Short Communication

X-Ray Study of a Pentacyclic Partially Saturated Benzothiazolo[2,3-*a*]isoindolone

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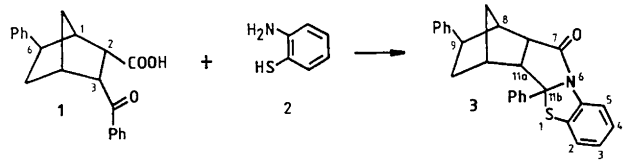
As part of our studies on various anorexigenic agents, the crystal structure of 12b-*p*-tolyl-3,6-methano-2a,3,6,6a,7,-8,9,10,11,12,12a-dodecahydro-3,1-benzoxazino[2,3-*a*]isoindol-8(12b*H*)-one was determined.[1] The definite structures of such partly saturated condensed isoindolones are difficult to elucidate by means of NMR owing to severe signal overlap.

As a continuation of these studies[1,2] we now report the crystal structure of 9,11b-diphenyl-8,11-methano-7a,8,9,10,11,11a-hexahydrobenzothiazolo[2,3-*a*]isoindol-7(11b*H*)-one (**3**) which was synthesized (Scheme 1) from 3-*endo*-benzoyl-6-*exo*-phenylbicyclo[2.2.1]heptane-2-*endo*-carboxylic acid (**1**) and 2-aminothiophenol (**2**).

The presence of the saturated terminal bicycle can lead to various stereopositions of the two hetero-rings, i.e., the position of the 11b-phenyl group relative to the hydrogen atoms at the norbornane–pyrrolidine fusion can be different. Furthermore the location and steric arrangement of the phenyl group on the norbornane moiety needed to be proved.

Experimental

Crystal data for **3**. $C_{27}H_{23}NOS$, monoclinic, space group $P2_1/a$, a = 13.949(4), b = 10.691(3), c = 15.203(3) Å, β = 110.00(2), V = 2130.5(9) Å^3, Z = 4, D_c = 1.277 g cm^{-3}, μ(Mo K_α) = 1.62 cm^{-1}, T = 296(1) K; colourless cubes.



Scheme 1.

Data collection, analysis and refinement. A Rigaku AFC5S diffractometer was used, with graphite-monochromated Mo K_α radiation (λ = 0.71069 Å), in the ω–2θ scan mode, with an ω scan rate of 8.0° min^{-1} and a scan width of (1.57+0.30tanθ). The weak reflections [$I < 10\sigma(I)$] were rescanned up to two times. The data obtained were corrected for Lorentz and polarization, but not for absorption effects. 3988 unique reflections were obtained ($2\theta_{max}$ = 50°). Direct methods and difference electron density ($\Delta\delta$) calculations were used. Refinement of structural parameters was by full-matrix least-squares refinement, with non-hydrogen atoms anisotropic, and hydrogen atoms with fixed isotropic temperature parameters (1.2 times B_{eq} of the carrying atom). In the final cycles, the 2261 data with $I > 2\sigma(I)$ yielded an R value of 0.046 (R_w = 0.051, w = $[\sigma^2(F_o)]^{-1}$) for 340 parameters; maximum/minimum $\Delta\delta$ = 0.19/−0.25 e Å^{-3}.

