Ring-*C* Aromatic Steroids. Part 5.† C-17 Hydroxylation and Side-chain Degradation of 18-Nor-17α(H)- and -17β(H)-pregna-4,8,11,13-tetraene-3,20-dione. *X*-Ray Structure of 17β-Hydroxy-18-nor-17β(H)-pregna-4,8,11,13-tetraene-3,20-dione

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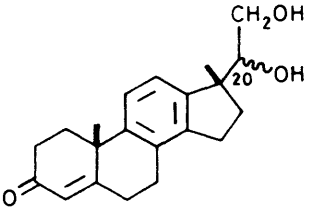
The procedure for 17-hydroxylation of pregnan-20-ones using oxygen, butoxide, and triethyl phosphite was extended to steroid analogues with aromatic *C*-rings, *viz.* 18-nor-17α(H)- and -17β(H)-pregna-4,8,11,13-tetraene-3,20-dione (and to 1-acetylindan). At temperatures higher than that we adopted (−50 °C), side-chain cleavage to give the 17-ketone (or equivalent) became prominent. Results of an *X*-ray crystallographic study on one of the two 17-epimeric *C*-aromatic products, 17β-hydroxy-18-nor-17β(H)-pregna-4,8,11,13-tetraene-3,20-dione, are presented. The crystals are orthorhombic, space group $P2_12_12_1$, with four molecules in a cell of dimensions a = 9.643(3), b = 17.043(4), c = 10.015(3) Å. The structure was solved by direct methods and refined by full-matrix least-squares calculations; R = 0.059 for 1 219 observed reflections. Ring *A* has a 1α,2β-half-chair conformation, ring *B* is in a 5α,6β-half-chair conformation, aromatic ring *C* is planar, and ring *D* is a C(16)β-envelope. Molecules are linked to form infinite chains by intermolecular O–H ··· O hydrogen bonds [O ··· O 2.801(4) Å].

During the course of a programme to synthesize analogues of the steroid hormones with an aromatic ring *C* (and therefore 18-nor) functionality,[1] we observed dramatic differences in the glucocorticoid and mineralocorticoid activities shown by the *C*-aromatic steroids (**1a**) and (**1b**) which differ only in the configuration at C-20.[2] To study the possible relation between the three-dimensional arrangement of groups on ring *D*[3] and hormonal activity, we have synthesized the 17-epimeric pair 17α- and 17β-hydroxy-18-norpregna-4,8,11,13-tetraene-3,20-dione (**2a**) and (**2b**). In this paper we give details of the formation of these two *C*-aromatic steroids by 17-hydroxylation of a mixture of 18-nor-17α(H)- and -17β(H)-pregna-4,8,11,13-tetraene-3,20-dione (**3a**) and (**3b**),‡ and also give the results of an *X*-ray crystallographic study of the 17β-hydroxy isomer (**2b**).

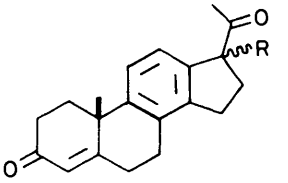
It was reported that steroids having the progesterone side-chain could be hydroxylated specifically at the C-17 position in a one-step procedure by reaction with oxygen and triethyl phosphite at −25 °C in the presence of sodium t-butoxide in dimethylformamide (DMF)–t-butyl alcohol.[4] Though the Δ^4-3-keto function was reported not to survive these conditions, we nevertheless explored the application of the method to the 17-hydroxylation of the ring-*C* aromatic analogue of progesterone, compound (**3a**), and its 17-epimer (**3b**).

Using 1-acetylindan (**4**) as a model, we found that when carried out at −25 °C the process of 1-hydroxylation [yielding product (**5**)] was accompanied by the loss of the acetyl side-chain, giving a comparable yield of indan-1-one (**6**). By working at −50 °C (which is the lowest temperature which does not cause freezing of the mixture) the side-chain cleavage was reduced, and the ratio of hydroxylation product to cleavage product was raised to 4:1, the overall reaction nevertheless reaching completion in 15 min. When progesterone (**7**) was subjected to the same reaction conditions, it was recovered unchanged, showing that the Δ^4-3-keto function is stable at the lower temperature we adopted.

