Conformational Studies. Part 10.[1] Crystal and Molecular Structure of 17β-Iodoacetoxy-4,4-dimethyl-5α-androst-7-en-3-one

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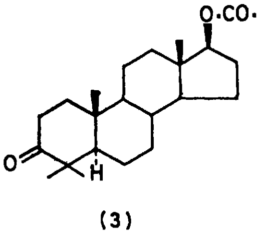
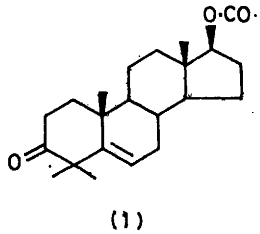
The crystal and molecular structure of the title compound, (2), $C_{23}H_{33}O_3I$, has been determined by single-crystal *X*-ray techniques. Crystals are trigonal, space group $P3_2$, with six molecules per unit cell (two independent molecules per asymmetric unit) of dimensions a = 22.982(3) and c = 7.547(1) Å. The structure was solved by the heavy-atom method and refined by least-squares calculations to R 0.064 for 1 686 observed reflections. The steroid frameworks of both molecules have essentially the same conformations, the only differences being in the orientations of the 17β-iodoacetoxy-side-chains. Ring A of the steroid skeleton has a very flattened chair conformation, ring B is a distorted half-chair, ring C a flattened chair, and ring D a distorted envelope.

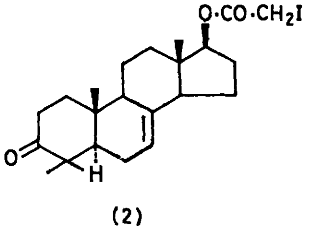
We have previously reported[2] upon the conformation of the steroidal nucleus in 17β-bromoacetoxy-4,4-dimethylandrost-5-en-3-one (1) and have described the effect of the 5,6-unsaturation on the shape of ring A in particular, which is constrained to adopt a skewed boat conformation. This paper describes a similar investigation applied to the isomeric system (2) with the double bond at C(7)–C(8). The unusual constraint placed upon androst-7-en-3-one (and similar steroids) by the presence of this double bond, as assessed *inter alia* by (*a*) direct methylation of androst-7-en-3-one at C(4),[3] in contrast to the normal methylation at C(2), (*b*) the very low rate of condensation of androst-7-en-3-one with benzaldehyde,[4] and (*c*) strain calculations,[5] combine to emphasise the desirability of a more detailed examination of (2).



(3)



(1)



(2)

Although there are two independent molecules in the asymmetric unit of the crystal, they have essentially identical dimensions with conformations which differ only in the orientation of the 17β-iodoacetyl moiety; in the discussion which follows mean dimensions will be used. A view of one of the molecules is in Figure 1 and details of mean torsion angles are in Figure 2.

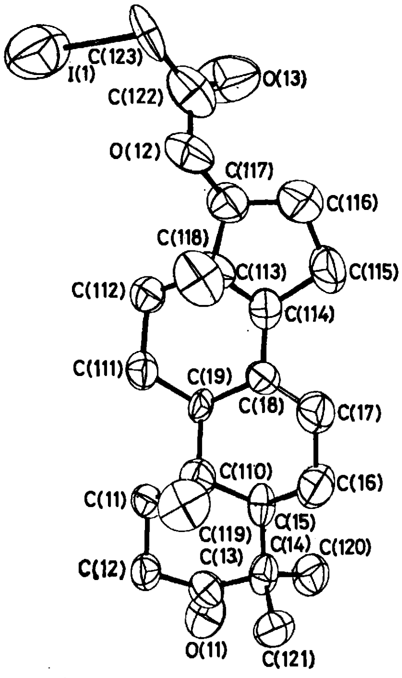


FIGURE 1 One of the two independent molecules, showing the atom numbering system. This follows the conventional steroidal scheme, but with a ' 1 ' placed before every atom number (to signify that this is molecule 1). See also Table 1

Ring A adopts a very flattened chair conformation principally to relieve methyl ··· methyl and hydrogen ··· methyl interactions between the axial groups at C(6) and C(10) with the axial methyl at C(4). This flattening is in the same geometrical sense as that observed in 17β-iodoacetoxy-4,4-dimethyl-5α-androstan-3-one, (3),[6] but more marked in accord with the expected

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[1] Part 9, J. S. E. Holker, W. R. Jones, M. G. R. Leeming, G. M. Holder, J. M. Midgley, J. E. Parkin, and W. B. Whalley, *J.C.S. Perkin I*, 1978, 253.