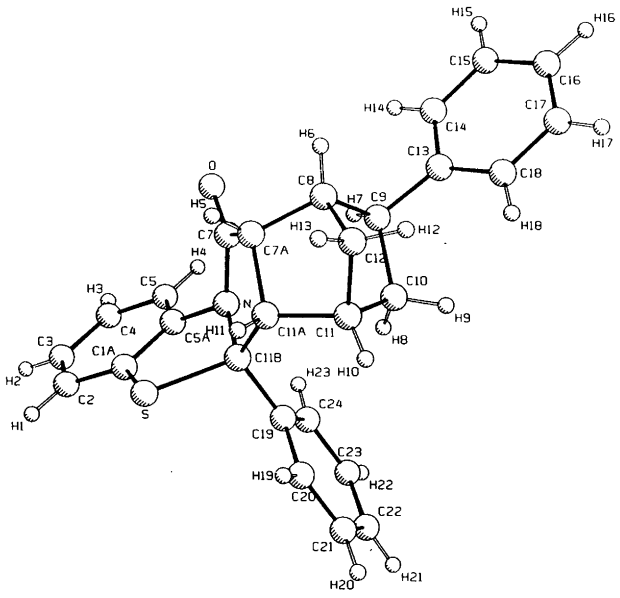


Fig. 1. Solid-state conformation of **3** by PLUTO drawing.

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Table 1. Positional parameters ($\times 10^4$) and B(eq) (Å^2) for non-hydrogen atoms.[a]

S	1318.6(7)	2593(1)	744.3(6)	3.87(4)
O	1123(2)	6656(3)	1144(2)	4.9(1)
N	1666(2)	4689(3)	1709(2)	3.0(1)
C1A	2365(3)	3527(4)	775(2)	3.6(2)
C2	3029(3)	3333(5)	282(3)	4.6(2)
C3	3789(4)	4211(6)	379(3)	5.8(3)
C4	3892(3)	5247(5)	933(3)	5.3(2)
C5	3219(3)	5457(4)	1424(3)	4.1(2)
C5A	2462(3)	4586(4)	1327(2)	3.4(2)
C7	933(3)	5625(4)	1365(2)	3.3(2)
C7A	−94(3)	5117(4)	1295(3)	3.3(2)
C8	−641(3)	5733(4)	1913(3)	3.4(2)
C9	152(3)	5959(3)	2905(2)	3.2(1)
C10	364(3)	4609(4)	3296(3)	3.7(2)
C11	−295(3)	3779(4)	2495(3)	3.9(2)
C11A	87(3)	3758(4)	1654(2)	3.2(2)
C11B	1216(2)	3475(3)	1779(2)	2.9(1)
C12	−1242(3)	4612(4)	2083(3)	4.4(2)
C13	−232(3)	6899(3)	3451(2)	3.3(2)
C14	−8(3)	8151(4)	3403(3)	3.8(2)
C15	−399(3)	9064(4)	3834(3)	4.6(2)
C16	−1017(4)	8743(4)	4324(3)	5.0(2)
C17	−1228(4)	7505(5)	4403(3)	5.7(2)
C18	−842(4)	6591(4)	3969(3)	4.9(2)
C19	1817(3)	2748(3)	2650(2)	2.9(1)
C20	1465(3)	1585(4)	2819(3)	3.8(2)
C21	1985(4)	922(4)	3614(3)	4.4(2)
C22	2868(3)	1393(4)	4255(3)	4.3(2)
C23	3229(3)	2525(4)	4089(3)	4.3(2)
C24	2709(3)	3202(4)	3292(3)	3.5(2)

[a]E.s.d.s are given in parentheses.

Neutral atomic scattering and dispersion factors were taken from Ref. 3. All calculations were performed with TEXSAN-89 software,[4] using a VAXSTATION 3520 computer. Figures were drawn with PLUTO[5] (cf. Fig. 1) software. The final atomic positional coordinates for non-hydrogen atoms are listed in Table 1, relevant bond lengths in Table 2 and relevant bond angles of non-hydrogen atoms in Table 3 and torsion angles in Table 4. Lists of the final positional coordinates for hydrogen atoms, complete lists of bond lengths and angles and anisotropic thermal

Table 2. Relevant bond lengths (Å).[a]