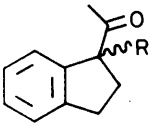
When a 3:1 mixture of 18-nor-17α(H)- and -17β(H)-pregna-4,8,11,13-tetraene-3,20-dione (**3a**) and (**3b**)‡ was likewise treated for 15 min at −50 °C, the two 17-hydroxylated *C*-aromatic products (**2a**) and (**2b**) and the side-chain-cleaved



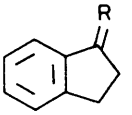
(**1a**) and (**1b**)



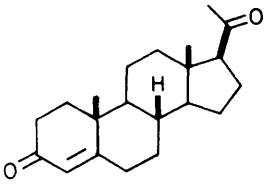
(**2a**) R = α-OH
(**2b**) R = β-OH
(**3a**) R = α-H
(**3b**) R = β-H



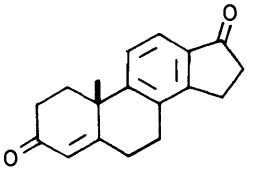
(**4**) R = H
(**5**) R = OH



(**6**) R = O
(**9**) R = >C(NC)–Me



(**7**)



(**8**)

† Part 4, ref. 1.
‡ As the hydroxylation reaction occurs *via* the 17,20 enolate, it was not necessary to start with a pure 17-epimer.

material (**8**) were obtained as a 1:1:1 mixture, separated by preparative high-pressure liquid chromatography (h.p.l.c.) into the pure components. As the side-chain-cleaved product (**8**) is the *C*-aromatic (18-nor) analogue of 17-dehydrotestosterone, we looked for a more efficient method of producing it. In the event, exclusive cleavage of the side-chain was achieved by omitting triethyl phosphite from the reaction mixture.

Only one of the 17-hydroxy products could be prepared in a crystalline form (see Experimental section) suitable for our *X*-ray studies which established that the material so examined is the 17β-hydroxy derivative (**2b**). The *X*-ray analysis did not establish the absolute configuration of compound (**2b**) but this is already known.[3] All the data for compound (**2b**) refer to this absolute configuration. A view of a molecule and our numbering scheme is in the Figure. The bond-length data, summarized

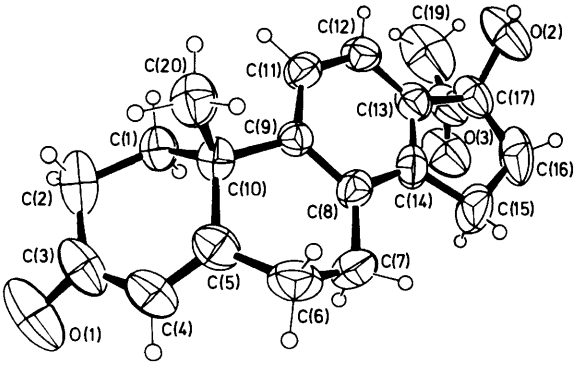
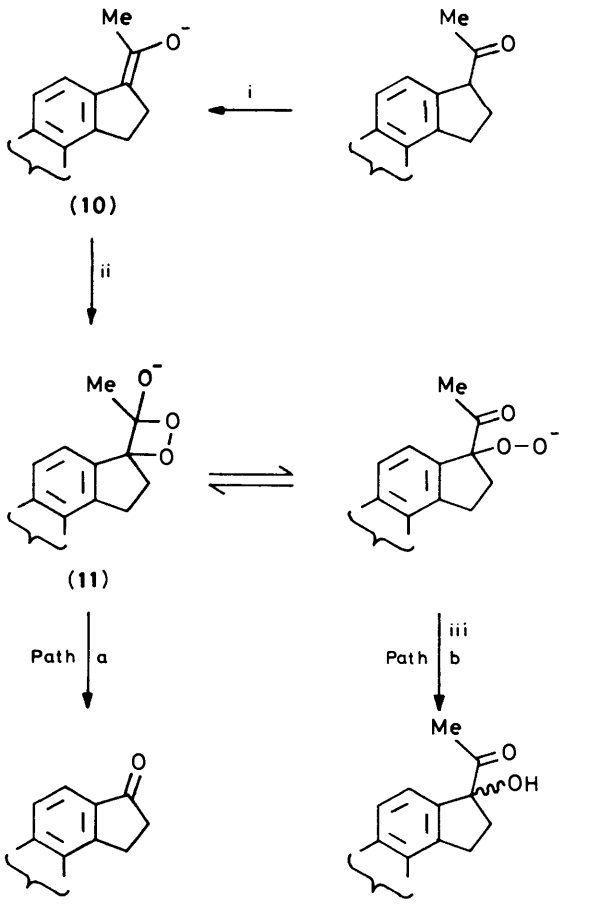