[2] G. Ferguson, W. C. Marsh, J. M. Midgley, and W. B. Whalley, *J.C.S. Perkin II*, 1978, 272.

[3] Y. Mazur and F. Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 6296.

[4] D. H. R. Barton, F. McCapra, P. J. May, and F. Thudium, *J. Chem. Soc.*, 1960, 1297, and references cited therein.

[5] M. J. T. Robinson and W. B. Whalley, *Tetrahedron*, 1963, **19**, 2123.

[6] G. Ferguson, E. W. Macaulay, J. M. Midgley, J. M. Robertson, and W. B. Whalley, *Chem. Comm.*, 1970, 954.

effect of the double bond (*vide infra*). The torsion angle C(3)–C(4)–C(5)–C(10) is only 36° in (2) compared with 47° in (3); for comparison, the 'standard' value suggested[7] for a non-overcrowded system is 56.5°. It is also of significance to observe that the C(2)–C(3)–C(4)–C(5) moiety has a smaller torsion angle than the geometrically equivalent C(1)–C(2)–C(3)–C(4) moiety. This is in accordance with views frequently expressed by one of us[8] concerning the non-vectorial equivalence of these two geometrically similar systems in the A ring of a 5α-3-oxo-steroid. These, and associated results will be discussed more fully in a later paper.

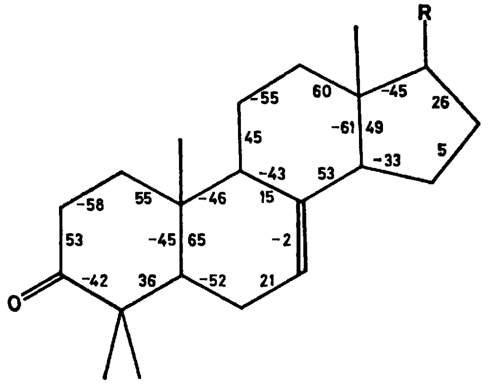

FIGURE 2 Mean torsion angles in the steroid skeleton of (2); the mean standard deviation in torsion angle is 2.6°

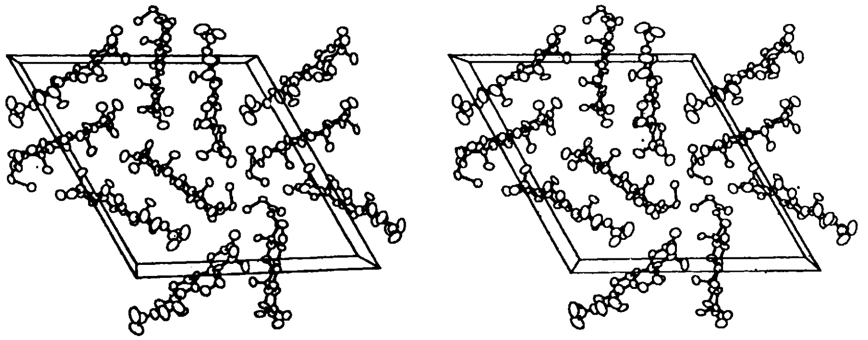

FIGURE 3 The molecular packing of (2) shown in stereoview down *c*

The 7,8-unsaturation causes ring B to adopt a half-chair conformation with C(5) 0.48 Å below the best plane through atoms C(6) · · · (9) and with C(10) 0.35 Å above this plane; associated with this is the large value (65°) of the C(9)–C(10)–C(5)–C(6) torsion angle. This conformation is of importance because it results in the axial hydrogen atom at C(6) being tilted slightly towards the axial methyl group at C(4). In undistorted molecular models the relevant H · · · Me distance would be reduced from a normal 2.58 in (3) to 2.1 Å. This extra intramolecular overcrowding, which is not present in (3), is undoubtedly the main reason for the increased flattening of ring A in (2), as this flattening would increase the Me · · · H separation.

