The Crystal Structure of 1-(Piperidin-1-yl)-4-*t*-butyl-7-thiabicyclo[4.2.0]octane 7,7-Dioxide [1α,4α,6α]

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The crystal structure of the title compound is described.

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Introduction.

In the course of our studies concerned with the heterocycloaddition reactions of anancomeric enamines [1], we have prepared two diastereoisomeric thiabicyclo[4.2.0]octane dioxide systems, which have been assigned the structures **1** and **2** respectively, on the basis of ^{1}H-nmr analysis [2] (Scheme).

1   2

Scheme. R = morpholin-4-yl, piperidin-1-yl, pyrrolidin-1-yl

The current X-ray study was undertaken to confirm the stereochemical assignments made and to establish the influence of the fusion on the structural parameters of the thietane 1,1-dioxide ring, as only crystal data of non-fused thietane 1,1-dioxide systems are reported in the literature [3,4].

X-ray Structural Investigation.

A single crystalline platelet of **1** measuring 0.40 mm × 0.30 mm × 0.20 mm was chosen for analysis. All crystallographic measurements were performed on a Philips PW 1100-four-circle diffractometer. The title compound was found to crystallize in the monoclinic space group $P2_1/c$. Unit cell parameters were determined from 25 carefully centered high angle reflections ($2\theta \geq 20°$) with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å).

A least squares fit of the measured 2θ values led to the lattice constants: a = 9.079(2) Å, b = 22.881(4) Å, c = 8.468(2) Å, β = 108.42(6)°. The calculated density of 1.192 g/cc assuming four molecules per cell is in good agreement with the experimentally measured density of 1.20 ± 0.02 g/cc.

Data collection was carried out using a θ scan technique with a scan speed of 0.04° s^{-1} and a scan width of 1.10° kept constant throughout the range $6° \leq 2\theta \leq 50°$. Two background counts were measured for 9s at each side of the peaks and then averaged. Two standard reflections measured every 120 minutes did not show any significant variation of the experimental conditions.

A total of 2923 independent reflections were collected, of which 1823 (62%) were considered as observed having $I \geq 3\sigma(I)$ (σ based on counting statistics). They were corrected for Lorentz and polarization factors and used in the subsequent analysis.

The structure was solved by the Multan 80 program [5]. The E-map with the highest figure of merit showed all the non-hydrogen atoms. The refinement was carried out using the SHELX program [6], by full matrix least squares with anisotropic thermal factors for all atoms (atomic scattering factors were taken from ref [7]). In the last cycles we

Table I

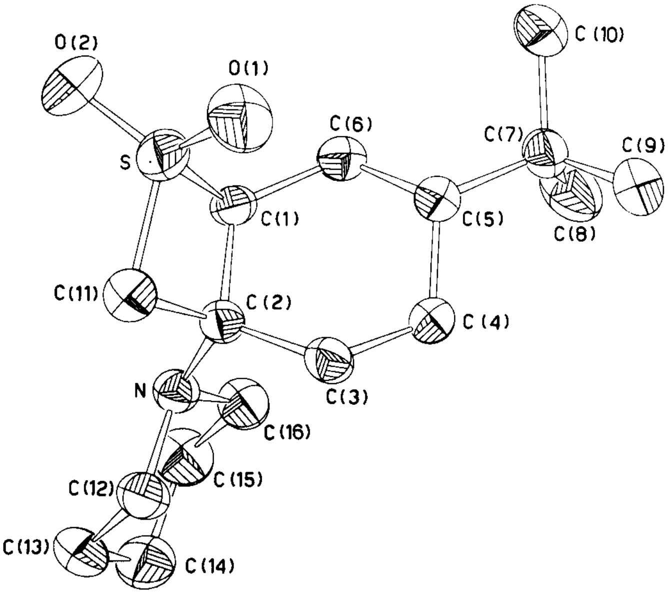
Fractional Coordinates (× 104) and Equivalent Isotropic Thermal Parameters (Estimated standard deviations in Parentheses refer to last decimal place)

