$V = 1043.3$ Å^3
$Z = 4$
$D_x = 1.39$ Mg m^{-3}
0.45 × 0.25 × 0.20 mm
Clear

Data collection

Stoe Stadi-2 diffractometer
ω scans
Absorption correction: none
957 measured reflections
772 independent reflections
557 observed reflections [$|F| > 4\sigma(|F|)$]
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 50°$
$h = -28 \rightarrow 28$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 9$
1 standard reflection per layer of k monitored every 25 reflections intensity variation: >2% of I

Refinement

Refinement on F
$R = 0.0465$
$wR = 0.0465$
$S = 0.74$
557 reflections
94 parameters
All H-atom parameters refined
Unit weights applied
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.12$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.05674 (11)	0.1495 (5)	0.2361 (3)	0.053 (2)
C(2)	0.06132 (13)	0.3522 (6)	0.3090 (4)	0.060 (2)
C(3)	0.11540 (14)	0.4519 (6)	0.3057 (4)	0.070 (2)
C(4)	0.16412 (13)	0.3382 (7)	0.2237 (4)	0.077 (2)
C(5)	0.16191 (13)	0.1389 (7)	0.1492 (5)	0.074 (2)
C(6)	0.10800 (13)	0.0428 (6)	0.1560 (4)	0.062 (2)
C(7)	0	0.0309 (7)	$\frac{1}{4}$	0.055 (2)
F(1)	0.21733 (8)	0.4348 (4)	0.2177 (3)	0.118 (3)
O(1)	0	−0.1663 (6)	$\frac{1}{4}$	0.088 (3)

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(2)	1.374 (4)	C(1)—C(6)	1.396 (4)
C(2)—C(3)	1.393 (4)	C(1)—C(7)	1.493 (3)
C(3)—C(4)	1.377 (5)	C(7)—O(1)	1.217 (5)
C(4)—C(5)	1.353 (5)	C(4)—F(1)	1.364 (3)
C(5)—C(6)	1.376 (4)		
C(7)—C(1)—C(2)	123.2 (3)	F(1)—C(4)—C(5)	118.9 (3)
C(7)—C(1)—C(6)	118.2 (3)	C(3)—C(4)—C(5)	123.8 (3)
C(2)—C(1)—C(6)	118.5 (3)	C(4)—C(5)—C(6)	118.4 (3)
C(1)—C(2)—C(3)	121.8 (3)	C(5)—C(6)—C(1)	120.8 (3)
C(2)—C(3)—C(4)	116.7 (3)	C(1)—C(7)—O(1)	119.3 (2)
F(1)—C(4)—C(3)	117.3 (4)	C(1)—C(7)—C(1′)	121.4 (2)

The data were collected, by two-circle diffractometer, in layers of k and, therefore, inter-layer scale factors were refined (final values of these ranged between 0.73 and 0.94). Structure solution was by *SHELXS*86 (Sheldrick, 1985) and the refinement used *SHELX*76 (Sheldrick, 1976).

Acknowledgement is made to both Liverpool University, for the use of the two-circle diffractometer, and to the SERC, for continued support of the Chemical Databank Service at the Daresbury Laboratory.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71516 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1056]

References

Granger, M. M. & Coillot, M. F. (1985). *Acta Cryst.* **C41**, 542–543.

Ito, Y., Matsuura, T., Tabata, K., Meng Ji-Ben, Fukuyama, K., Sasaki, M. & Okada, S. (1987). *Tetrahedron*, **43**, 1307–1312.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kojić-Prodić, B., Bresciani-Pahor, N. & Horvatić, D. (1990). *Acta Cryst.* **C46**, 430–432.

Shields, K. G. & Kennard, C. H. L. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 463–465.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Velden, G. P. M. van der & Noordik, J. H. (1979). *J. Cryst. Mol. Struct.* **10**, 83–92.

Velden, G. P. M. van der & Noordik, J. H. (1980). *J. Cryst. Mol. Struct.* **9**, 283–294.

