# MOLECULAR PACKING MODES. PART X.*
THE CRYSTAL AND MOLECULAR STRUCTURES OF
TRANS,TRANS-MUCONIC ACID

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ABSTRACT

trans,trans-Muconic acid $C_6H_6O_4$ crystallises in the space group $P\bar{1}$, with $a = 8.982$, $b = 9.895$, $c = 3.787$ Å, $\alpha = 103.68$, $\beta = 75.27$, $\gamma = 101.58°$, and two centrosymmetric molecules per unit cell. The structure was solved from 1671 reflections measured by an $\omega/2\theta$ scan with Mo $K\alpha$ radiation on an IBM 1800 computer-controlled Siemens diffractometer, and refined anisotropically (on F^2) to $R = 0.078$. The geometries in the carbon chains of the two independent molecules are essentially identical; their bond lengths match to within 0.003 Å. The carboxyl group of one molecule is statistically disordered (C-O 1.257, 1.275 Å) whereas in the second molecule the bond lengths differ significantly (1.236, 1.294 Å), indicating a greater degree of order. A careful consideration of the packing mode allows us to interpret the difference between the two molecules.

The crystal structure of *trans,trans*-muconic acid TTMA (I) was undertaken in furtherance of the studies of the packing modes of carboxylic acids [1] and the topochemical properties of the compound [2].

(I)
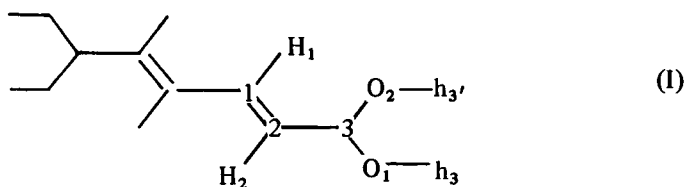
TTMA: Labelling of atoms (the carboxyl group was treated as disordered; two "hydrogen" atoms, labelled h(3) and h(3'), with adjustable occupancy factors, were attached to the oxygen atoms).

EXPERIMENTAL

Crystals of TTMA suitable for data collection were extremely difficult to grow. The diffraction data sets were collected on two separate crystals for reasons outlined below. The first crystal was the largest of a batch obtained by slow cooling of an ethanolic solution and measured approximately 0.06 x 0.12 x 0.06 mm. The structure was solved from the full set (Cu sphere) of data collected on this crystal. As the refinement was nearing completion we obtained from Mrs. Leah Muszkat of this Department a batch of crystals harvested from an ethanolic solution which had stood for about one year in a cold room (approx. 2°) and which yielded a specimen measuring 0.35 x 0.53 x x 0.48 mm. Approximately two-thirds of the reflections which had been too weak to be observed on the first crystal were strong enough to be observed on the second. Except where specifically noted, all remarks refer to measurements made on the second crystal.

Approximate cell constants for TTMA have been reported previously [3]. They were redetermined on the first crystal by a least-squares analysis of 24 high-angle spectra (Mo Kα radiation) measured on a Siemens diffractometer. Due to the large mosaic spread in this crystal the $K\alpha_1$, $K\alpha_2$ doublet was not sufficiently resolved to yield two readings for each reflection.

Crystal data
Triclinic $P\bar{1}$ (C_i)
$a = 8.982 \pm 0.004$, $b = 9.895 \pm 0.002$, $c = 3.787 \pm 0.001$ Å, $\alpha = 103.68 \pm 0.04°$,
$\beta = 75.27 \pm 0.04°$, $\gamma = 101.58 \pm 0.04°$.
$V = 312.8$ Å^3.
Formula: $C_6H_6O_4$, mol wt = 142.
$D_c = 1.51$ g/cm^3 with $Z = 2$.
μ(Mo Kα) = 1.4 cm^{-1}.

The crystal used for data collection was bounded by the *(201)*, *(1̄11̄)*, *(1̄20)*, *(22̄1̄)*, *(2̄1̄0)*, and *(110)* faces. With the crystal mounted along two different axes (a* + b* and 4a* + 6b* − c*) on a Siemens diffractometer controlled by an IBM 1800 computer, the *I(hkl)* for sinθ/λ ≤0.64 (Mo Kα radiation) were measured by the moving-crystal, moving-counter technique with balanced *Zr* and *Y* filters. Data reduction, including correction for absorption, was carried out as described previously [4]. The absorption factor, calculated using a Gaussian grid of 16 points, varied from 0.92 to 0.96.