Ring C has a chair conformation somewhat flattened at the B–C ring junction; the torsion angle C(14)–C(8)–C(9)–C(11) is −43 compared with −56° in (3). Ring C of (1) has essentially the same conformation as that in (3), even though the unsaturation in the B rings is differently located.

Ring D has a slightly distorted C(13) envelope conformation with C(13) 0.63 above and C(14) 0.14 Å below the plane through C(15)—(17). This conformation may also be described quantitatively in terms of a puckering angle ϕ_m of 50° and a phase angle Δ of 24°.[9] Again, this conformation is similar to that observed in (1) (ϕ_m 50° Δ 19°); in (3) ring D is closer to a half-chair (ϕ_m 48°, Δ −5°).

The interatomic distances and angles (Table 1) are not significantly different from accepted values.[10] Mean dimensions are $C(sp^3)$–$C(sp^3)$ 1.54(1), $C(sp^3)$–$C(sp^2)$ 1.49(1), C=C 1.33, C=O 1.19, $C(sp^3)$–O 1.44, $C(sp^2)$–O 1.32, $C(sp^3)$–I 2.20 Å.

In the crystal structure (Figure 3) the 3-oxo-oxygen [O(11)] of one of the molecules makes three short contacts with the iodoacetyl groups of neighbouring molecules [O · · · I 3.07(2), O · · · O 3.14(4), and O · · · C 3.21(4) (Table 1)] which are shorter than normal van der Waals contacts. These contacts appear to have no effect on the conformation of ring A, since the other independent molecule, which is devoid of such contacts, has the same ring A conformation (maximum difference in corresponding torsion angles is less than 2°). The orientations of the iodoacetyl moieties are different in the two molecules [ϕ C(116)–C(117)–O(12)–C(122) 76 and ϕ C(216)–C(217)–O(22)–C(222) 141°] an effect to be attributed, presumably, to improved packing which results in the unit cell.

EXPERIMENTAL

17β-*Hydroxy*-4,4-*dimethyl*-5α-*androst*-7-*en*-3-*one*.—A solution of 17β-acetoxy-4,4-dimethylandrost-5-en-3-one (1.25 g)

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[7] H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, 1967, **23**, 439.

[8] W. B. Whalley, first reported at the I.U.P.A.C. Symposium on Natural Product Chemistry, Brussels, June 1962, and in numerous lectures since that time.

[9] C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 1968, **24**, 33.

[10] L. E. Sutton, *Chem. Soc. Special Publ.*, No. 18, 1965.

in benzene (25 ml) containing 1,3-dibromo-5,5-dimethylhydantoin (0.8 g) was heated under reflux for 40 min, when xylene (5 ml) was added and the reaction mixture reduced to 5 ml by evaporation *in vacuo*. After addition of trimethyl phosphite (0.6 ml) dissolved in xylene (15 ml), the mixture was refluxed for 1 h. Purification of the product from acetone–light petroleum (b.p. 40—60 °C) gave 17β-*acetoxy*-4,4-*dimethylandrosta*-5,7-*dien*-3-*one* (0.62 g) in *prisms, m.p.* 162—164 °C; $[\alpha]_D^{21}$ −78.5° (*c* 0.54 in chloroform) (Found: C, 77.4; H, 8.9%; M^+ 356. $C_{23}H_{32}O_3$ requires C, 77.5; H, 9.0%; M^+ 356).

A solution of this diene (0.85 g) in ethanol (150 ml) containing Raney nickel (W4 activity) (0.8 g.) was shaken in an atmosphere of hydrogen at 50 °C and 10 atmospheres pressure during 14 h, to yield 4,4-dimethyl-5α-androst-7-en-3β,17β-diol 17-acetate, which was oxidised without purification with Jones reagent to yield 17β-*acetoxy*-4,4-*dimethyl*-5α-*androst*-7-*en*-3-*one* (0.47 g) as plates, m.p. 129—130 °C from methanol–ether; $[\alpha]_D^{21}$ −64° (*c* 2.04 in chloroform) (Found: C, 76.9; H, 9.6%; M^+ 358. $C_{23}H_{34}O_3$ requires C, 77.1; H, 9.6%; *M* 358).

