

O1—C1—C2—C7	-177.6 (2)	O1'—C1'—C2'—C7'	-179.6 (2)
C2—C7—C8—O2	175.7 (2)	C2'—C7'—C8'—O2'	177.1 (3)
O1—C1—C2—C3	-55.1 (3)	O1'—C1'—C2'—C3'	-57.1 (3)
O2—C8—C7—C6	53.6 (3)	O2'—C8'—C7'—C6'	54.6 (3)

La possibilité d'existence d'une maille orthorhombique *C*, de paramètres $\mathbf{a}' = -\mathbf{a}$, $\mathbf{b}' = \mathbf{a} + 2\mathbf{c}$, $\mathbf{c}' = \mathbf{b}$, a été rejetée; l'angle (\mathbf{a}'/\mathbf{b}') = 90,29 (1)° s'écartant significativement de 90°. La largeur de balayage est (0,75 + 0,5tg θ)°. Les intensités ont été corrigées des facteurs de Lorentz-Polarisation. La structure a été résolue par les méthodes directes (SHELXS86; Sheldrick, 1990), puis affinée par la méthode des moindres carrés (SHELXL93; Sheldrick, 1993).

Collection des données: CAD-4 EXPRESS (Enraf-Nonius, 1994; Duisenberg, 1992; Maciček & Yordanov, 1992). Affinement des paramètres de la maille: CAD-4 EXPRESS. Réduction des données: MolEN (Fair, 1990). Programme(s) pour la solution de la structure: SHELXS86. Programme(s) pour l'affinement de la structure: SHELXL93. Graphisme moléculaire: ZORTEP (Zsolnai, 1994). Logiciel utilisé pour préparer le matériel pour publication: SHELXL93.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: GS1003). Les processus d'accès à ces archives sont donnés au dos de la couverture.

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N-tert-Butyl-*N*-(1-dibenzylphosphono-2,2-dimethylpropyl)nitroxide

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Abstract

The crystal structure of the title compound, C₂₃H₃₃-NO₄P, has been determined by X-ray diffraction. It is the first example of a crystallized β -phosphorylated nitroxide.

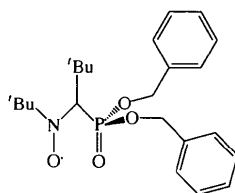
Comment

The use of stable nitroxide radicals is under extensive investigation. They have been shown to be useful electron spin resonance (ESR) spin probes (Zhdanov, 1992; Keana, 1984; Berliner, 1976) and contrast-enhancing agents for magnetic resonance imaging (MRI) (Kuppusamy *et al.*, 1995), and, recently, they have been employed in the field of living radical polymerization (Grimaldi *et al.*, 1997; Benoit *et al.*, 1997).

The chemistry of stable β -phosphorylated nitroxides has been extensively developed in our laboratory. For example, pyrrolidinylnitroxides can be easily prepared by oxidation of the corresponding α -aminophosphonates (Dembkowski *et al.*, 1993; Le Moigne *et al.*, 1991). We have applied this method to acyclic nitroxides bearing an electron-withdrawing β -phosphorylated group (Grimaldi *et al.*, 1998).

We report herein the structure of *N*-tert-butyl-*N*-(1-dibenzylphosphono-2,2-dimethylpropyl)nitroxide, (I),

determined by X-ray diffraction. It is the first example of a crystallized β -phosphorylated nitroxide.



(I)

In general, nitroxides bearing an H atom on the C_{α} atom bound to the nitroxide are prone to disproportionation resulting in a bimolecular transition state (Bowman *et al.*, 1971). Although the present nitroxide contains an H atom in this position, it appears to be stable. The torsion angles $\omega(O4-N-C15-H15)$ and $\omega(O4-N-C15-P)$ are -167.5 and -50.4° , respectively. As the $\omega(O4-N-C15-H15)$ angle is close to -180° , the H atom is in the nodal plane of the π system of the nitroxide. This conformation leads to inhibition of the disproportionation reaction and explains the stability of the nitroxide.