Acta Cryst. (1994). **C50**, 255–259

Substitution Effects on the Structure of *o*-Aryliminophosphoranes

ANTONIO L. LLAMAS-SAIZ AND
CONCEPCIÓN FOCES-FOCES*

Departmento de Cristalografía, Instituto de Química-Física 'Rocasolano', CSIC, Serrano 119, E-28006 Madrid, Spain

(*Received* 10 *February* 1993; *accepted* 15 *June* 1993)

Abstract

The iminophosphorane group in (*o*-dimethylaminophenylimino)triphenylphosphorane, $C_{26}H_{25}N_2P$, lies almost in the benzene plane [C6—C1—N11—P12 = −8.3 (3)°] giving rise to an inward distortion of the external angle at C1. The conformation adopted by the dimethylamino group reflects the electronic repulsion between both N-atom lone pairs and places one methyl almost eclipsed by the benzene ring [C3—C2—N31—C33 = −14.5 (3)°]. The optimized geometry (AM1) of *o*-dimethylaminobenzene shows both groups equally twisted (−27.8°) but to a lesser extent than in (*o*-dimethylaminophenylimino)triphenylphosphorane.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

Comment

The present study has been undertaken as part of a project on the influence of substituents on the molecular structure and properties of *peri*-naphthalene ['proton sponges'; 1,8-bis(dimethylamino)-naphthalene] and *ortho*-benzene derivatives when one or two basic centres are replaced by iminophosphorane groups (Laynez *et al.*, 1993; Llamas-Saiz *et al.*, 1992, 1993). As a result of the high basicity of these new proton sponges with a naphthalene skeleton and the instability of the iminophosphorane group in hydrolysis, none of the free bases could be obtained. We report here the crystal structure of (*o*-dimethylaminophenylimino)triphenylphosphorane (I) which is the free base available for the corresponding benzene derivatives. The crystal structures of (III) and (IV) have been published previously (Llamas-Saiz *et al.*, 1992).

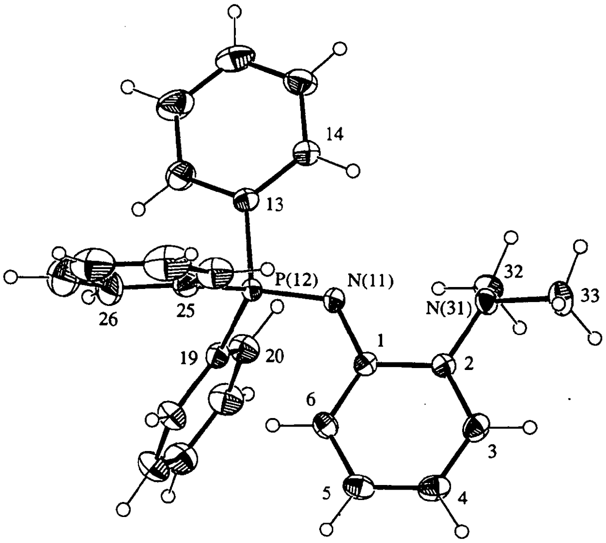
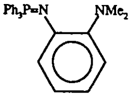
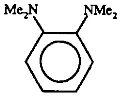


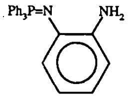
Fig. 1. A view of (I) showing the numbering scheme. Thermal ellipsoids are drawn at 30% probability level and H atoms are represented by spheres of 0.1 Å radius.



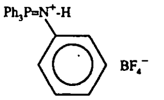
(I)



(II)



(III)



(IV)

For comparison purposes, we carried out a full geometrical optimization of *o*-bis(dimethylamino)-benzene (II) (Llamas-Saiz *et al.*, 1993) using the AM1 Hamiltonian as implemented in the *MOPAC*6.0 set of programs (Stewart, 1990), since it was liquid at room temperature. The geometry optimization of (I) has not been performed because unreliable theoretical results were obtained (Laynez *et al.*, 1993) as a consequence of the phosphorus parametrization in its pentavalent state. Table 2 shows the main geometric parameters of (II) together with the experimental geometry of (I), according to the numbering system displayed in Fig. 1 (Hall & Stewart, 1990). The theoretical calculations lead to a symmetrical molecule for (II), point group C_2, as shown in Fig. 2 (Motherwell & Clegg, 1978).

