	3 3	5	21.7	4 1	12.2	12.1	4 9	4.5	4.7	1 12	7.1	8.8	5 4	6.3	5.9
1 3	4.2	4.5	12 2	8.1	7.2	3 3	6	19.3	4 2	11.9	12.3	4 10	2.4	3.7	2 1	15.1	16.0	5 5	4.9	4.9
1 4	7.7	6.2	15 2	2.9	3.2	3 3	7	9.5	4 3	5.9	7.7	4 11	5.5	6.4	2 2	13.5	14.3	5 6	6.3	7.9
1 5	15.1	13.4	14 2	1.9	2.5	3 3	8	9.5	4 4	7.6	7.7	4 12	3.3	6.8	2 3	6.0	6.3	5 7	5.1	5.2
1 6	5.6	4.6	1 3	2.6	2.6	3 3	9	13.9	4 5	12.2	11.7	5 4	7.2	7.2	2 4	23.5	22.4	5 8	4.5	4.5
1 7	12.6	11.2	2 3	14.8	15.9	3 10	9.5	10.5	4 6	18.2	15.4	5 7	5.1	4.5	3 2	22.1	19.1	5 9	8.7	9.6
1 8	11.9	11.9	3 3	9.0	8.2	4 2	15.5	15.2	4 7	20.4	21.9	6 6	8.7	7.6	3 6	7.6	6.5	6 3	7.7	8.6
1 9	11.3	10.8	4 4	3.0	3.2	4 3	4.6	5.9	4 8	4.9	4.9	6 6	8.7	9.2	3 5	3.9	4.7	7 2	2.1	2.6
1 10	1.6	1.6	5 3	4.2	3.0	4 4	15.5	15.5	4 9	2.9	4.1	7 5	7.5	6.9	2 11	7.1	8.5	7 6	3.5	7.6
1 11	10.9	10.1	6 3	4.8	3.8	4 5	5.2	5.1	4 10	4.6	4.6	7 5	12.2	10.4	3 1	16.2	16.4	7 7	4.9	6.5
2 2	28.7	29.5	7 3	4.2	4.1	4 6	5.4	6.2	4 11	7.6	7.1	1 4	16.0	13.6	3 2	22.2	22.5	7 7	4.2	0.4
2 2	28.6	29.4	8 3	2.6	4.9	5 2	17.4	16.7	4 12	2.1	1.7	1 1	16.0	13.6	2 3	6.3	5.4	3 9	1.8	0.5
2 2	3	1.6	9 3	2.6	5.1	5 3	17.7	18.5	4 13	2.4	2.5	1 2	15.2	14.0	2 4	5.5	5.0	3 10	10.6	11.2
2 4	15.1	14.8	10 3	3.2	2.5	5 4	15.1	15.1	4 14	1.2	2.8	1 3	15.1	12.8	2 5	5.9	5.0	3 11	12.9	12.8
2 5	11.9	9.7	11 3	7.7	6.9	5 5	8	10.6	5 2	7.0	6.9	1 4	5.5	1.7	3 6	6.5	6.6	3 12	4.7	5.2
2 6	12.8	15.6	1 4	20.3	20.0	5 8	8	8.4	6 3	10.7	10.7	1 5	5.0	5.6	3 7	9.1	10.1	4 1	29.7	30.7
2 2	7	20.0	2 4	8.1	7.4	6 4	3	8.4	6 4	13.7	13.3	1 6	5.0	6.5	3 8	3.6	3.5	4 2	2.9	2.1
2 8	1.6	0.9	5 4	4.5	5.0	6 4	4	5.2	6 5	16.2	15.8	4 1	1.3	0.7	4 3	5.5	5.8	4 3	5.5	5.8
2 9	1.6	1.1	6 4	15.1	13.3	6 6	4	4.6	5 10	3.1	4.1	1 8	4.6	4.2	4 2	3.1	3.3	4 4	11.6	9.6
2 10	14.2	12.7	7 4	4	4.4	6 7	4	4.4	6 11	3.1	4.1	1 10	4.7	3.9	4 3	5.5	5.5	4 5	5.2	4.8
2 11	9.3	9.2	8 4	3.5	2.5	6 8	3	4.0	6 12	4.0	3.9	1 11	2.3	3.2	4 4	16.9	17.0	4 6	4.9	4.8
3 3	32.5	33.2	9 4	6.8	6.8	8 2	4.4	7.6	6 7	3.7	2.6	4 5	7	11.0	4 5	7	5.8	4 9	5.9	5.6
3 2	18.3	16.9	10 4	9.7	9.5	8 3	6.0	2.9	6 8	4.0	3.2	4 6	16.9	16.7	4 8	16.9	16.7	4 9	5.9	5.0
3 3	12.9	11.9	1 5	12.9	7.5	8 4	10.3	6.0	6 10	3.7	2.6	2 2	3	4.6	4 8	5.2	4.4	5 3	5.2	5.9
3 4	14.5	13.5	2 5	5	3.2	9 4	3	3.2	7 2	4.9	4.4	2 4	3.8	3.5	4 9	13.6	15.5	5 4	2.9	3.5