The crystal packing is governed by van der Waals interactions.

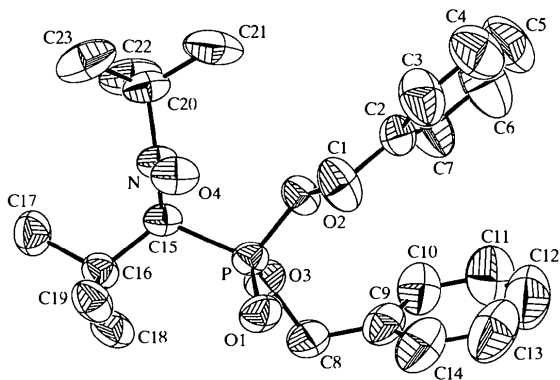


Fig. 1. ORTEP (Johnson, 1976) drawing of (I) with displacement ellipsoids at the 50% probability level.

Experimental

The title compound, *N-tert-butyl-N-(1-dibenzylphosphono-2,2-dimethylpropyl)nitroxide*, was synthesized by oxidizing with *m*-chloroperbenzoic acid, the corresponding dibenzyl *N-tert-butylamino(tert-butyl)methanephosphonate*, obtained by an aminophosphorylation reaction involving pivalaldehyde, *tert*-butylamine and dibenzyl phosphite (Grimaldi *et al.*, 1998). Crystals suitable for X-ray analysis were grown from a dichloromethane solution by slow evaporation.

Crystal data

$C_{23}H_{33}NO_4P$
 $M_r = 418.50$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Triclinic

$P\bar{1}$

$a = 6.027(3) \text{ \AA}$
 $b = 8.608(2) \text{ \AA}$
 $c = 22.935(4) \text{ \AA}$
 $\alpha = 97.75(2)^{\circ}$
 $\beta = 93.72(4)^{\circ}$
 $\gamma = 98.87(4)^{\circ}$
 $V = 1160(1) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.20 \text{ Mg m}^{-3}$

$D_m = 1.21(2) \text{ Mg m}^{-3}$

D_m measured by flotation in benzene/chloroform

Cell parameters from 25 reflections

$\theta = 11-14^{\circ}$

$\mu = 0.140 \text{ mm}^{-1}$

$T = 294 \text{ K}$

Prism

$0.70 \times 0.50 \times 0.15 \text{ mm}$

Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction: none

3721 measured reflections

3620 independent reflections

2491 reflections with

$I > 3\sigma(I)$

$R_{int} = 0.030$

$\theta_{max} = 28^{\circ}$

$h = -6 \rightarrow 6$

$k = -9 \rightarrow 9$

$l = 0 \rightarrow 26$

3 standard reflections

frequency: 60 min

intensity decay: 0.96%

Refinement

Refinement on F^2

$R = 0.049$

$wR = 0.067$

$S = 1.102$

2491 reflections

263 parameters

H atoms included but not

refined

$w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.2667 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.2482 \text{ e \AA}^{-3}$

Extinction correction:

isotropic (Zachariasen, 1963)

Extinction coefficient:

0.61×10^{-6}

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^{\circ}$)

