Crystal and Molecular Structure of (1*S*,3*S*,5*R*,7*S*,8*R*,9*R*)-9-*p*-Bromobenzoyloxy-1,4,4,8-tetramethyltricyclo[5.4.0.0^{3,5}]undecane†

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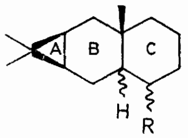
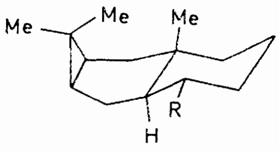
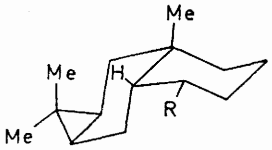
The crystal structure of the title compound has been determined from single-crystal *X*-ray data by the heavy-atom method. Crystals are monoclinic, $a = 23.165(1)$, $b = 6.000(1)$, $c = 14.538(1)$ Å, $\beta = 97° 4'$, space group $P2_1$, $Z = 4$, *i.e.* 2 independent molecules per asymmetric unit. Full-matrix least-squares refinement based on 2 814 independent reflections has reached R 0.069. The molecule contains a *cis*-decalin system in which ring B is considerably distorted by fusion with the cyclopropane ring.



(I)

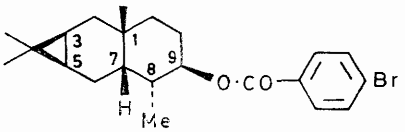


(II)



(III)

IN a recent series of papers[1-5] there is extensive discussion of the stereochemical inter-relations between a large number of bi- and tri-cyclic compounds derived from (—)-*cis*-caran-3-one. The tricyclic saturated compounds were of the form (I; R = H or Me) and the bicyclic ones resulted from opening ring A. Throughout those papers the compounds were regarded as derivatives of *trans*-decalin (II), but more recently Kirk *et al.*[6] deduced from chemical, c.d., and n.m.r. evidence that they all contain *cis*-decalin (III), and they showed that the formation and optical properties of these compounds are strongly influenced by intramolecular methyl–methyl repulsions. An *X*-ray study was thought desirable, partly to corroborate this revision, but also to provide evidence for the conformation of ring B in the tricyclic series. In Dreiding models this ring is abnormally flexible and they do not give the precise knowledge of its conformation that is needed for satisfactory interpretation of the c.d. and n.m.r. data in this series. The investigation was carried out on crystals of (1*S*,3*S*,5*R*,7*S*,8*R*,9*R*)-9-*p*-bromobenzoyloxy-1,4,4,8-tetramethyltricyclo[5.4.0.0^{3,5}]undecane (IV). This study has



(IV)

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† Reprints are not available.

[1] F. Fringuelli, A. Taticchi, and G. de Guili, *Gazzetta*, 1969, **99**, 219.

[2] F. Fringuelli, A. Taticchi, and G. Traverso, *Gazzetta*, 1969, **99**, 231.

[3] F. Fringuelli, A. Taticchi, and G. Traverso, *Gazzetta*, 1969, **99**, 247.

[4] F. Fringuelli and A. Taticchi, *J. Chem. Soc.* (*C*), 1971, 756.

[5] F. Fringuelli and A. Taticchi, *J. Chem. Soc.* (*C*), 1971, 1809.

[6] F. Fringuelli, A. Taticchi, F. Fernandez, D. N. Kirk, and M. Scopes, *J.C.S. Perkin I*, 1974, **10**, 1103.

confirmed the presence of *cis*-decalin and has shown that ring B is markedly flattened.

EXPERIMENTAL

Crystal Data.—$C_{22}H_{29}O_2Br$, $M = 405.4$. Monoclinic, $a = 23.165(1)$, $b = 6.000(1)$, $c = 14.538(1)$ Å, $\beta = 97.07(1)°$, $U = 2005.3$ Å^3, D_m (by flotation) 1.34, $Z = 4$, $D_c = 1.33$ g cm^{-3}. Optical activity and systematic absences indicate space group $P2_1$ (No. 4) so the asymmetric unit comprises two independent molecules. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 30.8 cm^{-1}.