3 5	11.9	11.2	3 5	8.1	9.0	1 1	38.1	37.4	7 3	8.5	9.6	3 1	11.6	11.4	4 10	4.2	3.6	6 2	4.9	5.1
3 6	10.3	9.1	4 5	8.1	10.6	1 2	16.8	16.0	7 5	4	2.9	3 2	8.5	5.8	4 11	5.2	3.0	6 5	11.9	11.6
3 7	6.4	6.6	1 6	8.1	10.6	1 3	4.0	4.7	7 7	10.7	8.0	3 3	2	4.4	5 1	4.4	3.8	6 7	12.5	12.6
3 9	9.3	6.9	2 6	3.2	3.4	1 4	14.0	14.7	8 3	4	4.8	3 4	4.4	7.8	5 2	3	7.7	6 8	2.6	3.8
3 10	10.3	9.3	1 7	1	0	1 5	1.9	0.1	8 4	2	4.9	3 5	4.4	4.0	5 3	9.9	10.1	6 9	2.9	4.6
4 1	14.5	15.1	1 8	2	5.9	1 6	21.7	20.1	8 5	4.3	2.8	3 6	18.4	18.7	5 4	10.4	10.0	6 10	2.3	3.2
4 3	7.7	7.9	2 2	2	85.9	1 7	14.3	14.4	8 6	8.9	7.0	3 7	12.5	12.7	5 5	7.1	7.7	7 2	6.4	6.4
4 5	11.9	10.2	3 2	4.5	3.5	1 8	3.1	2.9	9 5	7.6	4.2	3 8	7.9	8.6	6 1	4.4	5.0	7 3	3.2	3.9
4 6	7.1	6.8	4 2	7.7	7.7	1 9	9.9	8.3	1 1	2.4	2.3	3 10	3.8	4.7	6 2	12.5	11.6	7 4	9.3	9.6
4 7	15.1	15.0	5 2	8.1	8.5	1 10	6.4	6.9	1 11	2.4	2.3	3 11	3.8	4.5	6 3	9.7	10.4	7 5	3.2	3.3
4 8	20.6	20.9	6 2	1.6	1.3	1 11	12.5	12.7	1 12	20.3	21.1	4 1	4.4	6.0	6 4	6.2	7.2	7 6	3.2	3.2
6 1	7.7	6.3	1 4	45.7	44.7	1 12	2.1	2.5	1 13	8.1	8.2	4 2	2.9	2.8	6 5	18.0	19.0	1 1	12.2	13.3
6 2	11.9	9.5	2 4	14.5	12.1	2 2	3.4	4.0	4 3	25.7	24.4	4 3	11.7	12.6	6 6	8.3	8.2	1 2	13.3	14.3
6 4	15.3	15.3	4 4	10.9	7.9	1 5	22.7	21.9	4 4	5.5	4.6	4 4	4	5.5	6 7	4.9	4.7	1 3	4.9	3.3
6 5	9.8	9.5	5 2	8.1	8.5	2 3	10.1	10.2	4 5	15.2	15.7	4 5	15.2	15.7	6 8	7.3	7.3	1 4	4.2	2.3
k 1 (k=0)			h 1 (k=0)			2 4	4	7.6	4 6	3.0	3.5	1 5	24.2	21.9	6 9	2.6	1.0	1 5	24.2	21.9
1 1 (k=0)			1 2	160.4	156.4	2 5	11.6	12.3	5 1	4.4	5.4	1 6	4.4	5.5	7 1	1.3	2.4	1 6	8.7	8.3
1 1	13.2	15.7	2 2	3.2	1.7	2 6	9.5	9.3	6 1	3.5	3.7	2 7	5.5	4.4	7 2	5.3	3.2	1 7	5.7	5.7
2 1	33.8	36.9	3 2	19.0	21.2	2 7	11.6	11.2	6 2	11.6	11.2	2 8	3.8	3.8	7 3	5.5	4.4	2 8	10.8	9.9
3 1	10.9	7.1	4 2	29.7	31.4	2 8	9	8.2	6 3	6.0	8.6	3 9	2.8	3.7	7 4	5.9	3.9	3 9	17.9	17.6
4 1	19.3	19.1	5 2	3.2	3.6	2 9	2.8	3.8	6 4	11.6	11.5	4 0	6.1	5.7	8 1	58.2	58.2	4 0	8.7	7.1
4 1	41.2	40.5	6 2	5.5	5.0	2 10	9.2	10.0	6 5	2.3	2.3	1 1	58.2	58.2	1 2	53.9	54.9	5 0	8.0	4.0
6 1	8.4	8.0	h k (l=1)			2 11	2.1	1.6	6 6	3.8	3.8	2 9	9.6	10.5	1 2	53.9	54.9	6 0	6.1	5.7
7 1	15.8	13.2	1 1	18.5	18.9	2 12	4.3	6.3	6 7	7.9	7.6	3 0	12.5	11.6	1 3	12.5	11.6	6 1	5.9	6.3
8 1	18.0	14.4	1 2	22.9	22.5	2 13	3.0	2.0	6 8	7	7.6									

