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Crystallographic Studies of Dehydrohalogenation in Solid *meso*-Dibromobutane Derivatives. I. The Crystal and Molecular Structures of Dimethyl (*RSRS*)- *and* (*RRSS*)-α,α′-Dimethyl-β,β′-dibromoadipate

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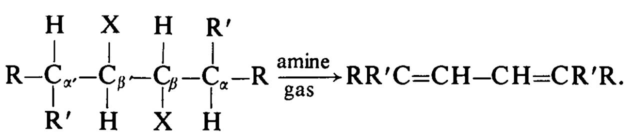
The structures of dimethyl (*RSRS*)- *and* (*RRSS*)-α,α′-dimethyl-β,β′-dibromoadipate were determined from diffractometer data by Patterson and heavy-atom techniques. Both crystals are monoclinic, space group $P2_1/c$, with $a = 9{\cdot}2632$, $b = 5{\cdot}4810$, $c = 13{\cdot}1657$ Å, $\beta = 92{\cdot}442°$, $Z = 2$; $a = 8{\cdot}865$, $b = 8{\cdot}872$, $c = 8{\cdot}339$ Å, $\beta = 96{\cdot}46°$, $Z = 2$ respectively. The structures were refined to $R = 0{\cdot}057$, $0{\cdot}049$. The two compounds react in the solid state with gaseous ammonia or amines and yield, by double dehydrobromination, the corresponding diester of 1,3-*trans,trans*-butadiene and 1,3-*cis,cis*-butadiene respectively. In both cases the reaction is strictly topochemical in the sense that the configurations of the products correlate directly with the conformations of the starting molecules in the crystal.

Introduction

The double dehydrohalogenation of solid *meso*-dihalogenobutanes by gaseous ammonia or amines has been performed by Friedman, Lahav & Schmidt (1969, 1974) in a series of compounds yielding quantitatively the corresponding 1,3-butadienes.



(1)

The configurations of the dienic products were established by chemical methods.

The stereo course of the reaction has been investigated in terms of the correlation between the molecular conformations of the starting compounds and the configurations of the products. We have already reported (Kaufman, Rabinovich & Schmidt, 1974) the structure of the dimethyl ester of *meso*-β,β′-dichloroadipic acid [(1): X = Cl; R = $COOCH_3$; R′ = H] and have shown that the reaction is controlled by the conformation of the molecule in the reacting crystal.

In a recent communication (Friedman, Gati, Lahav, Rabinovich & Shakked, 1975) we dealt with the stereo course of the reaction of solid dihalogenoadiponitriles [(1): X = Cl, Br; R = CN; R′ = H, CH_3] and shown that when R′ = H the reaction is not topochemically controlled. The apparent lack of control was attributed to a mechanism involving pre-reaction equilibrium of rotamers in the solid. The full X-ray structure analyses of some of the dihalogenoadiponitriles will be reported in part II of the present series.

In part I we present the detailed analyses of the two *meso*-diastereoisomers of another dimethyl adipate, dimethyl α,α′-dimethyl-β,β′-dibromoadipate [(1): X =

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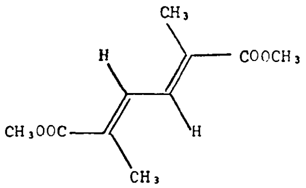
Br; R = $COOCH_3$; R′ = CH_3]. One isomer eliminates to the corresponding diester of 1,3-*trans,trans*-butadiene (2), the other to the corresponding 1,3-*cis,cis*-butadiene (3). In both cases the reaction is strictly topochemical in the sense that the configurations of the products correlate directly with the conformations of the starting molecules in the crystal.