The crystal chosen for intensity measurements was a plate *ca.* 0.15 × 0.60 × 0.02 mm^3 mounted about *b*. Intensities were measured on a Siemens off-line automatic four-circle diffractometer with filtered Cu-K_α radiation. A total of 2 814 independent reflections (to θ 55°) were measured by means of the θ—2θ scan technique with the five-value measuring procedure.[7] Of these, 210 reflections were judged to be unobserved, *i.e.* $I < 2.58\sigma(I)$.[7] The net count of the $15,0,\bar{1}$ reflection, measured as a reference every 50 reflections, did not alter significantly during data collection (*ca.* 110 h). Data were converted to a common arbitrary scale by use of this reflection and Lorentz and polarisation corrections were applied.

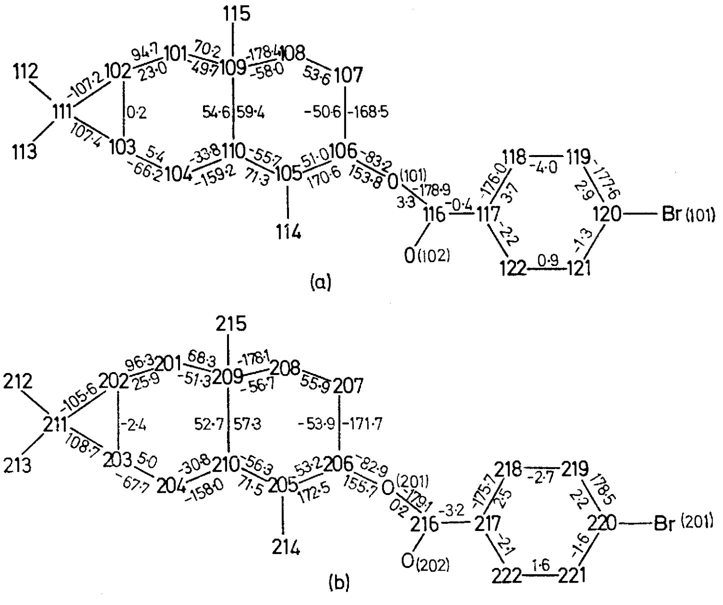

FIGURE 1 Comparison of the torsion angles (deg.) in the two independent molecules, (a) molecule (1), (b) molecule (2). The angle quoted is that required to rotate the projection of bond A→B to coincide with that of bond C→D, when looking down the B→C bond. A positive sign denotes clockwise rotation.

The structure was solved by means of a three-dimensional sharpened, origin-removed Patterson, and the heavy-atom method. Although the two independent Br atoms had very similar *y* co-ordinates they differed sufficiently to destroy the pseudosymmetry that occurs in this space group when either there is only one heavy atom or several having a common *y* co-ordinate, and this made interpretation much easier. Three cycles of isotropic least-squares refinement of the Br atoms only, gave *R* 0.39. The remaining non-hydrogen atoms were located from successive difference syntheses, and three cycles of isotropic refinement of all these atoms gave *R* 0.158.

At this stage an absorption correction was applied according to the method of Busing and Levy,[8] with crystal pathlengths determined by the procedure of Coppens *et al.*[9] Further isotropic refinement reduced *R* to 0.132, and still more, with the Br atoms only refined anisotropically, reduced *R* to 0.097. A difference synthesis now showed all 58 hydrogen atoms. Allowance for these, as fixed-atom contributions with isotropic thermal parameters equal to those of their parent carbon atom, gave a final *R* of 0.069. A Hughes-type weighting scheme [10] of the form $w = 1$ for $F < 15$, $\sqrt{w} = 15/F$ for $F \geqslant 15$ seemed to be optimum, but its application did not reduce *R*. A final difference synthesis was featureless except for a few peaks of *ca.* 0.5—0.7 eÅ^{-3} in the immediate vicinity of the Br atoms. The scattering factors used were taken from ref. 11, but for hydrogen from ref. 12; values for $\Delta f'$ and $\Delta f''$ were taken from ref. 13. Attempts to obtain the absolute configuration by comparison of R_+ and R_- were not successful, so the chemically known configuration has been adopted. All calculations were carried out on the University of London 7600 and 6600 computers by means of the '*X*-Ray' program system.[14]

Figure 1 shows the atomic numbering used: this follows that adopted by Kirk *et al.*[6] who found it preferable to adhere to the terpenoid–steroid numbering of (I) rather than that required by the tricycloundecane nomenclature. Table 1 lists final fractional co-ordinates for non-hydrogen atoms, and Table 2 the co-ordinates of the hydrogen atoms

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[7] F. H. Allen, D. Rogers, and P. G. H. Troughton *Acta Cryst.*, 1971, **B27**, 1325.

