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Structure of Benzo-1,2,3,4-tetrazine 1,3-Dioxide

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Abstract. $C_6H_4N_4O_2$, $M_r = 164.12$, orthorhombic, *Pcab*, $a = 13.602$ (1), $b = 14.477$ (2), $c = 6.969$ (1) Å, $V = 1372.3$ (3) Å^3, $Z = 8$, $D_x = 1.589$ Mg m^{-3}, $\lambda(Cu\,K\alpha_1) = 1.54050$ Å, $\mu = 1.025$ mm^{-1}, $F(000) = 672$, $T = 295$ K, final $R = 0.049$ for 692 reflections. The benzotetrazine ring is planar indicating extensive π-electron delocalization. Shortened semipolar N—O bonds [N(2)—O(5) 1.255 (4) and N(4)—O(6) 1.238 (4) Å] were observed.

Introduction. 1,2,3,4-Tetrazines, containing an unstable six-membered aza-aromatic ring system, are of interest from the viewpoint of their physical and chemical properties (Wiley, 1978; Neunhoeffer, 1984; Kaihoh, Itoh Yamaguchi & Ohsawa, 1990). However, 2-phenyl-1,2,3-triazole[4,5-*e*][1,2,3,4]tetrazine (Kaihoh, Itoh, Yamaguchi & Ohsawa, 1991) was the sole example and its structure was established by X-ray crystallography (Yamaguchi, Kaihoh, Itoh & Ohsawa, 1991). The crystal structure of the title compound, the second example of a 1,2,3,4-tetrazine, has been determined as part of a continuing study of 1,2,3,4-tetrazines.

Experimental. The preparation and physical properties are given by Churakov, Ioffe, Strelenko & Tartakovskii (1990). Crystal dimensions 0.10 × 0.08 × 0.55 mm, by recrystallization from C_2H_5OH, having m.p. 440–441 K. Rigaku AFC-5 four-circle diffractometer used with ω–2θ-scan method, ω-scan width $(1.3 + 0.5\tan\theta)°$ and scan speed 16° min^{-1}. Lattice parameters obtained from least-squares analysis of 20 reflections with 2θ values ranging from 42 to 46°. Of 1255 reflections scanned [within index range $h\,0$–15, $k\,0$–16, $l\,0$–7 up to $(\sin\theta)/\lambda < 0.56$ Å^{-1}], 1020 unique reflections $[F > \sigma(F)]$ classified as observed [125 unobserved reflections with

$\sigma(F) > F > 0$]. Three standard reflections measured every 150 reflections, intensity variation <3%. Intensities corrected for Lorentz and polarization factors, but absorption correction not applied. Structure solved using program package *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985). Refinement by full-matrix least-squares method with anisotropic temperature factors for non-H atoms. The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ with $w = 1/[\sigma^2(F_o) + 0.02(F_c)]$, $\sigma(F_o)$ from counting statistics. All H atoms located from the difference map and refined, initial thermal parameters set at equivalent isotropic thermal parameter of each bonded atom. Final discrepancy indices $R = 0.049$, $wR = 0.051$, $S = 1.276$ for 125 variables and 692 reflections with $F > 3\sigma(F)$. Maximum $\Delta/\sigma = 0.13$ in the final least-squares cycle. Final difference Fourier excursions 0.18 and -0.19 e Å^{-3}. All computations performed on a PANAFACOM computer with *RCRYSTAN* (Rigaku Corporation, 1985) X-ray analysis program system. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are listed in Table 1.* Bond lengths and angles are listed in Table 2. Fig. 1 shows an *ORTEP* drawing (Johnson, 1976) of the molecule with atomic labels.

The benzotetrazine ring system is almost planar, with maximum displacement out of the least-squares

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* Tables of H-atom coordinates, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54875 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0556]

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i{}^*a_j{}^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N(1)	0.3328 (2)	0.1245 (1)	1.2778 (4)	4.81 (9)
N(2)	0.3395 (2)	0.2136 (2)	1.2924 (5)	5.03 (9)
N(3)	0.3758 (2)	0.2753 (2)	1.1590 (5)	4.98 (10)
N(4)	0.4033 (2)	0.2386 (1)	0.9938 (5)	4.56 (9)
O(5)	0.3126 (2)	0.2523 (1)	1.4449 (4)	6.88 (10)
O(6)	0.4394 (2)	0.2916 (1)	0.8735 (4)	6.27 (9)
C(7)	0.3586 (2)	0.0901 (2)	1.1016 (5)	3.83 (9)
C(8)	0.3932 (2)	0.1441 (2)	0.9520 (5)	3.75 (9)
C(9)	0.4154 (2)	0.1082 (2)	0.7711 (6)	4.81 (11)
C(10)	0.4042 (3)	0.0157 (2)	0.7469 (7)	5.17 (12)
C(11)	0.3719 (2)	−0.0402 (2)	0.8965 (6)	4.90 (11)
C(12)	0.3493 (2)	−0.0051 (2)	1.0713 (6)	4.64 (11)

