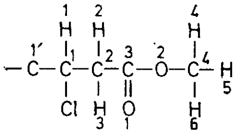
Conformational Studies. Part V.† The Crystal and Molecular Structures of Dimethyl *meso*-ββ'-Dichloroadipate

By **Hershel W. Kaufman, Dov Rabinovich,*** and (the late) **Gerhard M. J. Schmidt,** Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel

The crystal and molecular structures of the title compound have been solved from three-dimensional photographic data by Patterson techniques and refined by least-squares methods to R 0·060 for 837 observed reflections. The centrosymmetric molecule results in a conformation in which the two chlorine atoms are maximally separated; the halogen is gauche along the C_α–C_β bond in the methoxycarbonyl group. Crystals are monoclinic, a = 8·300(4), b = 5·626(2), c = 12·616(5) Å, β = 91·29(8)°, Z = 2, space group $P2/n$.

In the preceding paper [1] we discuss the reaction of solid dimethyl *meso*-ββ'-dichloro- and dibromo-adipates with gaseous amines. In order to ascertain that we were dealing with a solid-state reaction subject to the topochemical principle of minimum atomic and molecular motion, and that the course of the reaction was controlled by the conformation of the dihalogenoester in the solid state, the structure analysis of (I) was undertaken.



$$-\mathrm{C}-\mathrm{CH(Cl)}-\mathrm{CH_2}-\mathrm{C({=}O)}-\mathrm{O}-\mathrm{CH_3}$$

Dimethyl *meso*-ββ'-dichloroadipate, showing the atom numbering used in the analysis (only the asymmetric part of the molecule is shown)

EXPERIMENTAL

Cell constants were obtained by means of a least-squares procedure form 21 high-order reflections (2θ > 40°) measured on a Siemens diffractometer (Mo-$K_{\alpha1}$, and -$K_{\alpha2}$). Crystals, m.p. 120·6 °C (from ethanol), were needles elongated along [010] showing {001} and {101}.

Crystal Data.—$C_8H_{12}Cl_2O_4$, M = 243·1, a = 8·300(4), b = 5·626(2), c = 12·616(5) Å, β = 91·29(8)°, U = 589·0 Å^3, D_m = 1·36, Z = 2, D_c = 1·37, $F(000)$ = 252. Space group $P2/n$ or Pn from systematic absences: $h0l$ for $h + l$ odd; the former established as correct by the present analysis; molecular symmetry 2 or $\bar{1}$ in $P2/n$, the latter established by the analysis. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 5·16.

Partial three-dimensional data were collected from a needle 2·0 × 0·30 × 0·56 mm mounted about [010] along the dial axis of a Buerger precession camera (Zr-filtered Mo-K_α radiation) by the technique described elsewhere.[2] The levels recorded were: $hk0$—6, 0—4kl, and $hk[n-h]$ (n = 0—3). Intensities of symmetry-related reflections on each level were averaged, yielding a value for R_{sym} [$= \Sigma(\bar{I}-I_i)/\Sigma I_i$] of 0·06. The $I(hkl)$ on the various levels were brought to a common scale after the application of the Lorentz-polarisation correction. Absorption was not allowed for. 1807 Independent reflections were recorded, of which 970 were unobserved. Treatment of the unobserved reflections and assignment of weights $w(hkl)$ followed published procedures.[2,3]

A three-dimensional sharpened Patterson synthesis was computed, the interpretation of which by means of a molecular model of the *meso*-compound centred at (000) yielded trial co-ordinates of all atoms except hydrogen. Least-squares refinement, at first with isotropic temperature factors, led to R 0·26. Next, hydrogen atoms were inserted in chemically reasonable positions; the methyl group was oriented such that two hydrogens straddled the carbonyl oxygen of the ester group. Refinement was continued with anisotropic temperature factors of all but the hydrogen to R 0·060 and R' [$= \Sigma w(k^2F_o^2 - |F_c|^2)^2/\Sigma wk^4F_o^4$] 0·017. The methyl hydrogen atoms were relocated by a $\Delta\rho(xyz)$. Structure factors are listed in Supplementary Publication No. SUP 20899(20 pp., 1 microfiche).‡

Positional and thermal parameters together with their estimated standard deviations are in Tables 1 and 2. Standard deviations of all parameters were estimated from the usual formula with n (= 958) the number of reflections included in the last refinement cycle and s (= 88) the number of parameters adjusted. The scattering-factor curves used