[8] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[9] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[10] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[11] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[14] '*X*-Ray '67' System of Crystallographic Programs, University of Maryland, Technical Report 67 58, revised version, 1970.

as deduced from the difference map. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21576 (13 pp., 1 microfiche).†

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The two independent molecules not only have, as expected, the same chirality but they have almost identical conformations [see Figures 1(a) and (b), and

TABLE 1

Fractional co-ordinates (× 10^5 for Br, × 10^4 for C and O) and thermal parameters for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
(*a*) Molecule (1)				
Br(101)	−10 764(5)	50 000	−6 408(8)	*
O(101)	580(2)	8 292(11)	3 279(4)	3.8(1)
O(102)	62(3)	11 458(13)	3 028(5)	5.4(1)
C(101)	2 510(3)	9 849(18)	6 068(5)	4.4(2)
C(102)	2 243(4)	11 016(17)	6 846(6)	4.4(2)
C(103)	1 616(4)	10 664(17)	6 936(6)	4.4(2)
C(104)	1 249(3)	9 151(16)	6 247(6)	4.1(2)
C(105)	1 118(3)	7 169(15)	4 703(5)	3.5(1)
C(106)	913(3)	9 182(15)	4 118(5)	3.6(1)
C(107)	1 399(3)	10 610(16)	3 845(6)	4.4(2)
C(108)	1 838(4)	11 228(17)	4 667(6)	4.3(2)
C(109)	2 070(3)	9 139(15)	5 207(5)	3.6(1)
C(110)	1 558(3)	7 871(15)	5 532(5)	3.5(1)
C(111)	2 071(4)	9 839(19)	7 667(6)	4.6(2)
C(112)	2 169(4)	7 325(20)	7 807(7)	5.2(2)
C(113)	2 163(4)	11 056(20)	8 597(7)	5.5(2)
C(114)	612(4)	5 770(17)	4 961(6)	4.5(2)
C(115)	2 433(4)	7 702(19)	4 622(6)	4.9(2)
C(116)	175(4)	9 535(16)	2 828(6)	4.2(2)
C(117)	− 139(3)	8 383(16)	1 990(6)	4.0(2)
C(118)	15(4)	6 211(18)	1 758(6)	4.8(2)
C(119)	−250(4)	5 244(22)	960(6)	5.3(2)
C(120)	−693(4)	6 360(18)	422(6)	4.8(2)
C(121)	−859(4)	8 493(20)	649(7)	5.5(2)
C(122)	−576(4)	9 500(17)	1 454(6)	4.7(2)
(*b*) Molecule (2)				
Br(201)	17 398(4)	50 931(37)	21 710(6)	*
O(201)	3 736(2)	6 903(11)	−789(4)	3.8(1)
O(202)	3 801(2)	10 217(14)	−72(4)	4.7(1)
C(201)	4 932(3)	7 763(16)	−4 000(6)	4.1(2)
C(202)	5 498(3)	8 932(16)	−3 633(5)	3.9(2)
C(203)	5 726(3)	8 572(15)	−2 628(5)	3.7(1)
C(204)	5 391(3)	7 180(16)	−2 004(6)	4.0(1)
C(205)	4 434(3)	5 450(14)	−1 717(5)	3.3(1)
C(206)	4 163(3)	7 584(15)	−1 399(5)	3.4(1)
C(207)	3 858(3)	8 916(16)	−2 202(6)	4.0(2)
C(208)	4 258(3)	9 384(15)	−2 932(5)	3.7(1)
C(209)	4 515(3)	7 210(14)	−3 290(5)	3.2(1)
C(210)	4 830(3)	5 975(14)	−2 463(5)	3.3(1)
C(211)	6 053(3)	7 652(16)	−3 384(6)	3.8(2)
C(212)	6 074(4)	5 154(20)	−3 522(6)	4.8(2)
C(213)	6 598(4)	8 811(19)	−3 547(6)	5.0(2)
C(214)	4 737(3)	4 125(18)	−885(6)	4.4(2)
C(215)	4 033(3)	5 779(16)	−3 808(6)	4.2(2)
C(216)	3 592(3)	8 327(15)	−166(5)	3.3(1)
C(217)	3 169(3)	7 457(16)	413(5)	3.4(1)
C(218)	2 923(3)	5 351(17)	271(5)	3.9(1)
C(219)	2 500(4)	4 663(17)	789(6)	4.4(2)
C(220)	2 331(3)	5 985(15)	1 476(6)	3.8(2)
C(221)	2 574(4)	8 119(17)	1 642(6)	4.5(2)
C(222)	2 990(3)	8 776(17)	1 113(5)	4.0(2)