$$B_{eq} = 1/3\ \Sigma_{ij} a_i a_j a_i^* a_j^*\ Bij$$

Atom	X	Y	Z	Beq
S	-5351(1)	1715(0)	7293(1)	3.7(1)
O1	-6069(3)	2247(1)	6489(4)	5.3(2)
O2	-3952(3)	1524(1)	7007(4)	5.5(3)
N	-6649(3)	810(1)	9969(3)	2.7(2)
C1	-6768(3)	1145(1)	7113(4)	2.6(2)
C2	-6857(3)	1325(1)	8866(4)	2.6(2)
C3	-8283(4)	1715(2)	8711(4)	3.3(3)
C4	-9743(4)	1553(2)	7277(4)	3.3(3)
C5	-9447(4)	1597(2)	5599(4)	3.0(2)
C6	-8204(4)	1139(2)	5577(4)	3.2(3)
C7	-10924(4)	1551(2)	4060(5)	3.3(3)
C8	-11799(5)	985(2)	3999(6)	5.4(4)
C9	-12000(5)	2068(2)	4093(5)	4.7(4)
C10	-10473(5)	1604(2)	2459(5)	4.4(4)
C11	-5311(4)	1686(2)	9394(4)	3.3(3)
C12	-6390(5)	969(2)	11710(5)	3.5(3)
C13	-5895(5)	425(2)	12813(5)	4.3(4)
C14	-7106(5)	-47(2)	12302(6)	4.7(4)
C15	-7432(5)	-183(2)	10463(6)	4.5(4)
C16	-7892(5)	371(2)	9423(5)	3.6(3)

took into account the contribution of the hydrogen atoms kept fixed in the position found from a difference Fourier map with an optimized overall isotropic thermal factor. The function minimized was $\Sigma w(|F_o|-|F_c|_2)^2$ and the weighting scheme chosen as $w = k / (\sigma^2(F_o)+gF_o^2)$. The final, optimized values of k and g were 1.1015 and 0.002834 respectively. The conventional disagreement factor $R(= \Sigma||F_o|-|F_c|| / | |F_o|)$ was 0.0494, while the weighted R was 0.0595.

The fractional coordinates and equivalent isotropic thermal factors, bond distances, angles and torsion angles are reported in Tables I-IV. Lists of hydrogen fractional coordinates and anisotropic thermal factors and of the observed and calculated structure factors are available on request. An ORTEP [8] view of the molecule is supplied in Figure 1.



Discussion.

The X-ray crystallographic structure determination reported here confirms the assignment of structure **1** obtained by nmr analysis.

Bond distances involving the sulfur atom are significantly different between themselves and both are shorter than 1.80 Å , which is the value usually accepted for the carbon-sulfur bond [9]. However, both carbon-sulfur distances are equal within the experimental error to those observed in simple thietane 1,1-dioxide rings [3,4] and in *trans*-2,5-dibromo-7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide [10], which is the only bicyclo compound similar to ours, as far as we know. In the latter case however the presence of a double bond common to both rings prevents a full comparison.

The carbon-carbon distances of the four-membered ring (1.567(5) Å and 1.568(5) Å) fall in the upper part of the usual range of these bonds (from 1.532(5) Å of ref [4c] to

Table II

Bond Distances (Å)

(Standard Deviations in Parentheses refer to last decimal place)

01 - S	1.444(3)
02 - S	1.435(3)
C1 - S	1.805(3)
C11- S	1.770(4)
C2 - N	1.478(4)
C12- N	1.464(5)
C16- N	1.473(5)
C2 - C1	1.568(5)
C6 - C1	1.523(4)
C3 - C2	1.543(5)
C11- C2	1.567(4)
C4 - C3	1.534(4)
C5 - C4	1.530(5)
C6 - C5	1.544(5)
C7 - C5	1.550(4)
C8 - C7	1.512(6)
C9 - C7	1.541(6)
C10- C7	1.540(7)
C13- C12	1.535(6)
C14- C13	1.505(7)
C15- C14	1.522(7)
C16- C15	1.525(6)

Table III

Bond Angles (°)

