

Table 2. Comparison of the structure of 3-bromo- $\lambda^6$ -thietane 1,1-dioxide with related molecules

For title-compound e.s.d.'s, see Fig. 1.

	3-Bromo- $\lambda^6$ -thietane 1,1-dioxide	3-Chloro- $\lambda^6$ -thietane 1,1-dioxide	3-Hydroxy- $\lambda^6$ -thietane 1,1-dioxide
C(1)—C(2)	1.525 Å	1.536 Å	1.532 Å
C(1)—S	1.793	1.791	1.788(1.782)
S—O(1)	1.405	1.426	1.435
S—O(2)	1.416	1.419	1.436
C—X	1.940	1.776	1.415
(X = OH, Cl, Br)			
O(1)—S—O(2)	116.2°	117.9°	117.5°
C(1)—S—C(1')	82.2	81.5	82.4
S—C(1)—C(2)	87.9	89.3	88.8

The molecule has *m* symmetry in the crystal. The position of the Br atom with respect to the thietane ring was determined. The dihedral angle between planes C(1)SC(1') and C(1)C(2)C(1') is 171.0° while that between planes SC(1)C(2) and SC(1')C(2) is 171.4°. In general, the structural parameters agree with the previously reported structures of 3-chloro- $\lambda^6$ -thietane

1,1-dioxide (Andreotti, Bocelli & Sgarabotto, 1973a) and 3-hydroxy- $\lambda^6$ -thietane 1,1-dioxide (Andreotti, Bocelli & Sgarabotto, 1973b). A comparison of their structures is shown in Table 2.

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### 3-Hydroxy-1,2,3-benzotriazin-4(3H)-one, C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>

BY W. EDWARD HUNT\* AND CARL H. SCHWALBE

Department of Pharmacy, The University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET, England

AND KEITH VAUGHAN

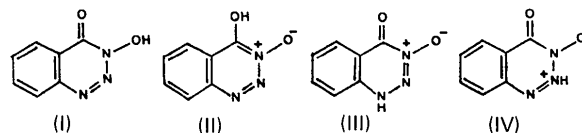
Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 2J5

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**Abstract.**  $M_r = 163.14$ ,  $P2_1/n$ ,  $a = 15.04$  (1),  $b = 4.29$  (2),  $c = 10.95$  (1) Å,  $\beta = 103.2$  (1)°,  $U = 687.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.575$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.130$  mm<sup>-1</sup>,  $F(000) = 336$ ,  $T = 293$  K. Final  $R = 0.109$  for 890 observed reflections. The ring N(1)—N(2) and carbonyl bond distances of 1.251 (7) and 1.221 (7) Å respectively show that these bonds are double, thus confirming the 3-hydroxy-4-one structure deduced chemically. A 2.589 (7) Å contact between O(3) and O(4) of an adjacent molecule related by the 2<sub>1</sub> axis is best explained by hydrogen bonding.

mers (II) and (III) on the basis of chemical reactivity (Harrison & Smith, 1960) and spectral characteristics (Ahern, Navratil & Vaughan, 1977). The IR spectrum of a Nujol suspension showed a broad carbonyl band at relatively low frequency (1660 cm<sup>-1</sup>) suggestive of intramolecular hydrogen bonding. Thermolysis leads to dimer formation minus the elements of N<sub>2</sub>O, apparently *via* stepwise loss of O and N<sub>2</sub> (Ahern *et al.*, 1977). The crystal-structure determination reported here was undertaken in order to confirm the structure and to relate it to these spectroscopic and chemical properties.

**Introduction.** The title compound has been assigned structure (I) in preference to the other feasible tauto-



\* Present address: Department of Materials, Queen Mary College, Mile End Road, London E1 4NS, England.

**Experimental.** Title compound crystallized as colorless needles elongated along **b**, specimen used for data collection had dimensions 0.24 mm between faces (1 0 1) and (-1 0 -1), 0.14 mm [(-1 0 1) and (1 0 -1)], and 0.80 mm [(0 1 0) and (0 -1 0)]; systematic absences  $h0l$ ,  $h + l$  odd and  $0k0$ ,  $k$  odd indicated space group  $P2_1/n$ , the centric distribution of normalized structure factors strengthening the preference for this space group over  $Pn$ ; unit-cell dimensions from Weissenberg and precession photographs optimized to fit observed setting angles on a Stoe STADI-2 two-circle diffractometer; intensities collected on the diffractometer for levels  $h0l$  to  $h4l$  to a maximum  $2\theta$  of  $55^\circ$  on every level with monochromated  $\text{Mo K}\alpha$  (monochromator  $2\theta = 12^\circ$ ); an  $\omega$  scan at  $0.01^\circ \text{ s}^{-1}$  used covering  $1.40^\circ$  for levels 0 and 1 and  $1.20 + 0.50 \times \sin \mu / \tan \theta'$  for upper levels, where  $\mu$  is the equi-inclination angle and  $\theta'$  half the angle between the diffracted ray and the direct beam when projected onto a plane perpendicular to the axis of rotation; background counts taken for 30 s on either side of scan; errors assigned on basis of counting statistics together with a 4% allowance for instrumental instability; 1637 independent reflections measured, of which 890 considered observed [ $F > 3\sigma(F)$ ]; corrections applied for Lorentz and polarization effects but not for absorption or extinction; phase determinations attempted with centrosymmetric direct-methods routine of *SHELX* (Sheldrick, 1976), resulting *E* maps repeatedly showed a feature produced by superimposing two images of the molecule separated by the  $\text{N}(3)\text{--O}(3)$  vector, which occurs four more times within the molecule and which therefore is the strongest bond vector; eventually, averaging atomic positions between the separate images yielded the structure; after initial isotropic refinement, H atoms were attached to C(5), C(6), C(7) and C(8) in calculated positions and constrained to ride on their C atoms but with refinable isotropic temperature factors; full-matrix least-squares refinement of all non-H coordinates and anisotropic thermal parameters decreased  $R$  to 0.109 and  $R_g$  to 0.105,  $w = 1/\sigma^2(F)$ .

