Stereochemistry of Hydroboronation and Osmylation of 3α,5-Cycloandrost-6-en-17-one

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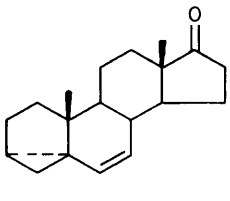
The stereochemistry of osmylation of a steroidal 6-ene is shown to be modified by the presence of a 3α,5-cyclopropane ring leading to predominantly β-face attack. Hydroboronation affords the 6α-, 7α-, and 7β-alcohols.

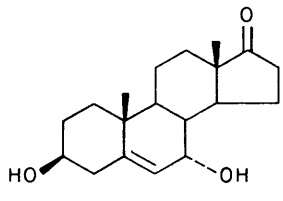
The facility with which a cyclopropane ring stabilizes an adjacent carbocation is amply demonstrated in the steroid series by the reactions of 6β-substituted-3α,5-cyclo steroids.[1] In previous work[2] we examined the participation of a 3α,5-cyclopropane ring in the epoxidation of a steroidal 6-ene. Thus treatment of 3α,5-cycloandrost-6-en-17-one (**1**) with *m*-chloroperbenzoic acid gave 3β,7α-dihydroxy-androst-5-en-17-one (**2**), 6β,7α-dihydroxy-3α,5-cycloandrostan-17-one (**3**), their 3β- and 6β-*m*-chlorobenzoates and a small amount of 6β-methoxy-7α-hydroxy-3α,5-cycloandrostan-17-one arising from methanol in the solvent. The formation of these products was rationalized in terms of 'α' attack by the reagent and a ready cleavage of the epoxide followed by stabilization of the incipient carbocation by the cyclopropane ring. The individual products were then determined by the nucleophilic components of the medium with a preference for attack at C-6β as found in the i-steroid system. Indeed the formation of such products may be a good test for any ionic character in a reaction. In this paper we examine two aspects of the role of the 3α,5-cyclopropane ring. Firstly the propensity for 6β-addition and secondly the effect on hydroboronation and osmylation, reactions that are conventionally considered to operate by cycloaddition mechanisms.

The optimum geometry of the cyclopropylcarbinyl cation has been calculated[3] and shown to be one in which the carbinyl cation bisects the cyclopropane ring. In the absence of stable crystalline salts,[4] to a first approximation, the conformation of 3α,5-cycloandrostane-6,17-dione (**4**)[5] may mimic the geometry of the corresponding cyclopropyl carbocation. We have determined the *X*-ray crystal structure of the diketone (see Figure 1) and this shows that the plane of O(1)–C(6)–C(7) adopts a favourable bisecting geometry. Furthermore the torsion angles O(1)–C(6)–C(5)–C(3) (−59.5°) and O(1)–C(6)–C(5)–C(4) (10°) indicate that the cyclopropane ring lies predominantly on the α face of the C-6 carbonyl group. If this structure does represent a reasonable model for the carbocation then there would be greater electron donation from the cyclopropane ring into the 'α'-lobe of the vacant '*p*' orbital at C-6 making the 'β' lobe more susceptible to nucleophilic attack thus possibly accounting for some of the propensity of the 3α,5-cycloandrostane cation to react at the 6β-position. The structure also reveals the cyclopropane ring deforming ring A so that it partly encumbers the 'α'-face of the molecule.

Treatment of 3α,5-cycloandrost-6-en-17-one (**1**)[2,6] in tetrahydrofuran with borane followed by oxidative hydrolysis with alkaline hydrogen peroxide gave the 6α-alcohol (**5**) and an inseparable mixture (1:1) of 7α-(**6**) and 7β-(**7**) alcohols. The ratio of the 6-:7-alcohols was 1:4. The 6α,17β-diol (**5**) was identified by oxidation to the 6,17-dione (**4**).[5] The stereochemistry of the 6-hydroxy group followed from the multiplicity of the n.m.r. signal (δ 5.10, d, *J* 4.4 and 11.5 Hz) in the corresponding acetate.[7] The 6β,17β-diacetoxy-3α,5-cycloandrostane (**8**) was prepared for comparison purposes from the i-steroid. In



