Structure of a β-Lactam, 2,6a-Di-*p*-tolyl-6,6a-dihydro-3*H*,5*H*-azeto[2,1-*b*]imidazol-5-one, C₁₉H₁₈N₂O*

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Abstract. $M_r = 290.37$, monoclinic, $P2_1/a$, $a = 19.176$ (2), $b = 5.745$ (1), $c = 15.144$ (2) Å, $\beta = 109.82$ (2)°, $V = 1569.5$ (5) Å³, $Z = 4$, $D_m = 1.22$ (1), $D_x = 1.229$ g cm⁻³, Ni-filtered Cu $K\alpha$, $\lambda(K\alpha_1) = 1.54056$, $\lambda(K\alpha_2) = 1.54439$ Å, $\mu(\text{Cu } K\alpha) = 5.70$ cm⁻¹, $F(000) = 616$, $T = 296$ K, $R = 0.046$ for 1467 observed reflexions. The compound was produced by a novel synthesis for inducing ring-opening reactions of azirines. The four- and five-membered rings are *cis* fused at C–N with a dihedral angle of 116.5 (4)° between their mean planes.

Introduction. A novel synthesis of β-lactams, which are an important class of antibiotics, has been described by Alper, Perera & Ahmed (1981). Although structure (I) could be assigned to the synthesized product on the basis of spectral data, i ers such as (II) could not be ruled out and the X-ray analysis was undertaken to resolve the ambiguity. The study has identified the product as (I).

(I)   (II)
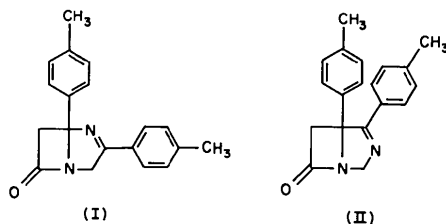
Experimental. Plate-like crystals, $0.40 \times 0.13 \times 0.03$ mm, Nonius CAD-4 diffractometer, cell parameters by least squares on setting angles of 11 reflexions, $70 < 2\theta < 80°$, intensities by ω–2θ scans for $\omega = 1.5°$ $(0.7 + 0.14 \tan\theta)$ at ω speed of $2.5°$ min⁻¹ maximum, three standard reflexions varied by $\pm2\%$ of mean intensities, hkl and $\bar{h}kl$ to $\theta = 65°$, 2665 independent reflexions, 1467 observed above $2\sigma(I)$ level, Lp correction but no absorption. Structure solving by symbolic addition (Karle & Karle, 1963), H atoms located in a difference map; anisotropic least-squares refinement (isotropic for H) on $\sum w(F_o - F_c)^2$, $w = [1 + (|F_o| - 20)/25]^{-1}$, excluding unobserved and three

very strong reflexions showing extinction effect, $R = 0.046$ for observed reflexions, $R_w = 0.047$, $S = 0.66$, mean shift $= 0.20\sigma$, maximum shift $= 0.8\sigma$ $(1.08\sigma$ for H), residual electron density within -0.11 and 0.15 e Å⁻³, f curves from *International Tables for X-ray Crystallography* (1974) and Stewart, Davidson & Simpson (1965) for H, NRC system of programs (Ahmed, Hall, Pippy & Huber, 1973) and *ORTEP* (Johnson, 1965).

Discussion. The atomic parameters are listed in Table 1,† a parallel projection of the molecular structure is shown in Fig. 1, and the bond lengths and angles are presented in Fig. 2. These results are in agreement with the expected formula (I), thus confirming the validity of the novel synthesis of Alper *et al.* (1981). The five-membered ring is best described as having the twist form (T) with puckering parameters $q_2 = 0.146$ (7) Å and $\varphi_2 = 261.3$ (5)° (Cremer & Pople, 1975). It is *cis* fused to the four-membered ring along N(4)–C(5) with a dihedral angle of 116.5 (4)° between their mean planes. The aromatic ring nearest the double bond N(1)=C(2) is nearly parallel to the mean plane of the five-membered ring [dihedral angle is 6.8 (5)°], while the other aromatic ring makes a dihedral angle of 57.2 (4)° with the five-membered ring. The angle between the two aromatic rings is 59.9 (5)°.

