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borane**

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3 α -Tosyloxymethyltropane(N⁸-B)-borane

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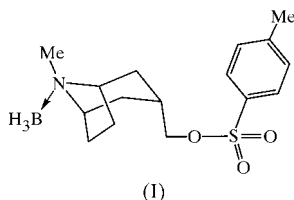
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The title compound [alternative name: 8-methyl-8-azabicyclo[3.2.1]octan-3-ylmethyl *p*-toluenesulfonate(N⁸-B)-borane], C₁₆H₂₆BNO₃S, has the tosyloxymethyl substituent in an *endo* position. The BH₃ group is equatorial and the (N-bonded) methyl group is axial, relative to the six-membered heterocycle. The N–B bond of 1.649 (8) Å is one of the longest known.

Comment

3 α -Tosyloxymethyltropane has been synthesized by Murr *et al.* (1992) by hydrogenation of 3-methylenetropane and tosylation of the resulting 3 α -oxymethyltropane. Repeating this process as part of a multi-stage synthetic route to littorine-type alkaloids (Tavasli, 1999), we accidentally obtained 3 α -oxymethyltropane(N⁸-B)-borane, (II), in the first stage and 3 α -tosyloxymethyltropane(N⁸-B)-borane, (I), in the second.



According to the ¹H and ¹³C NMR data, both (I) and (II) formed as 1:1 mixtures of two isomers. One isomer of (I) was isolated and studied in the present work.

The molecule has an *endo* configuration at C3. The BH₃ substituent at the N atom is equatorial and the methyl one axial with respect to the six-membered heterocycle (the opposite may be the case for the unidentified second isomer). A survey of the April 2000 release of the Cambridge Structural Database (Allen & Kennard, 1993) yielded 24 structures containing an N–B bond between a tertiary amine and a BH₃ group, the bond distance ranging from 1.60 to 1.66 Å and

averaging 1.625 Å. Thus, the N–B bond distance of 1.649 (8) Å in (I) is relatively long, probably due to steric overcrowding.

Experimental

HB(CHMeCHMe₂) was prepared by addition of BF₃·OEt₂ (26.7 mmol) to a solution of NaBH₄ (20 mmol) and 2-methyl-2-butene (53.4 mmol) in THF (10 ml). 3-Methylenetropane (4.5 mmol) was then added to the solution and the reaction stirred for 16 h at room temperature. A 30% solution of basic peroxide (NaOH/H₂O₂) in ethanol (8 ml) was added and the reaction stirred for another 4 h at 333 K. The mixture was then diluted with water and ether, filtered and the organics were extracted into ether, concentrated *in vacuo* and the products purified over silica gel, yielding (II) (70 mg, 10%) as a pale-yellow oil. A 1.6 M solution of *n*-BuLi (2.8 mmol) in hexane was added to a mixture of 2.6 mmol of (II) and 2 mg of Ph₃CH in THF (10 ml) at 273 K and the reaction was stirred for 15 min. A solution of tosyl chloride (2.6 mmol) in THF (5 ml) was then added and the mixture was stirred for 3.5 h at 273 K, diluted with Et₂O and washed with brine. After concentrating the organics *in vacuo*, a mixture of isomers of (I) was obtained as a white amorphous solid. One isomer was separated by chromatography on silica gel and recrystallized from petroleum ether (55 mg, 8%).

Crystal data

C₁₆H₂₆BNO₃S
M_r = 323.25
Orthorhombic, *Pna*2₁
a = 21.443 (2) Å
b = 7.959 (1) Å
c = 10.224 (2) Å
V = 1744.9 (4) Å³
Z = 4
D_x = 1.230 Mg m⁻³

Cu K α radiation
Cell parameters from 25 reflections
 θ = 20.5–25.2°
 μ = 1.731 mm⁻¹
T = 293 (2) K
Prism, colourless
0.28 × 0.22 × 0.11 mm

Data collection

Rigaku AFC-6S four-circle diffractometer
2 θ / ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.726, T_{max} = 0.837
2243 measured reflections
2157 independent reflections (see below)

1613 reflections with I > 2 σ (I)
R_{int} = 0.020
 θ_{max} = 75°
h = -16 → 26
k = -6 → 9
l = -8 → 12
3 standard reflections every 147 reflections intensity decay: 0.8%

Refinement

Refinement on F²
R[F² > 2 σ (F²)] = 0.043
wR(F²) = 0.103
S = 1.091
2157 reflections
208 parameters
H-atom parameters constrained

w = 1/[$\sigma^2(F_o^2) + (0.0473P)^2 + 0.4507P$]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = -0.001
 $\Delta\rho_{max}$ = 0.21 e Å⁻³
 $\Delta\rho_{min}$ = -0.17 e Å⁻³
Absolute structure: Flack (1983)
Flack parameter = 0.35 (3)

Table 1

Selected geometric parameters (Å, °).

S–O2	1.424 (4)	C1–C2	1.522 (6)
S–O3	1.432 (4)	C1–C7	1.523 (7)
S–O1	1.573 (3)	C2–C3	1.545 (6)
S–C11	1.745 (5)	C3–C9	1.513 (6)
O1–C9	1.467 (5)	C3–C4	1.541 (6)
N–C8	1.497 (7)	C4–C5	1.520 (6)
N–C1	1.502 (6)	C5–C6	1.523 (7)
N–C5	1.518 (6)	C6–C7	1.536 (7)
N–B	1.649 (8)		

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C8–N–C1	113.3 (4)	C8–N–B	106.0 (4)
C8–N–C5	112.6 (4)	C1–N–B	113.1 (4)
C1–N–C5	99.7 (3)	C5–N–B	112.3 (4)

1749 independent reflections and 408 of their Friedel equivalents were measured, of which 1229 and 384, respectively, had $I > 2\sigma(I)$. The crystal was a racemic twin with component contributions of 0.65 (3) and 0.35 (3). H atoms were treated as riding and the BH₃ group was treated as a 'rotating body' with the refined B–H distance converging to 1.19 Å.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure:

SHELXTL; software used to prepare material for publication: *SHELXTL*.

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