* Bromine anisotropic temperature factors (× 10^4) as they appear in $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(101)	36(1)	635(6)	76(1)	9(1)	−9(1)	−55(1)
Br(201)	29(1)	616(5)	57(1)	−37(1)	17(1)	−13(2)

TABLE 2

Hydrogen fractional co-ordinates (× 10^3) * derived from a ΔF map and unrefined

Atom	x	y	z
(*a*) Molecule (1)			
H(1011)	273	1 058	560
H(1012)	278	820	616
H(1021)	243	1 237	683
H(1031)	140	1 187	713
H(1041)	107	805	651
H(1042)	95	980	586
H(1051)	131	625	434
H(1061)	71	1 014	442
H(1071)	166	986	337
H(1072)	116	1 203	365
H(1081)	225	1 224	440
H(1082)	161	1 206	514
H(1101)	169	635	590
H(1121)	261	730	825
H(1122)	185	681	832
H(1123)	226	631	731
H(1131)	183	1 111	902
H(1132)	253	1 086	873
H(1133)	222	1 271	844
H(1141)	33	702	530
H(1142)	45	490	444
H(1143)	70	416	542
H(1151)	289	890	457
H(1152)	247	663	484
H(1153)	220	717	397
H(1181)	36	551	212
H(1191)	−26	380	73
H(1211)	−127	898	30
H(1221)	−70	1 098	162
(*b*) Molecule (2)			
H(2011)	470	919	−466
H(2012)	502	605	−406
H(2021)	545	1 030	−378
H(2031)	585	963	−230
H(2041)	557	630	−187
H(2042)	522	812	−147
H(2051)	406	461	−188
H(2061)	448	835	−107
H(2071)	342	848	−247
H(2072)	366	990	−204
H(2081)	403	964	−342
H(2082)	457	1 044	−272
H(2101)	497	462	−266
H(2121)	612	481	−411
H(2122)	628	425	−308
H(2123)	583	441	−357
H(2131)	662	1 019	−324
H(2132)	688	804	−330
H(2133)	688	859	−410
H(2141)	443	381	−54
H(2142)	486	318	−110
H(2143)	507	511	−60
H(2151)	371	518	−353
H(2152)	385	670	−430
H(2153)	426	441	−403
H(2181)	301	434	−29
H(2191)	226	307	65
H(2211)	239	924	217
H(2221)	317	1 030	121

* The first three digits of each hydrogen-atom label denote the carbon to which it is bonded.

TABLE 3

Other torsion angles (°) not shown in Figure 1

	Molecule (1) $M = 1$	Molecule (2) $M = 2$
C(*M*04)[C(*M*10)–C(*M*09)]C(*M*15)	170.6	170.3
O(*M*01)[C(*M*06)–C(*M*05)]C(*M*14)	−60.3	−60.3
C(*M*12)[C(*M*11)–C(*M*03)]C(*M*04)	−4.0	−2.3
C(*M*12)[C(*M*11)–C(*M*02)]C(*M*03)	109.0	107.9
C(*M*13)[C(*M*11)–C(*M*02)]C(*M*03)	−109.1	−107.6

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† See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

Table 3] and aspects as viewed down the *b* axis (see Figure 2) [15] though the crystallography does not require this. The close correspondence of the bond lengths, valence angles, and nonbonded intramolecular distances in the two molecules is apparent in the comparative data of Tables 4 and 5. All bond lengths agree well with accepted values. Figures 2 and 3 reveal the presence of *cis*-decalin ring systems and confirm the stereochemistry suggested by Kirk.

