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The Crystal and Molecular Structure of Dimethyl *trans, trans*-2,5-Dichloromuconate

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(*Received* 29 *January* 1973; *accepted* 5 *March* 1973)

The structure of dimethyl *trans,trans*-2,5-dichloromuconate, $C_8H_8O_4Cl_2$, was determined by single-crystal X-ray diffraction techniques. The unit cell is monoclinic, space group $P2_1/n$, with the following dimensions at 23 ± 2°C: $a = 3{\cdot}967\,(1)$, $b = 23{\cdot}339\,(5)$, $c = 5{\cdot}483\,(1)$ Å, $\beta = 95{\cdot}80\,(1)$°. There are two molecules in the unit cell; the molecules lie on centers of symmetry. The data were collected on an automated diffractometer. The structure was refined by full-matrix least-squares; the final value of the conventional R index is 0·041. The molecules lie in densely packed layers parallel to $(\bar{1}01)$. The carbonyl oxygen assumes the antiplanar conformation with respect to the β-carbon atom. Nonbonded intramolecular distances do not show a significant preference for one conformer over the other.

Introduction

The conformation of the carboxyl group, a representation of which is shown in Fig. 1, has been a subject of interest in a number of laboratories over the past few years. The preferred conformation at the carbon–carbon bond has been found to be the one which places the α, β carbon–carbon bond synplanar to the carbonyl (Leiserowitz & Schmidt, 1965). This preference is attributed by Leiserowitz and Schmidt to nonbonded interactions between the β-carbon and its hydrogen atoms, on the one hand, and the hydroxyl or carbonyl oxygen atoms, on the other. Chiefly due to the difference in carbon–carbon–carbonyl oxygen and -hydroxyl oxygen angles (characteristically about 122 and 114°, respectively), nonbonded β-carbon–oxygen and hydrogen–oxygen distances are 0·1 and 0·2 Å greater in the synplanar than in the antiplanar conformers.

This preference in conformation is amply confirmed for saturated acids, which are synplanar with only a few exceptions. However, the extension of this conformation to α,β-unsaturated acids on the basis of the same nonbonded interaction arguments is less satisfactory. Table 1 contains a list of α,β-unsaturated acids and esters whose structures are known, together with the respective conformations about the carboxyl carbon–carbon bond. Of the twenty-three crystallographically independent carboxyl groups represented in this table, nine are known to be antiplanar.

As Dunitz & Strickler (1968) point out, nonbonded interactions cannot be the sole factor determining conformations at the carbon–carbon bond in these compounds. They suggest that the bent-bond description of double bonds may be useful as a model of the interactions which produce the antiplanar conformation. If the carbonyl double bond is considered as two bent single bonds, then staggering about C–Cα in saturated acids leads to the synplanar conformation. However, in α,β-unsaturated acids, with two double bonds to be resolved into bent bonds, staggering about C–Cα gives the antiplanar conformation. In the latter case, the preference for the staggered conformation is in opposition to the steric factor and admits the possibility of antiplanar conformations.

While the bent-bond concept does rationalize the appearance of antiplanar conformations in unsaturated acids, it does not enable one to predict the conformations in such acids whose structures are not known.

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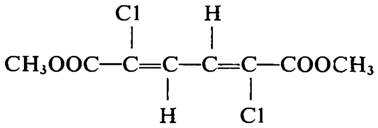
There is, however, one prediction which the bent-bond description does make: in α,β-unsaturated acids for which nonbonded interactions are ambivalent, the antiplanar conformation should be preferred. This suggests an investigation of α-substituted α,β-unsaturated acids. One such example was found in the literature: 2-methyl-*trans*-but-2-enoic acid (Porte & Robertson, 1959). The conformation of this compound places the double bonds antiplanar with distances of 2·76 Å between the carbonyl oxygen and α-methyl carbon and 2·72 Å between the hydroxyl oxygen and β-carbon. For a hypothetical synplanar conformer with the same bond distances and angles, nonbonded distances of 2·76 Å between carbonyl oxygen and β-carbon and 2·71 Å between hydroxyl oxygen and α-methyl carbon were calculated. The nonbonded interactions are clearly ambivalent in this case.

The compound dimethyl *trans,trans*-2,5-dichloromuconate was selected for this structure determination



$$CH_3OOC{-}\overset{Cl}{C}{=}\underset{H}{C}{-}\overset{H}{C}{=}\underset{Cl}{C}{-}COOCH_3$$

as an example of an α-substituted α,β-unsaturated ester whose structure would be pertinent to the conformational questions outlined above. It was a particularly appropriate choice because the structure of the unchlorinated parent compound, dimethyl *trans, trans*-muconate, had recently been determined (Filippakis, Leiserowitz & Schmidt, 1967) and found to be synplanar with respect to the carboxyl carbon–carbon bond. Calculations using representative values of bond distances and angles suggested that while the chlorine–oxygen nonbonded distance would be roughly 0·05 Å longer in the antiplanar conformer, the nonbonded distance between β-carbon and oxygen would be 0·05 Å longer in the synplanar conformer.

Experimental

A supply of the dichloromuconate was provided by Professor Bryan W. Roberts of the University of Pennsylvania, and portions were recrystallized by sublimation. The crystals were transparent, colorless, and most commonly in the form of thin laths. After several recrystallizations a crystal of suitable size and thickness was found. Attempts to cut samples from larger crystals were seldom successful, apparently the result of slippage parallel to the ($\bar{1}01$) plane.

Preliminary film work indicated the crystal has a monoclinic lattice. As indexed, systematic absences uniquely determine the space group as $P2_1/n$. The pertinent crystal data are listed in Table 2. The lattice constants are the result of a least-squares fit to 12 carefully centered 2θ measurements ranging between 40 and 65°. These measurements were made at 23 (2)°C using Cu $K\alpha$ radiation. The density of this material was estimated at between 1 and 2 g cm^{-3}.