Hydrolysis of this acetate (0.45 g) dissolved in methanol (20 ml) containing water (1 ml) and potassium hydroxide (0.2 g) at the boiling point for 1 h, gave 17β-*hydroxy*-4,4-*dimethyl*-5α-*androst*-7-*en*-3-*one* (0.4 g) as needles, m.p. 170—172° from ether; $[\alpha]_D^{21}$ −3° (*c* 0.50 in chloroform) (Found: C, 79.7; H, 10.2. $C_{21}H_{32}O_2$ requires C, 79.6; H, 10.3%).

17β-*Iodoacetoxy*-4,4-*dimethyl*-5α-*androst*-7-*en*-3-*one* (2).—17-Hydroxy-4,4-dimethyl-5α-androst-7-en-3-one was treated with pyridine–chloroacetic anhydride, to give 17β-*chloroacetoxy*-4,4-*dimethyl*-5α-*androst*-7-*en*-3-*one* as prisms, m.p. 129 °C from ether–light petroleum (b.p. 60—80 °C); $[\alpha]_D^{21}$ −50° (*c* 0.40 in chloroform) (Found: C, 70.4; H, 8.6%; M^+ 393. $C_{23}H_{33}O_3Cl$ requires C, 70.3; H, 8.5%; M^+ 393).

TABLE 1

Interatomic distances (Å) and angles (°) for (2)

(*a*) Bonded distances

C(11)–C(12)	1.53(4)	C(21)–C(22)	1.52(5)
C(11)–C(110)	1.54(5)	C(21)–C(210)	1.53(3)
C(12)–C(13)	1.52(4)	C(22)–C(23)	1.45(4)
C(13)–C(14)	1.47(5)	C(23)–C(24)	1.52(4)
C(13)–O(11)	1.23(5)	C(23)–O(21)	1.21(3)
C(14)–C(15)	1.60(4)	C(24)–C(25)	1.61(4)
C(14)–C(120)	1.52(5)	C(24)–C(220)	1.60(5)
C(14)–C(121)	1.47(5)	C(24)–C(221)	1.49(4)
C(15)–C(16)	1.51(6)	C(25)–C(26)	1.56(3)
C(15)–C(110)	1.59(5)	C(25)–C(210)	1.54(3)
C(16)–C(17)	1.47(5)	C(26)–C(27)	1.48(4)
C(17)–C(18)	1.33(4)	C(27)–C(28)	1.33(3)
C(18)–C(19)	1.54(4)	C(28)–C(29)	1.46(3)
C(18)–C(114)	1.45(4)	C(28)–C(214)	1.55(4)
C(19)–C(110)	1.58(3)	C(29)–C(210)	1.54(4)
C(19)–C(111)	1.52(4)	C(29)–C(211)	1.58(3)
C(110)–C(119)	1.55(5)	C(210)–C(219)	1.49(4)
C(111)–C(112)	1.61(4)	C(211)–C(212)	1.51(5)
C(112)–C(113)	1.55(5)	C(212)–C(213)	1.56(3)
C(113)–C(114)	1.56(5)	C(213)–C(214)	1.55(3)
C(113)–C(117)	1.48(4)	C(213)–C(217)	1.54(4)
C(113)–C(118)	1.55(5)	C(213)–C(218)	1.45(5)
C(114)–C(115)	1.59(6)	C(214)–C(215)	1.50(4)
C(115)–C(116)	1.52(6)	C(215)–C(216)	1.46(4)
C(116)–C(117)	1.54(5)	C(216)–C(217)	1.52(4)
C(117)–O(12)	1.49(5)	C(217)–O(22)	1.39(2)
O(12)–C(122)	1.30(4)	O(22)–C(222)	1.34(3)
C(122)–O(13)	1.13(5)	C(222)–O(23)	1.20(4)
C(122)–C(123)	1.52(7)	C(222)–C(223)	1.42(4)
C(123)–I(1)	2.23(4)	C(223)–I(2)	2.16(4)

TABLE 1 (*Continued*)