S–C1A	1.756(4)	C7–C7A	1.502(5)
S–C11B	1.882(3)	C7A–C8	1.546(5)
O–C7	1.208(4)	C7A–C11A	1.542(5)
N–C5A	1.423(4)	C8–C9	1.554(5)
N–C7	1.397(4)	C8–C12	1.535(5)
N–C11B	1.462(4)	C9–C10	1.550(5)
C1A–C2	1.392(5)	C9–C13	1.512(5)
C1A–C5A	1-389(5)	C10–C11	1.533(5)
C2–C3	1.386(7)	C11–C11A	1.544(5)
C3–C4	1.368(7)	C11–C12	1.539(5)
C4–C5	1.402(6)	C11A–C11B	1.549(5)
C5–C5A	1.378(5)	C11B–C19	1.517(4)

[a]Average bond lengths: C–H 0.95(3) Å and C–C (phenyl) 1.379(5) Å.

Table 3. Relevant bond angles (°) of non-hydrogen atoms.

C1A–S–C11B	89.6(2)	C7A–C8–C9	108.7(3)
C5A–N–C7	118.4(3)	C7A–C8–C12	100.4(3)
C5A–N–C11B	112.0(3)	C9–C8–C12	101.9(3)
C7–N–C11B	112.7(3)	C8–C9–C10	101.9(3)
S–C1A–C2	127.0(3)	C8–C9–C13	111.6(3)
S–C1A–C5A	112.8(3)	C10–C9–C13	117.7(3)
C2–C1A–C5A	120.1(4)	C9–C10–C11	104.5(3)
C1A–C2–C3	117.9(4)	C10–C11–C11A	112.6(3)
C2–C3–C4	122.0(4)	C10–C11–C12	100.7(3)
C3–C4–C5	120.5(5)	C11A–C11–C12	99.4(3)
C4–C5–C5A	117.6(4)	C7A–C11A–C11	102.6(3)
N–C5A–C1A	112.5(3)	C7A–C11A–C11B	105.4(3)
N–C5A–C5	125.6(3)	C11–C11A–C11B	121.6(3)
C1A–C5A–C5	121.9(3)	S–C11B–N	103.1(2)
O–C7–N	123.8(3)	S–C11B–C11A	111.1(2)
O–C7–C7A	127.2(4)	S–C11B–C19	107.2(2)
N–C7–C7A	109.0(3)	N–C11B–C11A	105.1(3)
C7–C7A–C8	117.4(3)	N–C11B–C19	113.3(3)
C7–C7A–C11A	106.2(3)	C11A–C11B–C19	116.3(3)
C8–C7A–C11A	104.0(3)	C8–C12–C11	94.5(3)

Table 4. Torsion angles (°).