P—O1	1.455 (2)	C6—C7	1.380 (7)
P—O2	1.574 (2)	C8—C9	1.477 (5)
P—O3	1.583 (2)	C9—C10	1.385 (6)
P—C15	1.832 (3)	C9—C14	1.369 (6)
O2—C1	1.446 (4)	C10—C11	1.379 (7)
O3—C8	1.458 (4)	C11—C12	1.376 (9)
O4—N	1.278 (3)	C12—C13	1.364 (8)
N—C15	1.479 (3)	C13—C14	1.407 (8)
N—C20	1.491 (4)	C15—C16	1.554 (5)
C1—C2	1.480 (6)	C16—C17	1.530 (5)
C2—C3	1.362 (5)	C16—C18	1.540 (4)
C2—C7	1.347 (5)	C16—C19	1.530 (5)
C3—C4	1.365 (8)	C20—C21	1.524 (6)
C4—C5	1.349 (7)	C20—C22	1.500 (5)
C5—C6	1.353 (7)	C20—C23	1.527 (6)
O1—P—O2	114.9 (1)	C10—C9—C14	118.7 (4)
O1—P—O3	114.7 (1)	P—C15—N	107.8 (2)
O1—P—C15	119.1 (1)	P—C15—C16	115.0 (2)
O2—P—O3	101.9 (1)	N—C15—C16	113.1 (2)
O2—P—C15	104.2 (1)	C15—C16—C17	108.8 (3)
O3—P—C15	99.6 (1)	C15—C16—C18	108.3 (2)
P—O2—C1	121.5 (2)	C15—C16—C19	112.8 (3)
P—O3—C8	120.6 (2)	C17—C16—C18	108.0 (3)
O4—N—C15	116.0 (2)	C17—C16—C19	109.0 (3)
O4—N—C20	116.6 (2)	C18—C16—C19	109.9 (3)

C15—N—C20	126.5 (2)	N—C20—C21	108.5 (3)
O2—C1—C2	109.6 (3)	N—C20—C22	111.9 (2)
C1—C2—C3	118.4 (3)	N—C20—C23	106.9 (3)
C1—C2—C7	123.3 (3)	C21—C20—C22	109.6 (3)
O3—C8—C9	111.9 (3)	C21—C20—C23	108.8 (3)
C8—C9—C10	119.5 (4)	C22—C20—C23	111.0 (3)
C8—C9—C14	121.8 (4)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *SDP-Plus*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1002). Services for accessing these data are described at the back of the journal.

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13,13-Ethylenedithio-3-mesyloxy-18-nor-13,17-secoestra-1,3,5(10)-triene-17-nitrile

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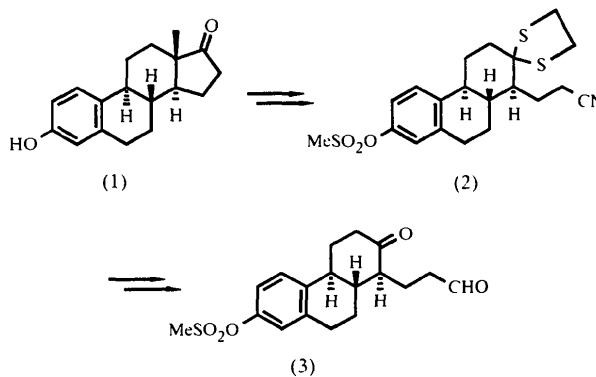
(Received 26 February 1998; accepted 14 April 1998)

Abstract

In the course of the partial synthesis of 18-norestradiol, an X-ray analysis of an appropriately crystallizing intermediate, C₂₀H₂₅NO₃S₃, was carried out in order to determine its absolute configuration. The unusual D-seco steroid displays configurations at C8, C9 and C14 not altered in comparison with the starting material, estrone.

Comment

In the context of our investigations directed towards the synthesis of 18-norsteroids, we examined an intramolecular coupling reaction of (3), a D-seco steroid prepared by a seven-step sequence starting from naturally occurring estrone, (1) (Kuhl, 1998). Since our first attempts to determine the configuration of (3) by NMR techniques led to ambiguous results and (3) was obtained as a non-crystallizing oil, we undertook the X-ray analysis of the title compound, (2), as a precursor of (3).



Although (2) displays in its D-seco moiety an unusual feature for steroids, some distortion effects typical of aromatic estrane derivatives are observed concerning rings A and B. Ring A displays typical characteristic aromaticity, with delocalization of π electrons producing an average C—C bond length of 1.381 (3) Å (Duax, 1972), with the exception of the C₂—C₃ bond, which is significantly shortened [1.325 (6) Å]. Additionally, the C₅—C₁₀—C₁ bond angle is reduced to a value of