F^2_{hkl} for equivalent reflections were averaged using statistical weights. Large discrepancies between the sets from the two crystal mountings were prevalent in, although not confined to, specific regions of reciprocal space. Careful examination of reflection profiles revealed that the crystal was partially split by about 0.2° but the large mosaic spread prevented us from precisely determining the orientation of this imperfection. It was felt that when a large discrepancy occurred between reflections in the two data sets, the lower intensity of one reflection resulted from

the fact that part of the intensity had not been measured due to the split crystal. For an individual reflection of an equivalent set for which
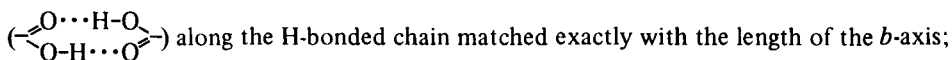
$$(\overline{F^2} - F_i^2)/\sigma_i(F_i^2) > 2$$

the reflection intensities were remeasured with the crystal mounted on the axis which gave the higher intensity in the first instance and the data were reaveraged. In the reaveraged final set of data, 233 of the 1352 measured reflections had $\overline{F^2} < \sigma(\overline{F^2})$ and were considered unobserved.

Since the larger crystal became available after the structure had been solved, we decided to collect additional reflections beyond the Cu sphere $(0.64 \leqslant \sin\theta/\lambda \leqslant \leqslant 0.77)$. Of the 1061 unique reflections in this shell of reciprocal space, 319 were calculated to have $|F_c| \geqslant 1.0$ and these were chosen to be measured, following the same procedure as that employed for the data within the Cu sphere. Of those measured nine were considered unobserved according to the criterion noted above. For the full set of data the agreement between equivalent reflections $R = \Sigma|\overline{F^2} - F_i^2|/\Sigma F_i^2$ is 0.075.

Structure determination and refinement

The structure was solved essentially from packing considerations. Although the space group is triclinic the diffraction data exhibit a pattern of absences and near-absences $h0l: h = 2n + 1, 0k0: k = 2n + 1$, indicating pseudo-monoclinic $P2_1/a$ symmetry. We therefore assumed that the structure consisted of two independent centro-symmetric molecules related by a pseudo two-fold screw axis. The molecules were assumed to lie in the *(201)* plane, *F(201)* being by far the strongest reflection. Using a molecular model based on the structure of dimethyl *trans,trans*-muconate [5] we found that the repeat distance between the TTMA carboxyl dimers

$(\overset{O\cdots H-O}{\underset{O-H\cdots O}{\diagdown}}-)$ along the H-bonded chain matched exactly with the length of the *b*-axis;

hence the H-bonded chains were assumed to lie along this axis.

The model was tested in a constrained-geometry least-squares programme on the 35 lowest-order reflections, in which only the molecular orientation parameters (three Eulerian angles for each molecule) and the scale factor were adjusted. After five cycles $R(=\Sigma|kF_o - |F_c||/\Sigma kF_o)$ stood at 0.07. Next, individual atomic parameters were refined, first with isotropic thermal parameters and fixed C-bonded hydrogen parameters, and finally with anisotropic vibration for all but the C-bonded hydrogens, whose parameters were now permitted to vary.

At convergence, difference syntheses $\delta(xyz)$ were computed in the planes of the two carboxyl dimers to locate the hydroxylic hydrogens, as the C-O bond lengths of both molecules (*A:* C-O(1) 1.279, C-O(2) 1.246;*B:* C-O(1) 1.288, C-O(2) 1.238 Å) indicated partial disorder. These hydrogens were not clearly resolved on the map although there were electron peaks at the expected hydroxyl hydrogen positions in both molecules. Therefore four half "hydrogens", with U of 0.035 Å^2, were inserted

