

The Crystal and Molecular Structure of the Low-Temperature Stable Modification of Octa-*trans*-2, *trans*-6-diene-1,8-dioic Acid

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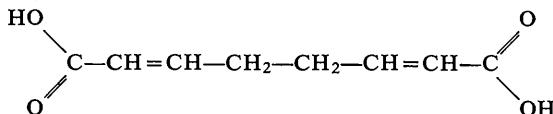
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Crystals of octa-*trans*-2, *trans*-6-diene-1,8-dioic acid are triclinic (*P* $\bar{1}$) with $a = 12.00 \pm 0.02$; $b = 3.94 \pm 0.01$; $c = 7.72 \pm 0.02$ Å; $\alpha = 121^\circ 21' \pm 30'$; $\beta = 139^\circ 24' \pm 30'$; $\gamma = 70^\circ 03' \pm 30'$. The unit cell contains one molecule. Three-dimensional X-ray diffraction data were collected by photographic methods. A trial structure was obtained by examination of the Patterson projections on the (010) and (001) planes. Refinement was carried out by least-squares methods. The molecules are associated in parallel rows in the crystal lattice. The aliphatic chain $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-$ between the two terminal carboxyl groups has the conformation: (*trans*) (*C*) (*T*) (*C*) (*trans*).

Introduction

Octa-*trans*-2, *trans*-6-diene-1,8-dioic acid:



(henceforth called octa-T,T) is dimorphous and undergoes a reversible, enantiotropic transition in the crystalline state at 166°C ($\Delta H = 15.5$ cal.g $^{-1}$; $\Delta S = 0.035$ cal.g $^{-1}$.deg $^{-1}$) (Corradini, Frasci & Martuscelli, 1969). This paper deals with the structural analysis of the low-temperature stable modification. Our interest in the X-ray study of octa-T,T is to gain new data on some conformational parameters (bond length, valence angles, torsional angles) in an unsaturated aliphatic molecule, in relation to a more general study, in progress in our laboratories, on the hindered rotation around the single bond C-C adjacent to the double bond C=C.

Experimental

Crystals of octa-T,T suitable for X-ray analysis were prepared by slow evaporation of aqueous solutions.

The values of the unit-cell parameters, summarized in Table 1, were determined from Weissenberg photographs taken with Cu $K\alpha$ radiation. The structure of octa-T,T is described in terms of an oblique non-reduced triclinic cell. The reduced cell is dimensionally near-monoclinic ($a = 6.59$, $b = 7.93$, $c = 3.94$ Å; $\alpha = 90^\circ 30'$, $\beta = 90^\circ 30'$, $\gamma = 78^\circ 30'$). Since systematic extinctions are not observed, both *P*1 and *P* $\bar{1}$ space groups are possible for octa-T,T. The space group *P* $\bar{1}$, assumed tentatively, was confirmed by the subsequent analysis of the crystal structure. Thus the molecule of octa-T,T is characterized by a symmetry centre on the central $-\text{CH}_2-\text{CH}_2-$ bond.

Table 1. Crystal data for octa-*trans*-2, *trans*-6-diene-1,8-dioic acid

$\text{C}_8\text{O}_4\text{H}_{10}$	M.W. 170.18
$F(000) = 90$	
Triclinic, space group	<i>P</i> $\bar{1}$
$a = 12.00 \pm 0.02$ Å	$\alpha = 121^\circ 21' \pm 30'$
$b = 3.94 \pm 0.01$	$\beta = 139^\circ 24' \pm 30'$
$c = 7.72 \pm 0.02$	$\gamma = 70^\circ 03' \pm 30'$
Density { X-ray	1.41 g.cm $^{-3}$
{ Experimental	1.39 g.cm $^{-3} \pm 0.01$
$Z = 1$	
$\mu = 9.75$ cm $^{-1}$ for $\lambda = 1.5418$ Å	

Intensity data have been collected with Cu $K\alpha$ radiation and the use of multiple-film equi-inclination Weissenberg photographs about the *b* axis for layer lines 0 to 2. The zero layers about the *a* axis and about the *c* axis have been recorded to provide cross correlation of the *b* axis data. Intensities were estimated visually by two observers using a calibrated intensity strip.

In all about 500 independent reflexions were used in the analysis. The intensities have been corrected for change of spot shape on upper and lower layer equi-inclination photographs (Phillips, 1954). The Lorentz and polarization factors were applied but no absorption correction was made.

Solution and refinement of the structure

Patterson projections along the two short axes were calculated to give information about the orientation of the molecules in the unit cell. The peaks lie in lines parallel to the crystallographic direction *a*.

Assuming angles and bond lengths reported in the literature for similar compounds a trial model was obtained which is in agreement with the Patterson peaks and gives reasonable molecular packing. For

this model the reliability index $R \left[R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right]$

is 0.42 for all the observed reflexions. A computation of the electron density projection on the (010) plane gives a good image of the proposed structure.

The refinement was initially carried out for the (010) and (001) projections by successive Fourier synthesis calculations. The coordinates obtained in this way were used for the final three-dimensional refinement, which was carried out by the block-diagonal-matrix least-squares method.