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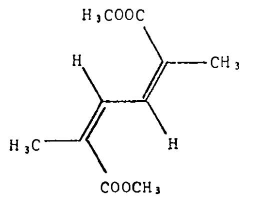


(3)

Experimental

Crystal data of the two diastereoisomers (I) and (II) are listed in Table 1. The two isomers crystallize in the monoclinic system in centrosymmetric space groups, the molecules occupying centres of inversion. Cell dimensions were derived by least squares from high-order reflexions. Intensities (two quadrants of the reciprocal sphere) were collected on an automatic Siemens diffractometer controlled by an IBM 1800 computer. The measurements were made at room temperature with Mo $K\alpha$ radiation by the balanced-filter technique (Irngartinger, Leiserowitz & Schmidt, 1970). The intensities were corrected for Lorentz–polarization and absorption effects. The two data sets of each crystal were averaged to one set of independent reflexions. The agreements between equivalent data sets were 3% for 1958 unique reflexions in (I) and 4% for 1432 unique reflexions in (II).

Structure determination and refinement

The structures were solved by sharpened Patterson and heavy-atom techniques. The coordinates of the Br atoms derived from the Patterson map of (I) were used to calculate the phases of nearly all the reflexions. These phases were used to calculate a Fourier map which yielded the positions of all non-hydrogen atoms. However, the Br atoms in (II) lie nearly on the screw axes, thus leading to pseudo-systematic absences, and the corresponding phases could not be determined. In this case the positions of the other non-hydrogen atoms were located from the Patterson map.

The non-hydrogen atoms of each structure were refined isotropically by full-matrix least squares. Next, the H atoms attached to C_α and C_β were inserted geometrically and the structures further refined anisotropically for non-hydrogen atoms and isotropically for H. Subsequent difference syntheses located the methyl H atoms and the refinement of the structures was continued until the parameter shifts were less than one third of their e.s.d.'s. The results are summarized in Table 2. The weighting scheme was as follows: The random error in a single observation was estimated to comprise 3% of the net intensity in addition to the statistical counting error.

$$\sigma^2(I-B) = [0{\cdot}03(I-B)]^2 + (I+B),$$

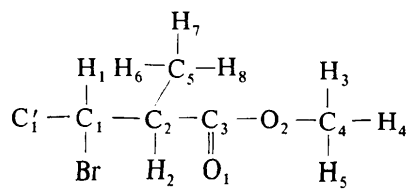
where I and B are the intensity and background measurements respectively. The statistical weight of each reflexion was taken as the sum of the calculated weights, $w = 1/\sigma^2$, of the symmetry-equivalent reflexions. Reflexions for which $F_o^2 < \sigma(F_o^2)$ were given threshold values $F_t = [\sigma(F_o^2)]^{1/2}$ and were included in the refinement only when $F_t < |F_c|$. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

Table 1. *Crystal data*

	(I)	(II)
Compound	$C_{10}H_{16}O_4Br_2$	$C_{10}H_{16}O_4Br_2$
M_r	327·8	327·8
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9·2632 (4)	8·865 (1)
b (Å)	5·4810 (2)	8·872 (2)
c (Å)	13·1657 (5)	8·339 (1)
β (°)	92·442 (6)	96·46 (1)
Z	2	2
D_c (g cm^{-3})	1·63	1·67
D_m (g cm^{-3})	1·62	1·68
V (Å^3)	667·8	651·7
μ (Mo $K\bar{\alpha}$) (cm^{-1})	64·3	65·9

Results

The numbering of atoms is given below. Atoms related by a centre of symmetry are primed.



(I), (II)

The final coordinates, the thermal parameters and their e.s.d.'s are in Tables 3 and 4. The bond lengths

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32108 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and angles, uncorrected for curvilinear thermal motion, and their e.s.d.'s are listed in Table 5. Intermolecular distances shorter than the corresponding van der Waals contacts are listed in Table 6. Figs. 1, 2 and 3 show stereoscopic views of (I), (II) and dimethyl *meso*-β,β'-dichloroadipate (III) (Kaufman, Rabinovich & Schmidt, 1974) with their thermal ellipsoids scaled to 50% probability (Johnson, 1965). Figs. 4 and 5 show

Table 2. *Results of the refinement*

Compound	R	r	D	n	s
(I)	0·057	0·071	1·53	1554	105
(II)	0·049	0·055	1·25	965	105

$R = \Sigma |kF_o - |F_c||/\Sigma kF_o$.
$r = [\Sigma w(k^2F_o^2 - |F_c|^2)^2/\Sigma wk^4F_o^4]^{1/2}$.
$D = [\Sigma w(k^2F_o^2 - |F_c|^2)^2/(n-s)]^{1/2}$.
n: Number of reflexions included in the last cycle of refinement.
s: Number of parameters refined.