The pattern of bond distances in the benzene ring, except that of C4—C5, is similar in both compounds, as are the conformations of the methyl groups. The axis of each N-atom lone pair makes angles of 45.5 (3) and 36.9° with the benzene plane, for (I) and (II), respectively (Fig. 2). The different coplanarity of the methyl groups [163.2 (2) *versus* 149.5°, Table 2] may be responsible for the different C2—N31—Me angles, *i.e.* the greater the bond angles, the nearer coplanarity. The iminophosphorane group is twisted by −8.3 (3)° with respect to the benzene ring. The external angular distortion at C1 is closely related to this coplanarity of the group. This may be caused by the overcrowding of the atoms at *ortho* positions and the intramolecular hydrogen-bond interactions. So

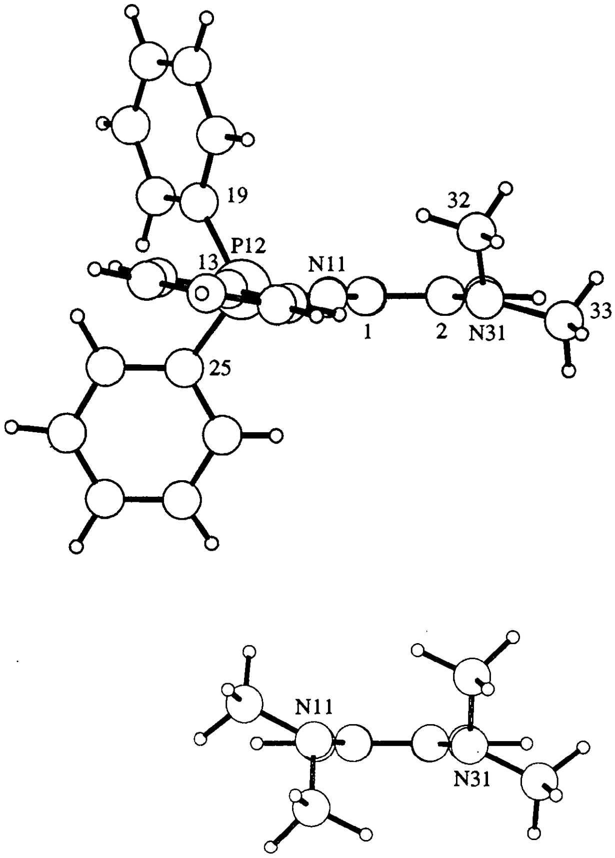


Fig. 2. Comparative view of molecules (I) and (II) with the aromatic ring perpendicular to the projection plane.

that, while the external C1—C2—N31 angles are close to 120° in (I) and (II), the C6—C1—N11 angle in (I) presents larger deformations than in (IV) [122.3 (4), 122.8 (3)°] and smaller than in (III) [125.9 (2), 126.6 (2)°] where an intramolecular interaction occurs. Therefore, these angular deformations suggest that the steric factors are more important than the electrostatic repulsion between both basic groups. The iminophosphorane group prefers to be coplanar with the benzene ring to allow the charge delocalization of the double bond, while only a twist of the dimethylamino group takes place to avoid the lone-pair electron repulsion. The corresponding N···N distances are 2.781 (3) and 2.878 Å for compounds (I) and (II), respectively.

The benzene ring in (I) is planar in terms of the achieved precision ($\chi^2 = 4.63$ *versus* 7.81 at 95% probability level) and both N atoms deviate [0.020 (2) and 0.063 (2) Å] from the least-square plane, while in (II), which is also planar, the N atoms are displaced at opposite sides of the benzene ring by ±0.046 Å.