Table 3 (cont.)

(c) Intermolecular distances

		$d(ij)$			$d(ij)$
C(1)–	–cC(2 ⁱⁱ)	3.73 Å	C(1)–	–cC(3 ⁱⁱ)	3.59 Å
C(1)–	O(1 ⁱⁱ)	3.33	C(1)–	–cO(1 ⁱⁱ)	3.75
C(1)–	–a, –cO(3 ⁱⁱ)	3.39	C(1)–	–a, –cO(4 ⁱⁱ)	3.53
C(2)–	–cC(3 ⁱⁱ)	3.45	C(2)–	–cC(4 ⁱⁱ)	3.59
C(2)–	O(1 ⁱⁱ)	3.40	C(2)–	–cO(4 ⁱⁱ)	3.73
C(3)–	C(3 ⁱⁱ)	3.53	C(3)–	–cC(4 ⁱⁱ)	3.39
C(3)–	O(1 ⁱⁱ)	3.72	C(3)–	–cO(3 ⁱⁱ)	3.55
C(4)–	C(4 ⁱⁱ)	3.57	C(4)–	aO(1 ⁱⁱ)	3.47
C(4)–	aO(2 ⁱⁱ)	3.47	C(4)–	–cO(3 ⁱⁱ)	3.37
C(5)–	aO(1 ⁱⁱⁱ)	3.28	C(5)–	2aO(4 ⁱⁱⁱ)	3.81
C(5)–	–cO(4 ⁱⁱ)	3.63	C(5)–	2a, b, cO(3 ⁱ)	3.64
O(1)–	O(1 ⁱⁱ)	3.60	O(1)–	O(2 ⁱⁱ)	3.79
O(1)–	–cO(2 ⁱⁱ)	3.74	O(1)–	–a, –cO(4 ⁱⁱ)	3.57
O(2)–	–a, –cO(3 ⁱⁱ)	3.39	O(2)–	aO(4 ⁱⁱⁱ)	3.54
O(3)–	O(3 ⁱⁱ)	3.72	O(3)–	O(4 ⁱⁱ)	3.57
O(3)–	–cO(4 ⁱⁱ)	3.71	O(4)–	2a, cO(4 ⁱ)	2.88
O(1)–	–a, –cO(3 ⁱⁱ)	2.63	} Hydrogen bond		
O(2)–	–a, –cO(4 ⁱⁱ)	2.74			

