Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Nitro-1-(triisopropylsilyl)-1*H*-pyrrole

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.059
wR factor = 0.123
Data-to-parameter ratio = 18.1

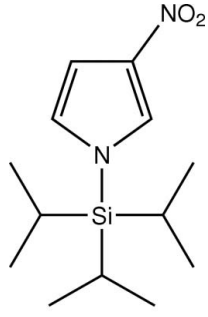
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 29 June 2006
Accepted 5 July 2006

The nitration of 1-(triisopropylsilyl)-1*H*-pyrrole leads to a mixture of products following partial acid cleavage of the triisopropylsilyl protecting group. Structural determination showed the isolated products to be the title compound, $C_{13}H_{24}N_2O_2Si$, and 2,4-dinitropyrrole. In the solid state, the title compound exists as discrete molecules with only weak C—H···nitro hydrogen bonds between them.

Comment

The quest for *N*-alkyl-substituted pyrroles bearing a nitro group at position three has led us to the use of the cleavable and bulky triisoproplysilyl (TIPS) group. This work is in connection with our research into minor-groove binding compounds (Khalaf *et al.*, 2004). These compounds are analogues of naturally occurring distamycin and netropsin, which bind primarily to the adenine-thymine-rich minor groove of DNA. 3-Nitropyrrole (Bray *et al.*, 1990) was required as a precursor; however, the straightforward nitration of pyrrole favours position two. To prevent the nitration from occurring at position two of the pyrrole, a TIPS protecting group was first attached to the nitrogen of the pyrrole ring. This led to the nitro group being directed to position three (as anticipated), giving rise to the desired product (I) (Fig. 1) in 32% yield. However, during the course of the reaction, and due to the presence of acetic acid, the TIPS group cleaved. The removal of the TIPS group allowed the nitration reaction to occur once again. However, this time it occurred at position two, leading to the formation of the undesired product, 2,4-dinitropyrrole (II), in 19% yield.



(I)

Despite the large number of substituted pyrroles reported in the Cambridge Structural Database (Version 5.27 with updates to May 2006; Allen, 2002), a search found only nine relevant 3-nitro derivatives. All of the ring bond lengths and angles (Table 1) of (I) fall within the ranges found for these nine structures, with the exception that in (I) the C2—N1—C5

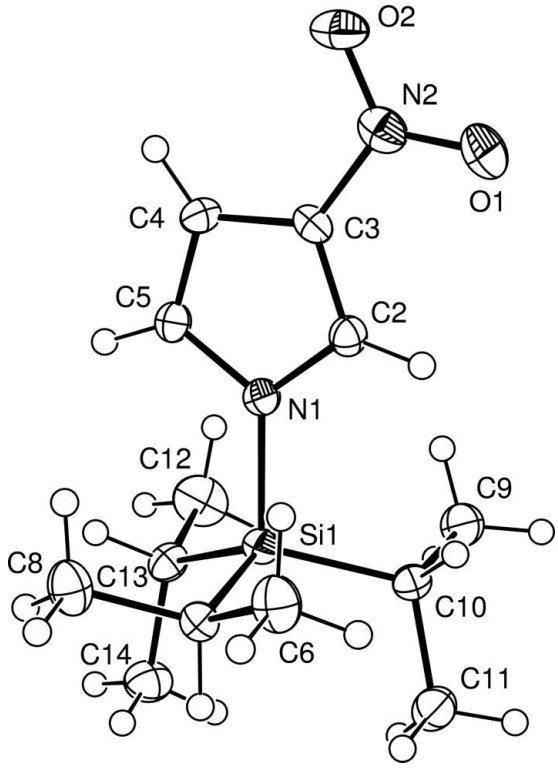


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level.

angle is slightly below the literature range [106.8 (2)° *cf.* 107.7–110.2°]. This is presumably due to the bulk and inductive effects of the attached TIPS group as no such relevant *N*-silyl substituent was found in the database. All of the literature nitro groups are approximately coplanar with their pyrrole rings; it can be seen from Table 1 that this is also the case for (I).

In the absence of obvious hydrogen-bonding groups, nitro aromatics often display nitro-to-nitro interactions of the type described by Wozniak *et al.* (1994); however, none is found in (I). The only intermolecular interactions of any note are weak C—H···O contacts utilizing both sp^2 and sp^3 CH groups (see Table 2). This can be rationalized as a consequence of the bulky triisopropylsilyl group, which ensures that the ring systems are widely separated from each other.

Experimental

A solution of cupric nitrate trihydrate (2.70 g, 11.2 mmol) in acetic anhydride (20 ml) was cooled to 273 K and 1-(triisopropylsilyl)-1*H*-pyrrole (2.50 g, 11.2 mmol) was added dropwise with stirring. The ice bath was removed and stirring was continued for 1 h at room temperature. The reaction mixture was poured slowly over a saturated sodium hydrogen carbonate solution with stirring. After extraction with diethyl ether the organic layer was collected, dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was subjected to flash chromatography on silica gel, using ethyl acetate/hexane (1:12) to elute (I). The solvents were removed under reduced pressure and a slow stream of air was passed over the residue to remove any volatile material. The product was obtained as colourless crystals [0.947 g, 32%; m.p. 325–327 K, literature m.p. 325–327 K (Bray *et al.*, 1990)]. Compound (II) was eluted using ethyl acetate–hexane (1:4). This material was obtained, after the removal of the solvents, as pale-yellow crystals [0.338 g, 19%; m.p. 422–423 K, literature m.p. 423–424 K (Sharnin *et al.*, 1975)].

Crystal data

$C_{13}H_{24}N_2O_2Si$
M_r = 268.43
Monoclinic, $P2_1/n$
a = 9.6924 (5) Å
b = 15.9437 (10) Å
c = 10.1267 (6) Å
β = 95.089 (4)°
V = 1558.74 (16) Å^3
Z = 4
D_x = 1.144 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 123 (2) K
Cut fragment, colourless
0.30 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: none
13088 measured reflections
3060 independent reflections
1685 reflections with $I > 2\sigma(I)$
R_{int} = 0.108
θ_{max} = 26.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.123
S = 1.01
3060 reflections
169 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.0035P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Si1—N1	1.805 (2)	C2—C3	1.365 (3)
N1—C2	1.365 (3)	C3—C4	1.410 (4)
N1—C5	1.395 (3)	C4—C5	1.358 (4)
C2—N1—C5	106.8 (2)	C5—C4—C3	105.3 (2)
C3—C2—N1	108.4 (2)	C4—C5—N1	110.3 (2)
C2—C3—C4	109.1 (2)		
O1—N2—C3—C2	−0.5 (4)	O2—N2—C3—C2	178.9 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O2^{i}	0.95	2.47	3.403 (4)	166
C10—H10···O1^{ii}	1.00	2.55	3.245 (4)	126

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

All H atoms were positioned geometrically, C—H = 0.95 (Csp^2), 0.98 (CH_3) or 1.00 Å (Csp^3), and refined using a riding model [U_{iso}(H) = 1.5U_{eq}(C) for CH_3 and 1.2U_{eq}(C) for all others].

Data collection: *COLLECT* (Hooft, 1988) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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