The crystal used for data collection was a rectangular prism of about 0·03 × 0·02 × 0·01 cm mounted with its long dimension (corresponding to the a axis) parallel to the glass fiber. Two quadrants of data (hkl and $h\bar{k}l$) were collected with Ni-filtered Cu $K\alpha$ radiation out to 150° 2θ using a highly modified, Datex-automated

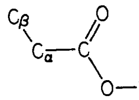


Fig. 1. The carboxyl group, synplanar conformer.

Table 1. *Conformations of α,β-unsaturated carboxylic acids and esters about the carboxyl carbon–carbon bond*

Compound	Conformation	Reference
Methyl *m*-bromocinnamate	*syn*	Leiserowitz & Schmidt (1965)
Methyl *p*-bromocinnamate	*syn*	
Crotonic acid	*syn*	
Sorbic acid	*syn*	
trans-β-2-Furylacrylic acid	*syn*	Filippakis & Schmidt (1967)
trans-β-2-Thienylacrylic acid, β form	*syn*	Block, Filippakis & Schmidt (1967)
trans-β-2-Thienylacrylic acid, γ form	*syn*	
Acrylic acid	*syn*	Higgs & Sass (1963); Chatani, Sakata & Nitta (1963)
Octa-2,6-*trans,trans*-dienedioic acid	*syn*	Martuscelli (1969)
Octa-2,6-*cis,trans*-dienedioic acid	*syn*	Martuscelli & Mazzarella (1969)
trans-β-Ionylidene crotonic acid	*syn*	Eichhorn & MacGillavry (1959)
Dimethyl *trans,trans*-muconate	*syn*	Filippakis, Leiserowitz & Schmidt (1967)
Monomethyl *trans,trans*-muconate, ester group	*syn*	Rabinovich & Schmidt (1967)
Monomethyl *trans,trans*-muconate, acid group	*anti*	
cis-β-Ionylidene crotonic acid	*anti*	Eichhorn (1957)
α-*trans*-Cinnamic acid	*anti*	Leiserowitz & Schmidt (1965)
2-Methyl-*trans*-but-2-enoic acid	*anti*	Porte & Robertson (1959)
α-Fumaric acid*	*anti*	Brown (1966)
β-Fumaric acid	*anti*	Bednowitz & Post (1966)
Verrucarin A *p*-iodobenzenesulfonate, *trans* end	*anti*	McPhail & Sim (1966)
Verrucarin A *p*-iodobenzenesulfonate, *cis* end	*syn*	

* This modification contains three crystallographically independent carboxyl groups, each antiplanar.

Table 2. *Crystal data*

Dimethyl *trans,trans*-2,5-dichloromuconate

$C_8H_8O_4Cl_2$

$P2_1/n$	M.W. 239·1
$a=$ 3·967 (1) Å	$F(000)=244$
$b=$23·339 (5)	$\varrho_{calc}=1\cdot57$ g cm^{-3}
$c=$ 5·483 (1)	$Z=2$
$\beta=$95·80 (1)°	$\mu/\varrho=36\cdot4$ cm^{2}g^{-1} (for Cu $K\alpha$ radiation)

G.E. XRD-5 diffractometer. This instrument is equipped with a quarter-circle goniostat, scintillation counter and pulse height analyzer. Peaks were scanned at a rate of 1° 2θ/min. Backgrounds were sampled for 30 s on both sides of a scan range which increased linearly from a minimum of 2·4° at 7° 2θ to 3·6° at 150° 2θ. Some thirty of the strongest reflections were recollected at reduced beam intensity. The intensities

Table 3. *Positional and thermal parameters*

Anisotropic temperature factors are expressed as:

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right].$$

E.s.d.'s are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	$(\times 10^4)$	$(\times 10^5)$	$(\times 10^4)$	$(\times 10^4)$	$(\times 10^5)$	$(\times 10^4)$	$(\times 10^4)$	$(\times 10^4)$	$(\times 10^4)$
Cl	2827 (1)	6955 (2)	3844 (1)	1018 (5)	181 (1)	297 (2)	4 (1)	−288 (4)	−9 (1)
O(1)	748 (5)	17609 (5)	1401 (3)	1467 (18)	121 (2)	487 (7)	−43 (3)	−447 (17)	−17 (2)
O(2)	−2255 (4)	13694 (5)	−1829 (2)	1086 (13)	106 (2)	352 (5)	33 (3)	−246 (13)	1 (2)
C(1)	− 389 (5)	2928 (7)	− 335 (3)	763 (16)	126 (3)	253 (6)	5 (4)	− 66 (15)	3 (2)
C(2)	522 (5)	7493 (7)	1023 (3)	704 (14)	130 (3)	256 (5)	− 1 (3)	− 53 (14)	2 (2)
C(3)	− 285 (5)	13531 (7)	257 (3)	780 (16)	120 (3)	317 (6)	− 8 (4)	−7 (16)	−5 (2)
C(4)	−3091 (11)	19331 (12)	−2810 (7)	1125 (33)	139 (5)	481 (12)	45 (6)	−124 (30)	30 (4)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	$(\times 10^3)$	$(\times 10^4)$	$(\times 10^3)$	$(\times 10^2)$	$(\times 10^4)$	$(\times 10^2)$	$(\times 10^3)$	$(\times 10^2)$	$(\times 10^3)$
H(1)	−165 (5)	364 (6)	−187 (3)	13 (2)	− 1 (3)	3 (1)	1 (4)	−4 (2)	−4 (2)
H(2)	−110 (7)	2093 (12)	−312 (6)	8 (2)	31 (8)	11 (2)	13 (7)	0 (4)	22 (6)
H(3)	−437 (7)	1889 (9)	−431 (5)	19 (4)	18 (6)	4 (1)	10 (7)	−8 (3)	3 (4)
H(4)	−418 (8)	2137 (11)	−166 (6)	16 (4)	20 (7)	7 (2)	12 (8)	−1 (4)	7 (5)

Table 4. F_o, F_c, *and* $\sigma(F_o)$ (× 10)

The final value of the secondary-extinction parameter (equation 3, Larson, 1967) is 4·6 (9) × $10^{-6}e^{-2}$.