(**1**)



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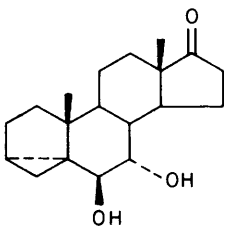
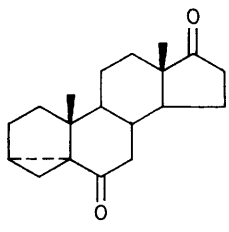
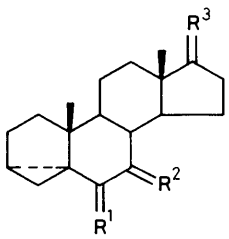


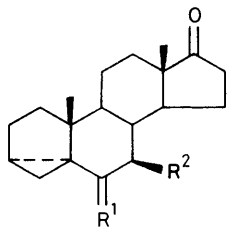
(**3**)



(**4**)



(**5**)—(**9**)



(**10**)—(**12**)

(**5**) R′ = α-OH,β-H; R^2 = H_2; R^3 = α-H,β-OH
(**6**) R′ = H_2; R_2 = α-OH, β-H; R_3 = α-H,βOH
(**7**) R′ = H_2; R^2 = α-H,β-OH; R^3 = α-H,β-OH
(**8**) R′ = α-H,β-OAc; R^2 = H_2; R^3 = α-H,β-OAc
(**9**) R′ = H_2; R^2 = O; R^3 = O
(**10**) R′ = α-H,β-OH; R^2 = OH
(**11**) R′ = α-H,β-OH; R^2 = OMs
(**12**) R′ = O; R^2 = OMs

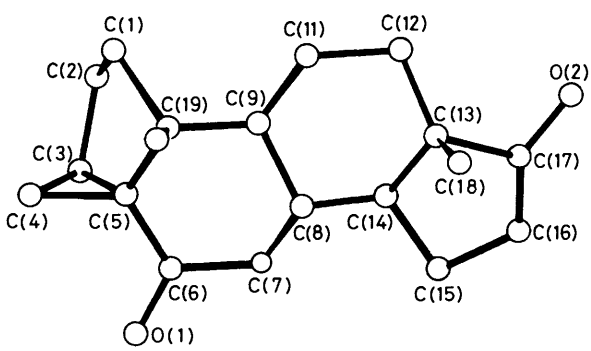
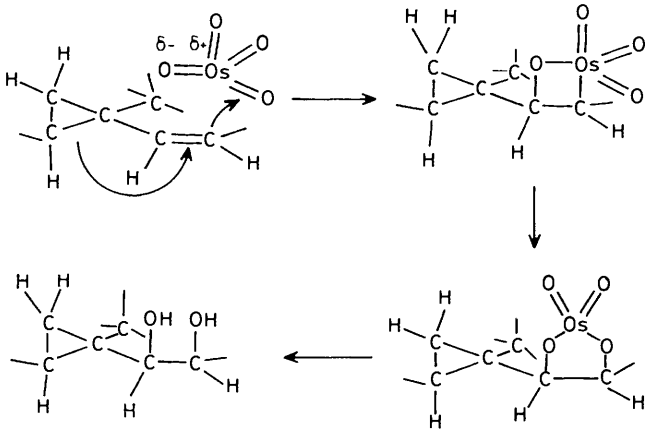


Figure 1. Crystal structure of compound (**4**)

this case the 6-H n.m.r. signal appeared at δ 4.49 (triplet, *J* 2.8 Hz). The 360 MHz ^{1}H n.m.r. spectrum of the 7-alcohol mixture showed 7-H C*H*(OH) signals at δ 3.35 (*J* 4.8 and 11.0 Hz, 7α-H) and 3.74 (broad singlet, 7β-H). Oxidation of the 7-alcohols with chromium trioxide gave the 7,17-dione (**9**). Although reduction with sodium borohydride regenerated the mixture of epimers, reduction with sodium in refluxing butanol [8] yielded the 7β,17β-diol (**7**) which was then acetylated. The 7-H resonance appeared (δ 4.56) as a triplet (*J* 10.9 Hz) of doublets (4.5 Hz). The formation of a significant amount (40%) of the 7β-alcohol in the hydroboronation is in contrast to the hydroboronation of 5α-cholest-6-en-3β-ol which is reported [9] to give a 1:1 mixture of the corresponding 3β,6α- and 3β,7α-diols. Although this difference may be rationalized in steric terms, if there is a small 'ionic' character ($H^- - BH_2^+$) to the *cis*-hydroboronation, then the cyclopropane ring might be expected to direct it in the observed sense.