Table 2. Final fractional atomic coordinates and their standard deviations

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
C(1)	0.1454	0.0153	-0.0312	0.001	0.003	0.002
C(2)	0.2471	-0.0073	-0.0706	0.001	0.003	0.002
C(3)	0.4178	0.0391	0.1493	0.001	0.003	0.002
C(4)	0.5435	0.0346	0.1499	0.001	0.003	0.002
O(1)	0.2037	0.0272	0.1912	0.0008	0.002	0.001
O(2)	-0.0191	-0.0199	-0.2555	0.0009	0.003	0.001
H(2)	0.182	-0.064	-0.287			
H(3)	0.474	0.087	0.358			
H(4a)	0.627	0.318	0.321			
H(4b)	0.631	-0.198	0.214			

Table 3. Comparison between observed (F_o) and calculated (F_c) structure factors of octa-trans-2-trans-6-diene-1,8-dioic acid

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	0	0	3.9	2.2	13	0	4	0.5	0.4	0	2	1	17.0	15.0	1	4	7.0	7.5	
2	0	0	4.3	3.6	0	0	5	0.3	0.2	0	3	1	6.0	6.0	2	4	1.0	1.2	
3	0	0	8.9	8.7	1	0	5	0.9	0.8	0	1	2	4.5	4.5	3	4	1.5	1.6	
4	0	0	8.2	8.1	1	0	5	1.0	-1.0	0	1	2	11.1	-9.7	4	4	6.7	-6.1	
5	0	0	9.3	9.6	2	0	5	1.2	-1.1	0	1	3	6.2	-7.9	4	1	4	2.0	
7	0	0	1.0	2.0	3	0	5	0.9	-0.7	0	2	3	5.2	-5.5	5	1	4	0.7	
9	0	0	1.0	0.2	4	0	5	0.9	1.0	0	4	0	1.2	1.1	1	4	1.4	1.6	
0	0	1	33.3	32.1	5	0	5	3.3	3.7	0	3	1	0.6	0.7	7	1	4	3.0	
1	0	1	0.7	-0.4	6	0	5	1.7	-2.2	0	4	1	2.4	-1.0	7	1	4	0.3	
1	0	1	4.6	4.0	7	0	5	4.2	4.6	0	2	2	1.7	-1.2	8	1	4	0.7	
2	0	1	5.0	-7.7	8	0	5	4.7	-5.0	0	2	2	0.5	-0.2	10	1	4	1.0	
3	0	1	6.5	-6.5	9	0	5	3.0	3.3	0	3	2	2.1	2.1	11	1	4	0.5	
3	0	1	14.0	-14.0	10	0	5	0.8	1.0	0	4	2	1.5	1.3	1	5	1.4	1.5	
4	0	1	0.6	0.6	11	0	5	2.4	3.1	0	1	3	2.1	-1.9	2	5	0.3	-0.3	
4	0	1	15.5	-11.1	14	0	5	2.6	-2.3	0	2	3	0.6	-0.5	3	5	1.1	-1.1	
5	0	1	6.5	6.9	1	0	6	1.1	-1.1	0	3	3	1.7	-1.8	4	5	0.5	0.5	
6	0	1	3.3	-2.9	3	0	6	1.7	-1.9	0	1	4	0.7	0.1	5	2	0.7	3.1	
6	0	1	6.3	6.2	4	0	6	1.6	-2.0	0	3	4	1.0	-2.0	6	1	5	3.3	
7	0	1	4.2	4.4	5	0	6	0.9	1.0	0	4	4	1.1	-1.2	7	1	5	1.0	
8	0	1	0.4	-0.4	6	0	6	0.5	0.5	0	4	5	0.7	-0.8	8	1	5	1.7	
8	0	1	2.1	2.0	7	0	6	2.5	3.0	0	1	5	0.8	0.4	9	1	6	1.8	
9	0	1	15.5	-0.6	6	0	6	7.9	-8.2	0	2	6	0.4	0.4	10	1	6	3.2	
10	0	1	0.6	0.5	5	0	6	1.5	-1.6	0	1	0	1.0	0.7	11	1	6	0.8	
11	0	1	0.6	0.5	10	0	6	0.7	-0.7	1	1	1	3.7	4.4	12	1	6	1.0	
0	0	2	10.3	-10.6	11	0	6	1.0	2.4	1	1	1	6.9	-7.9	2	1	0	1.0	
1	0	2	2.4	-2.6	12	0	6	0.6	-0.6	2	1	1	2.7	-4.4	3	1	0	7.7	
1	0	2	2.6	-2.7	13	0	6	1.4	-1.3	3	1	1	5.4	-6.3	4	1	0	6.1	
2	0	2	3.2	-4.0	14	0	6	0.7	0.6	4	1	1	4.1	-5.4	5	1	0	4.6	
4	0	2	15.5	-14.4	4	0	7	0.8	-1.0	5	1	1	6.8	-6.8	6	1	0	0.7	
