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2-(1-Piperidinyl)-1,3-benzothiazole

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An unusual de-alkylation reaction between 2-chlorobenzothiazole and *N*-ethylpiperidine gave 2-(1-piperidinyl)-1,3-benzothiazole, $C_{12}H_{14}N_2S$, as pale-yellow orthorhombic crystals. Discrete molecules consist of a planar benzothiazole fragment with a piperidine ring in a chair conformation.

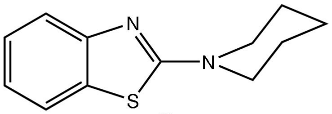
Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.065
Data-to-parameter ratio = 9.9

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

Comment

Research into minor groove binding drugs, such as distamycin, suggests that substitution of the head group with a heterocyclic moiety could enhance the selectivity of the binding to a specific strand of DNA. Benzothiazole and benzoxazole were examined as substitutes for the formyl group of distamycin; however, unexpected products were obtained from the reaction of 2-chlorobenzoxazole and 2-chlorobenzothiazole with the tail group of distamycin analogues. The products were proved to result from a de-alkylation of the dimethylamino tail group of the DNA binding compounds, prompting investigation of the reaction of other tertiary amines in combination with 2-chlorobenzothiazole or 2-chlorobenzoxazole (Khalaf *et al.*, 2000). Use of *N*-ethylpiperidine gave the title compound, (I), as a crystalline product.



(I)

The crystal structure of (I) consists of discrete molecules with no significant intermolecular interactions. The piperidine ring adopts a chair conformation whilst the other C, N and S atoms are coplanar [maximum deviation from the least-squares plane is 0.029 (2) Å for C1]. The bonding about N2 is distorted towards pyrimidal, with the N atom lying 0.219 (2) Å above the plane defined by its three bonded C atoms. Examination of the bond lengths and angles confirms the double-bond character between N1 and C7 [1.304 (3) Å] and shows the relative conjugation effects this bond has with N1—C2 and N2—C7 [1.395 (3) and 1.358 (3) Å, respectively]. The bonding

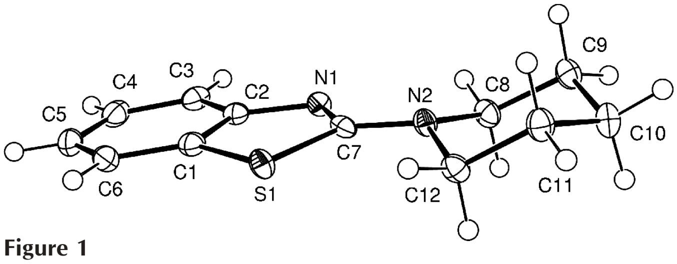


Figure 1
Fi. 1. The molecular structure of (I), shown with 50% probability displacement ellipsoids.

about S1 is slightly asymmetrical [S1—C1 and S1—C7 distances of 1.739 (2) and 1.771 (2) Å, respectively], but all geometric parameters are within the expected ranges and are consistent with those found for other amine derivatives of benzothiazole (Fehlmann, 1970; Chen *et al.*, 2003).

Experimental

2-Chlorobenzothiazole (0.504 g, 2.971 mmol) and *N*-ethylpiperidine (1.01 g, 8.91 mmol) were heated at 403 K for 5 d. Excess reagent was removed under reduced pressure and the crude product was applied to a chromatography column. Ethyl acetate/*n*-hexane (1:10) was used to elute the product, which was obtained as a pale-yellow crystalline solid (0.266 g, 41% yield); m.p. 363–364 K [literature m.p. 366–368 K (Nagarajan *et al.*, 1971)]. R_F = 0.33; ^{1}H NMR ($CDCl_3$): δ 1.68 (6H, *br*, *s*; 3 × CH_2), 3.56 (4H, *br*, *s*, CH_2NCH_2), 7.03–7.07 (1H, *dt*, *J* = 1.1 and 7.8 Hz, ArH), 7.26–7.31 (1H, *dt*, *J* = 1.1 and 7.8 Hz, ArH), 7.55–7.759 (2H, *m*, ArH). ^{13}C NMR ($CDCl_3$): δ 24.67, 25.71 (2 × C), 50.02 (2 × C), 119.21, 120.97, 121.44, 126.26, 131.12, 153.42, 169.25. IR (KBr): 2945, 2924, 2846, 1593, 1561, 1535, 1444, 1261, 762, 732 cm^{-1}.