(*b*) Angles

C(110)–C(11)–C(12)	114(2)	C(210)–C(21)–C(22)	112(2)
C(11)–C(12)–C(13)	108(2)	C(21)–C(22)–C(23)	110(3)
C(12)–C(13)–C(14)	122(3)	C(22)–C(23)–C(24)	122(2)
C(12)–C(13)–O(11)	117(3)	C(22)–C(23)–O(21)	120(2)
O(11)–C(13)–C(14)	122(3)	O(21)–C(23)–C(24)	118(2)
C(13)–C(14)–C(15)	109(2)	C(23)–C(24)–C(25)	108(3)
C(13)–C(14)–C(120)	108(3)	C(23)–C(24)–C(220)	104(2)
C(13)–C(14)–C(121)	105(2)	C(23)–C(24)–C(221)	111(3)
C(15)–C(14)–C(120)	105(2)	C(25)–C(24)–C(220)	114(2)
C(15)–C(14)–C(121)	116(3)	C(25)–C(24)–C(221)	109(2)
C(120)–C(14)–C(121)	113(2)	C(220)–C(24)–C(221)	111(2)
C(14)–C(15)–C(16)	118(2)	C(24)–C(25)–C(26)	111(2)
C(14)–C(15)–C(110)	118(2)	C(24)–C(25)–C(210)	118(2)
C(16)–C(15)–C(110)	106(3)	C(26)–C(25)–C(210)	110(2)
C(15)–C(16)–C(17)	115(3)	C(25)–C(26)–C(27)	109(2)
C(16)–C(17)–C(18)	122(3)	C(26)–C(27)–C(28)	123(2)
C(17)–C(18)–C(19)	123(3)	C(27)–C(28)–C(29)	124(2)
C(17)–C(18)–C(114)	123(3)	C(27)–C(28)–C(214)	119(2)
C(19)–C(18)–C(114)	113(2)	C(29)–C(28)–C(214)	116(2)
C(18)–C(19)–C(110)	111(2)	C(28)–C(29)–C(210)	110(2)
C(18)–C(19)–C(111)	112(3)	C(28)–C(29)–C(211)	112(2)
C(110)–C(19)–C(111)	114(2)	C(210)–C(29)–C(211)	113(2)
C(19)–C(110)–C(11)	109(2)	C(29)–C(210)–C(21)	110(2)
C(19)–C(110)–C(15)	108(2)	C(29)–C(210)–C(25)	106(2)
C(19)–C(110)–C(119)	111(3)	C(29)–C(210)–C(219)	109(2)
C(11)–C(110)–C(15)	109(3)	C(21)–C(210)–C(25)	109(2)
C(11)–C(110)–C(119)	109(2)	C(21)–C(210)–C(219)	110(2)
C(15)–C(110)–C(119)	110(3)	C(25)–C(210)–C(219)	112(2)
C(19)–C(111)–C(112)	114(2)	C(29)–C(211)–C(212)	115(3)
C(111)–C(112)–C(113)	107(2)	C(211)–C(212)–C(213)	110(2)
C(112)–C(113)–C(114)	106(3)	C(212)–C(213)–C(214)	107(2)
C(112)–C(113)–C(117)	112(3)	C(212)–C(213)–C(217)	115(2)
C(112)–C(113)–C(118)	109(3)	C(212)–C(213)–C(218)	109(3)
C(114)–C(113)–C(117)	100(3)	C(214)–C(213)–C(217)	99(2)
C(114)–C(113)–C(118)	117(2)	C(214)–C(213)–C(218)	115(2)
C(117)–C(113)–C(118)	114(3)	C(217)–C(213)–C(218)	112(2)
C(113)–C(114)–C(18)	116(2)	C(213)–C(214)–C(28)	111(2)
C(113)–C(114)–C(115)	102(3)	C(213)–C(214)–C(215)	101(2)
C(18)–C(114)–C(115)	121(3)	C(28)–C(214)–C(215)	122(2)
C(114)–C(115)–C(116)	102(3)	C(214)–C(215)–C(216)	104(2)
C(115)–C(116)–C(117)	108(3)	C(215)–C(216)–C(217)	110(2)
C(116)–C(117)–C(113)	103(3)	C(216)–C(217)–C(213)	100(2)
C(116)–C(117)–O(12)	111(4)	C(216)–C(217)–O(22)	114(3)
C(113)–C(117)–O(12)	107(3)	C(213)–C(217)–O(22)	114(2)
C(117)–O(12)–C(122)	116(3)	C(217)–O(22)–C(222)	124(2)
O(12)–C(122)–C(123)	110(3)	O(22)–C(222)–C(223)	113(3)
O(12)–C(122)–O(13)	125(4)	O(22)–C(222)–O(23)	120(2)
O(13)–C(122)–C(123)	124(4)	O(23)–C(222)–C(223)	127(3)
C(122)–C(123)–I(1)	108(3)	C(222)–C(223)–I(2)	112(2)

