The Crystal and Molecular Structures
of Three Related Planar Compounds Containing Heterocyclic Rings:
trans and *cis* Octa-2,4,6-triene-1:4,5:8-diolide
and *trans*-2,7-Dimethyl-octa-2,4,6-triene-1:4,5:8-diolide

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The crystal and molecular structures of *cis*- and *trans*-octa-2,4,6-triene-1:4,5:8-diolide, and of the *trans*-2,7-dimethyl derivative are reported and compared. All the monoclinic crystal structures have been determined by the use of the *hk*0, *hk*1 and *h0l* reflexions; owing to the particular orientation of the molecules, which are planar within the limits of accuracy, the molecular geometry is fairly well determined in the three cases. On account of the stereochemical similarity of the three compounds it has been possible to assign a standard error of the average molecular parameters (about ± 0.01 Å and $\pm 0.4°$ in bond lengths and angles respectively) which is smaller than that of the corresponding parameters obtained from the individual compounds.

Introduction

From the reaction between carbon monoxide and acetylenic hydrocarbons, carried out in the presence of $Co_2(CO)_8$ as a catalyst, the following unsaturated γ-dilactones have been obtained in the last few years (Albanesi & Tovaglieri, 1959; Albanesi, 1964; Sauer, Cramer, Hengelhardt, Ford, Holmquist, Howk, Marsh & Abrahamson, 1959):

$$2(-C{\equiv}C-)+4CO$$
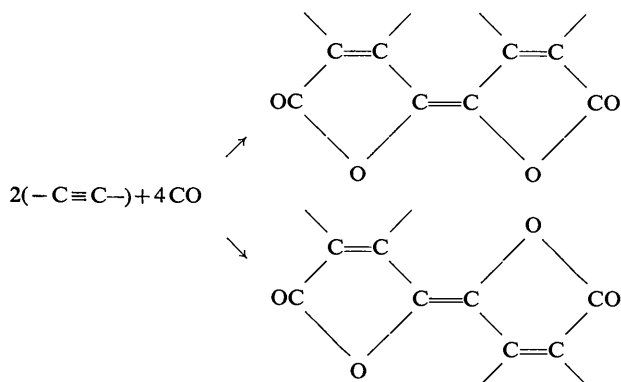
every compound of the above type being obtainable in either the *cis* or the *trans* stereoisomer or both.

As a result of the X-ray investigation carried out in our Institute on some of the above compounds (Allegra, 1960; Colombo & Allegra, 1964), we have recognized the *trans* (I) and *cis* (II) γ-dilactones obtained from the condensation of acetylene and carbon monoxide (the octa-2,4,6-triene-1:4,5:8-diolides). Moreover, it has been shown by X-ray investigation that the highest melting stereoisomer obtained from methylacetylene and carbon monoxide corresponds to *trans*-2,7-dimethyl-octa-2,4,6-triene-1:4,5:8-diolide(III):
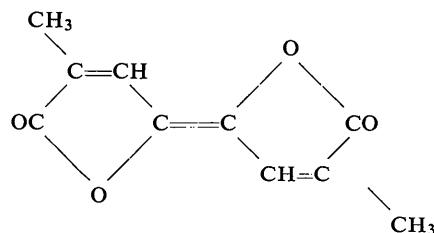
As could be predicted on stereochemical grounds, the X-ray analysis shows a practically planar molecular structure for all the molecules investigated. Owing to the interest inherent in the knowledge of the molecular dimensions of π-systems of the above type, we subjected to a parallel X-ray refinement both *cis* and *trans* octa-2,4,6-triene-1:4,5:8 diolide, as well as the *trans*-2,7-dimethyl derivative. Owing to the planar molecular conformation of the three compounds, and also to the particular disposition of the molecules inside the unit cells for each compound, we limited our refinement to three properly selected reciprocal layers. In particular, two layers, containing the *hk*0 and *hk*1 reflexions, were chosen in order to derive, as accurately as possible, the atomic coordinates within the average molecular plane, while the third layer, containing the *h0l* reflexions, allowed us to define the orientation of the molecular plane.

In spite of the limited accuracy in the determination of the molecular parameters for each compound considered separately, we think that the average value of the bond lengths and angles, which correspond to the common features of the three compounds, may be considered to be more reliable. In fact it seems a reasonable assumption, and indeed it is in agreement with our results, that the molecular conformation of every lactonic group cannot be appreciably distorted by modi-

fying the relative orientation of the adjacent group, or by substituting a hydrogen atom with a methyl group.

In the following, we shall make a parallel examination of the details of the X-ray investigation on the three compounds, their resulting molecular structures and the main features of the molecular packing of the crystalline state.

Experimental

Colourless, plate-shaped crystals of (I), (II) and (III) were obtained by recrystallization of mixtures of re-action products in suitable solvents. (I) and (II) were separated by fractional crystallization from acetic acid or acetone, profiting by the lower solubility of the *cis* isomer. (III) was separated from a mixture with the 2,6-dimethyl derivatives, with *cis* and *trans* configuration, by repeated crystallizations in benzene, (III) being characterized by an intermediate solubility with respect to the other two compounds.

Determination of the structure

By usual Weissenberg techniques, the X-ray analysis of single crystals of (I), (II) and (III) led us to the following assignment of space groups, unit-cell dimensions, number of molecules per unit cell, and calculated densities:

(I) $a = 8 \cdot 42 \pm 0 \cdot 03$, $b = 6 \cdot 01 \pm 0 \cdot 02$, $c = 6 \cdot 92 \pm 0 \cdot 03$ Å;
$\beta = 95 \cdot 9 \pm 0 \cdot 5°$. Space group $P2_1/c$; $Z = 2$; $D_{calc} = 1 \cdot 56$ g.cm^{-3}; ($D_{exp} = 1 \cdot 54$ g.cm^{-3}); $V = 349 \pm 3$ Å^3.