In previous work [10] we reported that osmylation of 3α,5-cycloandrost-6-en-17-one (**1**) afforded the 6β,7β-diol (**10**). This compound had been obtained [11] prior to our work by the microbiological transformation of 6β-hydroxy-3α,5-cycloandrostan-17-one. Nevertheless the result is surprising since it represents a complete reversal of the stereochemistry of osmylation of 3β-hydroxy-5α-cholest-6-ene which affords [12,13] the 6α,7α-diol. Consequently in order to check our previous work we examined the product of osmylation of 3α,5-cycloandrost-6-en-17-one further. The same 6β,7β-diol was formed by the action of the phase transfer oxidant, cetyltrimethylammonium permanganate, on 3α,5-cycloandrost-6-en-17-one. The 360 MHz ^{1}H n.m.r. spectrum revealed C*H*(OH) signals at δ 3.23 (doublet, *J* 3.6 Hz, 6α-H) and 3.46 (dd, *J* 3.6 and 10 Hz, 7α-H). Selective population transfer ^{1}H n.m.r. experiments linked the 3.46 signal both to that at δ 3.23 and to a quartet, δ 1.97 (*J* 10.0 Hz, 8-H). A nuclear Overhauser enhancement experiment based on irradiating the δ 1.06 methyl signal led to enhancements of a cyclopropyl CH resonance (δ 0.58, *J* 3.9 and 5 Hz, 4β-H), 8-H (δ 1.97), and the CH(O*H*) signals δ 2.16 and 2.38 (2%) both of which were exchangeable by a ^2H_2O wash. This n.O.e. experiment, which enhanced the hydroxy protons and the magnitude of the coupling constants together provide strong evidence for the stereochemistry of the diol.

The diol formed an unstable monomethanesulphonate (**11**) on treatment with methanesulphonyl chloride. Oxidation of this compound gave a ketone (**12**) in which the C*H*(OMs) signal was a clean doublet (*J* 11 Hz) corresponding to a diaxial coupling. Rather than undergoing elimination to form an α,β-unsaturated ketone, reaction of the methanesulphonate with lithium iodide, led to reduction to afford the ketone (**4**).



Scheme.

The stereochemistry of the diol may be interpreted in terms of the Sharpless mechanism for the *cis*-hydroxylation of alkenes.[14,15] This (see the Scheme) envisages an initial addition of the polarized oxo moiety to the alkene to form an organometallic intermediate which then rearranges to the cyclic osmate ester. In this case participation of the cyclopropane ring would favour the initial orientation of oxygen to the 6β-position and thence because of the cyclic nature of the intermediate, the formation of the 6β,7β-diol.

Experimental

Light petroleum refers to the fraction b.p. 60—80 °C, silica for chromatography was Merck 9385. Extracts were dried over sodium sulphate. ^{1}H N.m.r. spectra were determined on a Bruker WH 360 spectrometer for solutions in $CDCl_3$; i.r. spectra were recorded as Nujol mulls.