A difference Fourier synthesis, intended to reveal the remaining H atom and establish the tautomeric form, contained numerous peaks  $\approx 0.3 \text{ e } \text{\AA}^{-3}$  in height, most of which occupied stereochemically impossible positions near ring C atoms. However, the C(4)–O(4) distance of 1.221 (7) Å was inconsistent with the single bond of tautomer (II). The very short N(1)–N(2) distance of 1.245 (7) Å was incompatible with tautomers (III) and (IV); the N(1)–N(2) bond is 1.31 (1) and 1.293 (13) Å in two 2-substituted benzotriazines (Schwalbe, Stevens & Lowe, 1978; Hamid & Hargreaves, 1976) and 1.320 (7) Å in a 1,2-disubstituted benzotriazine (Ballard & Norris, 1975). An intermolecular O(3)···O(4)' contact of  $\approx 2.6$  Å is best explained as a hydrogen bond. Therefore the final model was based on tautomer (I) with an intermolecular hydrogen bond, and H(O3) was fixed 0.95 Å

from O(3) along the O(3)···O(4)' line with isotropic temperature factor  $U = 0.15 \text{ \AA}^2$ . Positional and thermal parameters for other atoms were refined as before until no shift exceeded  $0.06\sigma$ . The discrepancy indices remained at  $R = 0.109$ ,  $R_g = 0.105$ , and no bond distance or angle changed by more than  $\sigma$  from its value after the previous refinement.

**Discussion.** Final coordinates and equivalent isotropic temperature factors are in Table 1.\*

The molecule is pictured in Fig. 1, in which the upper values are bond distances (average  $\sigma = 0.007$  Å). In order to compare the strengths of C–C, C–N, N–N, and C–O bonds on a common basis, their bond lengths have been converted to  $\pi$ -bond orders by the linear relationship of Fischer-Hjalmars (1965) with the

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38357 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) (all  $\times 10^4$ ) with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
N(1)	5742 (4)	7140 (15)	4179 (5)	739 (23)
N(2)	6513 (3)	5963 (17)	4251 (5)	744 (24)
N(3)	6616 (3)	4039 (14)	3299 (4)	577 (19)
O(3)	7462 (3)	2705 (12)	3506 (4)	775 (19)
C(4)	5973 (3)	3146 (16)	2267 (5)	499 (21)
O(4)	6149 (2)	1249 (13)	1524 (4)	680 (17)
C(4a)	5104 (3)	4543 (14)	2198 (5)	471 (20)
C(5)	4354 (3)	4075 (16)	1191 (5)	562 (22)
C(6)	3552 (4)	5447 (17)	1195 (6)	626 (24)
C(7)	3456 (4)	7406 (18)	2169 (6)	694 (28)
C(8)	4181 (4)	7898 (18)	3163 (6)	704 (27)
C(8a)	5008 (4)	6531 (16)	3167 (5)	561 (23)

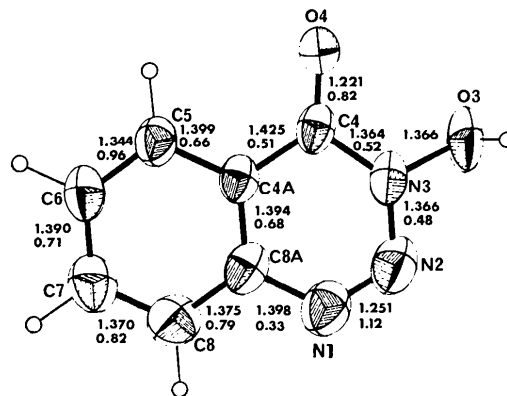
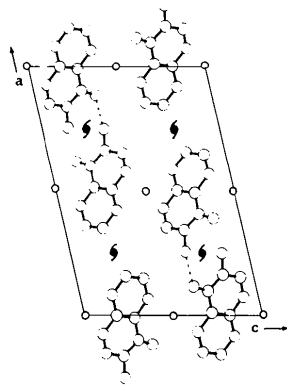


Fig. 1. The title compound (I) drawn by *ORTEP* (Johnson, 1971). Upper numbers are bond distances (Å) (*e.s.d.*'s 0.006–0.009 Å, average 0.007 Å); lower numbers are calculated  $\pi$ -bond orders for C–C, C–N, N–N, and C–O bonds. Thermal ellipsoids are at the 50% probability level.