The fusion of ring B with the cyclopropane ring A and the steric interaction between C(10) and methyl C(12) (3.45 and 3.47 Å) have distorted ring B (see the stereopair in Figure 3). It has the flattened skew conformation typical of cyclohexene. Thus, as shown in Table 6, the atoms C(1)—(4) are closely coplanar [especially in molecule (1)] and the atoms C(9) and C(10) are displaced unequally on opposite sides of this plane (means −0.53 and 0.10 Å). The ring angles at C(1)—(4) are enlarged to a mean of 118° in both molecules and at C(5) to 114°, but the angle at the tetrasubstituted atom C(9) is only 110 and 111°. The conformation of ring C is not very

TABLE 4

Bond lengths (Å) and bond angles (°), with standard deviations in parentheses

(*a*) Distances

	Molecule (1) *M* = 1	Molecule (2) *M* = 2
Br(*M*01)–C(*M*20)	1.872(9)	1.877(8)
O(*M*01)–C(*M*06)	1.46(1)	1.47(1)
O(*M*01)–C(*M*16)	1.31(1)	1.32(1)
O(*M*02)–C(*M*16)	1.23(1)	1.23(1)
C(*M*01)–C(*M*02)	1.53(1)	1.52(1)
C(*M*02)–C(*M*03)	1.49(1)	1.51(1)
C(*M*03)–C(*M*04)	1.53(1)	1.51(1)
C(*M*04)–C(*M*10)	1.54(1)	1.56(1)
C(*M*05)–C(*M*06)	1.52(1)	1.52(1)
C(*M*06)–C(*M*07)	1.51(1)	1.52(1)
C(*M*07)–C(*M*08)	1.52(1)	1.52(1)
C(*M*08)–C(*M*09)	1.54(1)	1.55(1)
C(*M*09)–C(*M*10)	1.53(1)	1.52(1)
C(*M*09)–C(*M*01)	1.57(1)	1.53(1)
C(*M*10)–C(*M*05)	1.54(1)	1.54(1)
C(*M*11)–C(*M*02)	1.48(1)	1.50(1)
C(*M*11)–C(*M*03)	1.49(1)	1.51(1)
C(*M*11)–C(*M*12)	1.54(1)	1.51(2)
C(*M*11)–C(*M*13)	1.53(1)	1.49(1)
C(*M*14)–C(*M*05)	1.53(1)	1.54(1)
C(*M*15)–C(*M*09)	1.53(1)	1.53(1)
C(*M*16)–C(*M*17)	1.51(1)	1.46(1)
C(*M*17)–C(*M*18)	1.40(2)	1.39(1)
C(*M*18)–C(*M*19)	1.37(1)	1.37(1)
C(*M*19)–C(*M*20)	1.38(1)	1.37(1)
C(*M*20)–C(*M*21)	1.39(2)	1.41(1)
C(*M*21)–C(*M*22)	1.41(1)	1.36(1)
C(*M*22)–C(*M*17)	1.37(1)	1.39(1)

(*b*) Angles

	M = 1	*M* = 2
C(*M*02)–C(*M*01)–C(*M*09)	116(1)	117(1)
C(*M*01)–C(*M*02)–C(*M*03)	119(1)	117(1)
C(*M*01)–C(*M*02)–C(*M*11)	124(1)	122(1)
C(*M*03)–C(*M*02)–C(*M*11)	60(1)	60(1)
C(*M*02)–C(*M*03)–C(*M*04)	120(1)	121(1)
C(*M*04)–C(*M*03)–C(*M*11)	124(1)	125(1)
C(*M*02)–C(*M*03)–C(*M*11)	60(1)	60(1)
C(*M*03)–C(*M*04)–C(*M*10)	118(1)	117(1)
C(*M*06)–C(*M*05)–C(*M*10)	111(1)	110(1)
C(*M*10)–C(*M*05)–C(*M*14)	114(1)	114(1)
C(*M*06)–C(*M*05)–C(*M*14)	112(1)	111(1)
C(*M*05)–C(*M*06)–C(*M*07)	114(1)	112(1)
C(*M*05)–C(*M*06)–O(*M*01)	106(1)	106(1)
C(*M*07)–C(*M*06)–O(*M*01)	109(1)	109(1)
C(*M*06)–C(*M*07)–C(*M*08)	113(1)	112(1)
C(*M*07)–C(*M*08)–C(*M*09)	111(1)	112(1)
C(*M*01)–C(*M*09)–C(*M*08)	110(1)	110(1)
C(*M*08)–C(*M*09)–C(*M*10)	109(1)	108(1)
C(*M*01)–C(*M*09)–C(*M*10)	110(1)	111(1)
C(*M*01)–C(*M*09)–C(*M*15)	104(1)	106(1)
C(*M*08)–C(*M*09)–C(*M*15)	111(1)	110(1)
C(*M*10)–C(*M*09)–C(*M*15)	113(1)	111(1)
C(*M*04)–C(*M*10)–C(*M*05)	110(1)	109(1)
C(*M*04)–C(*M*10)–C(*M*09)	114(1)	114(1)
C(*M*05)–C(*M*10)–C(*M*09)	111(1)	113(1)
C(*M*02)–C(*M*11)–C(*M*03)	60(1)	60(1)
C(*M*02)–C(*M*11)–C(*M*12)	122(1)	121(1)
C(*M*02)–C(*M*11)–C(*M*13)	118(1)	116(1)
C(*M*03)–C(*M*11)–C(*M*12)	120(1)	119(1)
C(*M*03)–C(*M*11)–C(*M*13)	119(1)	117(1)
C(*M*12)–C(*M*11)–C(*M*13)	111(1)	114(1)
C(*M*17)–C(*M*16)–O(*M*01)	113(1)	114(1)
O(*M*01)–C(*M*16)–O(*M*02)	125(1)	123(1)
C(*M*17)–C(*M*16)–O(*M*02)	122(1)	123(1)
C(*M*16)–C(*M*17)–C(*M*18)	121(1)	122(1)
C(*M*16)–C(*M*17)–C(*M*22)	119(1)	120(1)
C(*M*18)–C(*M*17)–C(*M*22)	121(1)	118(1)
C(*M*17)–C(*M*18) C(*M*19)	120(1)	120(1)
C(*M*18)–C(*M*19)–C(*M*20)	120(1)	121(1)
C(*M*19)–C(*M*20)–C(*M*21)	121(1)	120(1)
C(*M*19)–C(*M*20)–Br(*M*01)	120(1)	121(1)
C(*M*21)–C(*M*20)–Br(*M*01)	119(1)	118(1)
C(*M*20)–C(*M*21)–C(*M*22)	119(1)	118(1)
C(*M*21)–C(*M*22)–C(*M*17)	120(1)	123(1)
C(*M*06)–O(*M*01)–C(*M*16)	119(1)	119(1)