Table 4. *Fractional coordinates of* H *atoms* ($\times 10^3$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U(A^2)
(I)				
H(1)	38 (3)	332 (6)	431 (2)	−3 (7)
H(2)	232 (3)	382 (6)	543 (2)	1 (8)
H(3)	325 (5)	13 (9)	260 (3)	38 (13)
H(4)	342 (6)	292 (8)	223 (5)	57 (18)
H(5)	447 (7)	178 (10)	305 (4)	62 (20)
H(6)	202 (5)	879 (8)	506 (3)	36 (14)
H(7)	187 (5)	786 (7)	597 (3)	32 (12)
H(8)	360 (6)	804 (8)	557 (3)	49 (15)
(II)				
H(1)	3 (5)	344 (5)	42 (4)	−2 (12)
H(2)	220 (3)	429 (4)	−91 (4)	−12 (9)
H(3)	329 (7)	835 (8)	215 (7)	65 (23)
H(4)	307 (8)	901 (9)	38 (9)	89 (35)
H(5)	446 (7)	834 (8)	97 (7)	58 (23)
H(6)	409 (7)	281 (7)	72 (7)	72 (23)
H(7)	281 (5)	294 (6)	218 (6)	31 (17)
H(8)	231 (6)	205 (6)	51 (6)	32 (18)

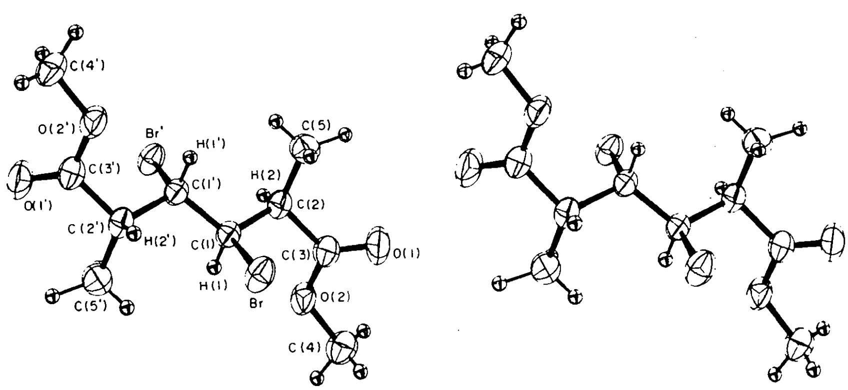


Fig. 1. Stereoscopic view of dimethyl *meso*-(*RSRS*)-α,α'-dimethyl-β,β'-dibromoadipate (I).

Table 3. *Fractional coordinates and anisotropic temperature factors* (Å^2)

Bromine parameters × 10^5, all other values × 10^4. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U^{11}h^2a^{*2} + \ldots + 2U^{13}hla^*c^*)]$.

Dimethyl *meso*-(*RSRS*)-α,α'-dimethyl-β,β'-dibromoadipate (I)

	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
Br	1451 (4)	70785 (7)	34694 (3)	4471 (22)	5776 (27)	3817 (19)	602 (21)	1191 (19)	796 (14)
C(1)	563 (3)	4786 (7)	4608 (2)	342 (18)	333 (21)	339 (16)	4 (16)	−5 (15)	75 (14)
C(2)	2137 (4)	5158 (7)	4973 (2)	317 (18)	428 (23)	388 (18)	22 (16)	33 (17)	63 (15)
C(3)	3139 (4)	4629 (7)	4112 (2)	365 (19)	428 (24)	459 (19)	41 (18)	25 (17)	66 (16)
C(4)	3643 (6)	1781 (11)	2832 (4)	424 (25)	856 (40)	598 (27)	68 (29)	−193 (28)	165 (22)
C(5)	2478 (5)	7585 (8)	5470 (3)	438 (22)	554 (33)	568 (23)	−11 (22)	−142 (22)	48 (20)
O(1)	4124 (3)	5883 (5)	3881 (2)	527 (17)	626 (18)	770 (19)	−180 (16)	−71 (16)	306 (15)
O(2)	2801 (3)	2530 (4)	3675 (2)	428 (14)	459 (18)	608 (15)	−16 (13)	−111 (12)	223 (12)