The internal bond angles in the benzene rings agree well with the calculated values after performing the angular corrections tabulated by Domenicano & Murray-Rust (1979) for the —NMe$_2$ group and by us for —N=PPh$_3$ (Llamas-Saiz *et al.*, 1993) [angles at C1–C6: 117.4, 118.7, 121.8, 119.9, 119.4, 122.7° and 118.2, 118.2, 120.0, 119.3, 119.3, 122.0° for (I) and (II), respectively]. The values of the angular deformation parameters place both groups among electrodonor substituents on aromatic rings.

The N=P distance [1.564 (2) Å] is significantly shorter than that displayed by the protonated groups and the groups accepting a hydrogen bond (partial protonation) [1.632 (1) and 1.577 (1) Å on average, respectively (Llamas-Saiz *et al.*, 1992, 1993)]. The iminophosphorane group displays a slightly distorted parallel conformation around the N=P bond. The greater deformation ($\chi_{19,25}$) corresponds to the phenyl rings alternated with C1, Table 3 (Cano, Foces-Foces & García-Blanco, 1979). The crystal packing is stabilized by C—H···phenyl contacts (Table 3). Moreover, some partial stacking between the C25–C30 phenyl rings related through a symmetry centre at (0, $\frac{1}{2}$, $\frac{1}{2}$) is also present. The interplanar distance is 3.902 (1) Å while the distance between their centroids is 4.132 (2) Å, giving rise to a displacement of 1.350 (2) Å between them.

Experimental

Crystal data

$C_{26}H_{25}N_2P$
M_r = 396.5
Monoclinic
$P2_1/c$
a = 12.5702 (9) Å
b = 9.1053 (6) Å
c = 19.1700 (14) Å
β = 90.798 (9)°
V = 2193.9 (3) Å^3
Z = 4

D_x = 1.200 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 78 reflections
θ = 2–45°
μ = 1.187 mm^{-1}
T = 295 K
Prism
0.47 × 0.27 × 0.20 mm
Yellow

Data collection

Seifert XRD3000-S four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.739, $T_{\max}$ = 1.198
3186 measured reflections
3104 independent reflections

2519 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.035
$\theta_{\max}$ = 65°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 90 min
intensity variation: none

Refinement

Refinement on F
R = 0.047
wR = 0.050
S = 1.11
2519 reflections
362 parameters
All H-atom parameters refined

Empirical weights to give no trends in $\langle w\Delta^2F\rangle$ *versus* $\langle|F_{\rm obs}|\rangle$ and $\langle\sin\theta/\lambda\rangle$
$(\Delta/\sigma)_{\max}$ = 0.18
$\Delta\rho_{\max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\min}$ = −0.18 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.3790 (2)	0.4055 (3)	0.34402 (11)	0.0334 (7)
C2	0.4257 (2)	0.4831 (3)	0.28769 (11)	0.0340 (7)
C3	0.5296 (2)	0.5360 (3)	0.29557 (15)	0.0463 (9)
C4	0.5876 (2)	0.5165 (3)	0.35700 (15)	0.0504 (9)
C5	0.5433 (2)	0.4421 (3)	0.41172 (14)	0.0458 (9)
C6	0.4405 (2)	0.3879 (3)	0.40496 (13)	0.0405 (8)
N11	0.2754 (2)	0.3549 (2)	0.33584 (10)	0.0395 (7)
P12	0.21272 (4)	0.25406 (7)	0.38698 (3)	0.0322 (2)
C13	0.0862 (2)	0.2160 (3)	0.34498 (12)	0.0388 (7)
C14	0.0581 (2)	0.2852 (4)	0.28371 (13)	0.0499 (9)
C15	−0.0409 (2)	0.2587 (4)	0.25311 (16)	0.0652 (11)
C16	−0.1118 (2)	0.1634 (4)	0.28380 (19)	0.0684 (12)
C17	−0.0844 (3)	0.0965 (4)	0.34503 (22)	0.0747 (13)
C18	0.0144 (2)	0.1207 (4)	0.37549 (17)	0.0606 (11)
C19	0.2711 (2)	0.0751 (3)	0.40501 (12)	0.0382 (8)
C20	0.2690 (2)	−0.0275 (3)	0.35121 (14)	0.0500 (9)
C21	0.3199 (3)	−0.1612 (4)	0.35811 (17)	0.0594 (11)
C22	0.3737 (3)	−0.1949 (4)	0.41903 (18)	0.0603 (11)
C23	0.3777 (3)	−0.0946 (4)	0.47291 (16)	0.0590 (11)
C24	0.3267 (2)	0.0407 (3)	0.46606 (14)	0.0486 (9)
C25	0.1782 (2)	0.3379 (3)	0.46933 (13)	0.0445 (9)
C26	0.1383 (3)	0.2612 (5)	0.52612 (15)	0.0660 (12)
C27	0.1060 (3)	0.3368 (7)	0.58486 (18)	0.0903 (19)
C28	0.1128 (3)	0.4874 (7)	0.58701 (22)	0.0964 (20)
C29	0.1533 (3)	0.5631 (6)	0.53228 (25)	0.0893 (17)
C30	0.1867 (3)	0.4897 (4)	0.47273 (18)	0.0627 (12)
N31	0.3645 (2)	0.5094 (2)	0.22600 (10)	0.0380 (6)
C32	0.3392 (2)	0.3781 (3)	0.18617 (14)	0.0462 (9)
C33	0.4052 (3)	0.6229 (4)	0.17955 (16)	0.0582 (11)