(Standard deviations are in parentheses)

02 -S- 01	118.0(2)
C1 -S- 01	111.4(1)
C1 -S- 02	114.2(2)
C11-S- 01	111.6(2)
C11-S- 02	114.8(2)
C11-S- C1	81.1(2)
C12-N- C2	112.7(3)
C16-N- C2	114.4(2)
C16-N-C12	110.4(3)
C2 -C1-S	88.8(2)
C6 -C1-S	118.3(2)
C6 -C1-C2	121.7(3)
C1 -C2-N	110.7(3)
C3 -C2-N	116.8(3)
C3 -C2-C1	111.3(2)
C11-C2-N	108.4(2)
C11-C2-C1	95.7(3)
C11-C2-C3	111.8(3)
C4 -C3-C2	114.8(3)
C5 -C4-C3	110.9(3)
C6 -C5-C4	108.1(3)
C7 -C5-C4	114.7(3)
C7 -C5-C6	112.6(3)
C5 -C6-C1	114.5(3)
C8 -C7-C5	113.1(3)
C9 -C7-C5	108.5(3)
C9 -C7-C8	109.2(4)
C10-C7-C5	109.6(3)
C10-C7-C8	108.7(4)
C10-C7-C9	107.5(3)
C2-C11-S	90.1(2)
C13-C12-N	109.5(3)
C14-C13-C12	111.1(3)
C15-C14-C13	109.3(4)
C16-C15-C14	110.5(4)
C15-C16-N	110.1 (3)

Table IV

Torsion Angles (°)

(Standards derivations are estimated to be about 1°)

S-C1-C2-N	129
S-C11-C2-N	-131
S-C11-C2-C1	-17
S-C1-C2-C3	-100
S-C11-C2-C3	99
S-C1-C6-C5	77
S-C1-C2-C11	17
O1-S-C1-C2	95
O1-S-C11-C2	-95
O1-S-C1-C6	-31
O2-S-C1-C2	-128
O2-S-C11-C2	127
O2-S-C1-C6	106
N-C2-C3-C4	92
N-C2-C1-C6	-108
N-C12-C13-C14	59
N-C16-C15-C14	-58
C1-S-C11-C2	15
C1-C2-C3-C4	-37
C1-C6-C5-C4	49
C1-C6-C5-C7	177
C1-C2-N-C12	-168
C1-C2-N-C16	65
C2-C1-C6-C5	-31
C2-C3-C4-C5	60
C2-C1-S-C11	-15
C2-N-C12-C13	170
C2-N-C16-C15	-170
C3-C2-C1-C6	23
C3-C4-C5-C6	-64
C3-C4-C5-C7	169
C3-C2-N-C12	63
C3-C2-N-C16	-64
C4-C5-C7-C8	59
C4-C5-C7-C9	-63
C4-C5-C7-C10	-180
C4-C3-C2-C11	-143
C6-C5-C7-C8	-65
C6-C5-C7-C9	173
C6-C5-C7-C10	56
C6-C1-S-C11	-141
C6-C1-C2-C11	140
C11-C2-N-C12	-64
C11-C2-N-C16	169
C12-N-C16-C15	61
C12-C13-C14-C15	-55
C13-C12-N-C16	-61
C13-C14-C15-C16	55

1.572(6) Å of ref [3]).

The bond angles involving the sulfur atom have the expected values, as well as the other angles of the thietane ring.

The puckering angle of the heterocyclic ring defined as the dihedral angle between the planes defined by the atoms C1-S-C11 and C1-C2-C11 is 157.7°. This value is to be compared with those found for simple thietane 1,1-dioxide systems, namely 162.1° [4a], 170.6° [4b] and 173.2° [4c], and is indicative of a substantial flattening of the thietane 1,1-dioxide ring. Also the cyclohexane ring is considerably flattened along the junction, as shown by the values of the relative torsion angles (C5-C6-C1-C2, −31°, and C6-C1-C2-C3, 23°). This marked flattening however seems to have but a small influence on the axiality of the S-C1 bond (C6-C1-S, 118.3°).

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