Hydroboronation of 3α,5-Cycloandrost-6-en-17-one.—The steroid (900 mg) in dry tetrahydrofuran (20 ml) under nitrogen was treated with 1M-borane in tetrahydrofuran (10 ml) and the reaction was left to stir overnight at room temperature. The mixture was cooled to 0 °C and aqueous potassium hydroxide (10%; 13 ml) and hydrogen peroxide (30%; 15 ml) were added. The mixture was then stirred at room temperature for a further 5 h whereupon it was neutralized with acetic acid, water was added, and the steroids were recovered in ethyl acetate. The extract was washed consecutively with aqueous sodium sulphite and water and then dried. The solvent was evaporated and the residue was chromatographed on silica. Elution with 20% ethyl acetate–light petroleum gave 6α,17β-dihydroxy-3α,5-cycloandrostane (65 mg) which crystallized from ethyl acetate–light petroleum as plates, m.p. 174—176 °C (lit.,[7] 176—177 °C, the stereochemical assignments in this paper should be reversed), $\nu_{max.}$ 3 460, 3 400, 3 330, and 3 080 cm^{-1}; δ 0.3 (1 H, m, cyclopropane), 0.7 (3 H, s, 18-H_3), 0.95 (3 H, s, 19-H_3), and 3.8 (2 H, m, 6-H and 17-H). The diacetate, prepared with acetic anhydride in pyridine, had m.p. 129—131 °C (lit.,[7] 130—130.5 °C); $\nu_{max.}$ 1 735 and 1 245 cm^{-1}; δ 0.3 (1 H, m, 4-H), 0.8 (3 H, s, 18-H), 0.92 (3 H, s, 19-H), 1.94 and 2.02 (each 3 H, s, OAc), 4.56 (1 H, t, *J* 7.8 Hz, 17-H), and 5.1 (1 H, dd, *J* 5.0 and 11.8 Hz, 6-H). Further elution with 30% ethyl acetate–light petroleum gave a 1:1 mixture of 7α- and 7β-, 17β-dihydroxy-3α,5-cycloandrostane (554 mg), $\nu_{max.}$ 3 350 cm^{-1}; δ 0.33, 0.75, and 0.77 (18-H_3), 0.91 and 0.92 (19-H_3), 3.35 (7α-H, *J* 4.8 and 11.0 Hz), 3.65 and 3.58 (t, *J* 8.6 Hz, 17-H), and 3.74 (br s, 7β-H).

Oxidation of 6α,17β-Dihydroxy-3α,5-cycloandrostane.—The steroid (100 mg) in acetone (10 ml) at 0 °C was treated with chromium trioxide reagent (4M; 0.3 ml) for 30 min. Methanol (2 ml) was added and the solution was concentrated, diluted with water, and the steroid recovered in ethyl acetate to give 3α,5-cycloandrostane-6,17-dione (80 mg) as needles, m.p. 189—192 °C (lit.,[7] 182—183 °C), $\nu_{max.}$ 1 735 and 1 690 cm^{-1}; δ 0.98 (3 H, s, 18-H_3) and 1.10 (3 H, s, 19-H_3).

3α,5-Cycloandrostane-7,17-dione.—The mixture of alcohols from the hydroboronation (250 mg) in acetone (15 ml) was treated with the chromium trioxide reagent (1 ml) at room temperature for 1 h. The solution was concentrated under reduced pressure and diluted with water. The steroid was recovered in ethyl acetate. The extract was washed consecutively with aqueous sodium hydrogen carbonate and water, and then dried. The solvent was evaporated and the residue crystallized from ethyl acetate–light petroleum to afford 3α,5-*cycloandrostane*-7,17-*dione* (200 mg) as needles, m.p. 145—146 °C, $[\alpha]_D^{20}$ +50° (*c*, 1 in $CHCl_3$) (Found: C, 79.7; H, 9.3. $C_{19}H_{26}O_2$ requires C, 79.7; H, 9.15%); $\nu_{max.}$ 3 050, 3 010, 1 720, and 1 710

cm^{-1}; δ 0.4 (1 H, m, cyclopropane), 0.89 (3 H, s, 18-H_3), and 1.18 (3 H, s, 19-H_3).