Table 2. *Selected bond distances, bond angles and torsion angles* (Å, °)

Experimental values for (I) and theoretical values (AM1) for (II).

	(I)	(II)
C1—C2	1.424 (3)	1.433
C1—C6	1.401 (3)	1.410
C2—C3	1.398 (3)	1.410
C3—C4	1.388 (4)	1.390
C4—C5	1.373 (4)	1.391
C5—C6	1.387 (4)	1.390
C1—N11	1.388 (3)	1.427
N11—P12	1.564 (2)	-
P12—C13	1.806 (2)	-
P12—C19	1.818 (3)	-
P12—C25	1.812 (3)	-
N11—C12	-	1.447
N11—C13	-	1.445
C2—N31	1.422 (3)	1.427
N31—C32	1.452 (4)	1.447
N31—C33	1.461 (4)	1.445
C2—C1—C6	117.4 (2)	118.4
C1—C2—C3	118.9 (2)	118.4
C2—C3—C4	121.8 (2)	121.8
C3—C4—C5	119.9 (3)	119.8
C4—C5—C6	119.4 (2)	119.8
C1—C6—C5	122.7 (2)	121.8
C1—N11—P12	127.2 (2)	-
N11—P12—C25	115.3 (1)	-
N11—P12—C19	116.1 (1)	-
N11—P12—C13	106.4 (1)	-
C6—C1—N11	124.2 (2)	121.2
C1—N11—C12	-	114.7
C1—N11—C13	-	115.3
C12—N11—C13	-	113.0
C2—C1—N11	118.3 (2)	120.4
C1—C2—N31	119.4 (2)	120.4
C3—C2—N31	121.7 (2)	121.2
C2—N31—C32	114.3 (2)	114.7
C2—N31—C33	115.8 (2)	115.3
C32—N31—C33	109.8 (2)	113.0
C6—C1—N11—P12	−8.3 (3)	-
C1—N11—P12—C13	−176.0 (2)	-
C1—N11—P12—C19	−59.3 (2)	-
C1—N11—P12—C25	68.8 (2)	-
N11—P12—C25—C30	15.1 (3)	-
N11—P12—C19—C20	−70.5 (2)	-
N11—P12—C13—C14	−6.6 (2)	-
N11—C1—C2—N31	1.6 (3)	4.8
C2—C1—N11—C12	-	−76.7
C2—C1—N11—C13	-	149.5
C1—C2—N31—C32	−67.7 (3)	−76.7
C1—C2—N31—C33	163.2 (2)	149.5

Table 3. *Deformation parameters around a bond and hydrogen interactions for* (I) (Å, °)

C(1–6) and C(13–18) denote the centroids of the corresponding phenyl rings.