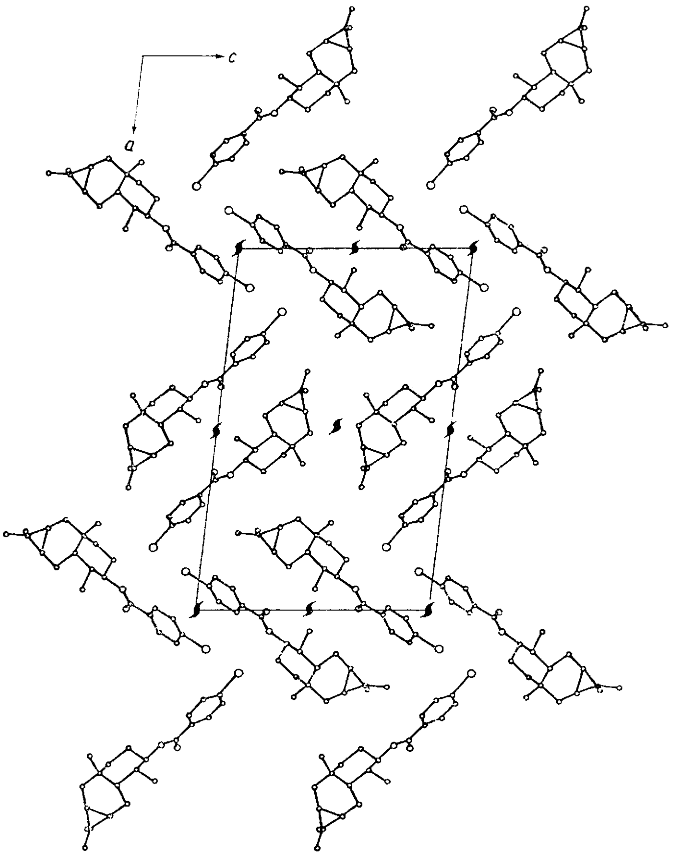

FIGURE 2 The [010] projection showing molecular packing.

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[15] C. K. Johnson, ORTEP Thermal Ellipsoid plotting program, Oak Ridge National Laboratory Report, 1965, ORNL 3794.

different from that of a typical chair, so the distortion of ring B has had little effect on ring C. This is evident from both the torsion angles [Figures 1 (a) and (b)] and the near coplanarity of C(6),C(7),C(9),C(10) (see Table 6).