Crystal data

$C_{12}H_{14}N_2S$
M_r = 218.31
Orthorhombic, $Pna2_1$
a = 15.3509 (6) Å
b = 11.6315 (4) Å
c = 5.9802 (2) Å
V = 1067.79 (7) Å^3
Z = 4
D_x = 1.358 Mg m^{-3}

Mo *K*α radiation
Cell parameters from 1447 reflections
θ = 1.0–27.5°
μ = 0.27 mm^{-1}
T = 123 (2) K
Cut needle, colourless
0.50 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
11 594 measured reflections
1341 independent reflections
1208 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.039
$\theta_{\rm max}$ = 27.5°
h = −19 → 19
k = −14 → 15
l = −7 → 7

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.065
S = 1.07
1341 reflections
136 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.2439P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.17 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.739 (2)	N2—C7	1.358 (3)
S1—C7	1.771 (2)	N2—C12	1.466 (3)
N1—C7	1.304 (3)	N2—C8	1.471 (3)
N1—C2	1.395 (3)		
C1—S1—C7	88.60 (10)	N1—C2—C1	115.55 (19)
C7—N1—C2	110.18 (18)	N1—C7—N2	124.30 (19)
C6—C1—S1	128.72 (18)	N1—C7—S1	116.05 (15)
C2—C1—S1	109.62 (15)	N2—C7—S1	119.62 (16)
C3—C2—N1	125.1 (2)		