(II) $a = 19 \cdot 44 \pm 0 \cdot 08$, $b = 5 \cdot 70 \pm 0 \cdot 02$, $c = 7 \cdot 28 \pm 0 \cdot 03$ Å;
$\beta = 121 \cdot 7 \pm 0 \cdot 5°$. Space group Cc or $C2/c$; $Z = 4$; $D_{calc} = 1 \cdot 59$ g.cm^{-3}; ($D_{exp} = 1 \cdot 57$ g.cm^{-3}); $V = 686 \pm 6$ Å^3.

(III) $a = 10 \cdot 48 \pm 0 \cdot 04$, $b = 6 \cdot 24 \pm 0 \cdot 02$, $c = 6 \cdot 83 \pm 0 \cdot 03$ Å;
$\beta = 90 \cdot 0 \pm 0 \cdot 5°$. Space group $P2_1/c$; $Z = 2$; $D_{calc} = 1 \cdot 43$ g.cm^{-3}; ($D_{exp} = 1 \cdot 43$ g.cm^{-3}); $V = 447 \pm 4$ Å^3.

The space group assignment to (I) and (III), based upon the systematic extinction of the *h*0*l*, *l* odd and the 0*k*0, *k* odd reflexions, was unambiguous; the ambiguity arising for (II), where the *hkl*, *h* + *k* odd and *h*0*l*, *l* odd reflexions are absent, was subsequently solved on structural grounds.

The presence of only two molecules in the unit cell of (I) and (III) could be explained only by assuming that every molecule occupies a crystallographic centre of symmetry, and therefore is in itself centrosymmetrical: the conclusion is that, in both cases, the configuration of the lactone rings is of the *trans* type and that, in the dimethyl derivative (III), the two methyl groups must be attached at either 2,7 or 3,6: these are in fact the two only possibilities that preserve the molecular centrosymmetry. In the case of (II), if the space group is $C2/c$ then the molecule may contain a crystallographic symmetry element, namely a twofold axis, and a *cis* molecular configuration could easily satisfy this crystallographic demand: therefore, we assumed as a starting hypothesis that $C2/c$ was the most probable space group.

The orientation of the average molecular plane was readily derived from inspection of the intensity distributions. In particular, in (I) and (II) the $\frac{1}{2}l, 0, l$ and 00*l* reflexions respectively are outstandingly intense, while in (III) the intensity distribution of the *h*0*l* reflexions is characterized by outstanding values for *h*/*l* ratios ranging between $\frac{1}{2}$ and $\frac{3}{4}$. Consequently we argued that the average molecular plane is, to a good approximation, parallel to the (102) plane in (I), and to the (001) plane in (II); in (III), it should be taken as roughly parallel to the ($\bar{2}$03).

From the above, we concluded that, in all cases, the *c* axis, which is inclined at an angle of no less than about 60° to the molecular plane, should provide a suitable direction for obtaining electron density projections, if any atomic superposition could be eliminated. Since two molecules, with different orientations, are contained in every unit cell, and the difference in the average *z* fractional coordinates is $\frac{1}{2}$ in every case, we used the technique of modulated projections in order to obtain electron density maps free from inter-molecular superpositions. In fact, both the planarity of the molecules and the approximate parallelism among them are favourable features for obtaining good modulated projections. The technique described below represents a useful way of applying modulated projections to crystals containing planar molecules which are parallel to one another.

Let us suppose that two molecules lie on parallel planes defined by the following equations, in terms of fractional coordinates:

$$z_1 = ax + by + c; \quad z_2 = ax + by + c + \frac{1}{2n} \quad (n \text{ integral}) . \quad (1)$$

From the expression

$$\varrho_n(x,y) = \frac{c}{2} \int_0^1 \varrho(x,y,z) \, [1 + \cos 2\pi n(z - z_1)] dz \quad (2)$$

it can be easily seen that $\varrho_n(x,y)$ represents only the electron density projection of the molecule lying on z_1, because the coefficient $[1 + \cos 2\pi n(z - z_1)]$ causes the density contribution of the other molecule to vanish, since $z_2 - z_1 = 1/2n$. By expressing $\varrho(x,y,z)$ in the most general way:

$$\varrho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + lz)] \quad (3)$$

and bearing (3) and (1) in mind, we obtain from (2) the following result:

$$\varrho_n(x,y) = \frac{1}{2A} \sum_h \sum_k (F(hk0) \exp[-2\pi i(hx + ky)]$$
$$+ \tfrac{1}{2} F(hkn) \exp[-2\pi i\{(h + a)x + (k + b)y + c\}]$$
$$+ \tfrac{1}{2} F(hk\bar{n}) \exp[-2\pi i\{(h - a)x + (k - b)y - c\}]), \quad (4)$$

where A is the area of the unit cell projected along **c**. If the structure under consideration is centrosymmetrical so that $F(hkl) = F(\bar{h}\bar{k}\bar{l})$, and the exponentials in (3) and (4) are replaced by cosine terms, then (4) easily reduces to:

$$\varrho_n(x,y)= \frac{1}{2A} \sum_h \sum_k (F(hk0) \cos 2\pi[hx+ky]+F(hkn)$$

$$\cos 2\pi[(h+a)x+(k+b)y+c]) . \quad (5)$$

We have applied (5) to the three compounds under investigation. For the sake of simplicity in performing the calculations, we rounded off the values of the a

and b parameters that define the molecular plane orientation [see (1)] to the nearest rational numbers, *i.e.*

for (I) $\quad a=-\frac{1}{2} \quad b=0 \quad c=0$ ⎫
for (II) $\quad a=0 \quad\quad b=0 \quad c=\frac{1}{4}$ ⎬ $n=1$
for (III) $a=\frac{1}{2} \quad\quad b=0 \quad c=0$ ⎭

