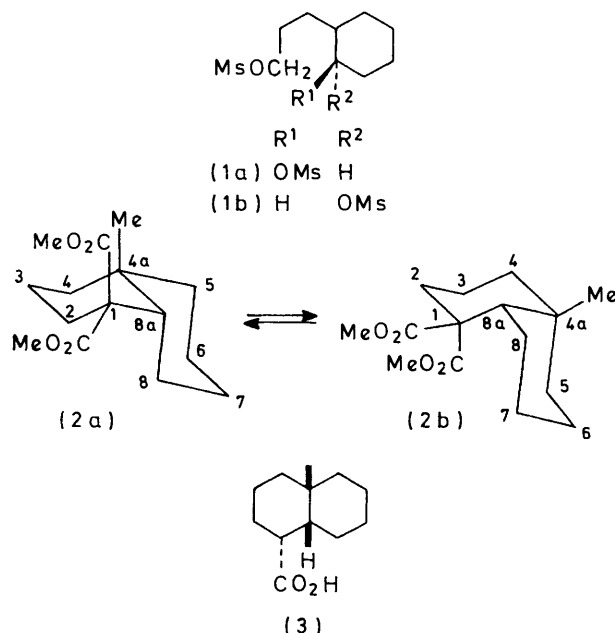


Crystal and Molecular Structure of *cis*-1,1-Bismethoxycarbonyl-4a-methyldecahydronaphthalene

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Single-crystal X-ray analysis of the title compound has established its molecular dimensions and preferred conformation. Crystals are monoclinic, space group $P2_1/c$, $a = 11.52(2)$, $b = 7.68(1)$, $c = 20.10(3)$ Å, $\beta = 125.58(20)^\circ$, $Z = 4$. The structure was solved by direct phase-determining methods and refined by full-matrix least-squares calculations to $R = 0.103$ over 2156 independent reflections. The presence of 1,3-diaxial interactions leads to significant deviations in bond lengths and valency angles from their normal values. The C=O ester groups are approximately in a *syn*-planar orientation with respect to the C(α)-C(β) bonds.

KRÖNIGER and WHEELER¹ reported recently that the reaction of a mixture of the epimeric dimesylates, (1a) and (1b), with malonic ester in the presence of base gave the compound (2a). The structure and stereochemistry [including the conformation (2a) as opposed to (2b)] was suggested on the basis of mechanistic considerations and spectroscopic (particularly n.m.r.) data. However the monocarboxylic acid (3) obtained from (2a) had m.p. close to that of a known 9-methyldecalin-carboxylic acid for which a *trans*-ring-junction had been suggested.²



None of this latter material was available as a sample. We therefore examined compound (2a) by X-ray crystallography to determine definitely its structure and stereochemistry.

EXPERIMENTAL

Crystal Data.— $\text{C}_{15}\text{H}_{24}\text{O}_4$, m.p. 91° , $M = 268.4$. Monoclinic, $a = 11.52(2)$, $b = 7.68(1)$, $c = 20.10(3)$ Å, $\beta = 125.58(20)^\circ$, $U = 1440$ Å³, $D_m = 1.23$, $Z = 4$, $D_c = 1.238$,

¹ A. Kröniger and D. M. S. Wheeler, *Tetrahedron*, 1972, **28**, 255.

² N. S. Basu, U. R. Ghatak, G. Sengupta, and P. C. Dutta, *Tetrahedron*, 1965, **21**, 2641.

³ J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

⁴ J. Karle and H. Hauptmann, *Acta Cryst.*, 1956, **9**, 635.

$F(000) = 584$. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $0k0$ when $k \neq 2n$, and $h0l$ when $l \neq 2n$. $\text{Cu-K}\alpha$ radiation, $\lambda = 1.542$ Å; $\mu(\text{Cu-K}\alpha) = 7.3$ cm⁻¹.