Figure. A view of molecule (**2b**) with the crystallographic numbering scheme. Atom C(18), which is not labelled, is behind the C(13)–C(17) bond

in Table 3, are unexceptional and serve to define the structure. The cyclohexene ring *A* has a 1α,2β-half-chair conformation with C(1) 0.561 Å below and C(2) 0.069 Å above the C(3),C(4),C(5),C(10) plane. Ring *B* is also in a half-chair conformation (5α,6β) with C(5) 0.106 Å below and C(6) 0.607 Å above the C(7)—C(10) plane. Aromatic ring *C* is planar as expected, and five-membered ring *D* is a C(16) β-envelope with C(16) 0.302 Å above the C(13),C(14),C(15),C(17) plane. An essentially identical conformation was found for the steroidal skeleton in the closely related molecule 20α,21-diacetoxy-17β-methyl-18-nor-17β(H)-pregna-4,8,11,13-tetraen-3-one.[3] The conformation of the 17α-CH_3CO side-chain with respect to the steroidal framework is defined by the O(2)–C(17)–C(18)–O(3) torsion angle (146.1°) and would appear to be dictated by intra- and inter-molecular packing effects, as carbonyl oxygen O(3) takes no part in any intermolecular hydrogen bonding. In the crystal structure, molecules are linked in the *a*-direction by O(2)–H···O(1) hydrogen bonds [O···O 2.801(4) Å] between the 17β-hydroxy group of one molecule and the carbonyl oxygen O(1) of a neighbouring molecule, to form infinite chains.

Although we have observed the loss of the acetyl side-chain from the *C*-aromatic steroids (**3a**) and (**3b**) [as well as from 1-acetylindan (**4**)], a similar cleavage of the acetyl side-chain was not reported for 17β-acetyl steroids.[4] The difference in behaviour may be related to the relative thermal stability of the cyclic peroxide intermediates.[5,6] The activation energy for thermal decomposition of the peroxide intermediate (**11**) formed from the aromatic compounds (**3a**), (**3b**) or (**6**) (see Path a in the Scheme) is lowered considerably by conjugation of the forming ketone-function in the transition state with the aromatic system. It is also to be noted that the hydroxylation α to an acetyl group



Scheme. *Reagents:* i, Base; ii, O_2; iii, $(EtO)_3P$

Table 1. ^1H N.m.r. data[a]

Compound	4-H	11-H[b]/12-H[b]		19-H_3	21-H_3
(**2a**)	5.95	7.05 d	7.25 d	1.59	2.10
(**2b**)	5.95	7.05 d	7.3 d	1.59	2.08
(**8**)	5.95	7.35 d	7.65 d	1.59	

Compound	MeCO	5-H—8-H	1-H	2-H	3-H
(**5**)	2.02	7.1—7.4 m		2.2—2.6 m	3.1—3.3 m
(**4**)	2.20	7.25—7.3 m	4.1 t (*J* 7)	2.2—2.5 m	2.9—3.2 m

[a] Chemical shifts measured in $CDCl_3$ (to ±0.01 p.p.m. for Me and to ±0.05 p.p.m. for other signals). [b] *J* 8 Hz.

proceeds more readily when the acetyl group is attached to a benzylic carbon than when it is not. Thus at −50 °C when 1-acetylindan (**4**) and *C*-aromatic steroids (**3a**) and (**3b**) undergo hydroxylation, progesterone (**7**) was recovered unchanged (see above). The difference in reactivity may be related to the increased ease of enolization to an aromatic-conjugated enolate [see *e.g.* enolate (**10**)].

Experimental

N.m.r. data as given in Tables 1 (^1H) and 2 (^{13}C) were collected using a JEOL FX 90Q spectrometer operating in the Fourier transform mode at 89.6 and 22.5 MHz respectively. Light petroleum refers to that fraction boiling within the range 40—

Table 2. ^{13}C N.m.r. chemical shifts[a]