A trial model of the molecular structure of *cis*- and *trans*-octatrienediolides was sketched as a starting point

Table 1. *Fractional coordinates, corresponding standard deviations and isotropic thermal factors for the three compounds*

trans-Octatrienediolide (I)

	x/a	y/b	z/c	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	B (Å²)
C(1)	0·2773	0·2018	−0·1328	0·0078	0·0086	0·0320	3·38
C(2)	0·3037	−0·0384	−0·1455	0·0086	0·0116	0·0394	3·68
C(3)	0·1820	−0·1465	−0·0872	0·0086	0·0098	0·0358	3·46
C(4)	0·0692	0·0112	−0·0331	0·0063	0·0093	0·0304	3·14
O(1)	0·3513	0·3659	−0·1683	0·0064	0·0069	0·0259	4·15
O(2)	0·1293	0·2241	−0·0619	0·0052	0·0060	0·0214	2·90
H(1)	0·4087	−0·1133	−0·1958		not evaluated		4·50
H(2)	0·1686	−0·3258	−0·0808		not evaluated		4·50

cis-Octatrienediolide (II)

	x/a	y/b	z/c	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	B (Å²)
C(1)	0·1421	−0·0547	0·2577	0·0093	0·0129	0·0433	3·48
C(2)	0·1477	−0·3093	0·2580	0·0070	0·0116	0·0363	3·86
C(3)	0·0838	−0·3987	0·2545	0·0075	0·0090	0·0322	3·26
C(4)	0·0340	−0·2061	0·2518	0·0071	0·0094	0·0305	3·00
O(1)	0·1843	0·1012	0·2600	0·0069	0·0070	0·0264	4·13
O(2)	0·0712	0·0030	0·2539	0·0047	0·0061	0·0211	2·99
H(1)	0·1941	−0·4215	0·2605		not evaluated		4·50
H(2)	0·0738	−0·5790	0·2540		not evaluated		4·50

trans-2,7-Dimethyloctatrienediolide (III)

|	x/a	y/b	z/c	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	B (Å²)
C(1)	0·2242	0·1984	0·1590	0·0120	0·0120	0·0420	3·61
C(2)	0·2530	−0·0281	0·1794	0·0111	0·0126	0·0415	4·15
C(3)	0·1523	−0·1369	0·1080	0·0105	0·0101	0·0360	3·50
C(4)	0·0556	0·0145	0·0394	0·0114	0·0132	0·0430	4·10
C(5)	0·3788	−0·0995	0·2686	0·0127	0·0108	0·0221	3·48
O(1)	0·2843	0·3611	0·2016	0·0076	0·0075	0·0264	4·12
O(2)	0·1023	0·2189	0·0725	0·0097	0·0086	0·0320	3·36
H(1)	0·3842	−0·2729	0·2724		not evaluated		4·50
H(2)	0·3852	−0·0377	0·4154		not evaluated		4·50
H(3)	0·4558	−0·0377	0·1810		not evaluated		4·50
H(4)	0·1425	−0·3093	0·1010		not evaluated		4·50
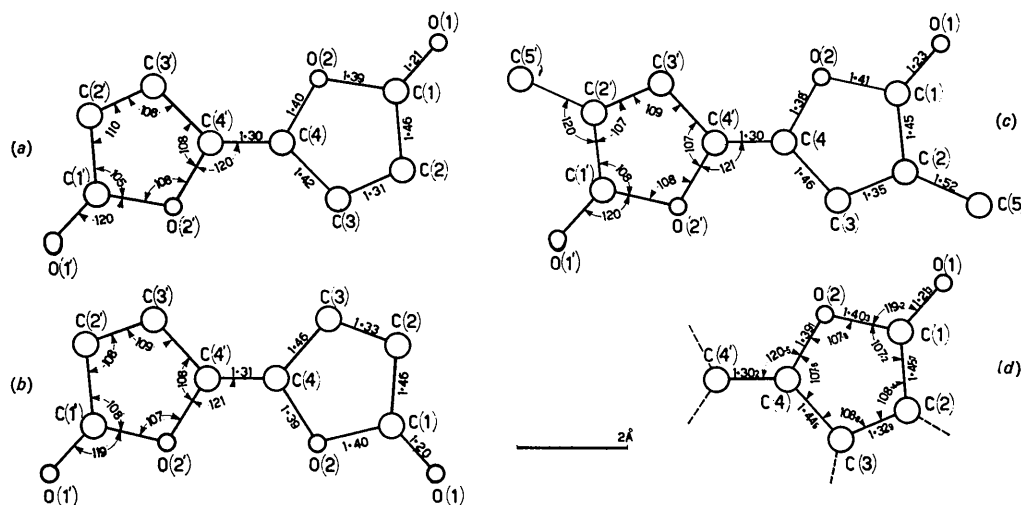
Fig. 1. Resulting molecular parameters for (I), (II) and (III) (see text) shown in (*a*), (*b*) and (*c*) respectively. In (*d*) the average parameters for the lactonic ring are also reported.