Equations for least-squares planes through various portions of the molecule are:

through all atoms

$$X + 0.0959Y - 1.9318Z - 0.8132 = 0 \quad (A)$$

through C(1)~C(5)

$$X + 0.1085Y - 1.9558Z - 0.8000 = 0 \quad (B)$$

through O(1), C(1), O(2)

$$X + 0.1045Y - 1.8676Z - 0.8924 = 0 \quad (C)$$

through O(3), C(4), O(4)

$$X - 0.0366Y - 1.9353Z - 0.4764 = 0 \quad (D)$$

Deviations from plane *B* are given in Table 4. The angles between the various planes and their direction cosines referred to orthogonal axes *a*, *b*, *c'* (where *c'* is normal to *a* and *b*) are in Table 5.

Table 4. Deviation of atoms from plane *B* and their e.s.d.'s

	Deviation	Δd
C(1)	–0.004 Å	0.012 Å
C(2)	0.006	0.012
C(3)	0.002	0.011
C(4)	–0.003	0.012
C(5)	–0.001	0.014
O(1)	0.004	0.009
O(2)	0.009	0.009
O(3)	0.061	0.009
O(4)	–0.083	0.010

Table 5. Planes in the molecules

(a) Direction cosines *l*, *m*, *n* of the normals to the planes

	<i>l</i>	<i>m</i>	<i>n</i>
Plane (A)	0.4593	0.0441	–0.8872
Plane (B)	0.4547	0.0494	–0.8893
Plane (C)	0.4715	0.0493	–0.8805
Plane (D)	0.4590	–0.0168	–0.8833

(b) Angles between various planes

Planes (B) & (C)	1.2°
Planes (B) & (D)	3.6

The crystal structure

Figs. 2, 3, and 4 show views of the structure projected down *c*, *b*, and *a* respectively. The molecules are arranged in chains along *a*, adjacent molecules (related by unit translation along *a* and *c* followed by the *c* glide) being linked by hydrogen bonds of 2.63 and 2.74 Å between the oxygen atoms of their opposing carboxyl groups. O(4) is also linked with a centrosymmetrically related (but translated by 2*a* and *c*) oxygen atom by a hydrogen bond of 2.88 Å. Thus the 2.74 and 2.88 Å hydrogen bonds must be regarded as bifurcated hydrogen bonds, as has been reported in a number of structures (*e.g.* Parry, 1951; Gupta, Prasad, Sahu & Sahu, 1972). The C–O(H)···O angles in the 2.63 and 2.74 Å hydrogen bonds are 113.7 and 116.2°, whereas in the 2.88 Å hydrogen bond the C–O(H)···O(H) angle is 164.9°. Other contact distances represent weak van der Waals forces.

The molecular structure

The C=O bonds (1.24 and 1.23 Å) are both on the same side of the central C=C bond. Thus they are not in the *trans* configuration, and the alternative name, methylfumaric acid, is misleading in this respect. A second consideration shows why the two C=O bonds cannot be regarded as being *trans*. Because of the bifurcated hydrogen bond system (2.74, 2.88 Å), O(4) must be regarded as of type O(H). Consequently, the other oxygen atom O(3) in the same carboxyl group has no hydrogen atom to donate. But, if the C=O bonds in the molecule are assumed to be *trans*, –*a*, –*c*O(3ⁱⁱ) is similar to O(1) and there cannot be a hydrogen bond between them, as neither has a hydrogen atom to donate. However, experiment shows that there is a hydrogen bond between them, and the only way to overcome this difficulty is to discard the assumption that