3	0	2	1.7	-1.9	6	0	7	0.9	0.8	6	1	1	2.3	-3.1	3	1	1	10.6	
3	0	2	6.3	-7.0	7	0	7	1.6	1.7	4	1	1	1.6	1.6	4	1	1	1.3	
4	0	2	1.3	-1.5	8	0	7	2.7	-3.4	1	1	1	1.8	1.7	5	1	1	7.0	
4	0	2	17.5	-17.7	9	0	7	2.5	-2.6	2	1	1	5.0	5.2	6	1	1	5.0	
5	0	2	1.1	-1.0	10	0	7	0.4	-0.3	3	1	1	3.4	3.4	7	1	1	3.7	
5	0	2	22.0	-20.5	11	0	7	0.7	0.7	4	1	1	2.5	2.6	8	1	1	1.3	
6	0	2	1.3	-1.1	14	0	7	1.0	-1.1	5	1	1	2.4	-2.4	9	1	1	4.7	
7	0	2	0.3	0.2	5	0	8	0.5	0.4	6	1	1	0.6	-0.5	2	1	1	12.0	
7	0	2	0.3	0.2	9	0	8	1.2	-1.3	7	1	1	1.8	-1.2	3	1	1	9.3	
7	0	2	0.6	0.6	10	0	8	1.2	1.3	8	1	1	0.5	0.4	4	1	1	15.4	
0	0	3	3.6	3.4	12	0	8	0.0	0.6	1	1	2	0.8	-0.4	5	1	1	15.1	
9	0	3	6.0	-6.5	13	0	8	1.4	1.5	1	1	2	4.5	-5.5	6	1	1	4.1	
10	0	3	1.4	-1.5	1	1	0	0.7	0.6	2	1	2	6.4	-6.5	7	1	1	4.2	
11	0	3	0.3	-0.3	1	1	0	4.9	5.7	3	1	2	6.4	-6.5	8	1	1	1.4	
12	0	3	0.5	0.6	2	1	0	0.6	0.9	4	1	2	4.5	-5.2	9	1	1	2.7	
0	0	4	4.5	-4.4	2	1	0	2.0	2.1	5	1	2	0.7	-0.2	10	1	1	6.3	
1	0	4	6.5	6.7	3	1	0	5.6	-7.2	6	1	2	2.4	-2.4	10	1	1	1.0	
2	0	4	0.7	0.4	3	1	0	8.2	-8.1	4	1	2	7.5	-8.6	1	1	1	0.8	
2	0	4	0.6	-0.6	4	1	0	5.2	5.3	5	1	2	1.4	-1.5	2	1	1	13.1	
3	0	4	6.5	-6.3	4	1	0	7.5	6.8	6	1	2	9.2	-11.0	3	1	1	11.4	
4	0	4	0.5	-0.3	1	1	0	4.5	4.6	7	1	2	1.4	-1.5	4	1	1	5.5	
4	0	4	2.6	-3.0	1	1	0	7.7	7.8	8	1	2	2.3	-2.4	5	1	1	23.0	
5	0	4	15.3	-15.1	6	1	0	1.1	1.0	9	1	2	13.8	-13.9	6	1	1	2.8	
6	0	4	1.6	1.5	7	1	0	1.5	1.6	10	1	2	0.5	0.4	7	1	1	2.8	
7	0	4	0.2	-0.1	7	1	0	1.7	1.8	7	1	2	0.4	0.3	8	1	1	5.0	
9	0	4	5.0	5.4	9	1	0	1.0	0.5	8	1	2	3.5	3.9	9	1	1	3.9	
9	0	4	7.5	-7.6	1	2	0	1.0	0.5	9	1	2	5.6	-5.4	10	1	1	1.6	
10	0	4	3.7	-4.0	2	2	0	2.1	1.2	10	1	2	1.3	-1.2	11	1	1	0.3	
11	0	4	1.3	-1.5	3	2	0	1.0	-1.3	1	2	3	0.3	-0.4					
12	0	4	0.3	0.2	3	2	0	4.1	-4.1	1	2	3	6.2	7.4	1	1	2	1.1	
1	0	5	0.5	-0.1	4	2	0	1.6	1.4	2	1	3	3.6	-3.3	2	1	2	4.5	
1	0	5	4.7	4.7	4	2	0	1.4	1.5	3	1	3	1.6	1.7	3	1	2	15.9	
2	0	5	0.4	0.3	5	2	0	3.0	2.0	4	1	3	3.4	3.2	4	1	2	11.0	
2	0	5	2.7	-2.9	7	2	0	0.9	0.8	5	1	3	0.4	0.3	5	1	2	2.7	
3	0	5	0.0	0.0	4	2	0	4.1	4.2	6	1	3	0.6	-0.4	6	1	2	5.0	
4	0	5	0.0	0.0	5	2	0	1.2	-1.1	7	1	3	0.0	1.4	7	1	2	5.5	
4	0	5	0.0	0.0	6	2	0	1.6	-1.7	8	1	3	1.1	1.2	8	1	2	6.7	
5	0	5	3.1	3.0	0	4	0	1.3	1.1	9	1	3	3.2	3.3	9	1	2	0.5	
7	0	5	5.0	5.3	0	1	0	50.0	50.5	7	1	3	4.0	-4.3	12	1	2	0.5	
8	0	5	3.4	3.0	0	1	1	13.2	13.0	10	1	3	4.4	-5.4	1	3	2	1.8	
9	0	5	1.0	1.1	0	1	1	34.9	34.2	11	1	3	1.0	-0.9	2	1	3	2.0	
10	0	5	0.9	-1.1	0	2	1	3.5	3.4	12	1	3	0.3	0.2	3	1	3	-0.2	