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Table 2. *Comparison between observed and calculated structure factors for the three compounds*

From left to right, in every column: h, $10F_o$ and $10F_c$ are reported. Starred reflexions are probably affected by extinction.

trans-Octatrienediolide (I)

h00		
0	—	1680
1	145	196
*2	236	-383
3	97	90
4	222	-233
5	158	-150
6	72	67
7	28	22
8	25	-23
9	32	-31
10	<4	-3

h10		
*1	176	-328
2	59	39
3	114	-114
4	148	-150
5	89	90
6	108	98
7	94	77
8	<6	-4
9	72	-63
10	14	-16

h20		
0	107	-137
1	50	-52
2	114	112
3	163	170
4	101	88
5	19	-1
6	37	-32
7	93	-83
8	101	-89

9	<5	-13
10	16	9

h30		
1	137	147
2	122	140
3	24	-23
4	22	-14
5	16	-19
6	103	-109
7	24	-11
8	52	46
9	<4	-2

h40		
0	56	47
1	110	120
2	46	40
3	30	-30
4	<6	6
5	97	-107
6	63	-68
7	44	43
8	<5	3
9	7	-7

h50		
1	14	-7
2	117	-144
3	28	-29
4	56	68
5	<6	-1
6	<5	1
7	5	7
8	12	-10

h60		
0	40	47
1	9	9
2	<6	-5
3	17	19
4	<5	11
5	9	4
6	<3	-5

h70		
1	19	18
2	<4	-8
3	<4	-2
4	<3	-1

h02		
0	150	193
*1	430	998
-1	247	-338
2	85	65
-2	108	91
3	172	-182
-3	211	-242
4	48	46
-4	195	-185
5	126	-139
-5	90	79
6	94	-96
-6	31	28
7	35	38
-7	28	-22
8	19	13
-8	30	-37
9	20	-21
-9	<9	-9
10	30	-23
-10	20	17

h04		
0	184	-163
1	116	118
-1	66	45
*2	315	432
-2	132	-143
3	43	23
-3	168	-153
4	83	-88
-4	65	59
5	14	23
-5	26	30
6	58	-65
-6	37	-20
7	48	-52
-7	21	-36
8	12	16
-8	<9	-12
9	14	7
-9	27	19
-10	14	-14

h06		
0	27	16
1	96	-82
-1	54	-61
2	81	77
-2	117	-100
3	187	204
-3	24	26
4	28	10
-4	16	25
5	40	-40
-5	42	-20
6	<7	10
-6	16	-32
7	24	-25

-7	<8	-10
-8	24	17

h08		
0	13	-18
1	<7	3
-1	59	-52
2	43	-35
-2	<8	6
3	40	40
-3	<7	16
-4	33	-15
-5	17	-24

h11		
*0	217	355
*1	218	316
-1	77	93
2	66	73
-2	101	-117
3	95	-90
-3	47	34
4	43	30
-4	5	5
5	22	-6
-5	131	-121
6	97	-86
-6	27	26
7	24	21
-7	17	-16
8	22	-21
-8	102	-96
9	65	-66
-9	14	2
10	9	3
-10	28	18

h21		
0	170	-202
1	171	198
-1	10	27
2	32	-40
-2	133	154
3	107	-112
-3	81	-84
4	57	58
-4	118	109
5	99	-89
-5	28	24
6	10	-12
-6	137	-135
7	98	98
-7	<6	-5
8	<6	3
-8	40	36
9	20	-24
-9	<5	7
10	4	-6
-10	15	13

h31		
0	15	4
1	<4	-2
-1	57	-59
2	40	-45
-2	171	193
3	169	172
-3	94	96
4	71	69
-4	98	-85
5	73	-66
-5	13	1
6	<6	-3

h51		
0	110	125
1	88	117
-1	7	-20
-2	8	4
3	<6	6
-3	16	16

-6	57	-54
7	52	-46
-7	87	-81
8	59	-56
-8	8	2
9	<4	2
-9	<4	3

h41		
0	63	-62
1	65	65
-1	66	-62
2	61	53
-2	42	43
3	50	-42
-3	<5	-6
4	<6	12
-4	59	-57
5	56	47
-5	64	64
6	55	-55
-6	81	82
7	58	-59
-7	23	-21
8	20	17
-8	21	-24
9	<2	15
-9	<3	-3

4	14	13
-4	69	-55
5	57	-54
-5	48	-52
6	39	-41
-6	11	2
7	6	2
-7	5	12
8	<2	8
-8	<3	-9

h61		
0	49	51
1	53	-53
-1	65	62
2	58	-57
-2	27	26
3	26	-23
-3	16	18
4	14	-14
-4	16	-21
5	15	17
-5	9	-10
6	7	6
-6	<3	-2

h71		
0	6	-8
1	<4	-6
-1	33	36
2	34	33
-2	<4	-2
3	<3	-3
-3	4	-9
4	<2	-7
-4	32	26

Table 2 (*cont.*)

trans-2,7-Dimethyloctatrienediolide (III)

h00		
0	—	2000
*1	220	327
*2	321	-447
3	<5	12
4	69	-61
5	160	-154
6	244	-230
7	<7	2
8	90	99
9	58	-62
10	-24	-10
11	<10	10
12	22	-23
13	26	23

h10		
1	213	-283
2	190	-219
3	136	146
4	206	-226
5	202	-213
6	106	112
7	87	91
8	95	102
9	75	77
10	36	-33
11	42	-50
12	26	-32
13	<4	-2

h20		
0	70	-59
1	104	-117
2	76	80
3	173	186
4	148	137
5	80	91
6	20	7
7	15	-7
8	26	-23
9	101	-101
10	76	-80
11	<7	-12
12	<6	4
13	<3	-2

h30		
1	202	202
2	111	103
3	126	128
4	56	-60
5	54	-52
6	29	34
7	91	-111
8	59	-58
9	23	32
10	<7	4
11	18	12
12	<4	-2

h40		
0	31	0
1	147	128
2	109	101
3	28	-26
4	30	37
5	30	-30
6	102	-96
7	83	-88
8	<8	-13
9	53	62
10	<6	-3
11	14	-11

h50		
1	30	29
2	133	-111
3	131	-122
4	31	24
5	62	61
6	21	-13
7	16	-16
8	20	16
9	<6	0
10	13	-11

h60		
0	50	37
1	33	32
2	31	-32

3	<8	-6
4	57	57
5	15	-11
6	<7	-5
7	18	13
8	27	-18
9	<2	-12

h70		
1	<7	-12
2	<7	6
3	34	-26
4	<6	8
5	18	12
6	38	-32

h80		
0	<3	24
1	<3	7

h02		
0	179	-219
1	215	-202
-1	912	1075
2	19	16
-2	636	801
3	109	-94
-3	231	-239
4	236	-233
-4	95	-101
5	220	-193
-5	15	22
6	121	123
-6	73	-80
7	48	24
-7	136	-123
8	97	-76
-8	79	-80
9	30	28
-9	71	68
10	<11	-18
-10	<11	0
11	<10	-8
-11	46	-36
12	47	31