Dimethyl *meso*-(*RRSS*)-α,α'-dimethyl-β,β'-dibromoadipate (II)

	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
Br	3155 (5)	49513 (8)	28028 (5)	4070 (24)	8178 (39)	2973 (21)	762 (42)	219 (41)	88 (15)
C(1)	481 (4)	4443 (6)	514 (5)	313 (23)	340 (34)	313 (24)	−23 (20)	−18 (18)	6 (16)
C(2)	2190 (5)	4342 (5)	303 (6)	262 (23)	287 (28)	408 (27)	78 (22)	19 (22)	−8 (19)
C(3)	3130 (5)	5671 (6)	971 (6)	274 (25)	395 (33)	425 (27)	3 (24)	37 (25)	6 (21)
C(4)	3414 (8)	8317 (8)	949 (9)	497 (40)	389 (44)	774 (47)	−89 (34)	−14 (38)	2 (34)
C(5)	2863 (7)	2871 (7)	1019 (8)	407 (35)	455 (44)	602 (45)	12 (33)	−48 (35)	−114 (29)
O(1)	4241 (4)	5576 (4)	1921 (4)	491 (22)	474 (25)	895 (29)	−27 (18)	54 (20)	−382 (20)
O(2)	2600 (3)	6967 (4)	356 (4)	320 (21)	400 (24)	499 (23)	−19 (19)	36 (20)	−104 (16)

Table 5. *Bond lengths* (Å), *angles* (°) *and e.s.d.'s of dimethyl meso-(RSRS)-α,α'-dimethyl-β,β-dibromoadipate* (I) *and dimethyl meso-(RRSS)-α,α'-dimethyl-β,β'-dibromoadipate* (II)

	(I)	(II)
C(1)–C(1')	1·517 (6)	1·508 (8)
C(1)–Br	1·981 (3)	1·982 (4)
C(1)–C(2)	1·530 (5)	1·548 (6)
C(2)–C(3)	1·523 (5)	1·513 (7)
C(2)–C(5)	1·510 (6)	1·528 (8)
C(3)–O(1)	1·192 (5)	1·195 (5)
C(3)–O(2)	1·318 (4)	1·323 (6)
O(2)–C(4)	1·443 (6)	1·455 (8)
C(1)–H(1)	0·90 (3)	0·98 (4)
C(2)–H(2)	0·96 (3)	1·02 (3)
C(4)–H(3)	1·02 (5)	1·02 (6)
C(4)–H(4)	1·02 (6)	0·81 (8)
C(4)–H(5)	0·80 (6)	0·93 (6)
C(5)–H(6)	0·94 (5)	1·14 (6)
C(5)–H(7)	0·90 (4)	0·97 (5)
C(5)–H(8)	1·07 (6)	0·95 (5)
C(1')–C(1)–C(2)	116·1 (3)	118·1 (4)
C(1')–C(1)–Br	107·4 (2)	107·4 (3)
C(2)–C(1)–Br	107·8 (2)	107·6 (3)
C(1)–C(2)–C(3)	110·1 (3)	114·7 (4)
C(1)–C(2)–C(5)	115·6 (3)	110·4 (4)
C(5)–C(2)–C(3)	111·6 (3)	110·3 (4)
C(2)–C(3)–O(1)	125·3 (3)	124·6 (5)
O(1)–C(3)–O(2)	124·2 (3)	123·2 (5)
C(2)–C(3)–O(2)	110·5 (3)	112·2 (4)
C(3)–O(2)–C(4)	117·2 (3)	116·3 (4)
H(1)–C(1)–C(1')	108 (2)	111 (2)
H(1)–C(1)–Br	102 (2)	102 (2)
H(1)–C(1)–C(2)	114 (2)	110 (2)
H(2)–C(2)–C(1)	104 (2)	104 (2)
H(2)–C(2)–C(3)	103 (2)	110 (2)
H(2)–C(2)–C(5)	112 (2)	108 (2)
H(3)–C(4)–O(2)	106 (2)	105 (4)
H(4)–C(4)–O(2)	109 (3)	106 (5)
H(5)–C(4)–O(2)	105 (4)	119 (4)
H(6)–C(4)–C(2)	107 (3)	107 (3)
H(7)–C(5)–C(2)	110 (2)	106 (3)
H(8)–C(5)–C(2)	116 (2)	108 (3)
H(3)–C(4)–H(5)	105 (4)	118 (7)
H(3)–C(4)–H(4)	116 (5)	101 (5)
H(4)–C(4)–H(5)	115 (5)	108 (7)
H(6)–C(5)–H(7)	91 (4)	112 (4)
H(7)–C(5)–H(8)	109 (4)	109 (5)
H(6)–C(5)–H(8)	119 (4)	114 (5)