Crystallographic Measurements.—Unit-cell dimensions were obtained from precession photographs taken with $\text{Mo-K}\alpha$ ($\lambda = 0.7107$ Å) radiation, and an $h0l$ Weissenberg photograph taken with $\text{Cu-K}\alpha$ radiation. Intensity data for the $h0$ — $7l$ layers were recorded photographically by the equi-inclination multiple-film Weissenberg method and estimated visually by comparison with a calibrated intensity strip. After the usual Lorentz, polarization, and spot-shape corrections were applied, 2156 independent structure amplitudes were obtained.

Structure Determination.—The data were placed on an approximately absolute scale and normalized structure factor magnitudes $|E_H|$ derived. The structure was solved by use of direct phase-determining methods employing the symbolic addition procedure³ and tangent formula⁴ refinement. Three origin-defining reflections $4,7,4$, $|E| = 2.79$; $8,6,11$, $|E| = 2.93$; $3,7,2$, $|E| = 2.60$, were assigned phases of zero, and three other reflections $6,1,16$, $|E| = 2.51$; $0,0,14$, $|E| = 2.76$; $2,7,13$, $|E| = 2.66$, were assigned symbolic phases. The most probable values for the symbolic phases were obtained through application of a local version of the iterative programme originally written by Drew⁵ and modified by Larson and Motherwell.⁶ A three-dimensional E -map was computed using the phases thus derived for 344 reflections with $|E| > 1.0$, and this distribution revealed clearly positions for all the non-hydrogen atoms.

Atomic positional and isotropic thermal parameters were then refined for four cycles of full-matrix least-squares calculations which minimized $\Sigma w(F_o - F_c)^2$. At the end of this procedure the individual scale factors were adjusted to ensure $\Sigma k|F_o| = \Sigma |F_c|$, and R was reduced from its initial value of 0.34 for the model derived from the E -map to 0.18. Subsequently, the carbon and oxygen atoms were allowed to assume anisotropic thermal parameters. Two cycles decreased R to 0.13. Approximate positions for the ring hydrogen atoms were calculated by assuming C-H 1.07 Å and tetrahedral angles at the carbon atoms. For the methyl groups the model employed was, at C(9) a staggered C-H arrangement with respect to the C(4a)-C bonds was assumed; in the ester groups one hydrogen atom was taken to be in the plane of the ester group and *trans* to the C=O

⁵ See e.g., M. G. B. Drew, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1969, **B**, **25**, 261.

⁶ See e.g., O. Kennard, D. L. Wampler, J. C. Coppola, W. D. S. Motherwell, D. G. Watson, and A. C. Larson, *Acta Cryst.*, 1971, **B**, **27**, 1116.

bond while the other two were assumed to be equally displaced above and below the ester group plane. A three-dimensional difference electron-density map was then computed and this revealed significant positive density at all positions calculated for the hydrogen atoms. Inclusion of the hydrogen atoms in the next round of structure-factor calculations reduced R to 0.112. Two further cycles of least-squares adjustment of the carbon and oxygen parameters brought the refinement to convergence at R 0.103.

For all structure-factor calculations, scattering factors for neutral atoms were taken from ref. 7. In the least-squares iterations, the weighting scheme used was $\sqrt{w} = 1$ for

placements of selected atoms from some least-squares planes are in Table 3.

The X-ray analysis confirms the structure deduced from spectroscopic evidence.¹ The molecule adopts conformation (2a) with both cyclohexane rings in chair conformations, and the methyl substituent and one of the methoxycarbonyl groups are axially oriented on the same ring. The alternative conformation (2b) would involve more severe, unfavourable 1,3-diaxial interactions between the methoxycarbonyl and hydrogen atoms on C(5) and C(7). By contrast, n.m.r. data¹ suggest that