(*c*) Intermolecular contacts <3.5 Å

I(2) · · · $O(11^{I})$	3.07(2)	C(222) · · · O(11)	3.21(4)
C(123) · · · $O(23^{II})$	3.22(6)	O(22) · · · O(11)	3.14(4)
C(119) · · · $C(221^{III})$	3.49(5)		

Roman numeral superscripts refer to the following equivalent positions:

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

When a solution of this chloroacetate in acetone containing an excess of potassium iodide was heated under reflux for 3 h, 17β-*iodoacetoxy*-4,4-*dimethyl*-5α-*androst*-7-*en*-3-*one* (2) was formed quantitatively, as needles, m.p. 129 °C, from ether–light petroleum (b.p. 40—60 °C) (Found: C, 57.3; H, 7.2%; M^+ 484. $C_{23}H_{33}O_3I$ requires C, 57.0; H, 6.9%; *M* 484).

TABLE 2

Final positional parameters for (2)

	x	y	z
C(11) [a]	3 057(13)	3 403(14)	−4 447(33)
C(12)	3 521(14)	4 165(15)	−4 649(33)
C(13)	3 600(15)	4 482(15)	−2 833(42)
C(14)	3 831(14)	4 262(14)	−1 288(31)
C(15)	3 454(14)	3 455(16)	−1 255(36)
C(16)	3 729(17)	3 129(18)	−31(36)
C(17)	3 319(18)	2 391(16)	100(43)
C(18)	2 882(14)	2 021(14)	−1 152(32)
C(19)	2 746(12)	2 321(13)	−2 816(31)
C(110)	3 313(14)	3 074(15)	−3 106(33)
C(11)	2 603(15)	1 877(14)	−4 435(30)
C(112)	2 069(15)	1 094(17)	−4 101(41)
C(113)	2 343(14)	856(14)	−2 555(42)
C(114)	2 412(18)	1 309(18)	−932(39)
C(115)	2 488(22)	902(21)	669(39)
C(116)	2 077(23)	184(21)	18(45)
C(117)	1 827(18)	196(18)	−1 862(46)
C(118)	2 992(15)	873(17)	−3 181(38)
C(119)	3 968(15)	3 118(15)	−3 811(44)
C(120)	3 598(15)	4 456(17)	383(35)
C(121)	4 567(15)	4 605(15)	−1 459(38)
C(122)	1 355(19)	−943(21)	−2 729(49)
C(123)	1 452(23)	−1 424(19)	−3 904(50)
O(11)	3 476(12)	4 945(12)	−2 731(32)
O(12)	1 837(11)	−327(10)	−2 999(29)
O(13)	977(15)	−1 110(14)	−1 615(43)
I(1) [b]	1 169(2)	−1 321(2)	−6 667
C(21)	−1 631(14)	3 264(14)	−4 387(35)
C(22)	−2 342(15)	3 135(18)	−4 071(39)
C(23)	−2 620(14)	2 740(13)	−2 468(37)
C(24)	−2 243(15)	2 944(15)	−713(36)
C(25)	−1 459(13)	3 227(13)	−1 125(32)
C(26)	−1 014(13)	3 616(16)	493(31)
C(27)	−306(13)	3 804(14)	126(31)
C(28)	−71(12)	3 828(12)	−1 500(30)
C(29)	−482(11)	3 661(12)	−3 106(25)
C(210)	−1 161(11)	3 631(11)	−2 839(28)
C(211)	−70(12)	4 103(15)	−4 750(32)
C(212)	626(13)	4 202(14)	−4 953(30)
C(213)	1 033(12)	4 483(13)	−3 195(31)
C(214)	655(11)	3 953(13)	−1 734(32)
C(215)	1 158(15)	4 218(14)	−249(31)
C(216)	1 808(13)	4 500(16)	−1 147(38)
C(217)	1 707(11)	4 494(13)	−3 146(29)
C(218)	1 117(13)	5 142(14)	−2 837(33)
C(219)	−1 039(14)	4 330(15)	−2 708(36)
C(220)	−2 404(13)	3 498(14)	67(36)
C(221)	−2 493(14)	2 353(15)	504(36)
C(222)	2 470(14)	4 995(15)	−5 601(36)
C(223)	2 915(13)	5 635(15)	−6 357(39)
O(21)	−3 149(11)	2 213(12)	−2 531(30)
O(22)	2 227(8)	5 039(8)	−4 018(22)
O(23)	2 251(10)	4 455(9)	−6 305(27)
I(2)	2 375(1)	6 053(1)	−7 693(4)