Table 3 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	
4	1	1	3.5	4.1	2.4	2.3	1.2	2.5	0.6	0.5	0.6	0.6	2.5	0.6	
4	1	1	3.3	7.5	2.0	2.0	1	2	1.1	1.1	1.1	1	2	2.0	
7	1	1	3.2	3.3	2.7	-2.0	1	2	2.3	2.3	2.3	1	2	2.0	
7	1	1	0.0	5.7	1.3	0.8	1	2	0.9	0.9	0.9	1	2	0.9	
8	1	1	4.0	-4.5	0.9	0.7	2	2	2.1	1.9	4	2	2	4.0	
9	1	1	4.8	5.2	2.1	1.9	4	2	0.1	-0.3	6	2	2	5.0	
10	1	1	4.4	2.0	1.4	-1.0	6	2	0.2	0.1	7	2	2	7.2	
11	1	1	3.2	3.4	4.3	-4.2	7	2	2.4	-3.1	8	2	2	3.1	
12	1	1	3.0	0.9	2.4	-3.1	8	2	1.3	1.7	9	2	2	1.2	
13	1	1	3.7	2.4	1.3	1.7	9	2	2.0	-2.2	10	2	2	1.9	
14	1	1	2.3	-1.7	4.3	-4.2	7	2	1.0	-1.7	5	2	2	3.1	
14	1	1	4.0	-4.1	2.4	-3.1	8	2	3.0	-3.4	10	2	2	0.4	
4	1	1	3.5	-3.4	2.3	-3.4	10	2	2.3	-3.5	10	2	2	1.4	
5	1	1	1.3	1.6	1.3	1.3	10	2	0.9	0.9	11	2	2	2.1	
5	1	1	0.0	0.6	2.3	-3.5	10	2	5.1	-5.9	1	2	2	2.4	
7	1	1	3.1	3.1	4.7	-4.1	1	2	4.7	-4.1	1	2	2	-0.6	
6	1	1	10.5	-14.4	0.0	-0.6	3	2	3.9	-4.5	4	2	2	-4.9	
5	1	1	2.1	-1.5	3.9	-4.5	4	2	1.3	1.7	5	2	2	-3.2	
11	1	1	1.2	-0.9	2.2	-2.1	6	2	2.5	2.6	7	2	2	2.5	
12	1	1	2.7	3.7	0.9	0.3	5	2	0.9	0.3	6	2	2	2.5	
11	1	1	1.0	-0.6	2.2	-2.1	6	2	1.7	1.8	11	2	2	0.7	
13	1	1	1.0	-1.0	2.5	2.6	7	2	2.7	12	2	2	1.3	-1.2	
13	1	1	1.6	1.1	0.9	0.3	5	2	0.7	-0.6	8	2	2	1.3	1.1
4	1	1	1.3	1.2	0.7	0.3	5	2	4.5	5.0	2	2	2	1.7	1.7
3	1	1	1.6	-1.1	1.7	-1.7	3	2	1.7	-2.1	3	2	2	1.7	-1.5
4	1	1	2.5	-2.1	1.2	1.1	4	2	1.2	1.1	4	2	2	2.9	-3.1
6	1	1	1.4	1.4	4.5	-5.2	5	2	1.4	1.1	6	2	2	0.5	0.4
7	1	1	3.3	3.1	1.4	1.1	6	2	5.3	5.2	7	2	2	2.0	1.9
8	1	1	7.5	-7.6	0.7	-0.6	13	2	2.3	-2.2	10	2	2	4.4	3.6
10	1	1	5.0	-4.0	0.7	-0.6	14	2	4.0	-4.4	9	2	2	13.4	-10.6
11	1	1	2.0	-0.9	1.7	1.8	11	2	2.3	-2.2	10	2	2	5.1	-5.0
11	1	1	1.4	1.0	1.2	1.1	4	2	0.8	-10.9	11	2	2	2.4	-2.6
12	1	1	0.4	-0.5	0.8	-10.9	11	2	0.8	1.1	12	2	2	1.7	2.7
13	1	1	1.4	-1.7	1.4	1.1	6	2	2.2	2.2	13	2	2	0.7	-0.8
14	1	1	1.6	-1.9	0.7	-0.6	13	2	0.9	0.7	14	2	2	1.7	-2.0
15	1	1	0.9	-1.0	1.5	1.5	15	2	1.5	1.5	15	2	2	1.0	-1.0
5	1	1	0.9	0.5	3.2	3.1	5	2	1.0	-1.7	6	2	2	0.7	0.5
5	1	1	2.1	1.6	1.0	-1.7	6	2	1.0	-1.7	6	2	2	2.3	2.3
7	1	1	1.0	0.9	1.0	-1.7	6	2	2.3	2.3	7	2	2	0.4	0.4
7	1	1	0.9	0.7	1.0	-1.7	6	2	0.8	-10.9	11	2	2	0.4	0.4
8	1	1	2.1	-1.9	0.8	1.1	12	2	1.5	1.5	15	2	2	1.0	1.1
10	1	1	1.0	1.6	0.7	-0.6	13	2	0.7	-0.6	13	2	2	1.7	2.0
12	1	1	1.0	1.7	0.9	0.7	14	2	1.0	0.5	13	2	2	0.4	0.4
13	1	1	2.5	2.3	1.5	1.5	15	2	1.5	1.5	15	2	2	2.5	-2.4
14	1	1	1.1	-1.1	3.2	3.1	5	2	0.2	-0.2	10	2	2	1.0	1.1
9	1	1	0.5	-0.4	1.0	-1.7	6	2	0.6	-0.5	11	2	2	0.0	0.0
10	1	1	2.3	-2.2	0.7	-0.6	13	2	1.5	1.5	15	2	2	1.7	2.0
11	1	1	1.2	-1.2	0.7	-0.6	13	2	1.0	0.5	13	2	2	2.1	2.1
11	1	1	0.7	0.5	1.5	-1.3	5	2	1.2	1.3	14	2	2	-1.5	-1.5
12	1	1	4.0	3.5	0.2	-0.2	10	2	4.0	-4.0	15	2	2	0.5	-0.5
13	1	1	20.0	15.7	13.0	11.8	7	4	13.0	11.8	7	4	4	1.3	1.4
14	1	1	0.0	0.6	0.2	-0.2	10	2	0.2	-0.2	10	2	2	0.4	0.4
15	1	1	1.0	0.0	1.0	0.0	13	2	1.0	0.0	13	2	2	1.0	0.0
15	1	1	1.0	0.4	1.2	1.3	14	2	1.2	1.3	14	2	2	-1.5	-1.5
15	1	1	0.3	0.4	4.0	-4.0	15	2	4.0	-4.0	15	2	2	0.5	-0.5
15	1	1	17.5	11.5	13.0	11.8	7	4	13.0	11.8	7	4	4	1.3	1.4
15	1	1	1.0	1.6	0.2	-0.2	10	2	0.2	-0.2	10	2	2	0.4	0.4
15	1	1	1.0	-1.1	0.2	-0.2	10	2	0.2	-0.2	10	2	2	0.4	0.4
15	1	1	0.5	-0.3	0.7	-0.6	13	2	0.7	-0.6	13	2	2	0.4	0.4
15	1	1	4.2	-4.1	1.2	1.1	4	2	1.2	1.1	4	2	2	1.7	1.7
15	1	1	1.5	-1.5	3.1	3.1	5	2	3.1	3.1	5	2	2	1.5	1.4
15	1	1	0.9	-0.9	1.7	1.7	3	2	1.7	1.7	3	2	2	4.2	4.2
15	1	1	5.0	-4.0	6.8	-6.8	14	2	6.8	-6.8	14	2	2	0.7	0.7
15	1	1	3.4	-4.3	3.2	3.1	5	2	3.2	3.1	5	2	2	3.9	3.9
15	1	1	1.0	-1.1	1.5	-1.3	5	2	1.5	-1.3	5	2	2	1.9	1.9
15	1	1	1.0	1.6	0.7	-0.6	13	2	0.7	-0.6	13	2	2	0.9	0.9
15	1	1	1.0	1.1	1.0	0.9	9	2	1.0	0.9	9	2	2	0.9	0.9
15	1	1	1.0	1.1	1.0	0.9	9	2	1.0	0.9	9	2	2	0.9	0.9