along the O···O lines at 1 Å from each oxygen, and their occupancy factors refined. The resulting C-O bond lengths (A: C-O(1) 1.275, C-O(2) 1.257; B: C-O(1) 1.294, C-O(2) 1.236 Å) clearly indicated that the carboxyl group on molecule A is highly disordered while that of molecule B is significantly less so. The values of the occupancy factors of these hydroxylic "hydrogens" (A: 0.52, 0.36; B: 0.66, 0.31) are consistent with this conclusion. The final agreement factors were $R = 0.078$ and $r[=\Sigma\omega(k^2F_o{}^2 - F_c{}^2)^2 / \Sigma\omega k^4 F_o{}^4] = 0.03$. Of the total 1671 reflections, 322 were excluded from the last cycle. These included: (a) five intense reflections suffering from extinction effects $[kF_o < F_c]$, (b) 157 (of 242) unobserved reflections for which $|F_c| < kF_t$, and (c) 160 observed reflections for which $\omega\Delta^2 > 6 \ \Sigma\omega\Delta^2 / (N - N_c) \sim 36$, where $\Delta = k^2 F_o{}^2 - F_c{}^2$, N is the number of observations, and N_c is the number of parameters refined. This set of 160 reflections showed the largest discrepancies between equivalent reflections measured in the two different orientations. The atomic scattering-factor curves were taken from the International Tables [6]. The positional and thermal parameters, together with their estimated standard deviations (e.s.d.), are listed in Tables I and II. The observed and calculated structure factors are available on request.

TABLE I. Fractional atomic co-ordinates and standard deviations referred to axes a, b, c.

Atom	x	y	z
	Molecule A		
C(1)	0.4822(3)	0.0708(2)	0.0288(6)
C(2)	0.5810(3)	0.1708(2)	-0.1266(7)
C(3)	0.5433(3)	0.3136(2)	-0.0689(6)
O(1)	0.6451(2)	0.3991(2)	-0.2410(6)
O(2)	0.4178(2)	0.3469(2)	0.1402(5)
H(1)	0.377 (3)	0.096 (3)	0.149 (8)
H(2)	0.681 (3)	0.151 (3)	-0.263 (7)
h(3)*	0.621	0.504	-0.180
h(3')*	0.389	0.432	0.165
	Molecule B		
C(1)	0.0163(3)	-0.4277(2)	-0.0287(6)
C(2)	-0.0778(3)	-0.3327(2)	0.1486(6)
C(3)	-0.0406(2)	-0.1878(2)	0.0826(6)
O(1)	-0.1413(2)	-0.1066(2)	0.2754(5)
O(2)	0.0780(2)	-0.1482(1)	-0.1396(5)
H(1)	0.121 (4)	-0.404 (4)	-0.189 (10)
H(2)	-0.173 (4)	-0.344 (4)	0.324 (8)
h(3)*	-0.119	-0.009	0.211
h(3')*	0.102	-0.043	-0.169

* The occupancy factors of the "hydrogen atoms" h(3)A, h(3')A, h(3)B, h(3')B are 0.52(7), 0.36(7), 0.66(8), and 0.31(8), respectively.

TABLE II. Observed thermal parameters ($\mathrm{\AA}^2$)
The Debye-Waller factor is defined as $\exp[-2\pi^2 \Sigma_i \Sigma_j a_i^* a_j^* h_i h_j u^{ij}]$ for C and O atoms, $\exp[-8\pi^2 U \sin^2\theta/\lambda^2]$ for hydrogen.

Atom	u^{11}	u^{22}	u^{33}	u^{12}	u^{23}	u^{13}
			Molecule A			
C(1)	.0471(11)	.0240(7)	.0442(11)	.0081(7)	.0116(7)	−.0004(8)
C(2)	.0489(11)	.0248(7)	.0514(13)	.0118(7)	.0147(8)	.0035(9)
C(3)	.0462(11)	.0236(7)	.0462(12)	.0044(7)	.0158(8)	−.0004(8)
O(1)	.0542(10)	.0275(6)	.0766(13)	.0083(6)	.0231(7)	.0151(8)
O(2)	.0569(10)	.0298(7)	.0766(13)	.0168(7)	.0207(8)	.0191(8)
H(1)	.028 (7)					
H(2)	.022 (7)					
h(3)	.035					
h(3')	.035					
			Molecule B			
C(1)	.0484(11)	.0207(6)	.0395(11)	.0057(7)	.0099(6)	−.0028(8)
C(2)	.0515(12)	.0218(7)	.0468(12)	.0059(8)	.0139(8)	.0045(9)
C(3)	.0476(11)	.0211(7)	.0459(12)	.0071(7)	.0132(7)	.0007(8)
O(1)	.0587(10)	.0255(7)	.0717(12)	.0152(6)	.0174(7)	.0165(8)
O(2)	.0547(10)	.0240(6)	.0637(11)	.0116(6)	.0186(6)	.0134(7)
H(1)	.037 (9)					
H(2)	.031 (8)					
h(3)	.035					
h(3')	.035					