-4	K	1	
1	41	38	2
2	26	-28	3
3	12	-6	5
4	57	-53	1
5	5	4	8
6	30	-26	2
7	6	-8	7
8	2	0	10
9	5	-5	8
10	12	11	4
11	5	3	7
12	25	21	2
13	0	-6	11
14	6	3	5
15	4	9	7
16	16	-15	2
17	6	-9	4
-4	K	2	
0	2	5	10
1	14	10	4
2	4	7	9
3	22	15	3
4	10	9	5
5	23	26	3
6	17	12	4
7	3	3	9
8	15	7	4
9	40	-43	2
10	2	2	10
11	28	-27	2
12	0	0	11
13	12	-8	3
14	23	-19	2
15	2	-3	7
16	14	-15	2
-4	K	3	
1	52	51	1
2	30	-35	2
3	26	22	2
4	2	-4	9
5	21	-21	3
6	8	3	5
7	35	-32	2
8	5	-8	6
9	22	-25	2
10	10	-3	4
11	5	0	6
12	11	12	3
13	24	23	1
14	7	7	3
-4	K	4	
0	0	4	10
1	18	-26	3
2	9	-2	4
3	32	-30	1
4	10	3	4
5	8	-3	4
6	17	19	2
7	7	1	4
8	13	14	2
9	9	5	3
-3	K	1	
0	48	-46	2
1	20	25	3
2	26	-26	3
3	13	3	5
4	39	37	2
5	21	23	3
6	81	81	1
7	16	16	4
8	61	57	1
9	85	-86	1
10	26	24	3
11	38	-38	2
12	20	-15	3
13	8	4	6
14	91	-88	1
15	17	-18	4
16	62	-62	1
17	19	16	3
18	8	-9	7
19	22	26	3
20	14	-12	3
21	10	12	4
22	25	27	2
23	7	-7	5
-3	K	2	
1	151	152	2
2	42	-46	2
3	44	42	2
4	68	63	1
5	54	-55	2
6	43	41	2
7	86	-83	1
8	44	-46	2
9	77	-78	1
10	63	-59	1
11	16	0	3
12	14	-14	5
13	61	64	1
14	25	21	3
15	40	39	2
16	20	-22	3
17	0	5	12
18	8	7	6
19	50	-51	1
20	43	46	1
21	57	-62	1
22	0	-4	9
-3	K	3	
0	66	67	2
1	93	-89	1
2	18	3	4
3	107	-108	1
4	9	-9	6
5	29	-29	3
6	34	39	2
7	0	-8	12
8	14	19	4
9	39	37	2
10	8	-4	6
11	68	66	1
12	25	-25	3
13	49	49	2
14	0	-8	12
15	20	-20	3
16	15	-12	4
17	78	-76	1
18	41	-45	1
19	17	-25	3
20	10	-12	3
-3	K	4	
1	18	16	3
2	3	8	9
3	2	-4	10
4	29	27	2
5	19	16	3
6	37	37	2
7	41	40	2
8	14	-10	4
9	15	14	4
10	24	-25	2
11	25	-29	2
12	11	-9	4
13	22	-24	2
14	6	-10	6
15	5	-7	6
16	0	3	10
17	19	-22	2
-3	K	5	
0	29	31	2
1	18	-14	3
2	33	33	2
3	33	-28	1
4	2	4	8
5	12	-13	3
6	18	-15	2
7	4	6	7
8	5	-6	6
9	17	18	2
10	11	-17	3
11	24	25	2
12	10	-3	3
13	9	15	3
-2	K	1	
1	312	317	3
2	13	-4	4
3	16	7	3
4	275	282	3
5	55	-56	1
6	161	162	1
7	74	-73	1
8	141	-142	1
9	137	-141	1
10	248	-242	2
11	16	0	4
12	106	-105	1
13	73	77	1
14	50	49	1
15	35	35	2
16	9	-8	6
17	10	6	5
18	82	82	1
19	100	-98	1
20	125	126	1
21	80	-83	1
22	27	-30	2
23	8	1	5
24	66	-66	1
25	21	-20	2
26	25	-27	1
-2	K	2	
0	384	390	4
1	218	-218	2
2	65	61	1
3	256	-256	2
4	103	-100	1
5	77	-75	1
6	39	40	1
7	38	-39	2
8	56	-58	1
9	101	102	1
10	54	-57	1
11	159	161	2
12	17	-15	4
13	96	97	1
14	55	57	1
15	24	-27	3
16	47	47	2
17	152	-152	2
18	112	-112	1
19	71	-72	1
20	71	-71	1
21	29	27	2
22	4	4	8
23	21	20	2
24	12	-16	4
25	36	38	1
-2	K	3	
1	11	-7	4
2	16	12	3
3	47	-49	1
4	41	43	2
5	55	56	1
6	47	48	2
7	177	177	2
8	12	-8	5
9	77	76	1
10	0	-3	13
11	79	-79	1
12	28	-21	2
13	85	-83	1
14	36	-37	2
15	48	-46	2
16	21	24	3
17	69	-69	1
18	10	-1	5
19	33	-31	2
20	19	13	3
21	43	45	1
22	30	36	2
23	31	37	1
24	27	-26	1
-2	K	4	
0	101	102	1
1	6	-11	8
2	113	113	1
3	8	-3	6
4	6	0	7
5	17	1	3
6	83	-82	1
7	0	4	11
8	29	-36	2
9	29	32	2
10	57	-55	1
11	19	19	3
12	8	5	6
13	9	-2	6
14	61	61	1
15	12	3	4
16	12	15	4
17	13	-8	3
18	13	-12	3
19	11	-12	4
20	42	-44	1
21	8	6	4
-2	K	5	
1	52	-49	1
2	72	-70	1
3	16	16	4
4	46	-46	2
5	52	49	1
6	16	-12	3
7	55	54	1
8	32	34	2
9	43	41	1
10	52	57	1
11	15	-13	3
12	50	53	1
13	52	-53	1
14	9	21	7
15	47	-52	1
16	41	-44	1
17	19	-24	2
-2	K	6	
0	5	-7	6
1	13	10	4
2	8	-2	5
3	33	36	2
4	19	19	3
5	45	61	--
6	20	24	2
7	18	25	3
8	0	9	10
9	22	-41	--
10	4	1	6
11	0	-27	--
-1	K	1	
0	1317	1309	14
1	310	-319	3
2	192	201	2
3	331	-337	3
4	328	-327	3
5	102	-99	1
6	28	8	1
7	64	-66	1
8	334	-343	3
9	135	134	1
10	170	-166	2
11	191	190	2
12	30	33	2
13	101	99	1
14	207	204	2
15	15	-19	4
16	198	194	2
17	151	-152	2
18	197	-197	2
19	85	-85	1
20	195	-191	2
21	24	25	3
22	19	-19	3
23	21	19	3
24	54	-51	1
25	41	39	2
26	6	-7	6
27	46	48	1
28	93	93	1
-1	K	2	
1	14	-14	3
2	54	-60	1
3	171	-170	1
4	76	-76	1
5	140	144	1
6	42	-35	1
7	422	427	4
8	47	41	1
9	158	160	1
10	194	193	2
11	141	-142	1
12	18	17	3
13	163	-162	2
14	81	-82	1
15	118	-118	1
16	49	49	2
17	121	-124	1
18	76	-78	1
19	62	-63	1
20	43	-47	2
21	89	88	1
22	74	73	1
23	96	97	1
24	9	-7	5
25	25	-25	2
26	10	9	4
27	41	-41	1
-1	K	3	
0	152	154	1
1	10	9	4
2	228	227	2
3	155	161	1
4	19	16	2
5	117	118	1
6	167	-166	2
7	30	-30	2
8	45	-47	1
9	48	45	1
10	96	-93	1
11	55	-55	1
12	9	10	6
13	104	-105	1
14	106	104	1