TABLE 1

(a) Fractional atomic co-ordinates ($\times 10^4$) and anisotropic temperature parameters * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	7125(3)	842(5)	6751(2)	61(2)	93(6)	17(1)	16(6)	40(2)	0(3)
C(2)	8148(4)	-717(6)	6996(2)	81(3)	119(7)	24(1)	49(7)	50(2)	-1(4)
C(3)	8057(4)	-2039(6)	7542(2)	120(4)	114(7)	26(1)	86(8)	60(3)	23(5)
C(4)	8337(4)	-1137(6)	8314(2)	102(3)	125(6)	21(1)	38(8)	47(2)	37(4)
C(4a)	7305(3)	390(5)	8107(2)	72(2)	109(6)	14(1)	6(7)	39(2)	10(4)
C(5)	7717(4)	1333(6)	8908(2)	103(3)	174(8)	14(1)	-8(9)	48(2)	1(4)
C(6)	9104(5)	2370(7)	9345(2)	99(4)	187(9)	14(1)	18(10)	23(3)	-9(5)
C(7)	9058(4)	3696(6)	8756(2)	91(3)	148(8)	18(1)	-56(9)	30(3)	-22(5)
C(8)	8776(4)	2767(6)	7997(2)	69(3)	124(7)	20(1)	-29(7)	38(2)	-5(4)
C(8a)	7370(3)	1738(5)	7532(2)	53(2)	90(6)	12(1)	9(6)	26(2)	2(3)
C(9)	5795(3)	-299(6)	7727(2)	82(3)	155(8)	25(1)	-9(8)	61(2)	23(4)
C(10)	7443(3)	2163(5)	6285(2)	63(2)	133(7)	17(1)	-18(7)	41(2)	-13(4)
C(11)	8310(3)	1935(5)	6136(2)	107(2)	193(6)	37(1)	14(6)	99(2)	14(4)
O(12)	6654(3)	3596(4)	6079(1)	105(2)	127(5)	28(1)	36(5)	77(2)	34(3)
C(13)	6890(5)	4910(7)	5639(3)	141(4)	158(9)	38(1)	-15(9)	91(3)	52(5)
C(14)	5579(3)	244(5)	6121(2)	75(3)	109(6)	12(1)	14(7)	38(2)	11(4)
O(15)	5257(3)	-1102(4)	5751(2)	105(3)	111(5)	25(1)	-22(6)	41(2)	-50(3)
O(16)	4636(2)	1426(4)	6028(1)	55(2)	135(5)	19(1)	5(5)	28(1)	-12(3)
C(17)	3154(4)	1011(7)	5427(2)	56(3)	206(9)	20(1)	-9(9)	21(3)	-6(5)

(b) Hydrogen atom † co-ordinates ($\times 10^3$), numbered according to the bonded carbon atoms

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H(2 α)	922	-24	732	H(8 α)	964	188	819
H(2 β)	788	-136	645	H(8 β)	873	372	759
H(3 α)	884	-304	773	H(8 γ)	652	264	732
H(3 β)	701	-261	720	H(9 α)	575	-121	812
H(4 α)	941	-65	867	H(9 β)	552	-95	718
H(4 β)	822	-208	866	H(9 γ)	508	76	758
H(5 α)	782	37	932	H(13 α)	803	488	600
H(5 β)	687	221	875	H(13 β)	655	604	579
H(6 α)	998	150	956	H(13 γ)	675	608	448
H(6 β)	925	305	986	H(17 α)	274	77	578
H(7 α)	1006	436	906	H(17 β)	316	-17	515
H(7 β)	822	462	857	H(17 γ)	254	198	498

* These are the values of b_{ij} in the expression $\exp(-B \sin^2 \theta / \lambda^2) = \exp - [(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

† For all the hydrogen atoms an isotropic temperature factor, B 3.5 Å², was used.

$|F_0| \leq 9.0$, and $\sqrt{w} = |F_0|/9.0$ for $|F_0| > 9.0$; this showed no systematic dependence of $\langle w\Delta^2 \rangle$ on $|F_0|$ or $\sin \theta$.