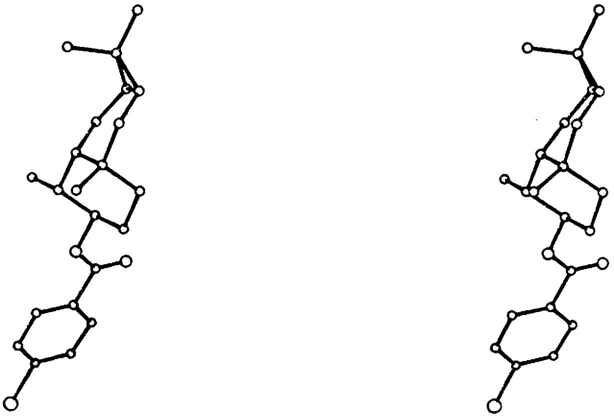

FIGURE 3 A stereopair of one molecule to emphasise the flatness of ring B

TABLE 5

Selected intramolecular contacts (Å)

	Molecule (1) $M = 1$	Molecule (2) $M = 2$
O(*M*01) · · · C(*M*14)	2.87	2.87
O(*M*01) · · · C(*M*18)	2.73	2.74
O(*M*02) · · · C(*M*05)	4.13	4.11
O(*M*02) · · · C(*M*06)	2.74	2.71
O(*M*02) · · · C(*M*07)	3.22	3.21
O(*M*02) · · · C(*M*14)	4.50	4.48
O(*M*02) · · · C(*M*22)	2.82	2.83
C(*M*01) · · · C(*M*12)	3.13	3.08
C(*M*02) · · · C(*M*08)	3.20	3.18
C(*M*04) · · · C(*M*06)	3.10	3.09
C(*M*04) · · · C(*M*08)	3.08	3.09
C(*M*04) · · · C(*M*12)	3.12	3.12
C(*M*04) · · · C(*M*14)	3.02	2.99
C(*M*05) · · · C(*M*15)	3.08	3.07
C(*M*07) · · · C(*M*15)	3.07	3.06
C(*M*07) · · · C(*M*16)	3.10	3.12
C(*M*10) · · · C(*M*11)	3.40	3.43
C(*M*10) · · · C(*M*12)	3.45	3.47
C(*M*12) · · · C(*M*15)	4.75	4.71

The bromobenzoate group is similarly inclined to ring C in both molecules. Thus the angles between the plane C(6),C(7),C(9),C(10) and the benzoate group are 75.5 and 76.3° in the two molecules. The bond lengths in the carboxy-groups are in close agreement and typical of carboxylic esters.[16] And, as usually occurs in esters, the atom C(6) is coplanar with the carboxy-group (0.005 and 0.033 Å from the entire bromobenzoate plane) with a consequently close contact between O(2) and C(6) (2.74 and 2.71 Å), and O(2) approaches C(6) on the hydrogen side. It is interesting, however, that atoms C(5) and C(7) are unequally displaced from the benzoate plane [means 0.609 and 1.448 Å]. As a consequence the hydrogen atom on C(6) is appreciably displaced from the plane of the ester, which is somewhat unusual. The very unequal nonbonded contacts between O(2)

TABLE 6

Mean planes through various sets of atoms

(*a*) Deviations (in Å × 10^3) of atoms from the planes
Rings *A*(1), *A*(2) defined by C(*M*02), C(*M*03), C(*M*11)

	B(1)	*B*(2)
C(*M*01)	1	6
C(*M*02)	−1	−11
C(*M*03)	1	11
C(*M*04)	−1	−6
C(*M*09) *	−500	−559
C(*M*10) *	124	73
C(*M*11) *	1 172	1 197

	D(1)	*D*(2)
Br(*M*01)	22	74
O(*M*01)	4	5
O(*M*02)	50	65
C(*M*16)	−2	21
C(*M*17)	−28	−35
C(*M*18)	−34	−32
C(*M*19)	27	4
C(*M*20)	9	−17
C(*M*21)	−10	−30
C(*M*22)	−38	−55
C(*M*05) *	−634	−589
C(*M*06) *	4	4
C(*M*07) *	1 418	1 473
C(*M*08) *	1 559	1 599
C(*M*09) *	991	1 017
C(*M*10) *	−481	−431
C(*M*15) *	1 837	1 843

	C(1)	*C*(2)
C(*M*05)	8	0
C(*M*07)	−8	0
C(*M*08)	8	0
C(*M*10)	−8	0
C(*M*06) *	−594	−635
O(*M*01) *	−323	−429
C(*M*09) *	710	699
C(*M*01) *	670	634