The N–C lengths spread over a wide range. The shortest is the N(1)=C(2) double bond, 1.287 (4) Å, which is comparable to N=C of 1.2849 (8) Å in glyoxime (Jeffrey, Ruble & Pople, 1982) and 1.278 (2)–1.288 (4) Å in the three oximes examined by Bertolasi, Gilli & Veronese (1982). Next is N(4)–C(7) = 1.403 (4) Å which is adjacent to C(7)=O(8). N(4)–C(3) and N(1)–C(5) are about equal at 1.464 (4) and 1.468 (4) Å, and the longest is N(4)–C(5) = 1.501 (4) Å which is the bond common to the two fused rings.

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† Lists of structure factors, anisotropic thermal parameters and some mean plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38361 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C—C lengths are comparable to the appropriate mean values given in *International Tables for X-ray Crystallography* (1962), except that the C(2)—C(9) bond of 1·470 (5) Å is relatively short as a result of lying between N=C and the aromatic ring. The C—H lengths are in the range 0·89 (3)–1·06 (3) Å, and all the intermolecular distances are above the sums of the van der Waals radii.

Table 1. *Fractional atomic coordinates* ($\times 10^4$; H $\times$ 10^3) *and equivalent isotropic temperature factors* ($\mathring{A}^2$)

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B/B_{eq}
N(1)	1836 (1)	8908 (4)	2406 (2)	4·1
C(2)	2029 (2)	7129 (5)	2951 (2)	3·8
C(3)	1510 (2)	5046 (6)	2664 (2)	4·8
N(4)	904 (1)	6051 (4)	1886 (2)	4·6
C(5)	1166 (2)	8317 (5)	1616 (2)	4·2
C(6)	442 (2)	9486 (6)	1644 (2)	5·3
C(7)	334 (2)	7213 (6)	2092 (2)	5·4
O(8)	−42 (1)	6550 (5)	2538 (2)	7·0
C(9)	2718 (2)	7048 (5)	3764 (2)	3·9
C(10)	3238 (2)	8799 (6)	3926 (2)	5·5
C(11)	3902 (2)	8652 (6)	4662 (2)	6·0
C(12)	4071 (2)	6751 (6)	5258 (2)	4·8
C(13)	3543 (2)	5049 (6)	5112 (2)	5·5
C(14)	2872 (2)	5181 (6)	4371 (2)	5·2
C(15)	4817 (2)	6564 (7)	6032 (2)	6·1
C(16)	1310 (2)	8404 (5)	701 (2)	4·2
C(17)	1087 (2)	6653 (6)	38 (2)	5·0
C(18)	1204 (2)	6893 (6)	−817 (2)	5·6
C(19)	1534 (2)	8823 (6)	−1029 (2)	5·0
C(20)	1757 (2)	10554 (6)	−363 (2)	5·7
C(21)	1648 (2)	10347 (6)	488 (2)	5·5
C(22)	1640 (2)	9065 (9)	−1968 (2)	7·8
H(3,1)	135 (2)	451 (6)	316 (2)	6·4 (8)
H(3,2)	175 (1)	366 (5)	246 (2)	4·9 (7)
H(6,1)	5 (2)	985 (6)	102 (2)	8·0 (9)
H(6,2)	52 (2)	1086 (6)	206 (2)	7·2 (9)
H(10)	315 (2)	1018 (5)	350 (2)	5·4 (7)
H(11)	424 (2)	1010 (7)	477 (2)	9·0 (10)
H(13)	364 (2)	358 (6)	552 (2)	7·4 (9)
H(14)	252 (2)	389 (6)	425 (2)	6·9 (8)
H(15,1)	483 (2)	500 (7)	638 (3)	9·8 (11)
H(15,2)	496 (2)	803 (8)	637 (3)	11·3 (12)
H(15,3)	523 (2)	654 (7)	575 (3)	9·9 (11)
H(17)	84 (2)	513 (6)	20 (2)	7·6 (9)
H(18)	104 (2)	558 (6)	−125 (2)	7·2 (9)
H(20)	200 (2)	1196 (6)	−49 (2)	7·0 (8)
H(21)	183 (2)	1171 (6)	99 (2)	7·6 (9)
H(22,1)	174 (2)	766 (8)	−218 (3)	12·9 (13)
H(22,2)	208 (2)	963 (8)	−194 (3)	12·1 (13)
H(22,3)	127 (2)	1005 (7)	−244 (3)	9·8 (11)