RESULTS AND DISCUSSION

Experimental bond lengths and angles of the two independent molecules are given in Fig. 1. Their e.s.d.s involving the heavy atoms only are 0.003 Å and 0.2° respectively. The equivalent bonds of the carbon chain of molecules A and B match each other in length with a "scatter" $\{=(\Sigma [r_A - r_B]^2/2)^{\frac{1}{2}}\}$ of 0.003 Å. On the reasonable assumption that this value may be taken as a measure of the degree of precision in bond length (i.e. $\sigma(r) = 0.003$ Å) the geometrically equivalent C-O bonds of molecules A and B compare poorly; a χ^2 test $(\Sigma(r_A - r_B)^2/[\sigma^2(r_A) + \sigma^2(r_B)] = 44$ for two degrees of freedom, the sum having been taken over two bonds) indicates that the two carboxyl groups are decidedly different; indeed the bond lengths of the molecules A and B of the first crystal (Fig. 1) also exhibit a very similar trend.

The C-O bond lengths of molecule A tend to be equal while the C-O bonds of molecule B are more unlike in length, indicating specific C=O carbonyl and C-OH hydroxyl bond character. The tendency towards equal C-O bond lengths in molecule A may arise either from proton delocalisation within its hydrogen-bonded
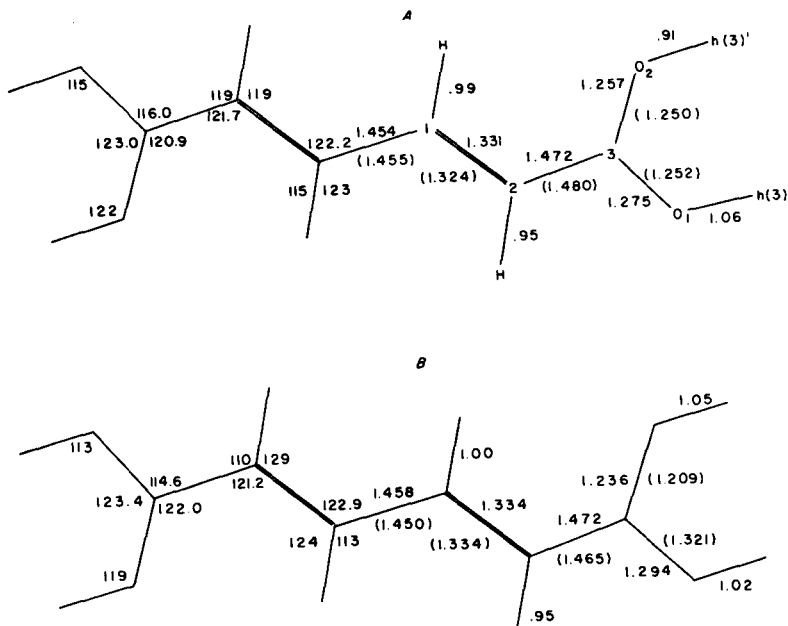
FIG. 1. TTMA. Bond lengths (Å) and bond angles (o) of molecules A and B. Bond lengths from the first crystal in parentheses.

dimer or from orientational disorder in the crystal lattice of carboxyl dimers

containing distinct C=O carbonyl and C-OH hydroxyl bonds ($-C\underset{O-H\cdots O}{\overset{O\cdots H-O}{<}}$,

$-C\underset{O\cdots H-O}{\overset{O-H\cdots O}{<}}$-). Proton delocalisation is precluded on the grounds that (a) the