Table 1

Atomic co-ordinates (Å × 10^4), with standard deviation in parentheses

Atom	x	y	z
Cl	14379(11)	5505(10)	15416(11)
C(1)	5019(29)	5767(23)	−239(31)
C(2)	14786(39)	4644(28)	−11378(42)
C(3)	23001(30)	17213(24)	−12958(36)
C(4)	42997(57)	25839(54)	−21768(74)
O(1)	19758(26)	27978(18)	−9488(35)
O(2)	34217(24)	14538(20)	−19139(29)
H(1)*	107(25)	1388(22)	−20(29)
H(2)	955(46)	440(36)	−1963(55)
H(3)	2096(36)	−278(30)	−1019(39)
H(4)	5021(68)	2213(46)	−2524(73)
H(5)	3791(46)	3197(40)	−2749(49)
H(6)	4070(60)	3317(47)	−1541(65)

* Hydrogen parameters × 10^3.

---

† Part IV, J. Bernstein and G. M. J. Schmidt, *J.C.S. Perkin II*, 1972, 951.

‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[1] G. Friedman, M. Lahav, and G. M. J. Schmidt, preceding paper.

[2] D. Rabinovich, *J. Chem. Soc.* (*A*), 1969, 2361.

[3] D. Rabinovich and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2030.

were from ref. 4 for chlorine, ref. 5 for carbon and oxygen, and ref. 6 for hydrogen.

TABLE 2

Observed thermal parameters † U_{ij} with standard deviations in parentheses (Å^2 × 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cl	781(7)	1040(8)	515(5)	−402(5)	35(5)	−134(6)
C(1)	514(16)	334(10)	438(17)	−64(11)	−47(13)	26(16)
C(2)	631(20)	381(11)	553(19)	−115(14)	−21(16)	183(20)
C(3)	542(17)	418(12)	496(19)	−102(12)	−8(13)	90(16)
C(4)	723(31)	870(29)	1221(52)	−343(25)	−20(34)	297(34)
O(1)	865(18)	370(8)	1197(27)	−118(11)	−34(14)	411(18)
O(2)	559(13)	649(17)	887(22)	−203(10)	−69(14)	262(13)

Atom	U^2	Atom	U^2
H(1)*	6(6)	H(4)	96(21)
H(2)	53(13)	H(5)	47(13)
H(3)	28(8)	H(6)	82(18)

* Hydrogen parameters ×10^3. † In the form: isotropic, $\exp(-8\pi^2U^2\sin^2\theta/\lambda^2)$; anisotropic, $\exp(-2\pi^2\Sigma h_ia^*_ih_ja^*_jU_{ij})$.

RESULTS AND DISCUSSION

Bond Lengths and Angles.—Table 3 gives the experimental bond lengths and angles. The mean σ for bond lengths and angles between heavier atoms is 0·004 Å and 0·26°; the corresponding values where one hydrogen is involved are 0·05 Å and 2·3°.

TABLE 3

Bond lengths and angles, with estimated standard deviations in parentheses

(*a*) Distances (Å)

C(1)–Cl	1·806(3)	C(1)–H(1)	0·90(2)
C(1)–C(1′)	1·531(5)	C(2)–H(2)	0·95(5)
C(1)–C(2)	1·502(5)	C(2)–H(3)	0·97(3)
C(2)–C(3)	1·512(4)	C(4)–H(4)	0·89(7)
C(3)–O(1)	1·179(3)	C(4)–H(5)	0·97(5)
C(3)–O(2)	1·320(4)	C(4)–H(6)	1·00(6)
O(2)–C(4)	1·459(6)		

(*b*) Angles (deg.)

C(1′)–C(1)–Cl	106·8(2)	H(2)–C(2)–C(1)	109(3)
C(1′)–C(1)–C(2)	113·9(2)	H(2)–C(2)–C(3)	101(2)
Cl–C(1)–C(2)	108·0(2)	H(2)–C(2)–H(3)	113(3)
C(1)–C(2)–C(3)	112·3(3)	H(3)–C(2)–C(1)	113(2)
C(2)–C(3)–O(1)	125·1(3)	H(3)–C(2)–C(3)	108(2)
C(2)–C(3)–O(2)	110·5(2)	H(4)–C(4)–O(2)	104(3)
O(1)–C(3)–O(2)	124·2(3)	H(4)–C(4)–H(5)	117(5)
C(3)–O(2)–C(4)	116·7(3)	H(4)–C(4)–H(6)	139(5)
		H(5)–C(4)–O(2)	107(3)
H(1)–C(1)–Cl	103(2)	H(5)–C(4)–H(6)	78(4)
H(1)–C(1)–C(1′)	113(2)	H(6)–C(4)–O(2)	108(3)
H(1)–C(1)–C(2)	111(2)		