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20528 (11 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Final atomic co-ordinates and temperature-factor parameters, with their estimated standard deviations, are listed in Table 1. A view of the molecular conformation is shown in Figure 1, and the molecular dimensions and some intermolecular separations are provided in Table 2. Torsion angles for the rings are given in Figure 2, and dis-

the conformation corresponding to (2b) becomes dominant when a benzene ring is fused at C(5)-C(6), and the unfavourable diaxial interaction between the methoxycarbonyl and a C(5) hydrogen no longer exists. Relief from overcrowding which results from the adoption of conformation (2a) is achieved through a combination of factors (i) bond-length extension, (ii) bond-angle deformations, and (iii) flattening of the cyclohexane rings in the central region of the molecule. Ring bonds C(1)-C(8a) and C(4a)-C(8a), mean 1.579 Å, are significantly longer than the other C(sp³)-C(sp³) bonds (mean 1.539 Å) which are close

* For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

† 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2

Interatomic distances (Å) and angles (deg.), with estimated standard deviations in parentheses

(a) Intramolecular distances

C(1)–C(2)	1.546(5)	C(5)–C(6)	1.525(7)
C(1)–C(8a)	1.576(5)	C(6)–C(7)	1.535(7)
C(1)–C(10)	1.559(5)	C(7)–C(8)	1.531(6)
C(1)–C(14)	1.537(5)	C(8)–C(8a)	1.537(5)
C(2)–C(3)	1.540(6)	C(10)–O(11)	1.209(5)
C(3)–C(4)	1.545(6)	C(10)–O(12)	1.330(5)
C(4)–C(4a)	1.545(6)	O(12)–C(13)	1.465(6)
C(4a)–C(5)	1.559(5)	C(14)–O(15)	1.198(5)
C(4a)–C(8a)	1.581(5)	C(14)–O(16)	1.342(5)
C(4a)–C(9)	1.531(5)	O(16)–C(17)	1.440(5)

(b) Valency angles

C(2)–C(1)–C(8a)	111.1(3)	C(4a)–C(5)–C(6)	115.0(4)
C(2)–C(1)–C(10)	107.0(3)	C(5)–C(6)–C(7)	110.5(4)
C(2)–C(1)–C(14)	109.5(3)	C(6)–C(7)–C(8)	110.2(4)
C(8a)–C(1)–C(10)	109.9(3)	C(7)–C(8)–C(8a)	112.4(3)
C(8a)–C(1)–C(14)	113.4(3)	C(1)–C(8a)–C(4a)	112.2(3)
C(10)–C(1)–C(14)	105.5(3)	C(1)–C(8a)–C(8)	110.0(3)
C(1)–C(2)–C(3)	112.4(3)	C(4a)–C(8a)–C(8)	112.1(3)
C(2)–C(3)–C(4)	110.7(4)	C(1)–C(10)–O(11)	124.6(4)
C(3)–C(4)–C(4a)	113.1(3)	C(1)–C(10)–O(12)	111.5(3)
C(4)–C(4a)–C(5)	110.5(3)	O(11)–C(10)–O(12)	123.9(4)
C(4)–C(4a)–C(8a)	109.7(3)	C(10)–O(12)–C(13)	115.0(3)
C(4)–C(4a)–C(9)	110.2(3)	C(1)–C(14)–O(15)	124.0(3)
C(5)–C(4a)–C(8a)	109.2(3)	C(1)–C(14)–O(16)	111.7(3)
C(5)–C(4a)–C(9)	104.5(3)	O(15)–C(14)–O(16)	124.3(3)
C(8a)–C(4a)–C(9)	112.7(3)	C(14)–O(16)–C(17)	115.9(3)

(c) Intramolecular non-bonded distances

C(2) ··· O(11)	2.74	C(8a) ··· O(12)	2.89
C(2) ··· O(15)	2.78	C(8a) ··· O(16)	2.83
C(8) ··· C(10)	2.86	C(9) ··· O(16)	3.13

(d) Intermolecular distances ≤ 3.6 Å

O(15) ··· O(15 ^I)	3.19	C(10) ··· O(15 ^I)	3.49
C(14) ··· O(15 ^I)	3.35	O(12) ··· O(15 ^I)	3.54
O(11) ··· C(17 ^I)	3.41	C(13) ··· C(13 ^{II})	3.54