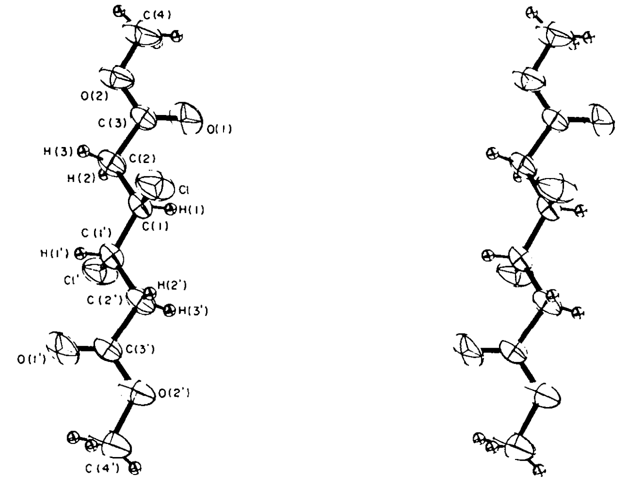


Fig. 3. Stereoscopic view of dimethyl *meso*-β,β'-dichloroadipate (III) (Kaufman, Rabinovich & Schmidt, 1974).

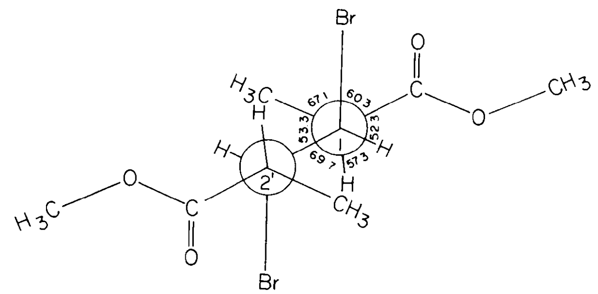


Fig. 4. Newman projection of (I) along C(1)–C(2).

Table 6. *Short intermolecular distances* (Å) *in the esters*

The second atom in each pair is related to the first by the corresponding symmetry and translation operations.

	(I)	(II)
Br···Br	3·75 [$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $\bar{1}00$]	3·77 [$\bar{x}, \bar{y}, \bar{z}$; 001]
O(1)···C(4)	3·16 [$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; 110]	3·27 [$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $1\bar{1}0$]

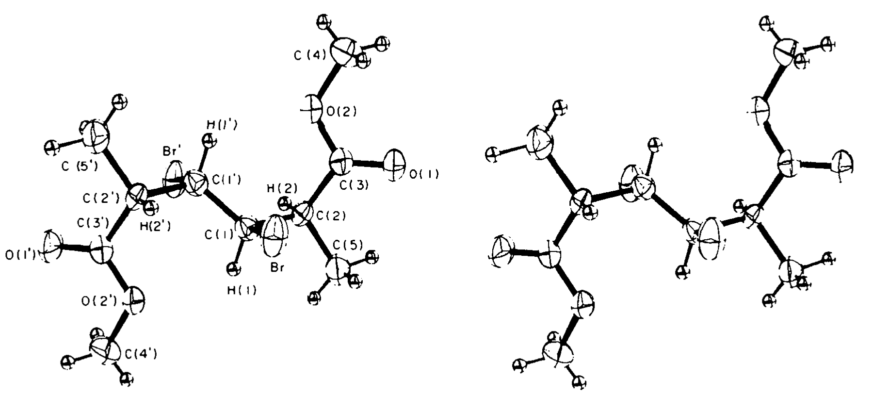


Fig. 2. Stereoscopic view of dimethyl *meso*-(*RRSS*)-α,α'-dimethyl-β,β'-dibromoadipate (II).