7β,17β-*Diacetoxy*-3α,5-*cycloandrostane*.—Sodium (480 mg) was added in portions to 3α,5-cycloandrostan-7,17-dione (400 mg) in refluxing butanol (50 ml) over 25 min. The solution was cooled, concentrated, and diluted with water, and the steroid was recovered in ethyl acetate. The crude product was chromatographed on silica. Elution with 15% ethyl acetate–light petroleum gave 7β,17β-dihydroxy-3α,5-cycloandrostane (370 mg) which was treated with acetic anhydride (0.5 ml) in pyridine (1 ml) overnight. The solution was poured into water and the steroid was recovered in ethyl acetate and chromatographed on silica. Elution with 10% ethyl acetate–light petroleum gave 7β,17β-*diacetoxy*-3α,5-*cycloandrostane* (345 mg) which crystallized from ethyl acetate–light petroleum as needles, m.p. 117—122 °C $[\alpha]_D^{20}$ +82° (*c*, 1 in $CHCl_3$) (Found: C, 74.0; H, 9.2. $C_{23}H_{34}O_4$ requires C, 73.8; H, 9.15%); $\nu_{max.}$ 3 050, 1 740, and 1 240 cm^{-1}; δ 0.31 (1 H, q, *J* 4.7 and 3.7 Hz, 4-H), 0.8 (3 H, s, 18-H_3), 0.90 (3 H, s, 19-H_3), 1.95 and 2.00 (each 3 H, s, OAc), 4.52 (1 H, t, *J* 7.8 Hz, 17-H), and 4.56 (1 H, dd, *J* 4.8 and 11.0 Hz, 7α-H).

Hydroxylation of 3α,5-*Cycloandrost*-6-*en*-17-*one*.—The steroid (620 mg) in t-butyl alcohol (17 ml) was treated with a solution of cetyltrimethylammonium permanganate (3 g) in t-butyl alcohol (20 ml) and water (5 ml) at room temperature for 24 h. Chloroform (50 ml) and aqueous sodium hydroxide (2%; 20 ml) were added and the solution was stirred for a further 30 min. The phases were separated and the organic solvents were evaporated under reduced pressure. The organic extract was taken up in chloroform, washed with water, and dried over sodium sulphate. The solvent was evaporated and the residue was chromatographed on silica to give 6β,7β-dihydroxy-3α,5-cycloandrostan-17-one (338 mg) which crystallized from acetone as needles, m.p. 165—167 °C (lit.,[10] 169—172 °C), δ(360 MHz), 0.36 (1 H, dd, *J* 5.5 and 8.0 Hz, 4-H), 0.58 (1 H, dd, *J* 4.2 and 5.5 Hz, 4-H), 0.93 (3 H, s, 18-H_3), 1.06 (3 H, s, 19-H_3), 3.23 (1 H, d, *J* 3.6 Hz, 6-H), and 3.46 (1 H, dd, *J* 3.6 and 10.0 Hz, 7-H). It was identical to material prepared by treatment of the steroid with osmium tetroxide in pyridine. The diacetate, prepared with acetic anhydride in pyridine was an oil, $\nu_{max.}$ 1 740 cm^{-1}; δ 0.40 (2 H, m, 4-H_2), 0.98 (3 H, s, 18-H_3), 1.05 (3 H, s, 19-H_3), and 1.98 and 2.09 (each 3 H, s, OAc), and 4.8 (2 H, m, 6-H and 7-H).

6β-*Hydroxy*-7β-*methylsulphonyloxy*-3α,5-*cycloandrostan*-17-*one*.—The above diol (360 mg) in dry pyridine (15 ml) was treated with methanesulphonyl chloride (1.5 ml) at 0 °C for 1 h. The mixture was poured into dilute hydrochloric acid and the steroid recovered in ethyl acetate. The extract was washed with aqueous sodium hydrogen carbonate and water and then dried. The solvent was evaporated to give a brown oil which was chromatographed on silica. Elution with 10% ethyl acetate–light petroleum gave 6β-*hydroxy*-7β-*methylsulphonyloxy*-3α,5-*cycloandrostan*-17-*one* (100 mg), m.p. 80 °C (Found: C, 62.5; H, 7.7. $C_{20}H_{30}O_5S$ requires C, 62.8; H, 7.9%); $\nu_{max.}$ 3 420, 1 735, and 1 170 cm^{-1}; δ 0.38 (1 H, dd, *J* 5 and 8 Hz, 4-H), 0.58 (1 H, dd, *J* 4 and 5 Hz, 4-H), 0.9 (3 H, 18-H_3), 1.05 (3 H, s, 19-H_3), 3.05 (3 H, s, OMs), 3.6 (1 H, d, *J* 3.5 Hz, 6-H), and 4.65 (1 H, dd, *J* 3.5 and 10.0 Hz, 7-H).