15	53	51	1
16	16	14	4
17	52	54	1
18	20	-16	3
19	13	16	5
20	75	-74	1
21	27	27	2
22	71	-70	1
23	12	-16	4
24	21	-19	1
25	35	-38	1
26	5	-1	4
-1	K	4	
1	23	-28	3
2	209	-208	2
3	77	77	1
4	147	-147	1
5	38	35	2
6	58	-59	1
7	14	7	4
8	83	82	1
9	48	44	1
10	168	170	2
11	13	-19	5
12	137	138	1
13	33	-47	--
14	52	52	1
15	29	-33	2
16	109	-106	1
17	41	-37	2
18	107	-110	1
19	9	3	5
20	25	-23	2
21	2	1	8
22	7	5	4
23	17	-20	1
-1	K	5	
0	78	-82	1
1	25	18	2
2	43	-46	2
3	53	52	1
4	42	43	2
5	120	118	1
6	96	96	1
7	63	65	1
8	85	87	1
9	88	-86	1
10	17	18	4
11	46	-46	2
12	74	-78	1
13	25	26	2
14	74	-75	1
15	3	-6	8
16	47	-46	1
17	14	12	3
18	10	-11	3
19	54	50	1
-1	K	6	
1	74	73	1
2	3	-12	10
3	10	13	4
4	6	2	6
5	32	-33	1
6	48	46	1
7	23	-22	2
8	3	1	7
9	39	-34	1
10	13	-14	4
11	22	-27	1
12	49	44	1
13	27	28	1
14	23	24	1
0	K	0	
2	286	282	3
4	484	-481	5
6	23	-28	3
8	598	-598	6
10	230	-225	2
12	57	58	1
14	312	306	3
16	289	287	3
18	238	-239	2
20	268	-264	3
22	43	-36	2
24	73	-72	1
26	15	-12	3
28	130	128	1
0	K	1	
1	196	192	2
2	168	-166	2
3	279	-278	3
4	506	-509	5
5	188	187	2
6	200	-195	2
7	517	521	5
8	134	137	1
9	98	101	1
10	549	533	5
11	137	-134	1
12	140	136	1
13	152	-153	1
14	123	-121	1
15	143	-145	1
16	51	50	1
17	110	-108	1
18	192	-191	2
19	110	-110	1
20	152	-150	2
21	64	62	1
22	94	92	1
23	123	123	1
24	56	52	1
25	41	-39	1
26	51	52	1
27	32	-32	1
28	8	0	4
29	26	23	1
0	K	2	
0	31	33	1
1	13	6	3
2	275	276	3
3	434	440	4
4	57	54	1
5	338	341	3
6	99	-103	1
7	118	-119	1
8	41	38	1
9	93	86	1
10	81	-82	1
11	154	-159	1
12	7	11	5
13	260	-260	2
14	11	8	4
15	124	129	1
16	42	-43	1
17	126	126	1
18	11	-10	4
19	46	50	2
20	67	-69	1
21	56	56	1
22	38	-40	2
23	43	-43	1
24	4	-1	8
25	78	-78	1
26	5	-8	5
27	56	-55	1
28	22	23	1
0	K	3	
1	132	129	1
2	395	-391	4
3	198	196	2
4	168	-168	2
5	64	-64	1
6	99	-99	1
7	180	-180	2
8	114	109	1
9	25	-26	2
10	274	272	3
11	16	-13	3
12	186	186	2
13	24	28	3
14	84	82	1
15	77	77	1
16	140	-140	1
17	27	-25	2
18	169	-169	2
19	34	-31	2
20	30	-24	2
21	52	-55	1
22	2	13	9
23	81	-82	1
24	43	41	1
25	18	20	2
26	46	47	1
0	K	4	
0	223	-221	2
1	29	-25	2
2	118	-117	1
3	35	-31	2
4	68	66	1
5	114	115	1
6	202	199	2
7	109	106	1
8	245	247	2
9	83	-83	1
10	44	46	2
11	10	10	5
12	175	-176	2
13	81	82	1
14	137	-134	1
15	35	-36	2
16	110	-108	1
17	27	-32	2
18	40	-42	2
19	40	35	1
20	104	101	1
21	30	33	2
22	68	69	1
23	31	-28	1
0	K	5	
1	143	136	1
2	54	55	1
3	22	20	3
4	61	63	1
5	80	-80	1
6	119	115	1
7	21	-20	3
8	11	-9	5
9	53	-53	2
10	84	-86	1
11	75	-79	1
12	27	23	2
13	58	57	1
14	24	24	2
15	76	78	1
16	11	1	4
17	13	3	3
18	37	36	1
19	25	-31	2
20	20	24	1
0	K	6	
0	17	-11	3
1	30	-29	2
2	36	-31	1
3	62	-59	1
4	17	-17	3
5	39	-44	1
6	72	65	1
7	16	19	3
8	69	66	1
9	63	66	1
10	9	-11	4
11	67	67	1
12	33	-33	1
13	57	58	1
14	31	-27	1
1	K	0	
1	433	419	4
2	114	-113	1
3	155	-148	1
4	604	-615	6
5	42	41	1
6	282	-279	3
7	188	193	2
8	211	210	2
9	109	-102	1
10	541	531	5
11	43	-40	1
12	194	193	2
13	7	-16	5
14	97	-97	1
15	54	-55	1
16	21	16	3
17	29	-32	2
18	190	-187	2
19	132	-132	1
20	190	-191	2
21	30	-30	2
22	71	70	1
23	67	69	1
24	94	92	1
25	36	-38	2
26	61	60	1
27	7	3	4
28	4	-2	5
1	K	1	
0	181	-173	2
1	39	-39	1
2	89	93	1
3	435	449	4
4	93	91	1
5	331	338	3
6	134	134	1
7	147	-143	1
8	152	149	1
9	145	134	1
10	6	0	5
11	139	-143	1
12	13	-1	3
13	261	-256	2
14	178	-170	2
15	137	137	1
16	119	-119	1
17	114	111	1
18	4	-1	8
19	36	37	2
20	33	-36	2
21	48	51	1
22	37	33	2
23	40	-39	1
24	30	30	2
25	69	-70	1
26	17	-19	2
27	57	-54	1
28	2	2	6
1	K	2	
1	343	346	3
2	389	-397	4
3	224	219	2
4	43	35	1
5	147	-147	1
6	51	-55	1
7	353	-353	3
8	65	67	1
9	127	-129	1
10	214	221	2
11	10	11	5
12	97	102	1
13	96	99	1
14	69	73	1
15	186	186	2
16	82	-88	1
17	8	7	6
18	128	-132	1
19	82	-81	1
20	0	12	12
21	101	-103	1
22	9	18	5
23	118	-119	1
24	12	-3	3
25	18	16	2
26	22	24	2
27	47	47	1
1	K	3	
0	231	-243	2
1	139	-131	1
2	132	-137	1
3	226	-216	2
4	54	52	1
5	10	8	4
6	211	217	2
7	98	98	1
8	334	338	3
9	17	18	4
10	48	46	1
11	166	163	2
12	232	-238	2
13	143	145	1
14	109	-110	1
15	64	-63	1
16	123	-124	1
17	112	-113	1
18	75	-78	1
19	44	-42	2
20	119	116	1
21	30	33	2
22	88	85	1
23	11	-2	4
24	23	22	2
25	2	-2	6