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

$$\text{I } 1 - x, -y, 1 - z \quad \text{II } 1 - x, 1 - y, 1 - z$$

TABLE 3

Equations of mean planes * in the form $AX + BY + CZ - D = 0$, and, in square brackets, displacements (Å) of some atoms from the planes. Atoms not included in the derivation of the plane are italicized

Plane (A): $-0.6162X - 0.6266Y - 0.4772Z + 5.857 = 0$
 [C(1) -0.005 , C(2) 0.005 , C(4) -0.005 , C(4a) 0.005 , C(3) 0.674 , C(8a) -0.656]

Plane (B): $-0.6260X + 0.5442Y - 0.5585Z + 6.589 = 0$
 [C(5) -0.002 , C(6) 0.002 , C(8) -0.002 , C(8a) 0.002 , C(4a) -0.641 , C(7) 0.690]

Plane (C): $-0.2489X - 0.4227Y - 0.8714Z + 9.933 = 0$
 [C(1) -0.001 , C(10) 0.002 , O(11) -0.002 , O(12) -0.002 , C(13) 0.000 , C(2) -0.065]

Plane (D): $0.5309X + 0.4438Y - 0.7219Z + 7.4706 = 0$
 [C(1) 0.011 , C(14) -0.008 , O(15) -0.001 , O(16) -0.015 , C(17) 0.013 , C(2) -0.333]

* Cartesian co-ordinates (X, Y, Z) are related to the fractional atomic co-ordinates (x, y, z) by the transformation [X, Y, Z] = [$xa + zc \cos \beta, yb, zc \sin \beta$].

to the normal length⁸ [1.537(5) Å]. Moreover, the exocyclic C(1)–C(10) and C(1)–C(14) bonds, mean 1.548 Å, are also significantly increased from the

⁸ Chem. Soc. Special Publ., No. 18, 1965.

⁹ B. E. Davison and A. T. McPhail, *J. Chem. Soc. (B)*, 1970, 660.

normal length [1.506(5) Å] for C(sp^3)–C(sp^2) bonds. Bond-angle deformation is apparent around C(1) and C(4) where C(10)–C(1)–C(14) 105.5° and C(5)–C(4a)–C(9) 104.5° are significantly smaller than the normal tetrahedral value (109.5°) while C(8a)–C(1)–C(14) 113.4° and C(8a)–C(4a)–C(9) 112.7° are enlarged. These angular changes serve to reduce the non-bonded interactions and the C(9) ··· C(14) distance is increased to 3.10 from the 2.62 Å separation of C(1) ··· C(4a). The former distance

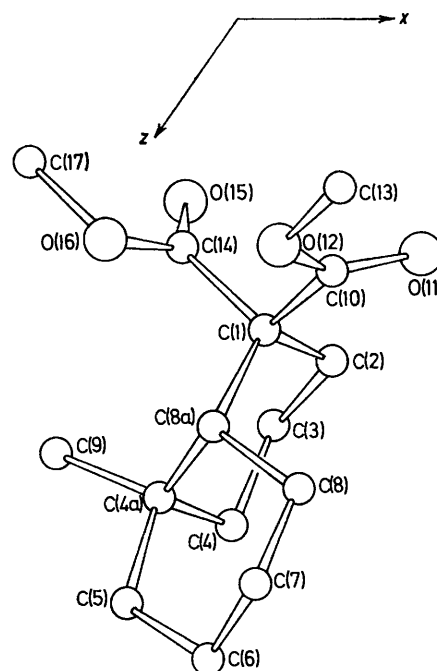


FIGURE 1 Molecular conformation and atomic numbering

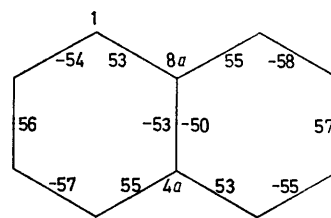


FIGURE 2 Torsion angles (deg.) in the rings of one enantiomer

then becomes comparable to that of 3.03 Å between diaxial carbon and oxygen atoms in methyl-4,6-*O*-benzylidene-2-*O*-*p*-bromobenzenesulphonyl-3-cyano-3-deoxy- α -D-altropyranoside.⁹ Furthermore, torsion angles around the C(4a)–C(8a) bond are smaller than average (55°) owing to flattening which occurs in the cyclohexane rings in order to reduce the 1,3-diaxial interactions.