7β-*Methylsulphonyloxy*-3α,5-*cycloandrostane*-6,17-*dione*.—The above alcohol (45 mg) in acetone (5 ml) was treated with the chromium trioxide reagent (0.5 ml) for 30 min. Methanol was added and the solution was then concentrated under reduced pressure. The steroid was recovered in ethyl acetate, washed with water, and dried. The solvent was evaporated to give 7β-*methylsulphonyloxy*-3α,5-*cycloandrostane*-6,17-*dione* (40 mg) which crystallized from ethyl acetate–light petroleum as needles, m.p. 174 °C (decomp.) (Found: C, 63.1; H, 7.3. $C_{20}H_{28}O_5S$ requires C, 63.1; H, 7.4%); $\nu_{max.}$ 1 740, 1 700, and 1 170 cm^{-1}; δ 0.83 (1 H, t, *J* 5 Hz, 4-H), 0.94 (3 H, s, 18-H_3), 1.06 (3 H, s, 19-H_3), 3.37 (3 H, s, OMs), and 4.93 (1 H, d, *J* 11 Hz, 7-H).

Reaction with Lithium Iodide.—The above methanesulphonate (50 mg) in 2,4,6-trimethylpyridine (2 ml) was treated with lithium iodide (200 mg) under reflux for 15 min. The mixture was cooled, poured into dilute hydrochloric acid and the steroid was recovered in ethyl acetate and chromatographed on silica. Elution with 5% ethyl acetate–light petroleum gave 3α,5-cycloandrostan-6,17-dione (20 mg), which crystallized from ethyl acetate–light petroleum as needles, m.p. 186—188 °C (lit.,[5] 182—184 °C) identical (i.r. and n.m.r.) with the material prepared by the oxidation of 6β-hydroxy-3α,5-cycloandrostan-17-one.

Crystal Structure Determination: Crystal Data.—$C_{19}H_{26}O_2$, M = 286.4, orthorhombic, space group $P2_12_12_1$, a = 6.456(9), b = 12.351(3), c = 19.571(4) Å, U = 1 560.4 $Å^3$, Z = 4, D_c = 1.22 g cm^{-3}; monochromated Mo-K_α radiation λ = 0.710 69 Å, μ = 0.7 cm^{-1}.

A crystal *ca.* 0.37 × 0.13 × 0.02 mm was mounted on an Enraf–Nonius CAD4 diffractometer. Intensities for unique reflections with $2 < \theta < 25°$ were measured with an $\omega - 2\theta$ scan with a maximum scan time of 120 s. No corrections were made for absorption. Out of 1 761 reflections measured, 530 with $|F^2| > \sigma(F^2)$ were used in the structure refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/\mathrm{Lp}$. The structure was solved using MULTAN and refined by full-matrix least squares. Only isotropic temperature factors were used owing to the limited amount of data and no attempt was made to include hydrogen atoms. Refinement converged at R = 0.160, R' = 0.160 with a weighting scheme of $\omega = 1/\sigma^2(F)$. A final difference map was everywhere <0.5 *e* $Å^{-3}$. All calculations were carried out on a PDP 11/34 computer using the Enraf–Nonius SDP-Plus program system. Fractional atomic co-ordinates, intramolecular

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	6 427(33)	7 585(16)	3 153(8)
O(2)	−3 084(36)	9 282(19)	586(10)
C(1)	99(41)	9 696(21)	4 161(10)
C(2)	901(45)	8 557(23)	4 410(12)
C(3)	3 126(55)	7 958(27)	4 243(14)
C(4)	4 898(44)	8 863(24)	4 343(13)
C(5)	3 796(38)	8 737(19)	3 639(10)
C(6)	4 751(40)	8 157(20)	3 066(11)
C(7)	3 410(48)	7 897(22)	2 415(12)
C(8)	2 210(39)	8 827(19)	2 223(10)
C(9)	943(40)	9 294(20)	2 819(10)
C(10)	2 325(36)	9 652(20)	3 436(10)
C(11)	−478(39)	10 189(20)	2 600(12)
C(12)	−1 844(41)	9 922(20)	1 975(12)
C(13)	−373(43)	9 563(23)	1 409(12)
C(14)	778(44)	8 508(21)	1 652(11)
C(15)	1 678(57)	8 019(27)	1 014(14)
C(16)	−122(58)	8 053(29)	538(16)
C(17)	−1 287(64)	8 939(34)	763(17)
C(18)	892(47)	10 479(23)	1 089(12)
C(19)	3 487(47)	10 648(23)	3 298(13)