Carbon Atom	(3a)[b]	(3b)[b]	(2a)	(2b)	(8)	Carbon Atom	Indan [c]
1	37.1	37.0	37.2	37.0	36.7		
2	34.6	34.7	34.7	34.4	34.5		
3	198.6	198.6	198.7	198.4	198.3		
4	124.1	124.2	124.3	123.9	124.7*		
5	169.3	169.2	168.9	168.9	167.8		
6	30.5	30.5	30.5	30.2	30.2		
7	28.3	28.3	29.4*	29.2*	27.0		
8	131.2	131.2	131.5	131.2	132.7	4	125.0
9	143.0*	143.1*	142.3	142.2	154.2**	5	126.4
10	39.2	39.1	39.3	39.1	39.8		
11	124.7	124.8	125.8	125.5	125.8*	6	126.4
12	123.1	123.1	121.8	121.6	122.0*	7	125.0
13	138.2	138.4	144.7	144.4	135.1	7a	144.1
14	142.7*	142.7*	140.7	140.6	150.4**	3a	144.1
15	30.5	30.4	28.1*	27.8*	24.6	3	33.6
16	28.0	28.2	37.0	36.7	36.4	2	25.6
17	58.6	58.7	88.9	88.7	206.5	1	33.6
19	27.6	27.7	27.6	27.4	27.5		
20	208.5	208.5	208.9	208.8			
21	28.0	27.7	23.7	23.6			

* ** Assignments within a vertical column may be reversed. [a] Unless otherwise stated, data are in p.p.m. downfield from $SiMe_4$ in $CDCl_3$, with $\delta(CDCl_3)$ 77.1 p.p.m. [b] Data taken from ref. 1. [c] Data of neat liquid adopted from H. L. Retcofsky and R. A. Friedel in 'Spectrometry of Fuels,' ed. R. A. Friedel, Plenum Press, New York, 1970, p. 95 by J. B. Stuthers, 'C-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 100.

60 °C. M.p.s were measured on a Reichert Kofler-block apparatus and are uncorrected. Solutions were dried over anhydrous sodium sulphate.

1-*Acetylindan* (**4**).[7]—A solution of n-butyl-lithium in hexane (31.6 ml of a 1.9M solution, 60 mmol) was added during 15 min to a solution of diethyl α-isocyanoethyl phosphate[8] (11.46 g, 60 mmol) in tetrahydrofuran (THF) (90 ml) at −70 °C.[9] A solution of indan-1-one (**6**) (7.51 g, 56.8 mmol) in THF (45 ml) was added to the mixture at −60 °C, which was then allowed to warm to room temperature during 45 min. Aqueous sodium chloride (10% w/v) (75 ml) was added, and THF was removed under reduced pressure. The product was extracted with diethyl ether (2 × 200 ml), and each extract was washed with 20% aqueous sodium chloride. The combined extracts were dried and the semi-crystalline solid (11.3 g) obtained on removal of solvent was chromatographed over neutral alumina, with elution by 0—10% diethyl ether in light petroleum containing one drop of triethylamine per 100 ml, to give the intermediate vinyl isocyanide (**9**) as a crystalline solid (6.95 g, 75%).

A solution of intermediate (**9**) (1.0 g, 5.9 mmol) in diethyl ether (100 ml) was treated at 0 °C with 10M-hydrochloric acid (2.95 ml, 29.5 mmol) and the mixture was stirred vigorously at room temperature for 2 h. Solid potassium carbonate was added until the mixture was neutral. The ether layer was decanted off and the remaining slurry was rinsed with diethyl ether. The combined ether extracts were dried and chromatographed over silica, with 2—5% diethyl ether in light petroleum as eluant to give 1-acetylindan (**4**) as a light yellow liquid (0.84 g, 89%), having the same ^1H n.m.r. data as those in the literature.[7]

1-*Acetylindan*-1-*ol* (**5**).—Sodium hydride (75 mg, 3.12 mmol) was dissolved in a mixture of t-butyl alcohol (1 ml) and DMF (1.5 ml) and a solution of triethyl phosphite (0.35 ml, 2.0 mmol) in DMF (1 ml) was then added. The mixture was cooled to −50 °C and oxygen was bubbled through for a few minutes. A solution of 1-acetylindan (**4**) (215 mg, 1.34 mmol) in THF (1.25 ml) was added and oxygen was bubbled through for 15 min at −50 °C before the mixture was flushed with nitrogen. The cooling bath was removed, the mixture was made faintly acidic with acetic acid, water (5 ml) was added, and the product was extracted with dichloromethane. All solvents were removed at 0.2 Torr and the residue was chromatographed over silica, with 5—10% diethyl ether in light petroleum as eluant, to give indan-1-one (**6**) (14 mg), and 1-acetylindan-1-ol (**5**) as a light yellow oil (54 mg), *m/z* (e.i.) 133.066 (100%, C_9H_9O or $M - CH_3CO$).