In the ester groups, the C(α)–CO–O–C(Me) atoms reveal the customary planarity (Table 5), and chemically equivalent bond lengths and valency angles are in excellent agreement. Mean dimensions are: C=O 1.204, C(sp^2)–O 1.336, C(sp^3)–O 1.453 Å; C(α)–C=O 124.3, C(α)–C–O(Me) 111.6, O=C–O(Me) 124.1, C–O–C(Me)

115.5°. Dunitz and Strickler¹⁰ have recently discussed the preferred conformations of carboxylic acids, esters, and amides and have shown that a *syn*-planar orientation of the C=O bonds with respect to the (C α)-C(β) bonds is a common feature of these molecules. A similar arrangement is present in (2a) for which projections along the C(α)-C(carbonyl) bonds are illustrated in Figure 3. The larger value of the C(2)-C(1)-C(14)-O(16) torsion angle (15°) may arise from a small rotation of the axial ester

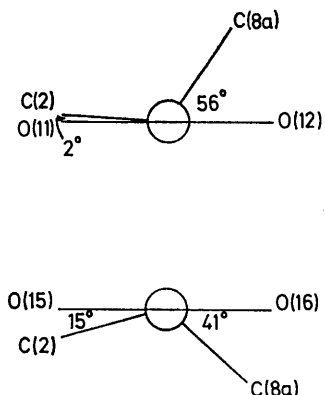


FIGURE 3 Torsion angles at the ester groups

group about the C(1)-C(14) bond to reduce intramolecular non-bonded interactions.

A view of the molecular packing in the crystal is shown

¹⁰ J. E. Dunitz and P. Strickler, in 'Structural Chemistry and Molecular Biology,' eds. A. Rich and N. Davidson, Freeman, San Francisco, 1968, p. 595.

in Figure 4. The shortest intermolecular separations (Table 2) correspond to normal van der Waals distances.

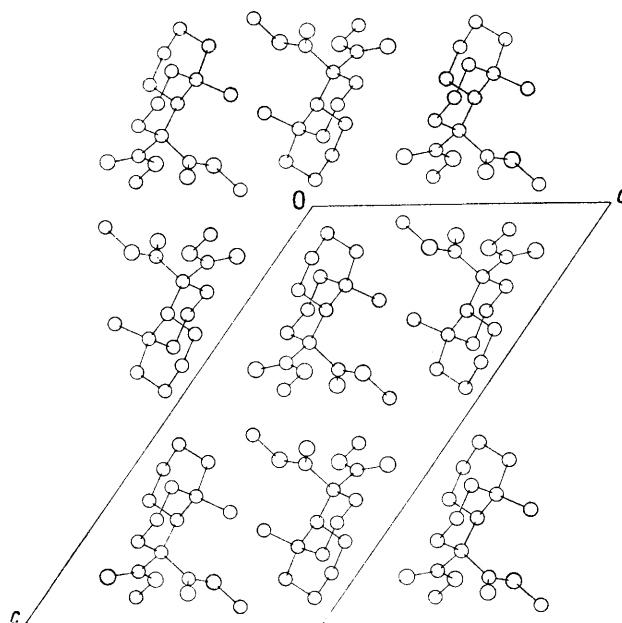


FIGURE 4 Crystal structure, viewed in projection on (010)

Crystallographic calculations were carried out on the IBM 370/65 computer located at the Triangle Universities Computation Centre, Research Triangle Park, North Carolina.

[2/1519 Received, 29th June, 1972]