Table 2. *Bond lengths (Å) and angles (°)*

N(1)—N(2)	1.297 (4)	N(1)—C(7)	1.371 (4)
N(2)—O(5)	1.255 (4)	N(2)—N(3)	1.380 (4)
N(3)—N(4)	1.322 (4)	N(4)—O(6)	1.238 (4)
N(4)—C(8)	1.406 (4)	C(7)—C(8)	1.386 (4)
C(7)—C(12)	1.400 (4)	C(8)—C(9)	1.396 (5)
C(9)—C(10)	1.358 (5)	C(10)—C(11)	1.391 (6)
C(11)—C(12)	1.355 (6)		

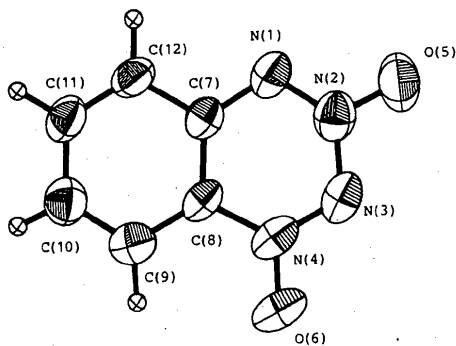|			
N(2)—N(1)—C(7)	114.5 (3)	N(1)—C(7)—C(12)	118.0 (3)
O(5)—N(2)—N(1)	119.2 (3)	C(8)—C(7)—C(12)	118.2 (3)
O(5)—N(2)—N(3)	112.8 (2)	C(7)—C(8)—C(9)	122.9 (3)
N(1)—N(2)—N(3)	128.0 (3)	C(7)—C(8)—N(4)	115.2 (3)
N(4)—N(3)—N(2)	115.4 (2)	C(9)—C(8)—N(4)	121.9 (3)
O(6)—N(4)—N(3)	117.0 (2)	C(10)—C(9)—C(8)	117.0 (4)
O(6)—N(4)—C(8)	120.1 (3)	C(9)—C(10)—C(11)	121.1 (4)
N(3)—N(4)—C(8)	123.0 (3)	C(12)—C(11)—C(10)	121.8 (3)
N(1)—C(7)—C(8)	123.8 (3)	C(11)—C(12)—C(7)	118.9 (3)

Fig. 1. *ORTEP* drawing. Ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

plane of 0.055 (8) Å for N(2). This planarity, as well as the endocyclic bond distances, indicates an extensive delocalization of the π electrons. The bond parameters of the tetrazine ring are close to those found in a triazolotetrazine (Yamaguchi, Kaihoh, Itoh & Ohsawa, 1991). However, shortened N(1)—N(2) and slightly lengthened N(4)—C(8) distances [1.297 (4) and 1.406 (4) Å, respectively] are observed. The angles N(1)—N(2)—N(3) 128.0 (3) and N(3)—N(4)—C(8) 123.0 (3)° involving the N-oxide moiety are greater than those found in the triazolotetrazine.

The opposite trend was observed in C(7)—N(1)—N(2) [114.5 (3)°] and N(2)—N(3)—N(4) [115.4 (2)°]. These differences may be ascribed to the N-oxide moiety. The N-oxide bond distances [N(2)—O(5) 1.255 (4) and N(4)—O(6) 1.238 (4) Å] indicate a contribution of double-bond character, and are consistent with those found in 1,2,3-triazine N-oxides (range from 1.243 to 1.251 Å) (Yamaguchi, Ohsawa & Itoh, 1990; Yamaguchi, Itoh, Kaihoh & Ohsawa, 1991). This feature suggests a back-donation effect of the unshared pair of electrons on the negatively charged oxygen atoms in tetrazines as observed in pyridine and 1,2,3-triazine N-oxides (Neunhoeffer, 1984; Yamaguchi, Ohsawa & Itoh, 1990). The semiempirical molecular orbital calculation using the MNDO-PM3 method* (Stewart, 1989) also suggests a back-donation effect. The calculated net atomic charges on O(5), N(2) and C(8) are −0.45, 1.00 and −0.49 e, respectively, and on O(6), N(4) and N(1) are −0.47, 1.10 and −0.42 e, respectively. These values exhibit a similar trend to those found in 1,2,3-triazines [respective values of −0.5, 0.99 and −0.21 e for the N(2)-oxide, and −0.54, 0.93 and −0.11 e for the N(1)-oxide] (Yamaguchi, Itoh, Kaihoh & Ohsawa, 1991). However, the greater contribution of this effect in 1,2,3,4-tetrazine dioxide is possibly a result of the more highly charged atoms located in the γ position with respect to the N-oxide moiety.