Investigation of the Effect of the Hydroxylation Conditions on Progesterone (**7**).—The hydroxylation reaction mixture was prepared as in the previous paragraph but at $\frac{1}{5}$ scale. A solution of progesterone (**7**) (82 mg, 3.4 mmol) in THF (0.25 ml) was added during a few minutes to the mixture at −50 °C, and oxygen was bubbled through for 15 min. The mixture was flushed with nitrogen and acidified with acetic acid. Water (10 ml) was added and the precipitate which formed was filtered off to give a white solid (40 mg) which was identified as progesterone by t.l.c. and ^1H n.m.r. spectroscopy.

Hydroxylation of 18-*Nor*-17α(*H*)- *and* -17β(*H*)-*pregna*-4,8,11,13-*tetraene*-3,20-*dione* (**3a**) *and* (**3b**).—The hydroxylation reaction mixture was prepared as in the previous two paragraphs, sodium hydride and other reagents being scaled up accordingly. A solution containing a 2:1 mixture of 18-nor-17α(H)- and -17β(H)-pregna-4,8,11,13-tetraene-3,20-dione (**3a**) and (**3b**) (400 mg, 1.36 mmol) in THF (2.3 ml) was added during a few minutes to the mixture at −50 °C and oxygen was bubbled through the resulting dark blue mixture for 15 min. After the mixture had been flushed with nitrogen the cooling bath was removed and the mixture was acidified with acetic acid. Water (80 ml) was added, and after being stirred overnight the mixture was filtered and the insoluble solid was dried to give the crude product mixture as a light yellow solid (284 mg). Extraction of the filtrate with dichloromethane gave a yellow oil (207 mg) which was shown by ^1H n.m.r. spectroscopy to be more of the crude product mixture but contaminated with triethyl phosphite. The combined crude products were chromatographed over silica with 5% acetone–dichloromethane as eluant to give partially separated products (293 mg). These were separated using h.p.l.c. with 3% acetone–dichloromethane as eluant to give 17β-*hydroxy*-18-*nor*-17βH-*pregna*-4,8,11,13-*tetraene*-3,20-*dione* (**2b**) (54 mg), crystallizing from benzene–light petroleum as needles, m.p. 169—172 °C; 17α-*hydroxy*-18-*norpregna*-4,8,11,13-*tetraene*-3,20-*dione* (**2a**) (52 mg) which could not be crystallized; and 18-*norandrosta*-4,8,11,13-*tetraene*-3,17-*dione* (**8**) (42 mg), crystallizing from benzene as needles, m.p. 211—214 °C [Found for compound (**2b**): C, 76.95; H, 7.55. $C_{20}H_{22}O_3$ requires C, 77.4; H, 7.15%. Found for compound (**8**): C, 81.05; H, 6.95. $C_{18}H_{18}O_2$ requires C, 81.15; H, 6.8%]. Compound (**2a**) gave *m/z* (CH_4 c.i.) 351 (5%, $M + C_3H_5$), 339 (15, $M + C_2H_5$), 311 (100, MH^+), 293 (80, $MH - H_2O$), 267 (20, $M - CH_3CO$); and *m/z* (e.i.) 267.139. (100%, $C_{18}H_{19}O$ or $M - CH_3CO$), 252.116 (18, $3_{17}H_{16}O_2$ or 267 − CH_3).

Side-chain Degradation of 18-*Nor*-17α(*H*)- *and* -17β(*H*)-*pregna*-4,8,11,13-*tetraene*-3,20-*dione* (**3a**) *and* (**3b**).—Sodium hydride (6.5 mg, 0.27 mmol) was dissolved in a mixture of t-butyl alcohol (0.085 ml) and DMF (0.13 ml). A further quantity of DMF (0.13 ml) was added, the mixture was cooled to −50 °C, and oxygen was bubbled through for a few minutes. A 2:1 mixture of the title compounds (**3a**) and (**3b**) (30 mg, 0.104 mmol) in THF (0.2 ml) was added in one portion and oxygen was bubbled through at −50 °C for 10 min. The mixture was flushed with nitrogen, the cooling bath was removed, and acetic acid was added to neutrality. All solvents were removed at 0.2

Table 3. Summary of mean bond lengths (Å) for compound (**2b**)

C=O	1.219(4)
$C(sp^3)$–OH	1.430(4)
$C(sp^3)$–$C(sp^3)$	1.522(4)
$C(sp^3)$–$C(sp^2)$	1.498(4)
$C(sp^2)$–$C(sp^2)$	1.447(4)
C=C	1.334(4)
C–C(aromatic)	1.387(4)

Table 4. Non-hydrogen atom positional parameters and estimated standard deviations