the corresponding projections along C(1)—C(2). Figs. 6 and 7 show stereoscopic views of the packing (Johnson, 1965). The analyses established the configuration of the two *meso*-diastereoisomers as *RSRS* for (I) and *RRSS* for (II).

Discussion

The discussion of the bond lengths and angles of the dibromobutane moiety, the molecular conformations and the course of the double elimination reaction is deferred to part III of this series, where the results of the analyses of an additional four adiponitriles are given. Here we discuss two aspects of the structures which are characteristic of these esters, namely the geometry of the ester group and the packing.

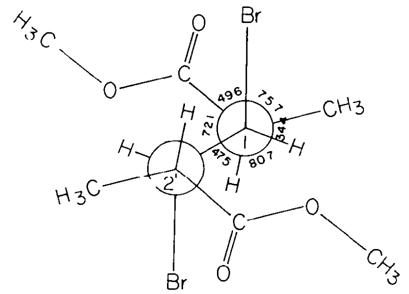


Fig. 5. Newman projection of (II) along C(1)—C(2).

The geometry of the ester group

The methoxycarbonyl groups in (I) and (II) are nearly synplanar. The twist angles about C(3)—O(2) are 3·0 and 2·3° for (I) and (II) respectively (α_1 in scheme 2). Two of the methoxy H atoms straddle the carbonyl O, the third being nearly antiperiplanar to C(3)—O(2) (Figs. 1, 2). This *anti* arrangement, which corresponds to the stable staggered orientation, is that usually observed in methyl esters. An exception has been observed in dimethyl *meso*-tartrate (Kroon & Kanters, 1973), where the methoxy H atoms are distributed in approximately equal weights over the *anti* and *syn* conformation.

Bond lengths and angles of the methoxycarbonyl groups of (I) and (II) together with other recently reported methyl esters are compiled in Table 7. The average values of C—O (1·328 Å) and C=O (1·198 Å) bonds

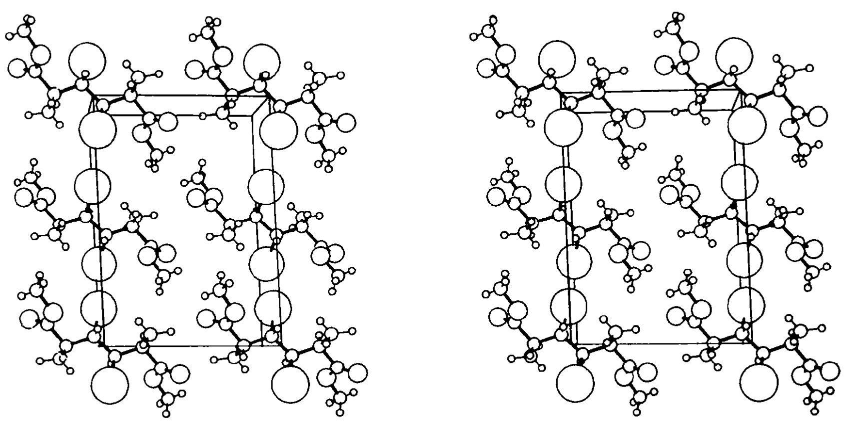


Fig. 6. Stereoscopic view of the packing arrangement of (I).