[a] The numbering scheme follows the convention for steroids with a '1' or a '2' placed before every atom number to identify the two independent molecules. [b] The z co-ordinate of this atom was arbitrarily fixed at the value given to define the origin.

The crystals of the iodoacetate were slender, colourless needles elongated along c. Preliminary unit-cell data were obtained from precession and Weissenberg photographs taken with Cu-K_α radiation ($\lambda = 1.541\ 8$ Å). Final values of the cell dimensions were found by a least-squares fit of the values of $\pm 2\theta$ for 12 strong general reflections measured on our diffractometer.

Crystal data for (2). $C_{23}H_{33}IO_3$, $M = 484.4$. Trigonal, $a = 22.982(3)$, $c = 7.547(1)$ Å, $D_m = 1.38$, $Z = 6$, $D_c = 1.40$, $F(000) = 1\ 488$. Mo-K_α radiation, $\lambda = 0.710\ 69$ Å; μ(Mo-K_α) = 14 cm^{-1}. Space group $P3_1$ (C_3^2) or $P3_2$ (C_3^3) from systematic absences ($00l$ when $l = 3n + 1$ or $3n + 2$), and the $\bar{3}$ symmetry of the reciprocal lattice; shown to be $P3_2$ from structure analysis.

Intensity measurements were made for a small needle crystal mounted in a general orientation on a Hilger and Watts Y 290 four-circle diffractometer. The intensities of the 2 068 independent reflections with 2θ (Mo-K_α) $< 40°$ were measured with experimental conditions as outlined previously.[11] Of these reflections 1 686 having $I > 3\sigma(I)$ were considered observed; other reflections were excluded from all refinement calculations. Data were corrected for Lorentz and polarization factors but not for absorption which is negligible.

Calculations were performed on the University of Guelph IBM 370 155 computer. Data processing was done by use of a locally modified version of DATCO 5 from the crystallographic package of programs contained in the '*X*-Ray' system (1972).[12] Mathematical methods are described in ref. 13.

Structure Determination and Refinement.—The structure was solved by the heavy-atom method with phases originally based upon the co-ordinates of the two iodine atoms, whose positions in the asymmetric unit were found from the three-dimensional Patterson function. Successive electron-density maps revealed all the non-hydrogen atoms positions which were initially refined with isotropic thermal parameters by full-matrix least-squares calculations to R 0.098. Space group $P3_2$ was chosen over $P3_1$ because it yielded a structure with the correct absolute configuration. A difference electron-density map was calculated at this stage and suitable positions for all the hydrogen atoms were obtained. The model was then refined by block-diagonal least-squares procedures using only observed data with the non-hydrogen atoms being allowed to vibrate anisotropically. The scattering functions used were those for neutral atoms from ref. 14 for non-hydrogen atoms and from ref. 15 for hydrogen atoms; that for iodine was corrected for the effects of anoamalous dispersion;[16] hydrogen atoms (positioned at calculated values assuming C–H 1.08 Å) were included in the structure-factor calculations with an overall isotropic thermal parameter U 0.051 Å^2, but excluded from the refinement. Absolute weights, based on counting statistics, were used in the refinement. At convergence, R was 0.064 and $R'\{[\Sigma\omega(F_o - F_c)^2/\Sigma\omega F_o^2]^{\frac{1}{2}}\}$ was 0.085.