	C(1′)	*C*(2′)
C(*M*06)	−35	−16
C(*M*07)	35	15
C(*M*09)	−34	−15
C(*M*10)	34	16
C(*M*05) *	−646	−659
C(*M*08) *	669	673
C(*M*14) *	−699	−685
C(*M*04) *	1 461	1 449
O(*M*01) *	−893	−831

	C(1″)	*C*(2″)
C(*M*05)	25	12
C(*M*06)	−25	−12
C(*M*08)	25	12
C(*M*09)	−25	−12
C(*M*01) *	681	704
C(*M*07) *	−613	−647
C(*M*10) *	691	668
C(*M*14) *	623	653

	E(1)	*E*(2)
C(*M*01)	4	9
C(*M*05)	−21	−19
C(*M*09)	19	19
C(*M*10)	−25	−1
C(*M*14)	23	10
O(*M*01) *	−936	−1 046
C(*M*02) *	−1 082	−1 101
C(*M*03) *	−1 681	−1 648
C(*M*04) *	−1 206	−1 167
C(*M*06) *	−1 168	−1 208
C(*M*07) *	−1 247	−1 258
C(*M*08) *	−1 208	−1 221

(*b*) Equations to the planes of the form: $Ax + By + Cz - D = 0$

	A	*B*	*C*	*D*
A(1)	−1.920	5.234	7.102	10.196
A(2)	12.184	5.103	−0.940	11.598
B(1)	3.792	−4.707	8.336	1.374
B(2)	12.545	−4.843	−4.359	4.165
C(1)	17.574	−3.180	−6.825	−3.532
C(1′)	−7.633	4.670	8.300	7.044
C(1″)	−11.492	2.149	12.299	6.014
C(2)	12.053	3.215	8.663	5.608
C(2′)	14.299	4.568	1.757	9.187
C(2″)	20.381	1.962	3.404	9.509
D(1)	17.320	2.246	−9.252	−0.171
D(2)	14.906	−2.296	8.414	3.324
E(1)	12.102	−5.091	−2.164	−3.293
E(2)	4.481	5.199	6.292	3.721

(*c*) Dihedral angles (°)

	Molecule (1)	Molecule (2)
(*A*)–(*B*)	65.8	66.3
(*B*)–(*C*)	71.7	72.1
(*B*)–(*C*′)	69.8	70.9
(*B*)–(*C*″)	83.6	82.4
(*C*)–(*D*)	54.8	55.2
(*E*)–(*A*)	34.5	33.0
(*E*)–(*B*)	45.6	45.3
(*E*)–(*C*)	28.6	29.4
(*E*)–(*D*)	83.1	84.4

* Atoms not included in derivation of plane.

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[16] ' Molecular Structures and Dimensions,' vol. A1, eds. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersen, and W. G. Town, 1972, Oesthoek, Utrecht, p. *S* 2.

and C(5) or C(7) (means 4.12 and 3.21 Å) show that the ester plane is tilted *ca.* 30° as far as it can go toward C(7); had it gone the other way it would quickly collide with methyl C(14). As a result, the plane O(1),C(6),C(7) is almost exactly perpendicular to the ester group. The close O(2) · · · C(6) contact is also probably responsible for enlarging the angle at O(1) to 119°, and reducing the angle C(5)–C(6)–O(1) to 106°, despite the close proximity (2.87 Å) between O(1) and methyl C(14).

The [010] projection of the crystal structure is shown in Figure 2. There are only two contacts <3.5 Å, both O · · · C, but neither is less than the sum of van der Waals radii. There is no obvious reason for the closely similar aspects of molecules (1) and (2), but it is curious that while the disposition of each molecule to its screw-related partner is very similar for the two independent pairs in the cell, the packing environment around each screw-related pair is quite different. The aromatic rings tend to congregate in one region and the aliphatic in another. Had this not occurred, and the columns of molecules (2) been inserted with reversed polarity of *y*, one would have had a structure in space group $P2_12_12_1$ and two pairs of overlapping aromatic rings instead of one, as here. We have not encountered such a polymorph.

We thank Dr. D. N. Kirk for helpful discussions and crystals of (IV), the S.R.C. for equipment, and the staff of the Computer Units of Imperial College and the University of London for their assistance.

[5/1387 *Received*, 14*th July*, 1975]