χ_T	−55.5 (1)
$\chi_{25,13}$	−4.8 (3)
$\chi_{19,25}$	8.1 (3)
$\chi_{13,19}$	−3.3 (3)

D(—H)···*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
N(11)···N(31)	-	2.781 (3)	-	-
C(22)—H(22)···C(1–6)^{i}	0.98 (4)	3.674 (4)	2.86 (4)	141 (2)
C(33)—H(333)···C(1–6)^{ii}	0.98 (4)	3.436 (4)	2.80 (4)	123 (3)
C(28)—H(28)···C(13–18)^{iii}	0.97 (5)	3.720 (6)	2.89 (6)	145 (4)

Symmetry codes: (i) $x, -1+y, z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, 1-y, 1-z$.

Compound (I) was prepared according to King & Clark-Lewis (1951) by the procedure of Horner & Oediger (1959) as described by Llamas-Saiz *et al.* (1993). Suitable crystals for the X-ray analysis were obtained by slow evaporation of a saturated solution in methylene chloride.

Data were collected on a four-circle Seifert XRD3000-S diffractometer with an oriented graphite monochromator, detector apertures of 1×1°, 1 min per reflection and a scan width of 1.5°. The structure was solved by direct methods using *SIR*88 (Burla *et al.*, 1989). Data processing, refinement and geometrical calculations were carried out on a VAX 6410 computer using the *XRAY*76 program package (Stewart *et al.*, 1976), *PESOS* (Martinez-Ripoll & Cano, 1975) and *PARST* (Nardelli, 1983). All H atoms were located in a difference Fourier synthesis.

Thanks are due to Professor P. Molina (University of Murcia) for the synthesis of the compound, and to the DGICYT of Spain for financial support for the acquisition of the Seifert diffractometer on behalf of the Programa Sectorial de Promocion General del Conocimiento (1989), and for the project, PB90-0070.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71412 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1048]

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Cano, F. H., Foces-Foces, C. & García-Blanco, S. (1979). *J. Cryst. Mol. Struct.* **9**, 107–116.

Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *User's Manual.* Univs. of Western Australia, Australia, and Maryland, USA.

Horner, L. & Oediger, H. (1959). *Ann. Chem. Warsaw*, **627**, 142–162.

King, F. E. & Clark-Lewis, J. W. (1951). *J. Chem. Soc.* pp. 3080–3085.

Laynez, J., Menéndez, M., Saiz Velasco, J. L., Llamas-Saiz, A. L., Foces-Foces, C., Elguero, J., Molina, P., Alajarín, M. & Vidal, A. (1993). *J. Chem. Soc. Perkin Trans.* 2, pp. 709–713.

Llamas-Saiz, A. L., Foces-Foces, C., Elguero, J., Molina, P., Alajarín, M. & Vidal, A. (1992). *Acta Cryst.* **C48**, 1940–1945.

Llamas-Saiz, A. L., Foces-Foces, C., Elguero, J., Molina, P., Alajarín, M. & Vidal, A. (1993). *Acta Chim. Acad. Sci. Hung.* **130**, 467–495.

Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS.* Unpublished program. Instituto Rocasolano, CSIC, Serrano 119, Madrid, Spain.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Stewart, J. J. P. (1990). *MOPAC*6.0. Frank J. Seiler Research Laboratory, United States Air Force Academy, CO 80840, USA.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System*. Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1994). C**50**, 259–260

(22*R*)-3β-*tert*-Butyldimethylsilyloxy-22-methylchola-5,23-diene

Akira Uchida

Department of Biomolecular Science, Toho University, 2-2-1, Miyama, Funabashi-shi, Chiba 274, Japan

Yuji Ohashi, Masayuki Arai and Eiichi Nakamura

Department of Chemistry, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan

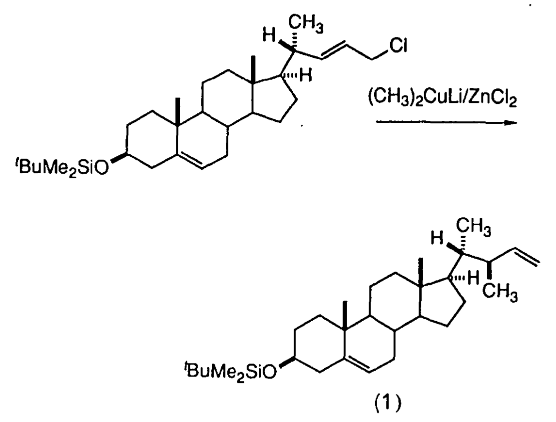
(*Received* 4 *May* 1993; *accepted* 4 *August* 1993)

Abstract

The structure determination of the title compound, $C_{31}H_{54}OSi$, based on single-crystal X-ray diffraction, shows that the absolute configuration at C22 is *R*.

Comment

The diastereoselectivity of nucleophilic additions to olefins bearing a chiral center on an adjacent C atom provides useful information for studies on the factors that control stereoselectivities of organic reactions (Nakamura, Sekiya, Arai & Aoki, 1989). In relation to studies on the diastereoselectivity of the S_N2'-allylation reaction of organocopper reagents, the reaction shown in the scheme below was examined and found to give the methylated product (1) as a single diastereomer (Arai, Kawasuji & Nakamura, 1993). Since no spectroscopic techniques were effective in determining the stereochemistry of this steroidal product, the X-ray crystal structure analysis was performed. The perspective view obtained (Fig. 1) reveals the absolute configuration at C22 to be *R*.



(1)

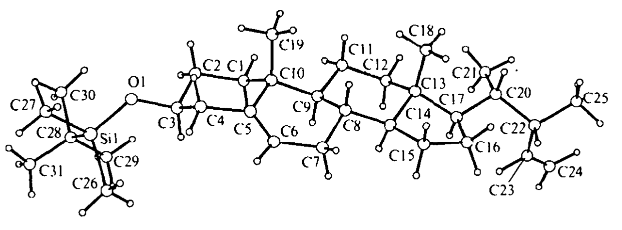


Fig. 1. Molecular structure of (22*R*)-3β-*tert*-butyldimethylsilyloxy-22-methylchola-5,23-diene with atomic numbering.

Experimental

Crystal data

$C_{31}H_{54}OSi$

M_r = 470.85

Orthorhombic

$P2_12_12_1$

a = 12.021 (1) Å

b = 40.218 (5) Å

c = 6.171 (1) Å

V = 2984 (1) Å^3

Z = 4

D_x = 1.05 Mg m^{-3}

Cu $K\alpha$ radiation

λ = 1.5418 Å

Cell parameters from 20 reflections

θ = 45–55°

μ = 0.818 mm^{-1}

T = 296 K

Plate

0.5 × 0.45 × 0.25 mm

Colorless

Data collection

Rigaku AFC-4 diffractometer

$\omega/2\theta$ scans

Absorption correction: none

2826 measured reflections

2815 independent reflections

2491 observed reflections [$F > 3\sigma(F)$]

R_{int} = 0.0348

θ_{max} = 62.5°

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 46$

$l = 0 \rightarrow 7$

3 standard reflections monitored every 50 reflections intensity variation: 2%

Refinement

Refinement on F

R = 0.068

wR = 0.108

S = 0.723

2491 reflections

376 parameters

Only H-atom U's refined

$w = 1/[\sigma^2(F) + 0.020545F^2]$

$(\Delta/\sigma)_{max}$ = 0.3

$\Delta\rho_{max}$ = 0.171 e Å^{-3}

$\Delta\rho_{min}$ = −0.316 e Å^{-3}

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978).