1	K	4	
1	106	107	1
2	154	160	2
3	12	14	5
4	150	151	2
5	92	-94	1
6	179	176	2
7	70	70	1
8	23	-21	3
9	3	0	10
10	159	-158	2
11	148	-151	1
12	43	-39	2
13	40	41	2
14	14	6	4
15	73	73	1
16	42	37	2
17	24	-26	2
18	93	91	1
19	20	-23	3
20	54	54	1
21	12	-3	2
22	33	-32	1
1	K	5	
0	70	70	1
1	30	-30	2
2	19	13	3
3	104	-97	1
4	42	-43	2
5	106	-105	1
6	16	20	3
7	27	26	2
8	25	28	3
9	120	122	1
10	43	-46	2
11	109	107	1
12	20	-19	2
13	90	86	1
14	24	24	2
15	8	-9	5
16	8	10	5
17	69	-69	1
18	16	-20	2
1	K	6	
1	79	-78	1
2	82	82	1
3	48	-48	1
4	83	79	1
5	79	77	1
6	54	52	1
7	90	90	1
8	7	7	4
9	42	44	1
10	45	-43	1
11	8	0	3
2	K	0	
0	134	-140	1
1	39	-38	1
2	58	-61	1
3	150	150	1
4	88	87	1
5	99	96	1
6	183	182	2
7	64	-64	1
8	130	129	1
9	130	122	1
10	54	50	1
11	20	-20	3
12	27	-25	2
13	102	-101	1
14	190	-186	2
15	70	68	1
16	122	-124	1
17	32	29	2
18	9	-3	5
19	11	-7	4
20	15	-14	4
21	13	12	4
22	57	57	1
23	11	-9	4
24	37	40	1
25	22	-21	2
26	16	-18	2
2	K	1	
1	307	314	3
2	149	-145	1
3	97	98	1
4	175	181	2
5	102	-100	1
6	54	53	1
7	266	-265	2
8	16	-7	3
9	128	-129	1
10	65	64	1
11	26	24	3
12	20	-20	3
13	78	80	1
14	29	29	2
15	158	157	2
16	7	-5	7
17	25	20	2
18	30	-33	2
19	96	-95	1
20	44	46	1
21	85	-86	1
22	16	10	3
23	81	-81	1
24	39	-40	1
25	0	4	9
26	12	-14	2
2	K	2	
0	52	-61	1
1	168	-166	2
2	48	-49	1
3	289	-289	3
4	12	-8	4
5	89	-90	1
6	109	109	1
7	46	46	1
8	219	219	2
9	119	121	1
10	11	0	5
11	248	250	2
12	168	-171	2
13	132	137	1
14	22	-17	3
15	62	-59	1
16	52	-53	1
17	136	-140	1
18	82	-84	1
19	103	-102	1
20	57	57	1
21	17	19	3
22	54	51	1
23	25	21	2
24	10	7	3
25	23	26	1
2	K	3	
1	17	-11	3
2	164	170	2
3	8	-8	6
4	159	160	2
5	49	-46	1
6	137	140	1
7	182	185	2
8	2	-8	11
9	85	86	1
10	115	-116	1
11	169	-171	2
12	74	-71	1
13	22	-20	3
14	7	-10	6
15	14	9	4
16	56	54	1
17	58	-63	1
18	88	85	1
19	9	0	5
20	50	50	1
21	43	44	1
22	30	-25	1
23	29	32	1
2	K	4	
0	139	140	1
1	0	0	12
2	76	74	1
3	53	-49	1
4	51	-52	1
5	93	-93	1
6	58	-55	1
7	27	28	2
8	34	-33	2
9	120	120	1
10	71	-73	1
11	72	72	1
12	0	2	5
13	61	62	1
14	85	84	1
15	8	0	5
16	50	47	1
17	46	-46	1
18	21	-19	2
19	30	-31	1
2	K	5	
1	120	-118	1
2	43	44	1
3	58	-59	1
4	0	3	11
5	105	103	1
6	24	24	2
7	124	124	1
8	39	39	1
9	69	69	1
10	4	3	6
11	5	0	6
12	17	17	2
13	98	-98	1
14	9	10	3
2	K	6	
0	54	56	1
1	35	36	1
2	26	28	1
3	K	0	
1	150	141	2
2	13	13	5
3	18	11	4
4	137	134	1
5	32	-25	2
6	63	65	1
7	92	-88	1
8	17	-15	4
9	54	-53	2
10	14	-16	4
11	13	13	4
12	48	-48	2
13	25	19	3
14	11	0	4
15	66	62	1
16	19	23	3
17	10	1	4
18	20	21	3
19	61	-63	1
20	33	35	2
21	34	-34	1
22	0	0	9
23	24	-25	1
3	K	1	
0	80	81	1
1	89	-91	1
2	30	31	2
3	175	-175	2
4	38	-39	2
5	89	-84	1
6	14	3	4
7	13	18	5
8	56	50	1
9	118	114	1
10	31	-33	2
11	180	178	2
12	65	-59	1
13	71	72	1
14	39	43	2
15	38	-37	2
16	10	13	5
17	86	-85	1
18	55	-56	1
19	83	-81	1
20	8	-6	4
21	12	4	3
22	8	8	3
3	K	2	
1	70	-72	1
2	79	77	1
3	25	-26	3
4	76	75	1
5	9	9	6
6	47	43	2
7	185	185	2
8	30	22	2
9	101	98	1
10	19	-8	3
11	115	-113	1
12	41	-36	2
13	56	-54	1
14	15	-11	4
15	32	-35	2
16	36	32	2
17	56	-60	1
18	33	29	1
19	10	8	4
20	14	14	3
21	51	57	1
3	K	3	
0	116	117	1
1	26	27	3
2	73	71	1
3	28	31	2
4	30	-34	2
5	26	-22	2
6	68	-66	1
7	21	21	3
8	48	-45	1
9	71	68	1
10	55	-57	1
11	14	7	4
12	4	4	7
13	9	8	5
14	79	80	1
15	15	12	3
16	47	45	1
17	0	0	9
18	10	-13	3
3	K	4	
1	86	-84	1
2	8	-7	6
3	35	-37	2
4	61	-63	1
5	73	70	1
6	13	-7	4
7	85	83	1
8	54	55	1
9	50	51	1
10	44	80	1
11	8	-3	4
12	55	57	1
13	68	-68	1
14	16	15	2
3	K	5	
0	9	1	5
1	43	46	1
2	7	-5	4
3	85	87	1
4	3	-3	6
4	K	0	
0	78	82	1
1	27	-19	3
2	34	37	2
3	57	-55	2
4	22	-25	3
5	43	-35	2
6	20	-26	3
7	13	12	4
8	18	-13	3
9	62	54	1
10	25	-26	3
11	77	71	1
12	11	-6	4
13	19	18	3
14	36	41	2
15	16	-14	2
16	15	21	3
17	22	-24	2
4	K	1	
1	49	-45	2
2	19	8	3
3	17	-18	4
4	1	0	10
5	21	16	3
6	12	-7	5
7	99	97	1
8	26	31	3
9	52	50	1
10	43	43	1
11	48	-47	1
12	4	2	7
13	36	-34	1
14	9	-4	4
15	30	-28	1
16	8	5	4
4	K	2	
0	47	47	1
1	28	26	2
2	30	26	2
3	47	50	1
4	11	-11	5
5	11	14	4
6	27	-24	2
7	16	12	3
8	21	-16	2
9	26	27	2
10	23	-22	2
11	18	-17	2
12	3	-4	6
13	12	-15	3
4	K	3	
1	26	-24	2
2	21	-20	2
3	11	-11	4
4	57	-57	1
5	23	21	2
6	11	-12	3
7	26	23	1
8	37	40	1