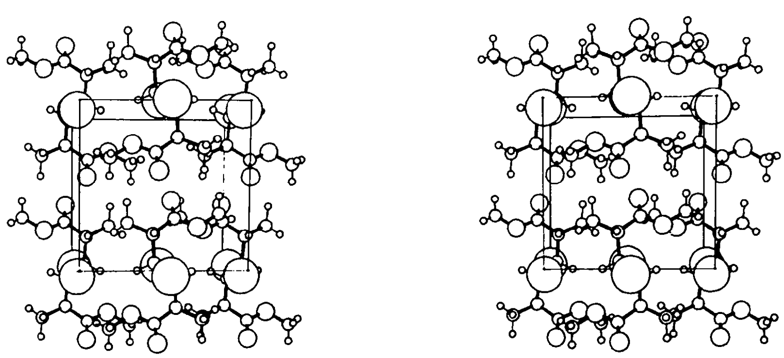
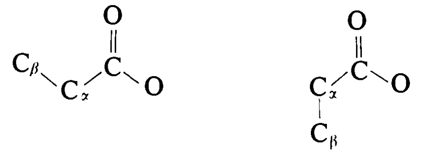


Fig. 7. Stereoscopic view of the packing arrangement of (II).

are different from the corresponding values in carboxylic acids (1·31 and 1·23 Å; Kanters, Kroon, Peederman & Schoone, 1967), reflecting a sharper distinction between single and double bonds of the carboxyl group moiety in the ester compared with that of free acids.

Equivalent bond lengths of the methoxycarbonyl group attached to quite different molecules show a relatively small variance as seen from the bond-scatter values (s) in Table 7. On the other hand, the O=C—O bond angle shows a larger variance resulting probably from the different arrangements of the methoxycarbonyl group with respect to the rest of the molecule.

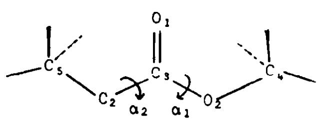
The orientation of the carboxyl and ester groups relative to C_α—C_β has been discussed by several authors. Leiserowitz & Schmidt (1965) claimed that the preferred conformation is the one which places the C_α—C_β bond synplanar to the carbonyl group. They attributed this preference to non-bonded repulsions between C_β and its H atoms on the one hand, and the hydroxyl or carbonyl O atoms on the other. Dunitz & Strickler (1968) pointed out that in addition to non-bonded interactions one should consider the bent-bond description of a double bond. If the carbonyl double bond is considered as two bent bonds, then staggering about C—C_α in saturated compounds leads to the synplanar conformation whereas in α,β-unsaturated compounds (where two double bonds are resolved into bent bonds) staggering about C—C_α gives the antiplanar conformation, scheme 1:



synplanar antiplanar

Thus, in unsaturated compounds, the preferred conformation according to the bent-bond model is opposite to the favourable conformation deduced from steric considerations, so that either conformation can exist (Einspahr & Donohue, 1973). In many saturated acids and esters the favourable conformation is the one where the α substituent or C_β eclipses the carbonyl O (synplanar conformation). The non-planarity of this system in other carboxylic acids has been attributed by Kanters *et al.* (1967) to the fact that a coplanar arrangement is unfavourable for hydrogen bonding, since the α substituent or C_β presents a close approach to one of the lone pairs of the carbonyl O. In saturated esters where hydrogen bonding is absent, the synplanar conformation is expected, provided that no steric repulsions are present.

In the esters (I) and (II) the α-methyl group is synplanar with respect to the methoxycarbonyl group, scheme 2:



	(I)	(II)
α_1 =	−3.0°,	−2.3°
α_2 =	3.7°,	0.0°

The staggered conformation of the α-methyl H atoms with respect to the substituents of C(2) results in the straddling of the carbonyl O by two H atoms similarly to that of the methoxy H atoms. It is reasonable to assume that the synplanar arrangement is stabilized by the interaction of the methyl H atoms and the carbonyl O. This assumption is substantiated by the following considerations. The synplanar arrangement leads to close 1 · · · 4 and 1 · · · 5 contacts of C and O atoms in (I) and (II) respectively [C(1) · · · O(2) in (I) and C(1′) · · · O(2) in (II), Figs. 1, 2]. The partial relaxation of the interaction in (II) is achieved by considerable angle-widening at C(1), C(2), and C(3) (Table 5) and by a large rotation (more than 10°) about C(1)—C(2) from the staggered orientation (Fig. 5) rather than by combined rotations about C(1)—C(2) and C(2)—C(3). Furthermore, in the *meso*-β,β'-dichloroadipate (III) the synplanar arrangement of C(1)—C(2) with respect to the methoxycarbonyl group is disturbed by even smaller steric effects; the methoxycarbonyl moiety is rotated from the plane of C(1)—C(2)—C(3) by as much as 24° (Fig. 3).