-12	<8	13
13	17	-17
-13	13	-15

h04		
0	74	-20
1	<9	-6
-1	189	-183
2	109	-106
-2	276	240
3	195	-172
*-3	378	500
4	87	-46
-4	29	32
5	119	111
-5	97	-102
6	49	-47
-6	<11	7
7	63	-30
-7	<11	-22
8	34	22
-8	49	-42
9	32	-32
-9	67	-65
10	35	22
-10	<9	8
11	28	13
-11	26	27

h06		
0	<11	-25
1	67	-60
-1	<11	5
2	101	-91
-2	82	-62
3	<11	31
-3	38	-6
4	53	42
-4	193	223
5	60	-54
-5	83	108
6	<10	9
-6	36	-51
7	<10	-5
-7	<10	-10
8	<9	-14

-8	<8	-6
9	34	28
-9	<7	-12

h08		
0	33	-36
1	37	-29
-1	<8	-14
2	15	34
-2	<8	-6
3	<7	-4
-3	<7	-10
4	28	-20
-4	12	-28
5	<5	10
-5	47	59

h11		
0	372	357
1	116	30
-1	519	548
2	43	35
-2	75	81
3	169	-175
-3	60	45
4	103	119
-4	97	-92
5	22	-17
-5	13	-21
6	154	-164
-6	60	75
7	35	41
-7	122	-108
8	<6	8
-8	34	-36
9	76	-88
-9	41	46
10	37	-41
-10	60	-54
11	<6	-3
-11	47	-44
12	28	28
-12	9	-12
13	<3	-4
-13	17	13

h21		
0	354	352
1	72	-94
-1	205	-192
2	180	-185
-2	146	-153
3	53	45
-3	204	219
4	54	-59
-4	11	8
5	74	-90
-5	16	1
-6	73	75
7	110	136
-7	55	54
8	99	114
-8	43	-38
9	61	-79
-9	121	-127
10	21	-26
-10	<6	11
11	10	8
-11	42	50
12	27	-26
-12	<4	-9

h31		
0	11	-18
1	77	-87
-1	50	30
2	121	142
-2	73	-78
3	236	254
-3	52	13
4	42	-10
-4	228	222
5	105	-109
-5	89	95
6	35	39
-6	91	-96
7	16	-15
-7	20	-10
8	78	-91
-8	19	21

9	41	-47
-9	61	-55
10	10	9
-10	50	-54
11	<5	4
-11	9	-7
12	29	-27
-12	12	10

h41		
0	99	116
1	63	52
-1	56	-61
2	24	16
-2	88	-93
3	27	-18
-3	25	-14
4	<6	-5
-4	17	-1
5	51	61
-5	27	22
6	59	-68
-6	46	-40
7	84	-105
-7	19	-1
8	16	-4
-8	86	93
9	19	19
-9	28	33
10	14	20
-10	18	-13
11	13	9
-11	11	-14

-5	57	47
6	43	-36
-6	79	-82
7	21	-25
-7	60	-49
8	17	29
-8	22	-23
9	8	22
-9	<5	2
10	13	-15
-10	18	30

h61		
0	91	-89
1	81	-69
-1	49	44
2	44	-39
-2	94	89
3	32	-31
-3	48	38
4	11	11
-4	39	36
5	10	11
-5	<6	2
6	12	16
-6	14	-11
7	<5	6
-7	10	-9
8	<4	3
-8	10	-11

h71		
0	<5	-7
1	36	29
-1	25	-28
2	<5	-5
-2	27	22
3	15	-10
-3	19	12
4	13	17
-4	14	-13
5	32	31
-5	<4	4
6	16	17
-6	28	24

Table 2 (cont.)

cis-Octatrienediolide (II)

h00

0	—	3360
*2	254	357
*4	448	-692
6	100	75
8	499	-531
10	204	-162
12	139	142
14	137	138
16	<15	-18
18	174	-194
20	37	-40

h10

*1	382	597
3	297	-321
5	199	171
7	116	-124
9	264	-266
11	<13	-3
13	<15	-12
15	123	119
17	39	49
19	57	-56
21	<5	-7

h20

0	339	453
2	25	33
4	233	-242
6	319	-300
8	271	-263
10	73	54
12	148	160
14	178	172
16	138	126

18	27	-13
20	40	-34

h30

1	254	271
3	175	-128
5	285	-307
7	90	-70
9	81	-97
11	17	-22
13	215	244
15	142	137
17	33	-27
19	<7	-5

h40

0	58	35
2	185	193
4	42	23
6	108	-110
8	17	11
10	118	-128
12	28	-37
14	72	68
16	<10	2

h50

1	191	170
3	206	241
5	150	-156
7	185	-189
9	21	-14
11	<13	8
13	33	36
15	<7	-13

h60

0	17	-4
2	55	-55
4	<13	11
6	37	-39
8	<11	-7
10	47	-44
12	<6	-3

h70

1	<9	1
3	<9	-5
5	60	-48

h02

*0	828	-2007?
2	179	-98
-2	366	-398
4	354	312
-4	446	663
6	43	-18
-6	121	-98
8	289	300
-8	447	605
10	153	104
-10	260	228
12	75	-84
-12	180	-180
14	98	-87
-14	193	-172
16	22	37
-16	<15	-16
-18	233	258
-20	50	73
-22	46	-37

h04

0	792	866
2	88	18
-2	293	252
4	185	-149
-4	372	-328
6	<15	3
-6	54	45
8	129	-140
-8	374	-385
10	77	-61
-10	224	-218
12	26	41
-12	159	151
-14	195	165
-16	59	35
-18	261	-268
-20	73	-100
-22	60	46
-24	83	-36

h06

0	356	-410
2	40	-8
-2	160	-174
4	83	67
-4	180	166
6	<10	1
-6	<15	-11
-8	189	172
-10	184	163
-12	80	-82
-14	145	-126
-16	30	-25
-18	212	217
-20	80	98