of three standard reflections ($0,\overline{10},\overline{1}$, 172, and $1\overline{23}$) were monitored every 45 reflections throughout the ten days of data collection. Variances, $\sigma^2(I)$, were obtained from counting statistics with an additional term, $(0{\cdot}02\ C)^2$, where C is the scan count. F^2 and $\sigma(F^2)$ were calculated in the usual fashion.

Because a previous data collection (Einspahr, 1970) had revealed a rather serious drop in scattering power with time, care was taken to record the time at regular intervals during collection of this data set. In this way, it was possible to assign to each datum a cumulative crystal-to-beam exposure time, good to within a quarter of a hour. Gaps during which the beam was shut off produced no perceptible decay.

Examination of the standard reflections showed that each had undergone a linear decay with time; however, rates of decay for these reflections were quite different. Over a 200 h period during which the crystal was exposed to the beam, the F values of $0,\overline{10},\overline{1}$, 172, and $1\overline{23}$ dropped to 95, 93, and 82% of initial values, respectively. A comparison of the two intensity-equivalent quadrants revealed a significant increase in percent decay at high angle. In addition, there were indications that this phenomenon was not spherically symmetric. A plot of F ratios of intensity-equivalent pairs averaged over the Miller index, k, on a grid in h and l suggested that the rate of increase in percent decay with angle was most severe in the reciprocal lattice plane $h=-l$. It is presumably this latter phenomenon which accounts for the difference in decay rates among the standards as the 2θ-values of the standards are all between 40 and 50°.