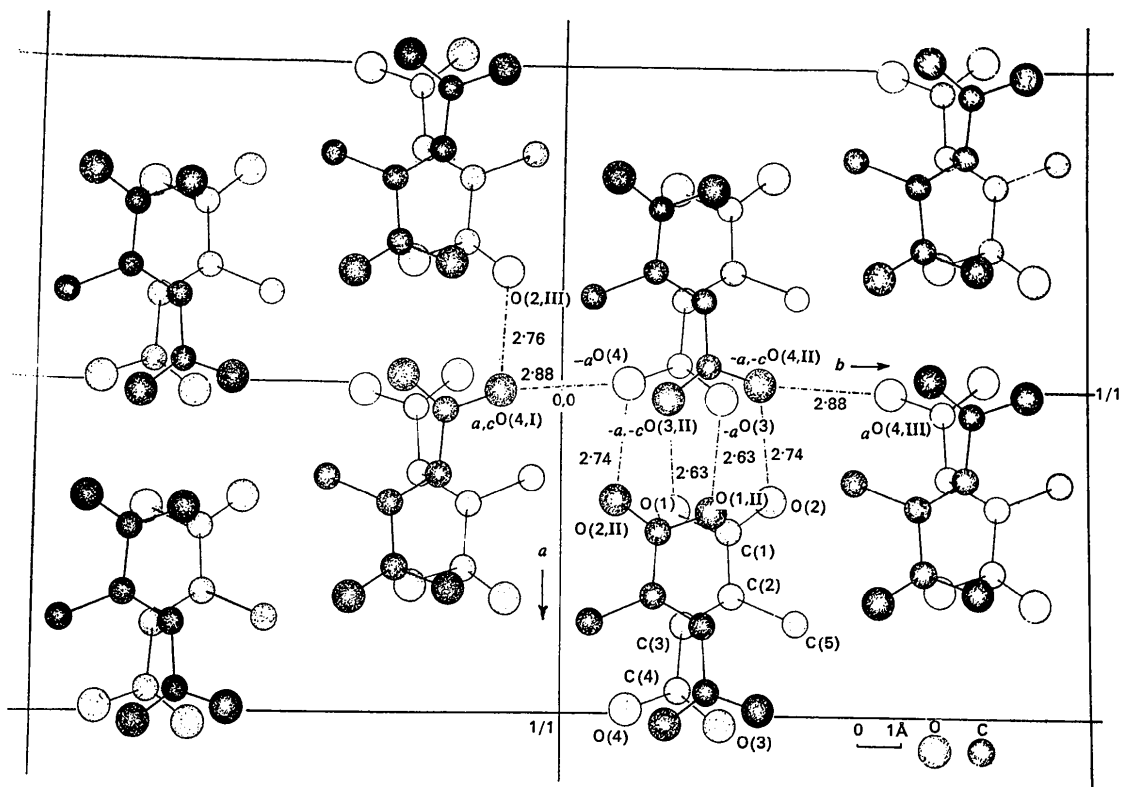


Fig. 2. The structure projected down *c*.