The central bond C(1)–C(1′) is significantly longer than the corresponding bond in adipic and suberic acids (1·531, 1·507, and 1·503 Å); it is however similar to the central bonds in the higher homologues, *i.e.* sebacic and dodecanedioic acids [7] (1·535 and 1·523 Å). It seems unlikely that the chlorine substitution is responsible for the larger central bond in (I) since in two related compounds, dichloro- and dibromo-cyanobutane the C_β–$C_{\beta'}$ bond is again shorter (*ca.* 1·50 Å).[8]

The C(1)–C(2) bond is shorter than the corresponding bond in saturated dicarboxylic acids with even number of carbon atoms where a mean value of 1·524 Å may safely be quoted.[7] Similarly, the C(2)–C(3) bond (sp^2–sp^3 bond) differs from the mean of 1·500 reported in ref. 7. The C–C–C angles seem to be in agreement with the observed tetrahedral angles in other compounds.

The C–Cl bond length (1·806 Å) seems a little long when compared with observed values in paraffinic compounds (ethyl chloride, 1·788, methyl chloride, 1·781 Å).[9] However, it compares favourably with C–Cl bond lengths in aliphatic ring compounds such as 2β,3α-dichloro-5α-cholestane (1·80 and 1·82 Å),[10] *trans*-2,3-dichloro-1,4-dithian (1·80 and 1·81 Å),[11] and *trans*-2,3-dichloro-1,4-thioxan (1·810 and 1·842 Å).[12]

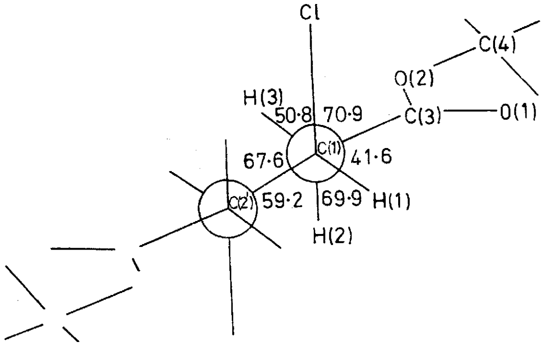


FIGURE 1 Newman projection

Bond lengths in the methoxycarbonyl group differ somewhat from those reported for the dimethyl *trans*,-*trans*-muconate [13] and methyl formate.[14] Both the C(3)–O(1) and C(3)–O(2) bond lengths in (I) (1·179 and 1·320 Å) are shorter than the corresponding bonds in the dimethyl muconate (1·218 and 1·347) and in methyl formate (1·200 and 1·334 Å); the O(2)–C(4) distance in (I) (1·459) agrees better with the value for dimethyl muconate but differs again by *ca.* 4σ from that in methyl formate (1·437 Å). It is doubtful whether the thermal libration correction which could not be applied since the molecule does not behave as a rigid body, can account for such differences. The bond angles around C(3) seem to agree better, their values being roughly the mean of those observed in refs. 13 and 14.

Molecular Conformation.—Figure 1 shows the molecule

---

[4] B. Dawson, *Acta Cryst.*, 1960, **13**, 403.

[5] J. Berghuis, I. J. M. Haanappel, M. Potters, B. O. Loopstra, MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[6] R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.

[7] J. Housty and M. Hospital, *Acta Cryst.*, 1966, **21**, 553.

[8] D. Rabinovich and Z. Shaked, to be published.

[9] R. H. Schwendeman and G. P. Jacobs, *J. Chem. Phys.*, 1962, **36**, 1245.

[10] H. J. Geise, C. Romers, and E. W. M. Rutten, *Acta Cryst.*, 1966, **20**, 249.

[11] H. T. Kalf and C. Romers, *Acta Cryst.*, 1965, **18**, 164.

[12] N. de Wolf, C. Romers, and C. Altona, *Acta Cryst.*, 1967, **22**, 715.

[13] S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1967, 290.

[14] R. F. Curl, *J. Chem. Phys.*, 1959, **30**, 1529.

projected down the C(1)–C(2) bond; it is evident from this scaled Newman projection that the molecules adopt at C(1) and C(2) an almost ideal staggered conformation which is energetically more stable. The somewhat larger twist angle [Cl C(3)] of 70·9° may be attributed to the greater repulsion between Cl · · · C(3) as compared with Cl · · · H(3). The C(2)–H(2) bond is very nearly anti periplanar to the C(1)–Cl bond, the angle between their projected vectors being 182·4° (70·9 + 41·6 + 69·9°). This result is thus in satisfactory agreement with the chemical evidence according to which the double elimination of HCl in the solid state goes with >96% yield to *trans,trans*-muconate. The steric requirements for β-elimination (antiperiplanar conformation of proton and halogen) are fulfilled, and the conformational change in the passage from (I) to the reaction product is minimal.