Table 2. Bond angles ( $^{\circ}$ ) with *e.s.d.*'s in parentheses

N(2)—N(1)—C(8a)	121.8 (6)	C(8a)—C(4a)—C(4)	118.0 (5)
N(3)—N(2)—N(1)	117.5 (5)	C(5)—C(4a)—C(8a)	118.8 (5)
C(4)—N(3)—N(2)	128.3 (5)	C(6)—C(5)—C(4a)	119.8 (6)
O(3)—N(3)—N(2)	113.0 (4)	C(7)—C(6)—C(5)	121.2 (6)
C(4)—N(3)—O(3)	118.5 (5)	C(8)—C(7)—C(6)	119.9 (6)
C(4a)—C(4)—N(3)	113.2 (6)	C(8a)—C(8)—C(7)	119.5 (6)
O(4)—C(4)—N(3)	121.2 (5)	N(1)—C(8a)—C(8)	118.2 (6)
C(4a)—C(4)—O(4)	125.5 (5)	C(4a)—C(8a)—C(8)	120.6 (5)
C(5)—C(4a)—C(4)	123.1 (5)	N(1)—C(8a)—C(4a)	121.2 (6)

Fig. 2. Contents of the unit cell drawn by *PLUTO* (Motherwell, 1972) in projection down *b*. H atoms have been omitted for clarity.

parameters of Hjortås (1973). These appear in Fig. 1 below the bond lengths. An extraordinarily strong bond joins N(1) to N(2); this  $N_2$  unit is connected to the rest of the ring by much weaker bonds. These strongly bonded atoms seem likely to stay together as the ring decomposes so that  $N_2$  would form more easily than  $N_2O$ , in agreement with the proposed thermolysis mechanism (Ahern *et al.*, 1977). The similar bond orders of N(2)—N(3), N(3)—C(4), and C(4)—C(4a) are consistent with tautomer (I). Indeed, all bond distances agree within  $3\sigma$  with those in 1,2,3-benzotriazin-4(3H)-one (B4-O) (Hjortås, 1973) except for C(4)—C(4a), C(5)—C(6), and C(8)—C(8a), which are all about  $4\sigma$  shorter in (I), possibly representing the encouragement of a quinonoid resonance structure by *N*-oxidation.

Bond angles (Table 2) are generally as expected for tautomer (I). However, the internal ring angle at N(1) exceeds  $120^{\circ}$  and apparently violates Chatar Singh's (1965) rule for unprotonated N atoms. Internal angles near or exceeding  $120^{\circ}$  at unprotonated N(1) atoms have been observed in other 1,2,3-triazines:  $119.7 (2)^{\circ}$  in B4-O;  $119.3 (4)$  and  $120.2 (4)^{\circ}$  in 4,5,6-tris(*p*-methoxyphenyl)-1,2,3-triazine (Oeser & Schiele, 1972). This anomaly can be attributed to the distortion

imposed on the three catenated N atoms by ring closure. All other bond angles in (I) agree with corresponding values in B4-O to within  $3.5\sigma$ .

Intermolecular interactions (Fig. 2) are dominated by successive  $O(3)\cdots O(4)'$  contacts in a spiral about a screw axis. The postulate of a highly polar intermolecular  $N-O-H\cdots O=C$  hydrogen bond seems adequate to explain both the short  $O\cdots O$  distance of  $2.589 (7) \text{ \AA}$  and the low  $C=O$  stretching frequency in the IR spectrum. A similar hydrogen-bonded spiral exists in B4-O, the linkage being  $N-H\cdots O=C$  in this case. In (I) the H atom in its calculated position forms a  $119 (1)^{\circ}$   $N-O-H$  angle and a  $134 (1)^{\circ}$   $H\cdots O=C$  angle; in B4-O the  $H\cdots O=C$  angle is well established to be  $131.9^{\circ}$  ( $\sigma$  not reported). Thus in both cases the H atom can approach an oxygen lone pair. Similar  $N-O-H\cdots O=C$  contacts of  $2.632 (3)$  and  $2.700 (3) \text{ \AA}$  have been observed in *p*-benzoquinone 4-oxime (Talberg, 1974). The association between molecules of (I) is further developed by stacking along *b* which places N(1) approximately under N(3)—C(4) and C(8) under C(4a)—C(5). The normal to each least-squares plane through the heterocyclic ring [maximum deviation of any ring atom  $0.025 (5) \text{ \AA}$ ] is inclined at  $38.5 (4)^{\circ}$  to the *b* direction, and successive planes in the stack have a perpendicular separation of  $3.36 (2) \text{ \AA}$ .

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