O-H···O distances for molecules A and B are equal (2.605, 2.614 Å) and (b) the
IR spectrum* of crystalline TTMA shows no evidence of the carboxylate anion

($-C\underset{O}{\overset{O}{<}}$-); the spectrum contains a band at 1680 cm^{-1} — a doublet with a

small peak separation of 10 cm^{-1} — due to the carbonyl stretching mode. We
therefore tend to the view that the equality of the C-O bonds of A is due to
orientational disorder of the carboxyl dimer A in the crystal. The question as
to what are the primary factors which induce the differences in the orientational
order/disorder of the carboxyl dimers of molecules A and B shall be discussed
presently.

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* The IR spectrum of crystalline TTMA was measured in a KBr pellet on a Perkin-Elmer
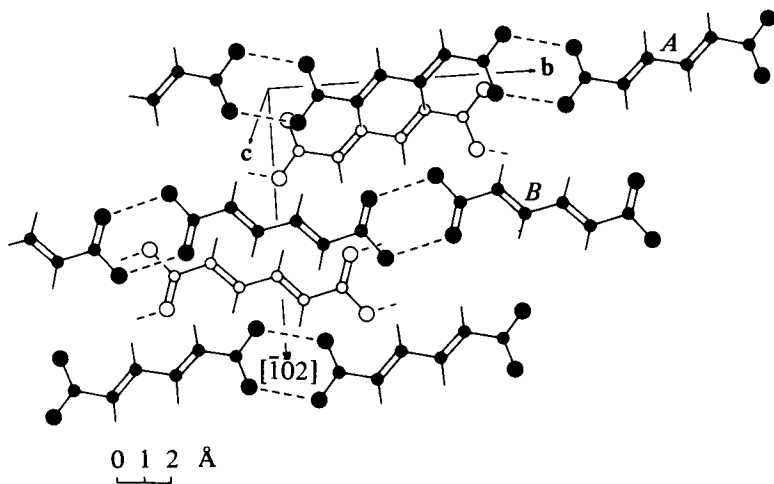457 A grating infrared spectrophotometer.

FIG. 2. TTMA. Intra- and interlayer packing arrangement seen normal to the best plane through the shaded *A* and *B* molecules.
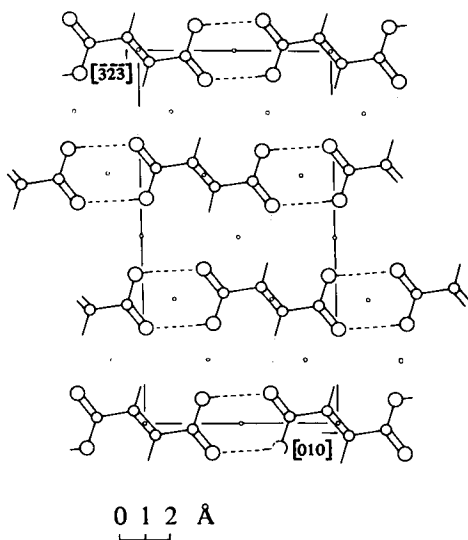

FIG. 3. Fumaric acid. The intralayer structure of the triclinic form which is almost identical to the intralayer structure of the monoclinic form (see Fig. 4a). The vector 3a+2b+3c is 15.20 Å long which compares well with the corresponding axis of the monoclinic form (15.01 Å). The angle between the vectors [010] and [323] is 90.7°. The layer structure is planar to within 0.2 Å. Some interatomic distances are C–H•••O 3.547, O–H•••O 2.670, C–OH 1.290, and C=O 1.228 Å.

TABLE III. Equations of best planes: $m_1 x + m_2 y + m_3 z - d = 0$, where x, y, z are fractional co-ordinates

		m_1	m_2	m_3	d
I*	Molecule A	5.494	−0.028	3.309	2.747
II	Molecule B	5.997	−0.067	3.183	0.033
III	Molecular Sheet containing A and B	6.203	−0.039	3.117	3.118

Deviations (Å) from best planes

Atom	Plane I	Plane II	Plane III	
	A	B	A	B
C(1)	−0.004	0.002	0.041	−0.026
C(2)	0.022	−0.005	−0.084	0.008
C(3)	0.001	−0.001	−0.024	−0.011
O(1)	−0.011	0.003	−0.116	0.016
O(2)	0.002	0.000	0.104	−0.052
H(1)	−0.182	0.116	0.316	−0.174
H(2)	0.122	−0.020	−0.281	0.056
h(3)	0.056	−0.074	−0.153	0.081
h(3')	−0.077	0.042	0.210	−0.104

* Planes are defined by the non-hydrogen atoms in the molecule; for plane III the co-ordinates of molecule B have been shifted to $1+z$.