The two quadrants were collected such that some 1000 intensity-equivalent pairs were separated by the same difference in cumulative exposure time. This subset of pairs was used as the basis of a least-squares fit of a two parameter equation, $F_k=F_{\bar{k}}\exp(A+B\sin^2\theta/\lambda^2)$. The function minimized was $\sum w[ln(F_{\bar{k}}/F_k)+A+B\sin^2\theta/\lambda^2]^2$ where $w=[(1/4F_k^4)\sigma^2(F_k^2)+(1/4F_{\bar{k}}{}^4)\sigma^2(F_{\bar{k}}{}^2)]^{-1}$. About 350 pairs for which one of the measured F's was missing or for which the ratio, $F_{\bar{k}}/F_k$, was less than 0·5 or greater than 1·5 were excluded, effectively removing the very weak or unobserved reflections. For an average difference in exposure time of 96·0 h, this calculation yielded values of A and B of 0·039 (3) and 0·27 (2) Å^2, respectively, corresponding to corrections of from 4% at low angle to 10% at high angle.

A correction, $F_{\text{corr}}=F\exp[A'+B'\sin^2\theta/\lambda^2]t$, where $A'=A/96{\cdot}0\ \text{h}^{-1}$, $B'=B/96{\cdot}0\ \text{Å}^2\ \text{h}^{-1}$, and t is the cumulative exposure time in hours, was now applied to each datum. A corresponding correction was applied to the $\sigma(F^2)$. The data collected at reduced beam intensity were scaled up to full beam and corrected F values and weights, $1/\sigma^2(F^2)$, for intensity-equivalent reflections were averaged. A total of 1042 independent data were obtained in this manner.

A plot of corrected F values of the standard reflections *versus* time revealed, as expected, that the two-parameter fit had not accounted for the abberant variation in decay rates. On the other hand, this correction appears to have centered the variation in decay rates about zero. After a 200 h exposure period, F values of the standards (reported in the same order as previously) were 107, 105, and 93% of original values. While sufficient data exist to permit expanding the number of parameters in the model, there is no clear indication of the form this expansion should take. No further work along this line is contemplated.

Structure determination and refinement

The solution of this structure has been described elsewhere (Einspahr, 1970). Briefly, the chlorine y and z coordinates were obtained from a Patterson projection, Pvw, constructed from photographic data. A fourfold superposition on the chlorine position revealed the projected positions of the other nonhydrogen atoms. The model was completed by solving graphically for the x parameters assuming an ideal planar molecule.

A refined version of this model was used as a starting model for full-matrix least-squares refinement with the scan data described above. This refinement minimized the function $\sum w(F_o{}^2-1/k^2F_c{}^2)^2$ where $w=1/\sigma^2(F_o{}^2)$. After six cycles of isotropic and two cycles of anisotropic refinement of the nonhydrogen atom parameters, a general plane difference electron-density map revealed the positions of the methyl hydrogens. The position of the fourth hydrogen was calculated. Subsequent refine-

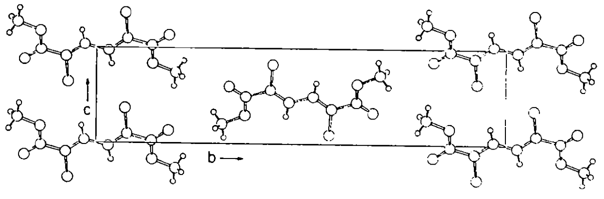


Fig. 2. A representation of the unit cell viewed along **a***.

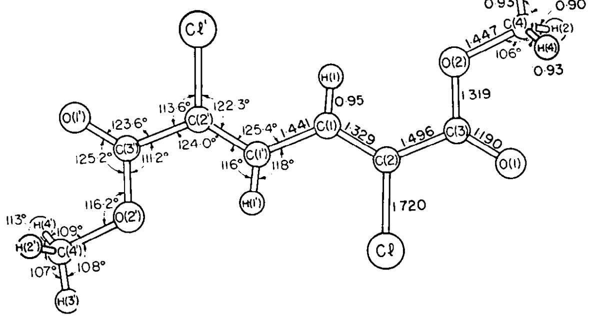


Fig. 3. Bond distances (Å) and angles (°). Primed atoms occupy equivalent positions ($\bar{x},\bar{y},\bar{z}$). E.s.d.'s for distances and angles not involving H atoms are 0·005 Å and 0·2°, respectively; those involving H atoms are 0·04 Å and 2°.

ment, which ultimately included as parameters the positions and anisotropic temperature factors for the hydrogen atoms as well as a secondary extinction coefficient (Equation 3, Larson, 1967), converged in seven cycles. Form factors for Cl, C, and O were taken from *International Tables for X-ray Crystallography* (1962). The form factor for H was that of Stewart, Davidson & Simpson (1965). The final value of the R index $\sum||F_o|-|F_c||/\sum|F_o|$, is 0·041; the goodness of fit is 1·45. Final values of the parameters are listed in Table 3. Table 4 contains values of the observed and calculated structure factors for each reflection. While the final value of the β_{22} parameter for H(1) is negative by about one-third of its standard deviation, this is not considered a significant departure from a physically realistic model.

A final difference-electron-density map produced no peaks or troughs with magnitudes greater than 0·15 e Å^{-3}. A section of this map through the mean plane of the molecule showed that the six largest peaks (0·10–0·15 e Å^{-3}) occurred at positions near the midpoints of bonds between nonhydrogen atoms, the only bond lacking a peak being the carbonyl bond C(3)–O(1). The standard deviation of electron density is estimated to be 0·1 e Å^{-3}.

Results and discussion

The results of a molecular best plane calculation, shown in Table 5, indicate that the molecule is roughly planar despite significant deviations on the part of the oxygen and chlorine atoms. The normal to this plane makes an angle of 5° with the normal to $(\bar{1}01)$, the direction cosines of which are (−0·8477,0,0·6134) to the monoclinic axes. As $(\bar{1}01)$ contains the center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, it is clear that the crystal is composed of layers parallel to $(\bar{1}01)$ approximately one carbon atom thick. The separation between layers is 3·5 Å.