Fig. 2. (a) Bond lengths (Å), e.s.d.'s = 0·004–0·005 Å; and (b) bond angles (°), e.s.d.'s = 0·2–0·3°.
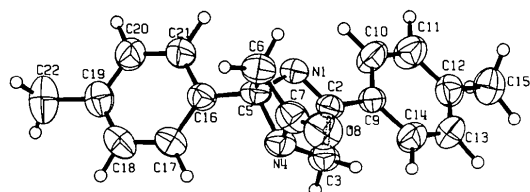
Fig. 1. A parallel projection of the molecular structure with the thermal ellipsoids drawn at 50% probability. The H atoms are drawn as equal small circles.
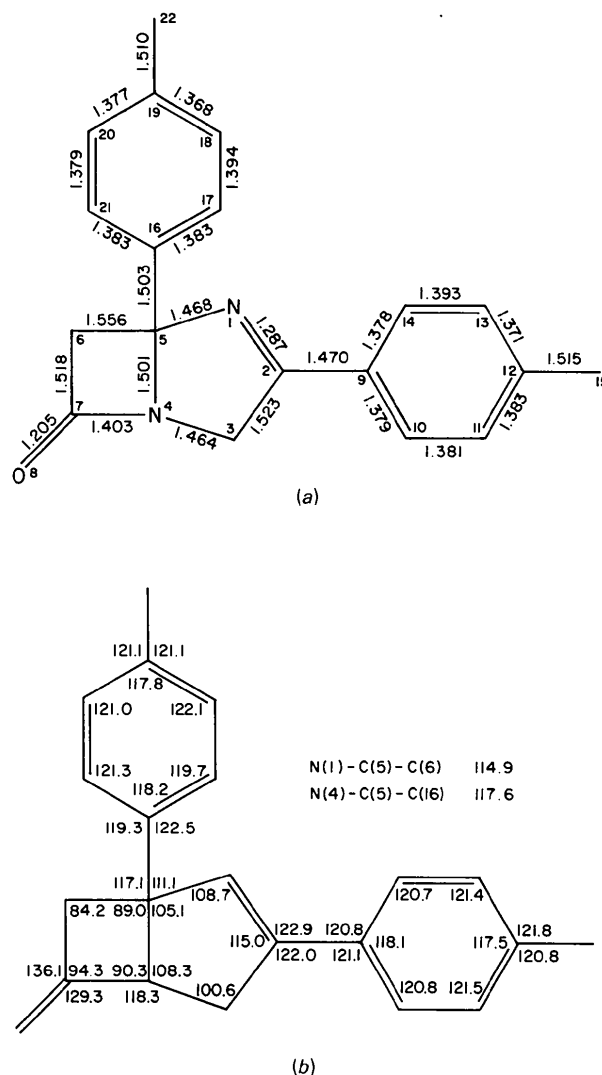
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Structure of 3-Bromo-λ^6-thietane 1,1-Dioxide, $C_3H_5BrO_2S$

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Abstract. $M_r = 184 \cdot 9$, orthorhombic, *Pnma*, $a = 16 \cdot 664$ (10), $b = 6 \cdot 617$ (3), $c = 5 \cdot 103$ (4) Å, $Z = 4$, $V = 562 \cdot 78$ Å^3, $D_x = 2 \cdot 182$ Mg m^{-3}, λ(Mo $K\alpha$) = $0 \cdot 71069$ Å, $F(000) = 360$. Final $R = 8 \cdot 0\%$ for 404 observed reflections. The structure is isomorphous to 3-chlorothietane 1,1-dioxide reported earlier.