Molecules A and B each form hydrogen-bonded chains along the b direction. These two independent molecules are almost antiparallel, the angle between their planes being 175°43' (see Table III), and moreover constitute a layer structure very nearly in the *(201)* plane (see Table III). Furthermore, within this plane, the angle between the b-axis and the -a+2c axis is 89°57'; therefore the arrangement of the A and B molecules within the *(201)* layer approximates closely to $P2_1/(-a+2c)$ as seen in Fig. 2. Within this layer all C-H bonds are clearly directed at oxygen atoms of neighbouring molecules (Fig. 2) with very similar C···O distances of 3.51, 3.52, 3.57, and 3.58 Å (see Table IV). This suggests the possibility that within the layer the structure is stabilised by C-H···O interactions.

In this context it is relevant to review some of the structural features of the triclinic [7] *(P1̄, Z = 1)* and monoclinic [8] *($P2_1/c, Z = 6$)* forms of fumaric acid, the lower analogue of TTMA. Fumaric acid lies in layers in both forms; moreover these layers are isostructural (see Figs. 3 and 4). The two forms differ only in their interlayer arrangement. In the monoclinic structure the layers are related by two-fold screw axes (Fig. 4a); in the triclinic crystal they are related by translation (Fig. 4b). The conformation of the C=C-C=O group is *anti*planar in both structures, in contrast to the usually observed *syn*planar conformation [9]. The *anti*planar conformation must be due primarily to intralayer forces; the interlayer interactions are ruled out on the grounds that the packing of the layers is different in the two structures. Within the layer the molecules are so arranged that the C-H bonds are directed towards neighbouring carbonyl oxygens along the line of sight of their lone-pair lobes,
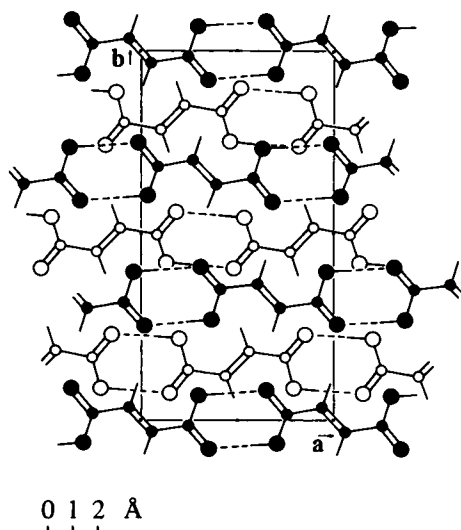
0 1 2 Å

0 1 2 Å

FIG. 4a. The interlayer structure of mono-
clinic fumaric acid. Some averaged interatomic
distances are: C-OH 1.293, C=O 1.224,
O-H⋯O 2.684, and the intralayer
C-H⋯O 3.40 Å. The layer structure is
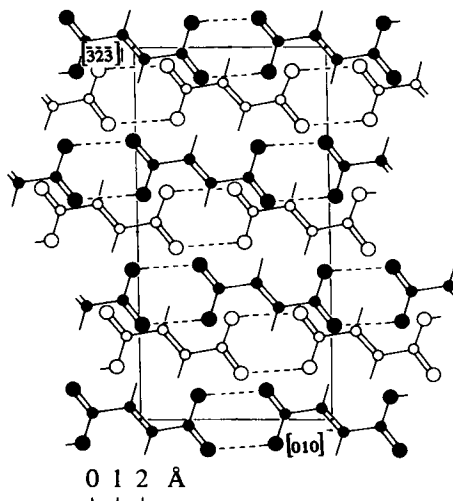planar to within 0.2 Å.