Interatomic distances and angles are shown in Table 1, and atom co-ordinates in Tables 2 and 3. Figure 1 shows a view of one of the two molecules in the asymmetric unit and Figure 2 contains mean torsion-angle data. Details of all the torsion angles in both molecules, anisotropic

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[11] G. Ferguson, D. F. Rendle, J. M. Midgley, and W. B. Whalley, *J.C.S. Perkin II*, 1978, 267.

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

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thermal parameters, mean plane calculations, and measured and calculated values of the structure factors have been deposited as Supplementary Publication No. SUP 22268 (33 pp., 1 microfiche).*

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TABLE 3

Calculated positional parameters ($\times 10^3$) for the hydrogen atoms in (2). The carbon atom to which each is bonded is in square brackets

Atom	x	y	z	Atom	x	y	z
H(11)[C(11)]	256	332	−395	H(21)[C(21)]	−163	280	−459
H(12)[C(11)]	298	317	−571	H(22)[C(21)]	−141	358	−556
H(13)[C(12)]	400	426	−514	H(23)[C(22)]	−236	359	−404
H(14)[C(12)]	330	436	−554	H(24)[C(22)]	−267	283	−522
H(15)[C(15)]	293	328	−86	H(25)[C(25)]	−139	280	−142
H(16)[C(16)]	424	329	−43	H(26)[C(26)]	−103	408	73
H(17)[C(16)]	378	336	134	H(27)[C(26)]	−119	332	171
H(18)[C(17)]	336	212	128	H(28)[C(27)]	5	392	125
H(19)[C(19)]	228	232	−267	H(29)[C(29)]	−59	317	−356
H(110)[C(111)]	243	208	−552	H(210)[C(211)]	−36	387	−591
H(111)[C(111)]	308	192	−488	H(211)[C(211)]	−4	459	−457
H(112)[C(112)]	158	104	−382	H(212)[C(212)]	60	374	−528
H(113)[C(112)]	202	80	−531	H(213)[C(212)]	87	457	−603
H(114)[C(114)]	191	126	−73	H(214)[C(214)]	61	347	−210
H(115)[C(115)]	302	103	83	H(215)[C(215)]	112	462	45
H(116)[C(115)]	231	98	192	H(216)[C(215)]	107	383	68
H(117)[C(116)]	238	−4	1	H(217)[C(216)]	216	500	−71
H(118)[C(116)]	166	−7	95	H(218)[C(216)]	204	418	−82
H(119)[C(117)]	130	13	−177	H(219)[C(217)]	166	403	−375
H(120)[C(118)]	320	82	−210	H(220)[C(218)]	141	537	−164
H(121)[C(118)]	289	54	−430	H(221)[C(218)]	138	551	−392
H(122)[C(118)]	338	138	−361	H(222)[C(218)]	63	512	−266
H(123)[C(119)]	416	290	−290	H(223)[C(219)]	−71	461	−160
H(124)[C(119)]	389	289	−509	H(224)[C(219)]	−81	462	−392
H(125)[C(119)]	435	366	−394	H(225)[C(219)]	−151	433	−252
H(126)[C(120)]	376	427	156	H(226)[C(220)]	−213	365	131
H(127)[C(120)]	384	499	49	H(227)[C(220)]	−221	394	−82
H(128)[C(120)]	307	423	44	H(228)[C(220)]	−293	331	27
H(129)[C(121)]	473	442	−31	H(229)[C(221)]	−223	248	178
H(130)[C(121)]	472	447	−266	H(230)[C(221)]	−302	215	79
H(131)[C(121)]	479	514	−137	H(231)[C(221)]	−243	196	−8
H(132)[C(123)]	196	−133	−395	H(232)[C(223)]	322	597	−528
H(133)[C(123)]	113	−195	−352	H(233)[C(223)]	326	559	−727

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

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