Atom	*x*	*y*	*z*
O(1)	0.6547(4)	0.3669(2)	0.0761(3)
O(2)	0.4233(4)	0.0760(2)	0.9674(3)
O(3)	0.7332(4)	0.0232(2)	0.8283(4)
C(1)	0.5710(4)	0.3472(2)	0.4222(4)
C(2)	0.5882(5)	0.3974(2)	0.2979(5)
C(3)	0.5866(5)	0.3507(3)	0.1753(4)
C(4)	0.5010(5)	0.2810(3)	0.1760(4)
C(5)	0.4354(4)	0.2538(2)	0.2838(4)
C(6)	0.3557(5)	0.1784(3)	0.2814(4)
C(7)	0.4253(5)	0.1205(2)	0.3741(5)
C(8)	0.4473(4)	0.1539(2)	0.5097(4)
C(9)	0.4501(4)	0.2343(2)	0.5319(3)
C10)	0.4441(4)	0.2946(2)	0.4179(3)
C(11)	0.4636(4)	0.2619(2)	0.6622(3)
C(12)	0.4797(5)	0.2125(2)	0.7697(4)
C(13)	0.4818(4)	0.1326(2)	0.7475(4)
C(14)	0.4646(4)	0.1039(2)	0.6198(4)
C(15)	0.4672(6)	0.0160(2)	0.6196(6)
C(16)	0.4586(6)	−0.0052(2)	0.7662(6)
C(17)	0.4998(5)	0.0664(2)	0.8462(4)
C(18)	0.6494(5)	0.0636(3)	0.8874(5)
C(19)	0.6985(7)	0.1127(4)	0.9990(8)
C(20)	0.3109(4)	0.3449(2)	0.4343(4)

Torr, dichloromethane (10 ml) was added, the solution was filtered, and the solvent was removed to give the crude product (25 mg). This was chromatographed over silica, with 5% acetone–dichloromethane as eluant, to give 18-norandrosta-4,8,11,13-tetraene-3,17-dione (**8**) as a crystalline solid (12 mg), recrystallizing from benzene as needles, m.p. 211—214 °C.

Crystal Data for 17β-*Hydroxy*-18-*nor*-17β(*H*)-*pregna*-4,8,11,13-*tetraene*-3,20-*dione* (**2b**).—$C_{20}H_{22}O_3$, M = 310.4, orthorhombic, a = 9.643(3), b = 17.043(4), c = 10.015(3) Å; U = 1 646(1) Å, Z = 4, D_c = 1.25 g cm^{-3}, F(000) = 664, Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 0.8 cm^{-1}. Space group $P2_12_12_1$, from systematic absences (axial reflections halved for *h*00, 0*k*0 00*l*).

The cell data and orientation matrix were determined from the setting angles of 25 reflections with $10 < \theta < 15°$. The intensities of 1 677 unique reflections with $2 < \theta < 25°$ were measured on an Enraf-Nonius CAD4 diffractometer using the $\omega/2\theta$ technique. After correction for Lorentz and polarization factors. [but not for absorption which is negligible with the small (0.2, 0.3, 0.3 mm) crystal used and the small μ value], the 1 219 reflections with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement.

The structure was solved with the aid of MULTAN 82.[10] Refinement* by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters, proceeded smoothly. Difference maps computed at various stages of refinement had maxima corresponding to the anticipated hydrogen-atom sites. In the final rounds of calculations the hydrogen atoms were allowed for in fixed idealized positions (C–H, O–H 0.95 Å). The final refinement cycle included 208 variables and converged with R = 0.059 and R_w = 0.072. The largest shift/error ratio in the last cycle was less than 0.01. Scattering factor data were taken from International Tables[11] and weights were derived from the counting statistics. A final difference map was devoid of any chemically significant features.

The final fractional co-ordinates for compound (**2b**) are in Table 4. A list of least-squares planes, dihedral angles, and hydrogen co-ordinates has been treated as a Supplementary Publications [SUP No. 56645 (4 pp.)].† Bond lengths, bond angles, torsion angles, and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.‡

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* All calculations were made on a PDP11/73 computer with the SPD Program System: B. A. Frenz and Associates, Inc., College Station, Texas, U.S.A., and Enraf-Nonius, Delft, Holland, 1983.

† For details of the Supplementary Publications Scheme, see Instructions for Authors (1987) Para 4.0, *J. Chem. Soc., Perkin Trans. 1*, 1987, issue 1.

‡ See Instructions for Authors (1987) Para. 5.6.3, *J. Chem. Soc., Perkin Trans. 1*, 1987, issue 1.