FIG. 4b. Fumaric acid. The interlayer
structure of the triclinic form.

assuming sp^2 hydridisation of the carbonyl oxygen. It is therefore not unreasonable
to suppose that neighbouring hydrogen-bonded chains of the fumaric-acid layer
structure are interlinked by C-H⋯O (carbonyl) contacts which indeed stabilise
the *anti*planar C=C-C=O conformation. An assumed *syn*planar C=C-C=O
conformation would lead to the less favoured C-H⋯O (hydroxyl) interaction.

Returning to the intralayer structure of TTMA, we note that efficient utilisation
of C-H bonds in the formation of C-H⋯O contacts involving all oxygen atoms
is possible only if the molecules *A* and *B* are related by a (pseudo) two-fold screw-
axis. This full complement of C-H⋯O contacts cannot be achieved with molecules
related by translation.

Since the intralayer environments of molecules *A* and *B* are essentially identical,
the difference in orientational order/disorder of their carboxyl groups must be
associated with interlayer environment. The direction of offset between successive
(201) layers is such that the interlayer contacts of molecules *A* and *B* are not alike;
this is evident particularly along the 4 Å stack axis. The stacking of the carboxyl
dimers of *B* is shown in (II).

(II)   (III)   (IV)
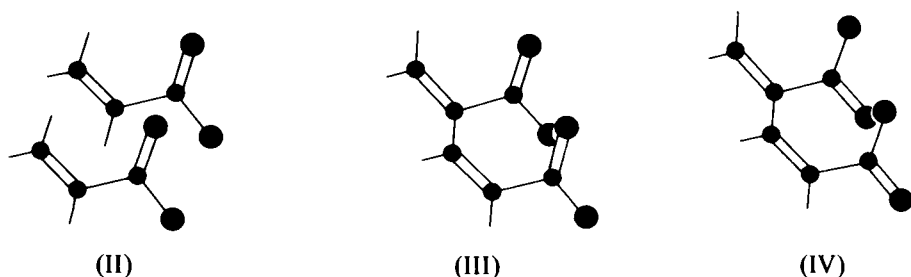
The crystal structure of monomethyl *trans,trans*-muconate [10] shows a stack arrange-
ment of carboxyl groups (see Fig. 5) very similar to that of (II) although the molecule
adopts an *anti*planar C=O–C=O conformation unlike the B molecule of TTMA. We
therefore tend to the view that (II) represents a favourable stack arrangement of
carboxyl dimers. The stacking patterns of carboxyl dimers of the A-molecules, assum-
ing *syn*planar and *anti*planar C=O-C=O conformations, are shown in (III) and (IV),
respectively. Of these two packing motifs of A, (IV) is the more similar to (II) and
so it is not unreasonable to suppose that intrastack packing forces favour the arrange-
ment (IV) over (III). However, as stack (III) contains molecules with the preferred
*syn*planar C=O–C=O conformation, the carboxyl group of molecule A is subjected
to two opposing effects leading to conformational disorder. As to the question why
only the *anti*planar C=O–C=O conformation is stabilised in the structure of mono-
methyl *trans,trans*-muconate – unlike the A molecules of TTMA – this is presumably
due to an intralayer C–H···O(carbonyl) interaction as in fumaric acid.
TTMA gives on irradiation in the solid state [2] the cyclobutane of symmetry *m*. However, we
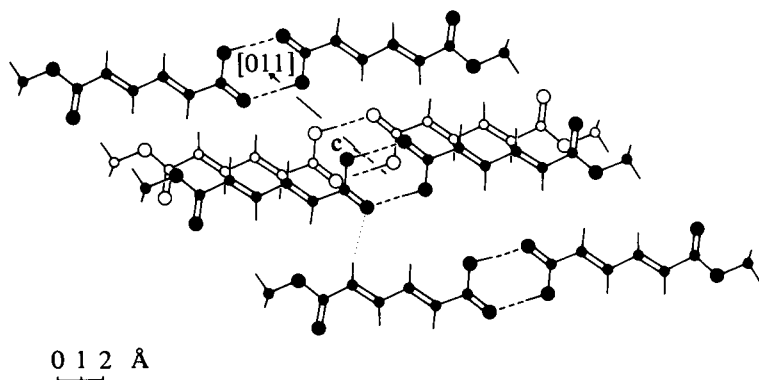