Introduction. The purpose of this study is to determine the geometry and the position of the Br atom with respect to the thietane ring. It is also our purpose to study the ring puckering. The sample was synthesized from λ^6-thietane 1,1-dioxide by bromination and recrystallized from chloroform–hexane.

Experimental. Sample supplied by Professor D. C. Dittmer of Syracuse University, nearly rectangular crystal, $0 \cdot 42 \times 0 \cdot 40 \times 0 \cdot 80$ mm; Nicolet *P3F* diffractometer, graphite monochromator, Mo $K\alpha$ radiation; 12 reflections used for measuring lattice parameters, no absorption correction applied, $2\theta_{max} = 45 \cdot 0°$, range of hkl: (0,0,−5) to (16,7,5), three reflections used as standards measured after intervals of 60 measurements, their intensities remained constant (within ±6%) during data collection; 406 reflections measured, 404 unique; structure solved by direct-phase determination using symbolic addition procedure and refined on all reflections by anisotropic full-matrix least squares (*ORFLS*, Busing, Martin & Levy, 1962) on heavy atoms with parameters for H atoms kept constant, positions of H atoms derived from a difference map; $R = 8 \cdot 0\%$ for the 404 reflections after six cycles of refinement (initial value of $R = 12\%$), $wR = 10 \cdot 27\%$, $S = 4 \cdot 56$, function minimized $\sum w(|F_o| - |F_c|)^2$ with weights, w, calculated according to Gilardi (1973); ratio of maximum least-squares shift-to-error = $0 \cdot 68$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

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Discussion. The structural parameters are shown in Fig. 1. (Note: the numbering system used here is different from the IUPAC nomenclature of the compound.) Coordinates and B_{eq} values for the non-H atoms are listed in Table 1.†

† Lists of structure factors, anisotropic thermal parameters and unrefined H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38296 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
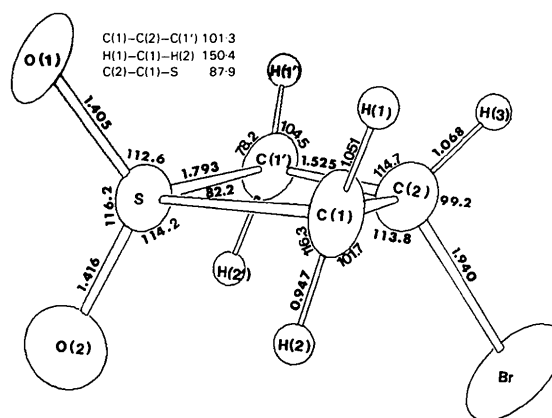

Fig. 1. The structure of 3-bromo-λ^6-thietane 1,1-dioxide. Bond distances in Å, angles in °. The e.s.d.'s for bond distances are in the range $0 \cdot 01$–$0 \cdot 02$ Å; for bond angles, $0 \cdot 6$–$1 \cdot 4°$.

Table 1. *Fractional coordinates and B_{eq} values for the non-H atoms of 3-bromo-λ^6-thietane 1,1-dioxide*

The e.s.d.'s for B_{eq} are near $0 \cdot 1$ Å^2. $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)
Br	0·2335 (1)	0·2500	0·2093 (6)	2·2
C(1)	0·3914 (6)	0·0718 (18)	0·2862 (24)	1·2
C(2)	0·3392 (10)	0·2500	0·3684 (36)	1·6
S	0·4587 (3)	0·2500	0·1386 (9)	0·9
O(1)	0·4540 (8)	0·2500	−0·1363 (26)	2·4
O(2)	0·5369 (6)	0·2500	0·2473 (28)	1·2