Table 7. *Bond lengths* (Å) *and angles* (°) *of the ester group in methyl ester compounds*

Compound	C=O	C—O	O—CH_3	O=C—O	C—O—C
1 (I)	1·192	1·318	1·443	124·2	117·2
2 (II)	1·195	1·323	1·455	123·2	116·3
3 (III)	1·179	1·320	1·459	124·2	116·7
4*a*	1·190	1·330	1·460	124·8	115·9
4*b*	1·200	1·330	1·460	125·5	116·2
5	1·194	1·339	1·445	121·2	116·0
6*a*	1·196	1·338	1·441	123·7	116·7
6*b*	1·203	1·333	1·451	123·1	117·5
7*a*	1·200	1·330	1·460	123·9	117·7
7*b*	1·209	1·332	1·439	123·7	115·7
8	1·200	1·341	1·441	123·4	116·3
9	1·187	1·313	1·455	122·2	116·3
10	1·201	1·321	1·467	124·5	115·5
11	1·208	1·329	1·443	123·6	115·4
12	1·200	1·326	1·461	126·7	115·2
13*a*	1·199	1·322	1·445	123·4	117·3
13*b*	1·214	1·332	1·443	125·0	116·3
Average ($\bar{r}$)	1·198	1·328	1·450	123·9	116·4
Bond scatter (s)*	0·008	0·008	0·010	1·2	0·7

References: (1), (2) This work. (3) Kaufman, Rabinovich & Schmidt (1974). (4) Atwood, Williams, Garner & Cone (1974). (5) Huber & Gabe (1974). (6) Cameron, Hair, Greengrass & Ramage (1974). (7) Abola, Pletcher & Sax (1974). (8) Harlow & Simonsen (1974). (9) Maverick, Smith, Kozerski, Anet & Trueblood (1975). (10) Dewulf, Putzeys & Van Meerssche (1975). (11) Dupont, Toussaint, Dideberg, Braham & Noels (1975). (12) Goldberg (1975). (13) Belsky & Voet (1976).

* $s = [(r_i - \bar{r})^2/(n-1)]^{1/2}$.

A similar synplanar arrangement is observed in *trans*-1,2-bis(2-carboxymethyl-2-propyl)cyclohexane (van Koningsveld, 1973), where one of the two methyl groups attached to C_α is nearly synplanar with the carbonyl group ($\alpha_1 = 5{\cdot}0°$, $\alpha_2 = 6{\cdot}2°$, scheme 2). An approximate synplanar arrangement of the α-methyl group with respect to a carboxyl group is observed in methylmalonic acid (Derissen, 1970), where the methyl group is nearly synplanar with one of the two carboxyl groups ($\alpha_2 = 8°$).

The packing of the esters

Although the packing arrangements of the two diastereoisomers (I) and (II) are entirely different (Figs. 6, 7), because of different molecular geometries, the types of interactions observed in the two structures are very similar (Table 6). The molecules are held together mainly by Br···Br and O···H_3C interactions. The Br atoms in both structures lie nearly on the (100) planes. The short Br···Br contact in (I) (3·75 Å) is between atoms related by screw axes, one of the C–Br···Br angles being almost linear (170°). The Br···Br contact in (II) (3·77 Å) is across a centre of inversion and the centrosymmetric C–Br···Br–C system is also nearly linear with an angle of 167°.

Short C=O···H_3C–O contacts generated by screw axes exist in both structures. The distances between the carbonyl O and the methoxy C are 3·16 and 3·27 Å in (I) and (II) respectively. The distances between the carbonyl O and the methoxy H atoms are similar and average 3·0 Å. The C=O···C and C···C–O angles are 143 and 170° in (I) and 146 and 162° in (II) respectively. These values reflect the similar geometry of this interaction in the two structures which may be regarded as a weak hydrogen-bonded system.

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