0 1 2 Å

FIG. 5. Monomethyl *trans,trans*-muconate. Intra- and interlayer structure pro-
jected onto the best plane of the central shaded dimer. Some interatomic dis-
tances are: C–OH 1.308, C=O 1.228, O–H···O 2.618, and C–H···O 3.49 Å.
The offset from coplanarity between successive molecular pairs, within the
layer, is 0.8 Å.

observe (see Fig. 2 and Table IV) that the C=C double bonds along the A stack, which are related across the centre at (½, 0, -½), are 3.78 Å apart. Therefore on topochemical grounds, we should expect some yield of the $\bar{I}$ photodimer. This point is at present being investigated.

TABLE IV. Interatomic distances. (Limiting radii of C, O = 1.90 Å; H = 1.40 Å)

D_{000}** $\bar{D}_{0\bar{1}\bar{1}}$

*C(1)'⋯C(1)'	3.581

$D_{00\bar{1}}$

C(1)⋯C(1)	3.788
C(2)⋯C(2)	3.788
C(3)⋯C(3)	3.788
C(3)⋯O(2)	3.563
O(1)⋯O(1)	3.788
O(1)⋯O(2)	3.372
O(2)⋯O(2)	3.788
C(1)'⋯C(1)'	3.788
C(1)'⋯C(2)'	3.789
C(2)'⋯C(2)'	3.788
C(3)'⋯C(3)'	3.788
C(3)'⋯O(1)'	3.698
O(1)'⋯O(1)'	3.788
O(2)'⋯O(2)'	3.788

$\bar{D}_{000}$

C(1)⋯C(1)'	3.640
O(2)⋯C(2)'	3.463
O(2)⋯C(3)'	3.654
O(2)⋯O(1)'	3.485
O(2)⋯H(2)'	3.132
H(1)⋯O(1)'	3.002
O(1)'⋯O(1)'	3.534
O(1)'⋯O(2)'	2.614
O(2)'⋯O(2)'	3.333

D_{000} D_{001}

C(1)⋯C(2)	3.405
C(1)⋯C(3)	3.780
C(2)⋯O(1)	3.682
C(3)⋯O(1)	3.358
C(2)'⋯C(3)'	3.563
C(2)'⋯O(2)'	3.335
C(3)'⋯O(2)'	3.294
O(1)'⋯O(2)'	3.455

$\bar{D}_{001}$

C(1)⋯O(1)'	3.512
O(2)⋯C(2)'	3.525
O(2)⋯O(1)'	3.749
O(2)⋯H(2)'	2.584
H(1)⋯O(1)'	2.624
C(3)'⋯O(1)'	3.718
O(1)'⋯O(1)'	3.483
O(1)'⋯O(2)'	3.722

$D_{10\bar{1}}$

H(2)⋯O(1)'	3.194

$\bar{D}_{10\bar{1}}$

C(1)⋯C(2)	3.780
C(2)⋯O(2)'	3.579
O(1)⋯C(1)'	3.568
O(1)⋯H(1)'	2.603
H(2)⋯O(2)'	2.703

* The unprimed atom is of molecule A, the primed atom of molecule B.
** Co-ordinates of equivalent positions: Symbol

x, y, z	D
$-x, -y, -z$	$\bar{D}$

D_{pqr} denotes fractional co-ordinates $p+x$, $q+y$, $r+z$.

TABLE IV (cont'd)

D_{000} $\overline{D}_{100}$		D_{110}	
$C(2) \cdots O(2)'$	3.521	$O(1) \cdots C(1)'$	3.621
$C(3) \cdots H(1)'$	3.294	$O(1) \cdots C(2)'$	3.574
$O(1) \cdots C(1)'$	3.386		
$O(1) \cdots H(1)'$	2.955		
$H(2) \cdots O(2)'$	2.953	$\overline{D}_{110}$	
$D_{11\bar{1}}$		$O(1) \cdots O(1)$	3.472
		$O(1) \cdots O(2)$	2.605
$O(1) \cdots H(2)'$	3.289	$O(2) \cdots O(2)$	3.379

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