Table 2. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonds

O(1)–C(6)	1.30(3)	O(2)–C(17)	1.28(5)
C(1)–C(2)	1.49(4)	C(1)–C(10)	1.66(3)
C(2)–C(3)	1.65(5)	C(3)–C(4)	1.61(4)
C(3)–C(5)	1.58(4)	C(4)–C(5)	1.56(3)
C(5)–C(6)	1.47(3)	C(5)–C(10)	1.53(3)
C(6)–C(7)	1.57(3)	C(7)–C(8)	1.43(4)
C(8)–C(9)	1.54(3)	C(8)–C(14)	1.50(3)
C(9)–C(10)	1.56(3)	C(9)–C(11)	1.50(4)
C(10)–C(19)	1.47(4)	C(11)–C(12)	1.54(3)
C(12)–C(13)	1.52(4)	C(13)–C(14)	1.57(4)
C(13)–C(17)	1.59(5)	C(13)–C(18)	1.53(4)
C(14)–C(15)	1.50(4)	C(15)–C(16)	1.49(5)
C(16)–C(17)	1.40(5)		

(*b*) Angles

C(2)–C(1)–C(10)	106(2)	C(1)–C(2)–C(3)	109(2)
C(2)–C(3)–C(4)	106(2)	C(2)–C(3)–C(5)	97(2)
C(4)–C(3)–C(5)	58(2)	C(3)–C(4)–C(5)	60(2)
C(3)–C(5)–C(4)	62(2)	C(3)–C(5)–C(6)	113(2)
C(3)–C(5)–C(10)	118(2)	C(4)–C(5)–C(6)	122(2)
C(4)–C(5)–C(10)	116(2)	C(6)–C(5)–C(10)	115(2)
O(1)–C(6)–C(5)	121(2)	O(1)–C(6)–C(7)	117(2)
C(5)–C(6)–C(7)	119(2)	C(6)–C(7)–C(8)	110(2)
C(7)–C(8)–C(9)	113(2)	C(7)–C(8)–C(14)	108(2)
C(9)–C(8)–C(14)	110(2)	C(8)–C(9)–C(10)	113(2)
C(8)–C(9)–C(11)	113(2)	C(10)–C(9)–C(11)	111(2)
C(1)–C(10)–C(5)	97(2)	C(1)–C(10)–C(9)	112(2)
C(1)–C(10)–C(19)	113(2)	C(5)–C(10)–C(9)	110(2)
C(5)–C(10)–C(19)	111(2)	C(9)–C(10)–C(19)	113(2)
C(9)–C(11)–C(12)	115(2)	C(11)–C(12)–C(13)	106(2)
C(12)–C(13)–C(14)	108(2)	C(12)–C(13)–C(17)	119(2)
C(12)–C(13)–C(18)	115(2)	C(14)–C(13)–C(17)	91(2)
C(14)–C(13)–C(18)	119(2)	C(17)–C(13)–C(18)	103(2)
C(8)–C(14)–C(13)	107(2)	C(8)–C(14)–C(15)	119(2)
C(13)–C(14)–C(15)	105(2)	C(14)–C(15)–C(16)	102(3)
C(15)–C(16)–C(17)	104(3)	O(2)–C(17)–C(13)	113(3)
O(2)–C(17)–C(16)	131(3)	C(13)–C(17)–C(16)	115(3)

distances and angles are given in Tables 1 and 2. Torsion angles and isotropic temperature factors are available on request from the Cambridge Crystallographic Data Centre.*

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* For details of the data deposition scheme, see 'Instructions for Authors (1988),' *J. Chem. Soc., Perkin Trans. 1*, 1988, issue 1, paragraph 5.6.3.

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