The function minimized was

$$R_w = \sum_{hkl} W(hkl) \left[F_o(hkl) - \frac{1}{K} F_c(hkl) \right]^2$$

with a unit value for all the weighting factors $W(hkl)$. Thermal parameters were allowed to vary isotropically at the first stage up to the conventional R index of 0.20. The refinement was then continued with anisotropic thermal parameters for the C and O atoms. In the last stage of the refinement the positions of the hydrogen atoms were calculated ($C-H=1.10 \text{ \AA}$) and introduced into the structure factor calculations with

the same isotropic temperature factor ($B=5 \text{ \AA}^2$). The carboxylic hydrogen atoms were not taken into account. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillivray & Veenendaal (1955) for carbon and oxygen atoms and of McWeeny (1951) for hydrogen atoms were used.

The refinement was considered to be complete when the coordinate shifts were less than the corresponding standard deviations. The final value of the reliability R index was 0.0982. The final atomic coordinates together with the corresponding standard deviations (Cruickshank, 1949) are reported in Table 2. In Table 3 observed and calculated structure factors are listed.

Table 4 shows the coefficients B_{ij} of the temperature factor in the form:

$$\exp \left[-\frac{1}{4}(h^2 a^2 B_{11} + k^2 b^2 B_{22} + l^2 c^2 B_{33} + 2hka^* b^* B_{12} + 2hla^* c^* B_{13} + 2klb^* c^* B_{23}) \right]$$

with the corresponding standard deviations.

A projection of the electron density distribution on the (010) plane is shown in Fig. 1.

Description of the structure

Molecules of octa-T,T acid are linked together to form chains by a double hydrogen-bonding system (broken lines in Figs. 2 and 3) between adjacent centrosymmetric related carboxylic groups in the manner already found in numerous other organic acids. The molecular rows are parallel and are oriented along the crystallographic axis a . The length of the hydrogen bond (2.624 \AA) compares favourably with those found in similar compounds.

Figs. 2 and 3 illustrate the molecular arrangement of octa-T,T molecules as seen along the b and the c axes respectively. The most significant intermolecular contacts are indicated. All the C---C intermolecular distances are larger than 3.80 \AA .

Molecular conformation

The various bond lengths, bond angles, torsional angles and their estimated standard deviations are shown in Table 5 with reference to Fig. 4.

The eight carbon atoms and the four oxygen atoms of the octa-T,T molecule are approximately in a plane. The least-squares best plane through these atoms, calculated by the method of Schomaker, Waser, Marsh &

Table 4. Final temperature parameters

Temperature factors are given in the form:

$$\exp \left[-\frac{1}{4}(h^2 a^2 B_{11} + k^2 b^2 B_{22} + l^2 c^2 B_{33} + 2hka^* b^* B_{12} + 2hla^* c^* B_{13} + 2klb^* c^* B_{23}) \right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
C(1)	5.93	7.33	6.15	1.14	4.94	3.42	0.48	0.66	0.50	0.45	0.46	0.49
C(2)	6.81	6.61	5.86	1.86	5.44	3.53	0.53	0.64	0.50	0.48	0.48	0.47
C(3)	6.17	6.69	4.94	1.32	4.63	2.97	0.48	0.64	0.44	0.46	0.43	0.47
C(4)	6.05	6.00	5.48	1.66	4.77	3.58	0.47	0.59	0.48	0.44	0.44	0.47
O(1)	5.97	11.54	6.17	2.77	5.08	6.09	0.35	0.60	0.36	0.37	0.33	0.41
O(2)	5.00	15.26	6.26	2.19	4.42	6.54	0.34	0.74	0.39	0.40	0.34	0.46