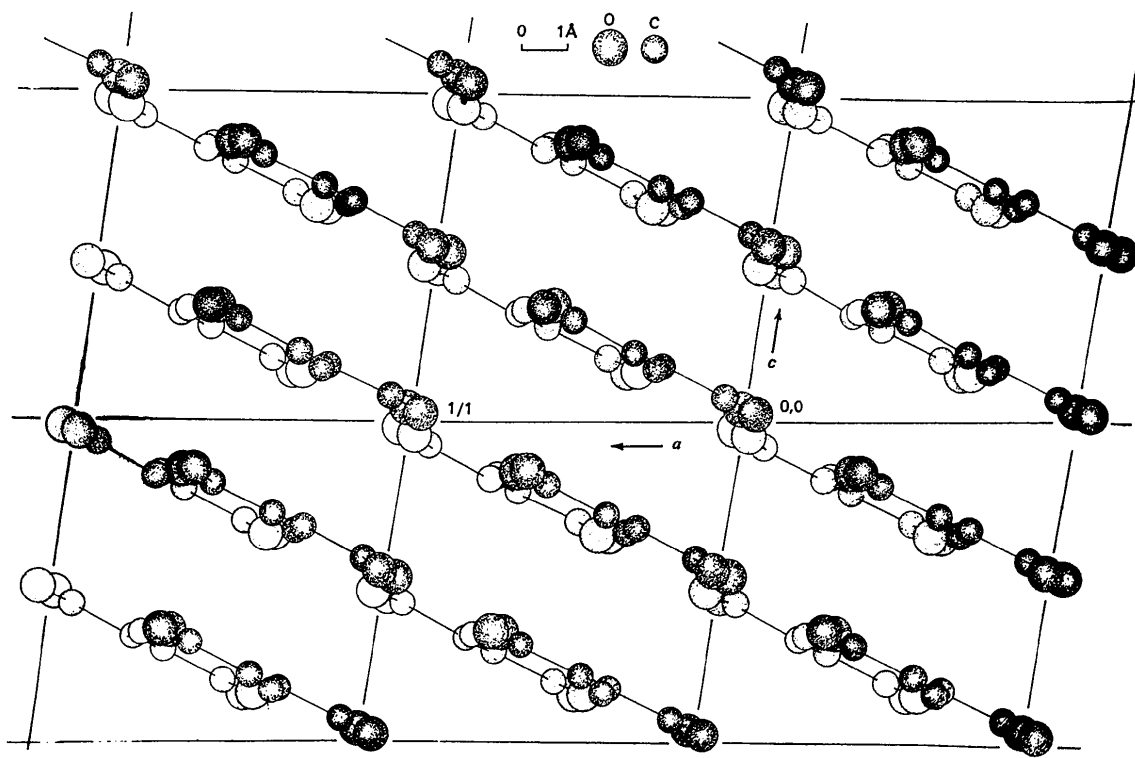


Fig. 3. The structure projected down *b*.

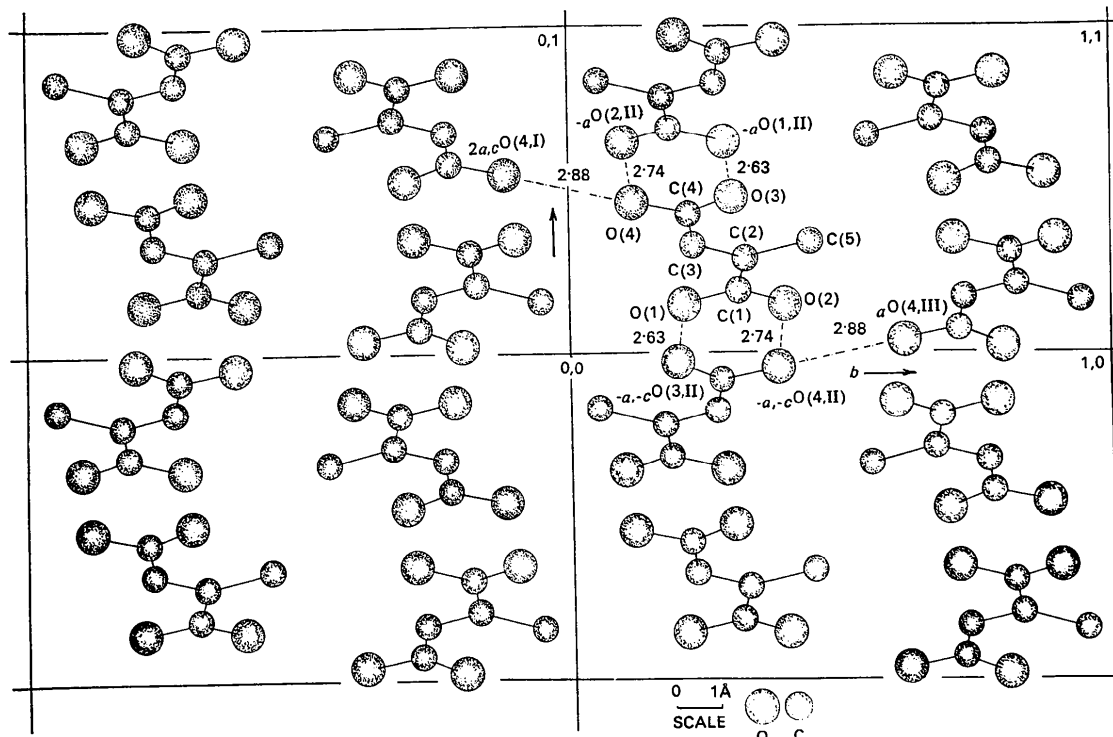


Fig. 4. The structure projected down a .

the C=O bonds in the two end carboxyl groups of the molecules are in the *trans* configuration.

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