-22	65	-43
-24	79	32

h08

-2	71	97
-4	58	-69
-6	<12	-6
-8	53	-61
-10	98	-95
-12	<13	28
-14	86	78
-16	<12	8
-18	171	-142
-20	62	-73
-22	<6	31

h11

1	542	557
-1	555	638
3	82	98
-3	121	144
5	183	-174
-5	257	-250
7	171	156
-7	238	217
9	63	-41
-9	45	-16
11	181	-169
-11	287	-256
13	78	76
-13	122	104
15	43	-49
-15	43	-49
17	114	-128
-17	201	-194
19	<8	-16

-19	<14	-23
-21	22	17

h21

0	438	-470
2	266	270
-2	255	264
4	174	131
-4	233	206
6	22	-33
-6	65	-83
8	213	220
-8	310	313
10	150	-145
-10	196	-174
12	135	-142
-12	190	-203
14	<15	-5
-14	30	9
16	36	-29
-16	69	-51
18	17	21
-18	33	32
-20	18	15

h31

1	35	-43
-1	53	-63
3	19	45
-3	41	70
5	288	-276
-5	337	-323
7	<14	13
-7	<12	-4
9	83	84
-9	133	127

11	18	-15
-11	46	-40
13	131	134
-13	174	175
15	49	43
-15	72	69
17	33	-35
-17	58	-57
-19	<10	3

h41

0	54	-58
2	113	-106
-2	111	-103
4	186	-172
-4	203	-193
6	85	94
-6	76	82
8	145	150
-8	192	199
10	108	-114
-10	140	-140
12	14	3
-12	<16	-14
14	108	109
-14	137	156
16	<7	3
-16	12	4
-18	<9	6

h51

1	32	34
-1	32	40
3	16	-37
-3	18	-40

5	<16	7
-5	<16	2
7	43	49
-7	56	58
9	18	-5
-9	20	-2
11	28	-36
-11	37	-47
13	<8	0
-13	<12	-4
-15	<10	11

h61

0	132	123
2	57	38
-2	60	45
4	<13	8
-4	<14	9
6	<12	10
-6	<14	15
8	16	-21
-8	20	-26
10	<7	-2
-10	<11	-1
-12	20	-19

h71

1	14	13
-1	15	20
3	47	-50
-3	53	-56
-5	51	49
-7	69	68

for the crystal structure resolution of (I) and (II). The molecular orientation within their average planes was derived by trial and error methods and the structures were then refined by differential Fourier synthesis technique, both in the modulated projection along c, following formula (5), and in the normal projection along b.

In the case of the *trans*-dimethyl derivative (III), the ambiguity in the substitution sites of the methyl groups was easily resolved by simple comparison of the intensity distribution over the $hk0$ reflexions and of the unit-cell dimensions between compounds (III) and (I). The molecular orientation with respect to the unit cell axes was thus recognized to be closely analogous to that of *trans*-octatrienediolide, and the methyl groups could not be arranged in the unit cell other than by attaching them in the 2,7 positions: this is in fact the only possibility of explaining the lengthening of the a cell edge in (III) with respect to (I) (Fig.3). The comparison between observed and calculated structure factors then provided a definite check for the above hypothesis, and the crystal structure refinement was carried out in strict analogy to the cases of (I) and (II).

As a conclusion, the X-ray crystal structure resolution and refinement of the three compounds under examination was carried out by Fourier techniques, using in every case the $hk0$, $hk1$ and $h0l$ observed reflexions. The molecular planarity and the parallelism amongst the molecular planes were the most significant features that suggested the above type of structural approach. Moreover, owing to the close analogy among the molecular structures under examination, the standard deviations of the average values of the corresponding molecular parameters may be assumed to be reduced by a factor that is approximately equal to $\sqrt{3}$

with respect to the values derived from a single X-ray refinement, provided every structural refinement leads to about the same accuracy.

Resulting structural data

Table 1 gives the resulting atomic fractional coordinates, the corresponding standard deviations and the isotropic thermal factors for (I), (II) and (III) (for the atomic symbols, see Fig. 1). The hydrogen atoms were introduced in the normally expected positions. The standard errors in the x and y coordinates were derived by Cruickshank's (1949) method. On account of the atomic overlaps in the projection along b, the $\sigma(z)$ standard errors were derived by the method applied by Ahmed & Cruickshank (1953) to the crystal structure of oxalic acid dihydrate, considering the $h0l$ reflexions; the order of magnitude of $\sigma(z)$ is about 3 times $\sigma(x) \simeq \sigma(y)$.

Table 2 compares observed and calculated structure factors for the three compounds. The disagreement index R, including non-observed reflexions, has the values 0·12, 0·11, 0·12 for the $hk0$ and $hk1$ reflexions and 0·15, 0·17, 0·17 for the $h0l$ reflexions, for (I), (II) and (III) respectively.

In Fig. 1 the resulting molecular parameters are reported for the three compounds. The average standard deviations corresponding to the various bond lengths and angles are given in Table 3, according to Ahmed & Cruickshank and Darlow (1960). In Fig. 2 the modulated electron density projections $\varrho_1(x,y)$ are shown together for the three compounds.