Table 5. *Deviations* (Å) *from the mean plane of the molecule*

Direction cosines of the plane normal are −0·8892, −0·0566, and 0·5415 to the *a*, *b*, and *c* axes, respectively. The plane passes throught the origin.

Cl	0·05	C(1)	0·00
O(1)	−0·08	C(2)	0·02
O(2)	0·07	C(3)	0·00
H(1)	−0·02	C(4)	0·00

There are no unusually close contacts between atoms in adjacent molecules. The closest approach separates molecules within the same layer. As seen in Fig. 2, the molecules pack such that a carbonyl bond of the origin molecule is directed toward a methyl group of the molecule centered at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The distance O(1)···C(4) in this case is 3·106 Å, although the shortest O···H distance is 2·78 Å. Each molecule makes four such contacts, one with each of its four nearest neighbors within the layer.

The layered nature of this crystal structure permits a rationalization of its tendency toward irreversible amorphic deformation when subjected to stress. The absence of all save van der Waals forces between layers suggests that slippage of layers over one another might be induced by application of mechanical stress.

The bond distances and angles are shown in Fig. 3. E.s.d.'s for distances and angles not involving hydrogen atoms are 0·005 Å and 0·2°, respectively; those involving hydrogen atoms are 0·04 Å and 2°. All of these distances and angles are within the ranges of values reported in the literature. Comparison of these results with those of the parent compound, dimethyl *trans*, *trans*-muconate (Filippakis *et al.*, 1967), shown in part in Table 6, reveal some of the effects of substitution of the bulky chlorine in the α position. The most noticeable effect is the expansion of angles C(1′)–C(1)–C(2) and C(1)–C(2)–C(3). While the C(2)–C(3) bond appears to have lengthened to accomodate the chlorine, the increase of 0·02 Å is of questionable significance.

Table 6. *Bond distances and angles for dimethyl trans, trans-muconate* (*Filippakis et al.*, 1967)

Primed atoms occupy the equivalent position $(\bar{x},\bar{y},\bar{z})$. The values listed are those before temperature corrections were applied. E.s.d.'s for distances and angles are quoted as 0·002 Å and 0·15°, respectively.

Distances		Angles	
C(1)–C(1′)	1·450 Å	C(1′)–C(1)–C(2)	123·1°
C(1)–C(2)	1·334	C(1) –C(2)–C(3)	120·9
C(2)–C(3)	1·476	C(2) –C(3)–O(1)	125·7
C(3)–O(1)	1·203	C(2) –C(3)–O(2)	111·0
C(3)–O(2)	1·338	O(1) –C(3)–O(2)	123·3
O(2)–C(4)	1·445	C(3) –O(2)–C(4)	115·6

The greatest effect of the addition of chlorine is to invert the conformation about C(2)–C(3) to antiplanar. As indicated in the introduction, this result had been anticipated. It remains, however, to determine whether addition of the chlorine forced the antiplanar conformer or whether nonbonded interactions are, as assumed, ambivalent. The pertinent nonbonded distances observed in the antiplanar conformer are Cl···O(1) of 2·904 Å, C(1)···O(2) of 2·722 Å, and H(1)···O(2) of 2·36 Å. For a hypothetical synplanar conformer with the same bond distances and angles, the pertinent distances would be Cl···O(2) of 2·685 Å, C(1)···O(1) of 2·900 Å, and H(1)···O(1) of 2·60 Å. While the Cl···O contact is 0·22 Å longer in the antiplanar conformation, the C···O and H···O contacts are 0·18 and 0·24 Å, respectively, shorter. The predicted van der Waals contacts are Cl···O of 3·2 Å, C···O of 3·1 Å, and H···O of 2·6 Å. [The value for the C···O contact was suggested by Dunitz & Strickler (1968).] Thus, while the Cl···O, C···O, and H···O contacts are 0·3, 0·4, and 0·2 Å, respectively, shorter than predicted for the antiplanar conformer, they are 0·5, 0·2, and 0·0 Å, respectively, shorter in the synplanar conformer. Although it may be argued that the Cl contact is the most important of these, it would be difficult to accept the hypothesis that this contact was the determining factor in fixing the conformation unless one were willing to accept the possibility of an attractive force between H(1) and O(2). This is hardly likely. While the valence angles for H(1) suggest (without statistical significance) that H(1) is leaning toward O(2), H(1) also makes contact with Cl′ across the center of symmetry at a distance of 2·72 Å, suggesting that H(1) is being pushed, not attracted, toward O(2). Dipole–dipole interactions resulting from the introduction of chlorine favor the synplanar conformer and do not complicate the analysis. It is suggested that this is another case in which nonbonded-interaction arguments are ambivalent and the conformation about the carboxyl carbon–carbon bond is antiplanar.

Fig. 4 is a stereo representation of the chloromuconate molecule. Thermal ellipsoids are drawn at the 50% probability level. For H(1), an isotropic temperature factor of 3·0 Å^2 has been substituted.

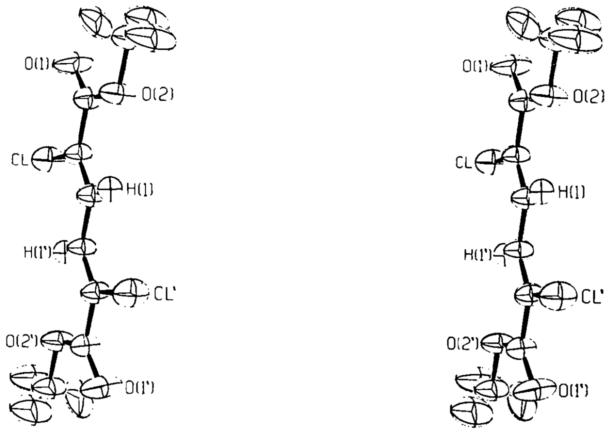


Fig. 4. A stereo representation of the molecule displaying the thermal ellipsoids.

We thank Dr R. E. Marsh for helpful discussions and interesting suggestions and Dr Sten Samson for assistance with data collection. This work was supported in part by the National Science Foundation and the Advanced Research Projects Agency of the Office of the Secretary of Defense and by the National Institutes of Health, Public Health Service, through Grant GM 16966.

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