Table 5. *Intramolecular distances and angles with standard deviations*

Distances		
C(1)—O(1)	1.24 ₅ Å	0.01 Å
C(1)—O(2)	1.28 ₃	0.01
C(1)—C(2)	1.43 ₃	0.01
C(2)—C(3)	1.32 ₂	0.01
C(3)—C(4)	1.49 ₉	0.01
C(4)—C(4')	1.54 ₃	0.01
C(2)⋯C(4')	2.96 ₅	0.03
O(1)⋯C(3)	2.84 ₁	0.04
O(2)⋯O(1')	2.62 ₄	0.03
Angles		
C(2)—C(1)—O(1)	124.9°	0.8°
C(2)—C(1)—O(2)	116.4	0.8
O(1)—C(1)—O(2)	118.2	0.9
C(1)—C(2)—C(3)	121.3	1.0
C(2)—C(3)—C(4)	128.5	0.9
C(3)—C(4)—C(4')	113.6	0.9
Dihedral angles		
O(1)—C(1)—C(2) \wedge C(1)—C(2)—C(3)	-9°	
O(2)—C(1)—C(2) \wedge C(1)—C(2)—C(3)	178	
C(1)—C(2)—C(3) \wedge C(2)—C(3)—C(4)	-178	
C(2)—C(3)—C(4) \wedge C(3)—C(4)—C(4')	0	
C(3)—C(4)—C(4') \wedge C(4)—C(4')—C(3')	180	(by symmetry)

Bergman (1959), attributing a unitary weight factor to all twelve atoms, is $0.119 X + 3.504 Y - 0.564 Z = 0.060$. This equation is referred to the axes of the unit cell, X, Y, Z being fractional coordinates.

In Table 6 the distances (Å) of the atoms from the plane are compared with their atomic standard deviations (Å). The value of the rotation angle around the single bond C(3)—C(4) adjacent to the double bond C(2)—C(3) is 0° ('*c*' or '*cis*' type). The aliphatic chain $-\text{CH}=\text{CH}-\text{CH}_2-\text{---}-\text{CH}_2-\text{CH}=\text{CH}-$, between the two carboxylic groups in the octa-*T, T* molecule, presents a conformation (*trans*) (*C*) (*T*) (*C*) (*trans*). The same conformation has been found for the same grouping (in brackets in Fig. 5) in the case of the low-temperature

stable modification of deca-*trans*-3,*trans*-7-diene-1,10-dioic acid (Martuscelli, 1967).

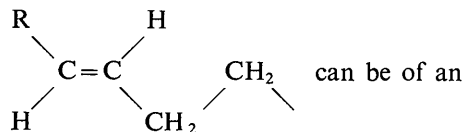
Table 6. *Distances (Å) of C and O atoms of the octa-T, T molecule from the least-square mean plane of equation:*

$$0.119 X + 3.504 Y - 0.564 Z = 0.060$$

and their atomic standard deviations (Å)

Distances	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	
(Å $\times 10^{-2}$)	(Å $\times 10^{-2}$)	(Å $\times 10^{-2}$)	(Å $\times 10^{-2}$)	
C(1)	2.8	1.5	1.4	1.7
C(2)	-1.6	1.5	1.3	1.6
C(3)	4.2	1.4	1.3	1.5
C(4)	4.2	1.4	1.2	1.5
C(4')	-4.2	1.4	1.2	1.5
C(3')	-4.2	1.4	1.3	1.5
C(2')	1.6	1.5	1.3	1.6
C(1')	-2.8	1.5	1.4	1.7
O(1)	-4.8	1.0	1.0	1.2
O(2)	1.2	1.1	1.2	1.3
O(1')	4.8	1.0	1.0	1.2
O(2')	-1.2	1.1	1.2	1.2

These results lead us to the conclusion that the dihedral angle around the single bond (CH₂—CH—) in a grouping such as



either skew \pm or *cis* type. The corresponding conformations are practically isoenergetic not only in the vapour and liquid phases as already found (Kilb, Lin & Wilson, 1957; Herschback & Krisner, 1958; Abraham & Pople, 1960; Bothner-By, Naar-Colin & Gunther, 1962) but also in the solid state. Therefore the possibility of finding a skew \pm or *cis* conformation for the above mentioned grouping, in the crystal state, is

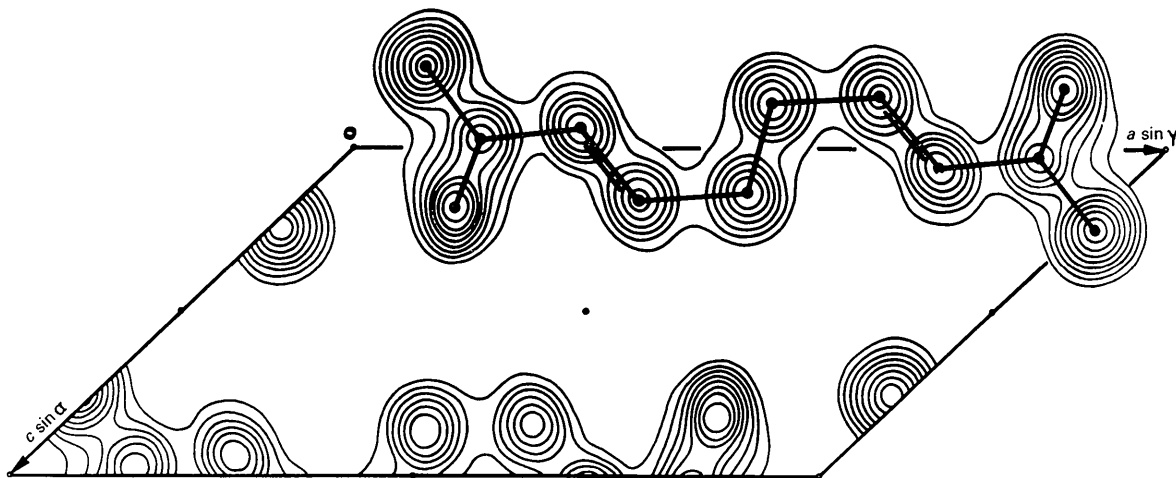


Fig. 1. Projection of the electron density distribution on the (010) plane. Levels are drawn at intervals of $1 \text{ e.}\text{\AA}^{-2}$ starting with $1 \text{ e.}\text{\AA}^{-2}$.

dependent only upon the conditions imposed by the packing forces.