In all the cases the molecular conformation is planar within the experimental error (± 0.03 Å). The resulting molecular geometry is in substantial agreement with
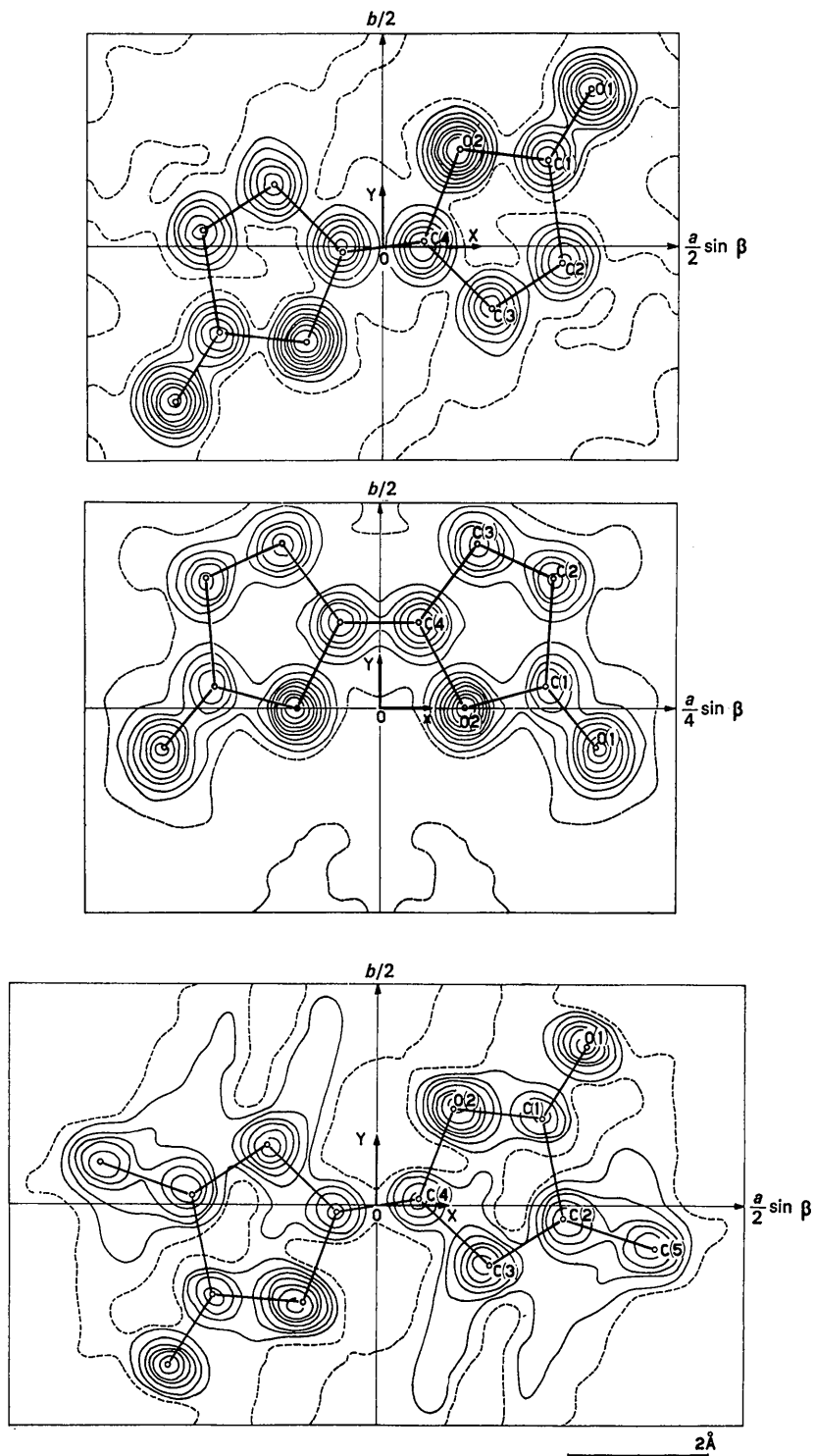
Fig. 2. Modulated electron density projections (see text) along the c axis for (I), (II) and (III) from top to bottom respectively. Contour lines are drawn at 1 (dashed line), 2, 3... e.Å^{-2}.
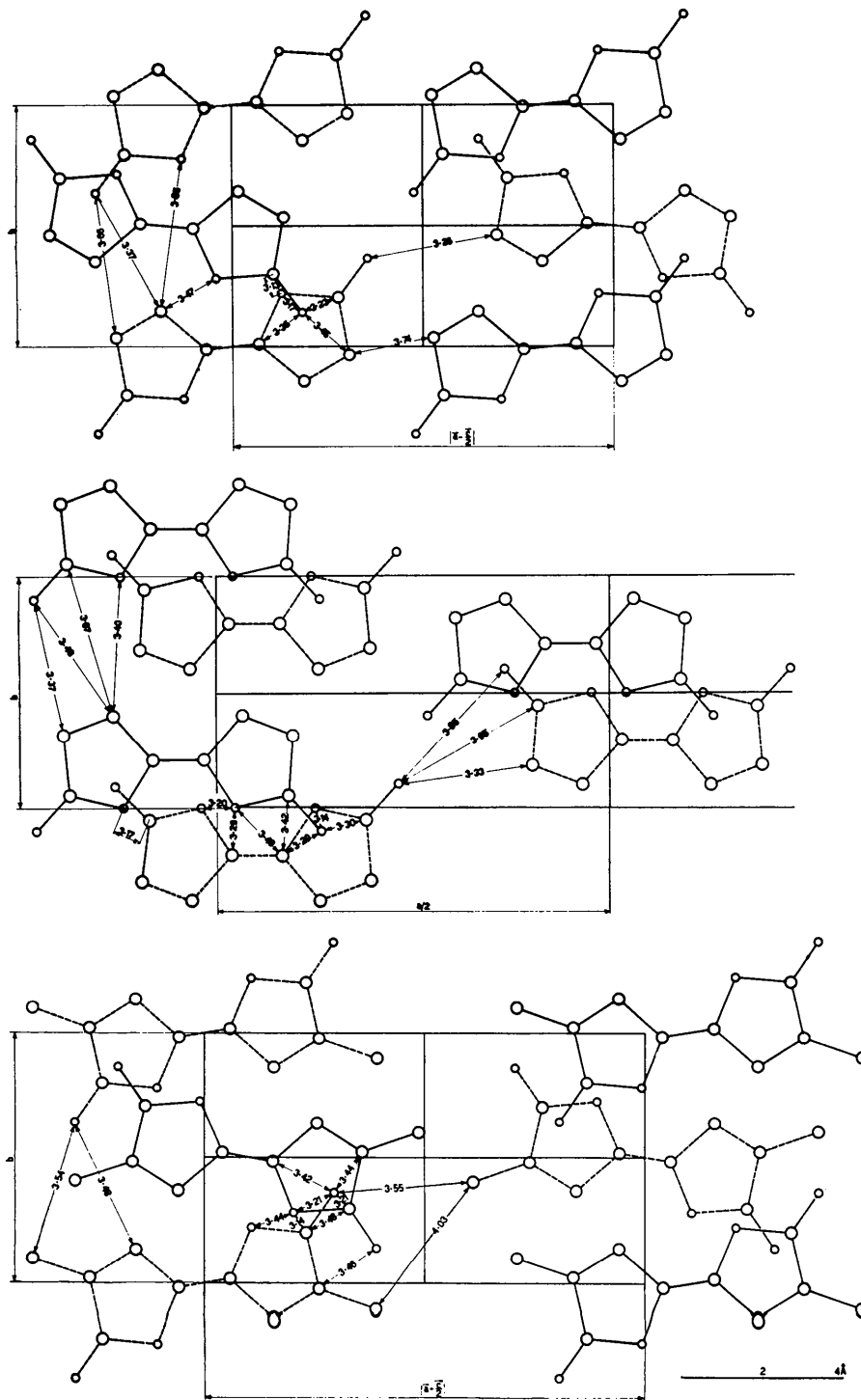
Fig. 3. Molecular packing in the crystal state of (I), (II) and (III) from top to bottom respectively. The molecules are projected perpendicular to their average planes. The most significant interatomic distances between different molecules are shown.