S–C1A–C2–C3	177.7(3)	C7–N–C11B–C11A	−12.8(3)
S–C1A–C5A–N	−2.3(4)	C7–N–C11B–C19	−140.8(3)
S–C1A–C5A–C5	−178.3(3)	C7–C7A–C8–C9	−42.7(4)
S–C11B–N–C5A	−32.8(3)	C7–C7A–C8–C12	−149.2(3)
S–C11B–N–C7	103.7(3)	C7–C7A–C11A–C11	119.9(3)
S–C11B–C11A–C7A	−98.4(3)	C7–C7A–C11A–C11B	−8.3(3)
S–C11B–C11A–C11	145.8(3)	C7A–C7–N–C11B	7.6(4)
S–C11B–C19–C20	−68.4(3)	C7A–C8–C9–C10	−71.2(4)
S–C11B–C19–C24	111.9(3)	C7A–C8–C9–C13	162.4(3)
O–C7–N–C5A	−37.2(5)	C7A–C8–C12–C11	56.1(3)
O–C7–N–C11B	−170.7(3)	C7A–C11A–C11–C10	−65.9(4)
O–C7–C7A–C8	−65.1(5)	C7A–C11A–C11–C12	39.8(3)
O–C7–C7A–C11A	179.2(3)	C7A–C11A–C11B–C19	138.6(3)
N–C5A–C1A–C2	174.5(3)	C8–C7A–C11A–C11	−4.6(4)
N–C5A–C5–C4	−174.8(3)	C8–C7A–C11A–C11B	−132.8(3)
N–C7–C7A–C8	116.7(3)	C8–C9–C10–C11	1.4(4)
N–C7–C7A–C11A	1.0(4)	C8–C9–C13–C14	−91.4(4)
N–C11B–S–C1A	26.0(2)	C8–C9–C13–C18	85.4(5)
N–C11B–C11A–C7A	12.4(3)	C8–C12–C11–C10	56.1(3)
N–C11B–C11A–C11	−103.3(4)	C8–C12–C11–C11A	−59.2(3)
N–C11B–C19–C20	178.6(3)	C9–C8–C7A–C11A	74.2(4)
N–C11B–C19–C24	−1.1(4)	C9–C8–C12–C11	−55.8(3)
C1A–S–C11B–C11A	138.1(3)	C9–C10–C11–C11A	68.6(4)
C1A–S–C11B–C19	−93.8(2)	C9–C10–C11–C12	−36.3(4)
C1A–C2–C3–C4	−0.5(7)	C9–C13–C14–C15	175.3(3)
C1A–C5A–N–C7	−109.2(4)	C9–C13–C18–C17	−175.5(4)
C1A–C5A–N–C11B	24.6(4)	C10–C9–C8–C12	34.3(3)
C1A–C5A–C5–C4	0.7(6)	C10–C9–C13–C14	151.4(4)
C2–C1A–S–C11B	168.9(3)	C10–C9–C13–C18	−31.8(6)
C2–C1A–C5A–C5	−1.5(5)	C10–C11–C11A–C11B	51.2(5)
C2–C3–C4–C5	−0.2(7)	C11–C10–C9–C13	123.7(3)
C3–C2–C1A–C5A	1.4(6)	C11–C11A–C11B–C19	22.9(5)
C3–C4–C5–C5A	0.2(6)	C11A–C7A–C8–C12	−32.3(4)
C5–C5A–N–C7	66.6(5)	C11A–C11B–C19–C20	56.6(4)
C5–C5A–N–C11B	−159.6(3)	C11A–C11B–C19–C24	−123.1(4)
C5A–N–C7–C7A	141.1(3)	C11B–C11A–C11–C12	157.0(3)
C5A–N–C11B–C11A	−149.3(3)	C11B–C19–C20–C21	−178.6(3)
C5A–N–C11B–C19	82.7(3)	C11B–C19–C24–C23	178.7(3)
C5A–C1A–S–C11B	−14.5(3)	C12–C8–C9–C13	−92.1(3)

parameters and observed and calculated structural factors are available from the authors on request.

Results and discussion

The X-ray analysis indicates that the phenyl substituent on the norbornane ring occupies the 9-*exo*-position. It was important to establish this because the phenyl group in the initial reactant **1**, prepared from bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride by addition and acylation of benzene in one step, could, in principle, be located at C10. The *exo* position of this phenyl group is not surprising since the saturation of the norbornene double bond generally results in *exo* substitution.

The *endo* phenyl group at C11B and the hydrogen atoms at C7A and C11A, namely H7A and H11A, are *trans* relative to the pyrrolidine ring. Fig. 1 shows the perspective view of the molecule.[5] One of the heterocyclic five-membered rings (C11B,S,...,N) attains an envelope form (E_1) with the puckering parameters Q = 0.327(1) Å and φ = 179.5(2)° and the ring torsion angles starting from C5A–N–C11B–S of −38.8(3), 26.0(2), −14.5(3), −2.3(4) and 24.6(4)°, respectively. The conformation of the second five-membered heterocycle (C11B,N,...,C11A) is a flattened ^1E envelope with the puckering parameters Q = 0.125(2) Å and φ = 353.9(7)° and the ring torsion angles starting from C11A–C11B–N–C7 of −12.8(3), 7.6(4), 1.0(4), −8.3(3) and 12.4(3)°, respectively.

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