The positively charged N(2) and N(4), as well as the shortened N—O bond lengths, indicate the participation of the free electrons on these oxygens in respective N—O bonds, which gives rise to the stability of this compound by prevention of the repulsive N—N bond cleavage to break the tetrazine ring.

An intramolecular attractive interaction [O(6)···H(9) 2.46 (4) Å, O(6)—H(9)—C(9) angle 96 (3)°] was observed.

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* Used with standard parameters as implemented in *MOPAC*. *Quantum Chemistry Program Exchange*, No. 455. Indiana Univ., USA.

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The Absolute Configuration of an Intermediate in the Asymmetric Synthesis of Unusual Amino Acids

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Abstract. (4R)-3-[(2'R,3'R)-2'-Bromo-3'-(phenylbutanoyl)]-4-(phenylmethyl)-2-oxazolidinone, $C_{20}H_{20}Br$-NO_3, $M_r = 402.30$, monoclinic, $P2_1$, $a = 11.542$ (2), $b = 7.625$ (1), $c = 11.667$ (1) Å, $\beta = 113.97$ (1)°, $V = 938.2$ (2) Å^3, $Z = 2$, $D_x = 1.42$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 21.8$ cm^{-1}, $F(000) = 412$, $T = 296 \pm 1$ K, final $R = 0.028$ for 2369 observed reflections. Since a D-chiral auxiliary was used the configuration at the α-carbon was R as expected. The two carbonyls are aligned in opposite directions to each other to overcome van der Waals repulsions.

Introduction. We have recently described our approach to the asymmetric synthesis of individual isomers of β-methylphenylalanines (Dharanipragada, Nicolas, Toth & Hruby, 1989) and β-methyltyrosines (Nicolas, Dharanipragada, Toth & Hruby, 1989). These compounds, by virtue of their biased side-chain rotamer populations, are very useful in controlling peptide topography (Hruby, Al-Obeidi & Kazmierski, 1990). The stereochemistry at the α-carbon for these compounds is controlled by utilizing chiral auxiliaries (Evans, Ellman & Dorow, 1987). Thus, face-selective halogenation of boron enolate (2) derived from (1) gave the crystalline bromide (3) as the major product, which was converted in several steps to the *threo*-L-β-methylphenylalanine (4). Determination of the absolute stereochemistry of (3) will support models for asymmetric induction (Evans, Ellman & Dorow, 1987; Evans, Britton, Ellman & Dorow, 1990). In the case reported here, since a D-chiral auxiliary was used, electrophilic bromination should give an R configuration at the 2' site. For the first time, an X-ray

structure determination is used to demonstrate directly that this occurs.

(1) → (2) [Bu$_2$BOTf]; (2) → (3) [NBS]; (3) → (4) [Many steps]
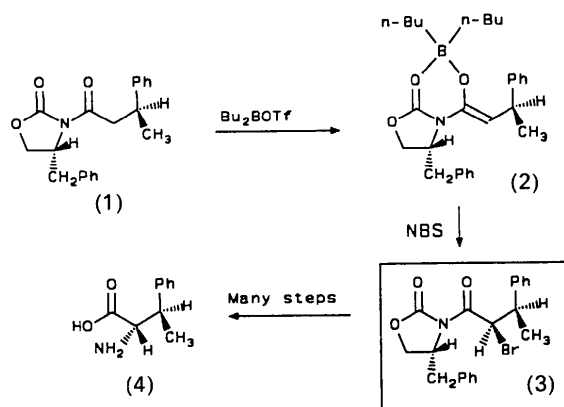
Experimental. Crystals of (3) were obtained from a solution of ethyl acetate and hexane. A colorless block crystal having approximate dimensions of 0.32 × 0.38 × 0.70 mm was mounted on a glass fiber for data collection. Data were collected on a Syntex $P2_1$ diffractometer, with graphite-monochromated Mo $K\alpha$ radiation using the θ–2θ scan mode. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $20 < 2\theta < 33°$. Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on a series of ψ scans was applied to the data. Relative transmission coefficients ranged from 0.760 to 0.998 with an average value of 0.889. Data were collected to a maximum 2θ of 50.0°, from the $+h+k\pm l$ and $-h-k\pm l$ quadrants. Three standard reflections were measured after every 97

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