In Table 7 are reported the values of the rotation angles about single bonds adjacent to double bonds in a series of low molecular weight and macromolecular compounds. These values have been determined by X-ray diffraction. Both in octa-T,T and in deca-*trans*-3,*trans*-7-diene-1,10-dioic acid the valence angles adjacent to the double bonds, $C(2)-C(3)-C(4)=128.5^\circ$

and $C(3)-C(4)-C(5)=132.1^\circ$ respectively (see Figs. 4 and 5), are substantially larger than the expected *normal* values.

Even accounting for the possible influence of the packing forces it appears that the main reason for such large deviations is the need for keeping carbon atoms $C(2)$ and $C(4')$ and $C(3)$ and $C(5')$ respectively, as far apart as possible. The equilibrium distances $C(2)\cdots C(4')$ and $C(3)\cdots C(5')$ are, in fact, still somewhat short

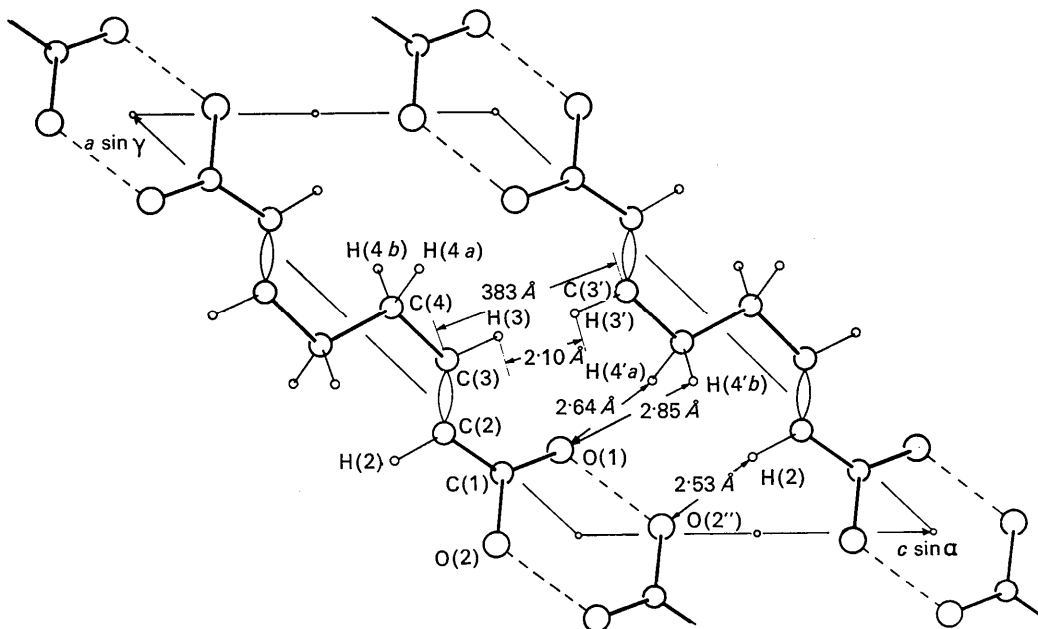


Fig. 2. Projection of the structure along [010].

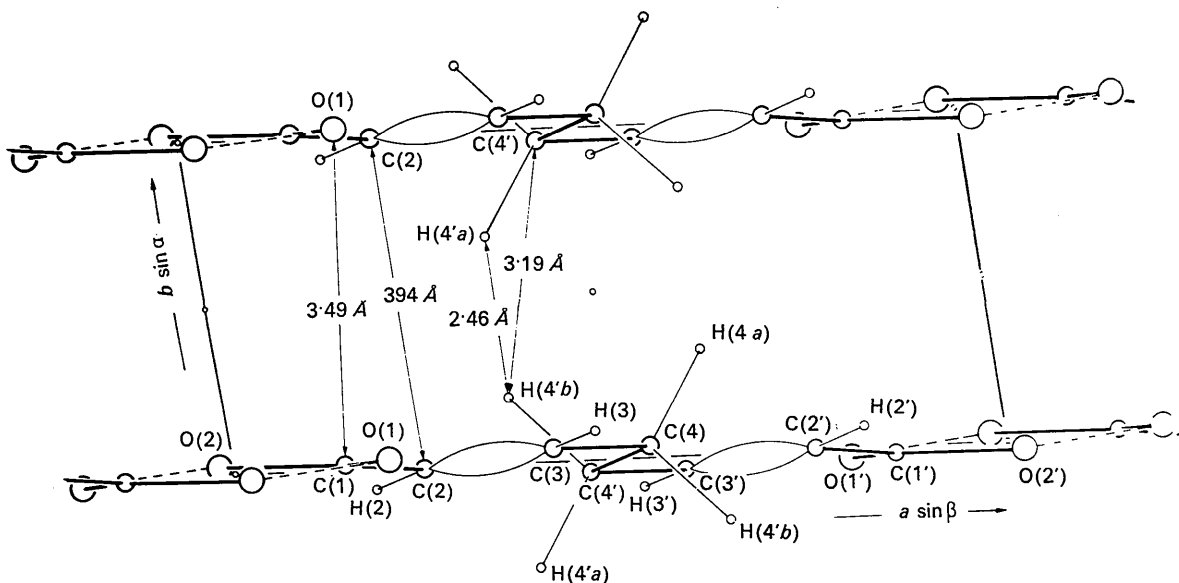
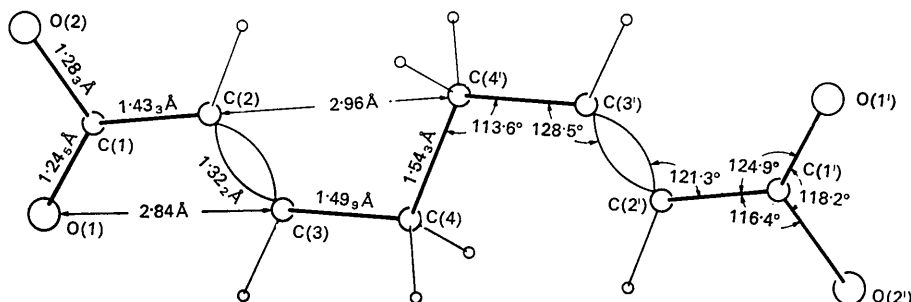