H atoms were included in the riding-model approximation, with C—H distances of 0.99 and 0.95 Å for CH_2 and CH groups, respectively, and with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. Initial refinement gave an intermediate Flack (1983) parameter with a large uncertainty. Thus, in the final model, Friedel pairs were merged and no Flack parameter was refined.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1988); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); 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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$F(000) = 464$
$D_x = 1.358$ Mg m^{-3}
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Cell parameters from 1447 reflections
$\theta = 1.0$–27.5°
$\mu = 0.27$ mm^{-1}
$T = 123$ K
Cut needle, colourless
0.50 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
11594 measured reflections
1341 independent reflections
1208 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.039$
$\theta_{\text{max}} = 27.5°$, $\theta_{\text{min}} = 2.2°$
$h = -19 \rightarrow 19$
$k = -14 \rightarrow 15$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.065$
$S = 1.07$
1341 reflections
136 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.2439P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.17$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.19$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
S1	0.39332 (3)	0.01583 (4)	0.40617 (11)	0.01893 (14)
N1	0.36236 (11)	0.11262 (14)	0.0187 (3)	0.0175 (4)
N2	0.47092 (11)	0.20489 (14)	0.2309 (3)	0.0164 (4)
C1	0.31266 (14)	−0.04382 (17)	0.2381 (4)	0.0187 (5)
C2	0.30605 (13)	0.01905 (17)	0.0379 (4)	0.0169 (4)
C3	0.24705 (13)	−0.01615 (17)	−0.1252 (4)	0.0210 (5)
H3	0.2406	0.0264	−0.2597	0.025*
C4	0.19756 (13)	−0.11476 (17)	−0.0881 (5)	0.0247 (5)
H4	0.1586	−0.1407	−0.2008	0.030*
C5	0.20427 (15)	−0.17589 (18)	0.1112 (4)	0.0248 (5)
H5	0.1691	−0.2421	0.1337	0.030*
C6	0.26155 (14)	−0.14147 (18)	0.2774 (4)	0.0217 (5)
H6	0.2660	−0.1829	0.4138	0.026*
C7	0.41108 (13)	0.12077 (16)	0.1966 (4)	0.0160 (4)
C8	0.49943 (14)	0.27153 (18)	0.0350 (4)	0.0197 (5)
H8A	0.4498	0.2817	−0.0688	0.024*
H8B	0.5457	0.2287	−0.0449	0.024*
C9	0.53401 (15)	0.38887 (17)	0.1046 (4)	0.0205 (5)
H9A	0.5589	0.4281	−0.0276	0.025*
H9B	0.4852	0.4363	0.1612	0.025*
C10	0.60356 (14)	0.37909 (19)	0.2851 (4)	0.0234 (5)
H10A	0.6553	0.3391	0.2243	0.028*
H10B	0.6216	0.4568	0.3341	0.028*
C11	0.56756 (14)	0.31233 (18)	0.4830 (4)	0.0212 (5)
H11A	0.5188	0.3557	0.5507	0.025*
H11B	0.6136	0.3034	0.5976	0.025*
C12	0.53554 (13)	0.19401 (14)	0.4101 (4)	0.0190 (4)
H12A	0.5854	0.1476	0.3568	0.023*
H12B	0.5092	0.1538	0.5394	0.023*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0234 (3)	0.0157 (2)	0.0176 (2)	−0.00208 (19)	−0.0005 (3)	0.0037 (3)
N1	0.0180 (8)	0.0155 (8)	0.0189 (9)	0.0001 (7)	0.0009 (8)	0.0004 (8)
N2	0.0195 (9)	0.0149 (8)	0.0147 (9)	−0.0022 (7)	−0.0014 (8)	0.0031 (7)
C1	0.0172 (10)	0.0185 (10)	0.0203 (11)	0.0020 (8)	0.0018 (9)	−0.0023 (9)
C2	0.0161 (10)	0.0166 (9)	0.0182 (11)	0.0022 (8)	0.0019 (9)	−0.0018 (9)
C3	0.0177 (10)	0.0238 (10)	0.0214 (13)	0.0030 (8)	0.0008 (10)	−0.0036 (10)
C4	0.0177 (10)	0.0254 (10)	0.0311 (12)	−0.0013 (8)	0.0012 (13)	−0.0076 (15)
C5	0.0201 (12)	0.0188 (10)	0.0355 (14)	−0.0034 (9)	0.0057 (11)	−0.0045 (10)
C6	0.0227 (11)	0.0173 (10)	0.0253 (13)	0.0013 (9)	0.0059 (10)	0.0015 (9)
C7	0.0209 (10)	0.0118 (9)	0.0153 (10)	0.0028 (8)	0.0027 (9)	−0.0001 (9)
C8	0.0241 (11)	0.0173 (10)	0.0178 (11)	−0.0012 (9)	0.0020 (10)	0.0042 (9)
C9	0.0255 (12)	0.0172 (10)	0.0186 (11)	−0.0031 (9)	0.0014 (9)	0.0021 (10)

C10	0.0237 (12)	0.0208 (11)	0.0256 (13)	−0.0075 (9)	0.0004 (10)	0.0006 (10)
C11	0.0230 (12)	0.0214 (11)	0.0192 (11)	−0.0038 (9)	−0.0024 (10)	0.0005 (9)
C12	0.0221 (10)	0.0169 (9)	0.0179 (10)	0.0004 (7)	−0.0036 (11)	0.0018 (12)

Geometric parameters (Å, º)

S1—C1	1.739 (2)	C6—H6	0.9500
S1—C7	1.771 (2)	C8—C9	1.523 (3)
N1—C7	1.304 (3)	C8—H8A	0.9900
N1—C2	1.395 (3)	C8—H8B	0.9900
N2—C7	1.358 (3)	C9—C10	1.522 (3)
N2—C12	1.466 (3)	C9—H9A	0.9900
N2—C8	1.471 (3)	C9—H9B	0.9900
C1—C6	1.400 (3)	C10—C11	1.519 (3)
C1—C2	1.406 (3)	C10—H10A	0.9900
C2—C3	1.393 (3)	C10—H10B	0.9900
C3—C4	1.394 (3)	C11—C12	1.525 (3)
C3—H3	0.9500	C11—H11A	0.9900
C4—C5	1.392 (4)	C11—H11B	0.9900
C4—H4	0.9500	C12—H12A	0.9900
C5—C6	1.386 (3)	C12—H12B	0.9900
C5—H5	0.9500		