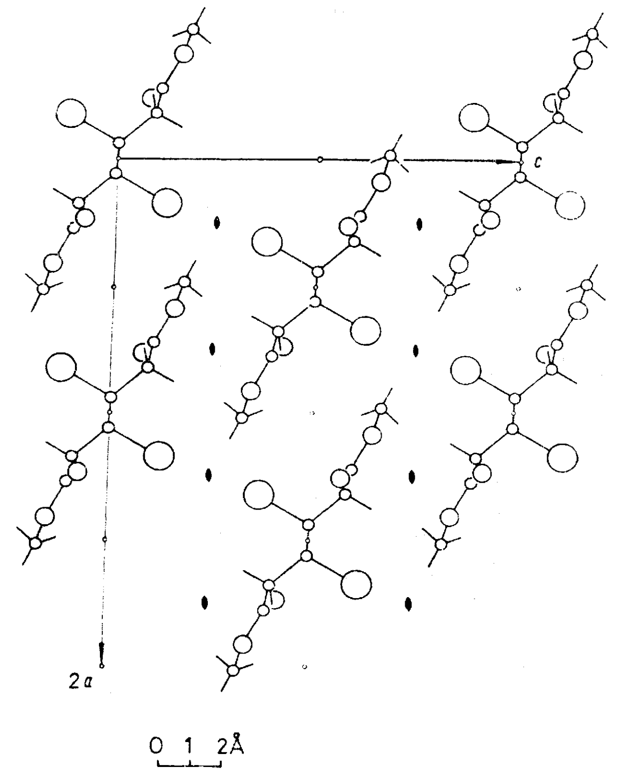


FIGURE 2 Packing arrangement seen along [010]

The C·CO$_2$Me group in (I) is nearly planar, in good agreement with results in refs. 13 and 14. Deviations of atoms from this plane, of equation (fractional coordinates) $3{\cdot}668x - 0{\cdot}904y + 11{\cdot}006z + 0{\cdot}4085 = 0$, are: C(2) −0·11, C(3) 0·12, C(4) −0·11, O(1) −0·001, and O(2) 0·012 Å.

The twist of the C(1)–C(2) bond, computed from the dihedral angle between the best planes through C(1)—(3) and the planar C·CO$_2$Me group is 22·5°.

Packing Arrangement.—Figure 2 shows the molecular packing arrangement seen along [010]; short intermolecular contacts are listed in Table 4. Viewed along [010], the molecules pack with their long axis parallel to the [$\bar{3}$01] direction, the structure being held together by short Cl · · · Cl and H(4) · · · H(4) contacts across the twofold axes. In the [010] direction the structure is locked together mainly by short C:O · · · H contacts.

TABLE 4

Short intermolecular distances (Å)

O(1) · · · H(3$^{\text{I}}$)	2·56	O(2) · · · H(2$^{\text{IV}}$)	2·64
O(1) · · · H(1$^{\text{II}}$)	2·73	H(4) · · · H(4$^{\text{V}}$)	2·74
Cl · · · Cl$^{\text{III}}$	3·44		

Roman numeral subscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $x, 1 + y, z$
II $x, 1 - y, z$
III $\frac{1}{2} - x, y, \frac{1}{2} - z$
IV $\frac{1}{2} - x, y, -\frac{1}{2} - z$
V $\frac{3}{2} - x, y, -\frac{1}{2} - z$

The Cl · · · Cl contact of 3·44 Å is shorter than the usually quoted van der Waals sum of radii of 3·6 Å. This phenomenon was noted by Sakurai *et al.*[15] and compared with other compounds in which this short contact occurs. The angles of 170° between C–Cl and Cl · · · Cl in (I) satisfy nicely one of the possible angles cited in ref. 15.

The geometry of the C:O · · · H·C contacts in (I) resembles generally, though not in details, that of similar contacts observed previously.[16,17]

We thank the National Research Council of Canada for a postdoctoral Fellowship (to H. W. K.).

[3/1074 *Received*, 24*th May*, 1973]

---

[15] T. Sakurai, M. Sundaralingam, and G. A. Jefferey, *Acta Cryst.*, 1963, **16**, 354.

[16] D. J. Sutor, *J. Chem. Soc.*, 1963, 1105.

[17] D. Rabinovich, G. M. J. Schmidt, and Z. Shaked, *J. Chem. Soc.* (*B*), 1970, 17.