Fig. 3. Projection of the structure along [001].

Table 7. Values of rotation angles about single bonds C-C adjacent to double bond C=C in a series of low-molecular-weight and macromolecular compounds

The rotation angles are measured following Natta, Corradini & Bassi (1961).

Name of compound	Chemical formula	Rotation angles	References
Geranylamine hydrochloride	$\text{CH}_3-\overset{\text{trans}}{\text{C}}=\overset{\sigma_3}{\text{CH}}-\text{CH}_2-\overset{\sigma_2}{\text{CH}_2}-\overset{\text{trans}}{\text{C}}=\overset{\sigma_1}{\text{CH}}-\text{CH}_2\text{NH}_2\text{Cl}$	$\sigma_1 = -117^\circ$ $\sigma_2 = 99^\circ$ $\sigma_3 = 132^\circ$	Jeffrey (1944)
Oleic acid	$\text{HO}-\text{C}(\text{O})-\text{(CH}_2)_6-\overset{\sigma_1}{\text{CH}_2}-\overset{\text{cis}}{\text{CH}}=\overset{\sigma_2}{\text{CH}}-\text{CH}_2-\text{(CH}_2)_6-\text{CH}_3$	$\sigma_1 = 132^\circ$ $\sigma_2 = -127^\circ$	Abrahamsson, Ryderstedt & Nahrngbauer (1962)
Poly- <i>t</i> -butylbutadiene	$\text{---CH}_2-\overset{\sigma_1}{\text{C}}=\overset{\text{cis}}{\text{CH}}-\overset{\sigma_2}{\text{CH}_2}-\text{CH}_2-\text{---C}=\overset{\text{cis}}{\text{CH}}-\text{CH}_2-\text{---}$	$\sigma_1 = 90^\circ$ $\sigma_2 = -90^\circ$	Cesari (1964)
Hexa- <i>trans</i> -3-ene-1,6-dioic acid	$\text{HO}-\text{C}(\text{O})-\text{CH}_2-\overset{\text{trans}}{\text{CH}}=\text{CH}-\text{CH}_2-\text{C}(\text{O})\text{OH}$	$\sigma = 130^\circ$	Ganis & Martuscelli (1966)
<i>trans</i> -Polyalkenes	$\text{---CH}_2\left[\overset{\sigma_1}{\text{---CH}}=\overset{\sigma_2}{\text{---CH}}-\text{(CH}_2)_n\right]_p\text{---CH}=\text{CH}-\text{(CH}_2)_n\text{---}$	$\sigma_1 = 130^\circ$ $\sigma_2 = -130^\circ$	Natta & Bassi (1967)
Deca- <i>trans</i> -3, <i>trans</i> -7-diene-1,10-dioic acid (Form I)	$\text{HO}-\text{C}(\text{O})-\text{CH}_2-\overset{\sigma_1}{\text{CH}}=\overset{\sigma_2}{\text{CH}}-\text{CH}_2-\text{CH}_2-\overset{\text{trans}}{\text{CH}}=\overset{\text{trans}}{\text{CH}}-\text{CH}_2-\text{C}(\text{O})\text{OH}$	$\sigma_1 = -126^\circ$ $\sigma_2 = -2^\circ$	Martuscelli (1967)
Octa- <i>trans</i> -2, <i>cis</i> -6-diene-1,8-dioic acid	$\text{HO}-\text{C}(\text{O})-\text{CH}=\overset{\sigma_1}{\text{CH}}-\text{CH}_2-\overset{\sigma_2}{\text{CH}_2}-\overset{\text{cis}}{\text{CH}}=\text{CH}-\text{C}(\text{O})\text{OH}$	$\sigma_1 = 127^\circ$ $\sigma_2 = -97^\circ$	Martuscelli & Mazzarella (1969)
Deca- <i>trans</i> -3, <i>trans</i> -7-diene-1,10-dioic acid (Form II)	$\text{HO}-\text{C}(\text{O})-\text{CH}_2-\overset{\sigma_1}{\text{CH}}=\overset{\sigma_2}{\text{CH}}-\text{CH}_2-\text{CH}_2-\overset{\text{trans}}{\text{CH}}=\overset{\text{trans}}{\text{CH}}-\text{CH}_2-\text{C}(\text{O})\text{OH}$	$\sigma_1 = 135^\circ$ $\sigma_2 = -123^\circ$	Martuscelli & Frasci (1969)
Octa- <i>trans</i> -2, <i>trans</i> -6-diene-1,8-dioic acid	$\text{HO}-\text{C}(\text{O})-\text{CH}=\overset{\text{trans}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\overset{\text{trans}}{\text{CH}}=\text{CH}-\text{C}(\text{O})\text{OH}$	$\sigma = 0^\circ$	Present work

Fig. 4. Molecular model of octa-*trans*-2-*trans*-6-diene-1,8-dioic acid.