C1—S1—C7	88.60 (10)	C9—C8—H8A	109.4
C7—N1—C2	110.18 (18)	N2—C8—H8B	109.4
C7—N2—C12	120.40 (17)	C9—C8—H8B	109.4
C7—N2—C8	117.44 (18)	H8A—C8—H8B	108.0
C12—N2—C8	115.24 (16)	C10—C9—C8	111.80 (18)
C6—C1—C2	121.6 (2)	C10—C9—H9A	109.3
C6—C1—S1	128.72 (18)	C8—C9—H9A	109.3
C2—C1—S1	109.62 (15)	C10—C9—H9B	109.3
C3—C2—N1	125.1 (2)	C8—C9—H9B	109.3
C3—C2—C1	119.35 (19)	H9A—C9—H9B	107.9
N1—C2—C1	115.55 (19)	C11—C10—C9	109.59 (17)
C2—C3—C4	119.0 (2)	C11—C10—H10A	109.8
C2—C3—H3	120.5	C9—C10—H10A	109.8
C4—C3—H3	120.5	C11—C10—H10B	109.8
C5—C4—C3	121.1 (2)	C9—C10—H10B	109.8
C5—C4—H4	119.5	H10A—C10—H10B	108.2
C3—C4—H4	119.5	C10—C11—C12	110.86 (19)
C6—C5—C4	120.9 (2)	C10—C11—H11A	109.5
C6—C5—H5	119.5	C12—C11—H11A	109.5
C4—C5—H5	119.5	C10—C11—H11B	109.5
C5—C6—C1	118.0 (2)	C12—C11—H11B	109.5
C5—C6—H6	121.0	H11A—C11—H11B	108.1
C1—C6—H6	121.0	N2—C12—C11	110.43 (16)
N1—C7—N2	124.30 (19)	N2—C12—H12A	109.6
N1—C7—S1	116.05 (15)	C11—C12—H12A	109.6

N2—C7—S1	119.62 (16)	N2—C12—H12B	109.6
N2—C8—C9	110.99 (18)	C11—C12—H12B	109.6
N2—C8—H8A	109.4	H12A—C12—H12B	108.1

C7—S1—C1—C6	178.0 (2)	C2—N1—C7—S1	−0.2 (2)
C7—S1—C1—C2	0.49 (15)	C12—N2—C7—N1	−166.66 (19)
C7—N1—C2—C3	−178.02 (19)	C8—N2—C7—N1	−17.2 (3)
C7—N1—C2—C1	0.6 (2)	C12—N2—C7—S1	15.4 (3)
C6—C1—C2—C3	0.3 (3)	C8—N2—C7—S1	164.88 (14)
S1—C1—C2—C3	177.97 (16)	C1—S1—C7—N1	−0.19 (17)
C6—C1—C2—N1	−178.43 (19)	C1—S1—C7—N2	177.93 (17)
S1—C1—C2—N1	−0.7 (2)	C7—N2—C8—C9	156.20 (18)
N1—C2—C3—C4	176.92 (19)	C12—N2—C8—C9	−52.7 (2)
C1—C2—C3—C4	−1.6 (3)	N2—C8—C9—C10	52.5 (2)
C2—C3—C4—C5	2.1 (3)	C8—C9—C10—C11	−55.4 (2)
C3—C4—C5—C6	−1.1 (3)	C9—C10—C11—C12	56.9 (2)
C4—C5—C6—C1	−0.3 (3)	C7—N2—C12—C11	−155.42 (19)
C2—C1—C6—C5	0.7 (3)	C8—N2—C12—C11	54.5 (2)
S1—C1—C6—C5	−176.51 (17)	C10—C11—C12—N2	−55.8 (2)
C2—N1—C7—N2	−178.20 (19)		