Table 3. *Standard errors for bond lengths and angles*

In the left hand column, the values refer to each compound separately and are obtained by averaging the corresponding figures for the three compounds [Fig.1(*a*), (*b*) and (*c*)]. In the right hand column, the probable values corresponding to the average model [Fig.1(*d*)] are given: these are derived by dividing the first-column values by $\sqrt{3}$.

	σ	σ_{av}
C(1)–C(2)	0·015 Å	0·009 Å
C(2)–C(3)	0·024	0·014
C(3)–C(4)	0·019	0·011
C(4)–C(4')*	0·029	0·017
C(2)–C(5)	0·024	—
C(1)–O(1)	0·015	0·009
C(1)–O(2)	0·019	0·011
C(4)–O(2)	0·013	0·007
C–Ĉ–C	1·2°	0·7°
C–Ĉ–O	1·1	0·6
C–Ô–C	0·8	0·5
O–Ĉ–O	1·0	0·6

* Symmetrical atoms

other cases of π-molecules already reported, with the sole exception of the ($\diagdown$C=C$\diagup$) length corresponding to the central double bond, which in all three cases is 1·31 Å within the experimental error. A possible reason for the shortening of this distance with respect to the usually accepted value of a (C=C) double bond (1·34 Å) could reside in the fairly strong distortion from the trigonal coordination which is observed around the carbon atoms involved, as it results from the valency angles reported in Fig.1.

The molecular packing

Significant analogies may be observed among the modes of molecular packing of all three compounds in the crystalline state (Fig.3). First of all, the molecular planes are approximately contained in parallel layers, which are $3\cdot10\pm0\cdot05$ Å apart, the deviation from the layer planes being more pronounced for the dimethyl derivative than in the other two cases. We may incidentally observe that this deviation is also responsible for the poor quality of the modulated electron density projection along c of compound (III) in comparison with (I) and (II) (Fig.2). The monoclinic unique axis *b* represents the shortest repetition vector within every layer; it is more or less perpendicular in all the cases

to the largest molecular dimension, and its length varies from 5·70 [for (II)] to 6·24 Å [for (III)]. The molecules are disposed within the layers according to a centred rectangular network, and molecules at van der Waals contact are so oriented as to keep their oxygen atoms as far apart as possible.

Two adjacent layers are relatively shifted so as to fill the space as uniformly as possible. It may be worth noting that in all the cases the carbonyl carbon atoms are at very short distances (< 3·3 Å) from the oxygen atoms of the molecules in neighbouring layers, while the carbonyl oxygen atoms tend to fill the holes within the lactone rings of the upper or of the lower layer molecules (Fig.3).

Finally, from inspection of the same figure we may observe that the lowest value of the O · · · O intermolecular distances is 3·14 Å; the corresponding limit for the C (trigonal) · · · O distances is expressed approximately by the same value, and is realized between non-coplanar molecules. The same happens for the C (trigonal) · · · C (trigonal) intermolecular distances which are never less than 3·42 Å (*cf.* graphite in which the least C · · · C distance between adjacent layers is 3·35 Å). Finally the C (methyl) · · · C and the C (methyl) · · · O shortest distances are 3·85 and 3·54 Å respectively.

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