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Structure and Atomic Charge Distribution of 4-Ethyl-3-methyl-1,2,3(4H)-benzotriazin-4-ol*

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Abstract. $C_{10}H_{13}N_3O$, $M_r = 191.23$, orthorhombic, *Pbca*, $a = 11.265$ (2), $b = 8.551$ (3), $c = 21.099$ (3) Å, $U = 2032.4$ Å^3, $Z = 8$, $D_m = 1.25$ (1), $D_x = 1.250$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.050$ mm^{-1}, $F(000) = 816$, $T = 293$ (3) K, final $R = 0.066$ for 760 observed reflections. The bicyclic system is relatively flat. As in similar 4-hydroxybenzotriazines, N(1) accepts a hydrogen bond from a nearby hydroxyl group. N(1) seems to be the preferred proton acceptor because of its accessibility as well as its negative charge, since N(1) bears only the third strongest negative charge in the molecule according to *ab initio* molecular-orbital calculations.

Introduction. The highly reactive N_3 unit in azides and triazenes can be rendered more stable by incorporation into the bicyclic system of a 1,2,3-benzotriazine. Comparison of two 4-hydroxybenzotriazine structures (Lai, Schwalbe, Vaughan, Lafrance & Whiston, 1985) showed reasonable consistency of bond distances but up to 37° variation in three key torsion angles determining puckering of the triazine ring. Crystals of both molecules contained O—H···N intermolecular

hydrogen bonds in which N(1) was the proton acceptor. The structure of the title compound (I) was determined in order to ascertain whether the triazine ring was puckered as in 3-ethyl-1,2,3(4H)-benzotriazin-4-ol (II) or flat as in 6-chloro-3-methyl-4-phenyl-1,2,3-benzotriazin-4-ol (III), and to describe the mode of intermolecular hydrogen bonding. The hypothesis that the proton acceptor would be the most negative atom in the molecule was checked by performing *ab initio* molecular-orbital calculations.

(I)   (II)   (III)
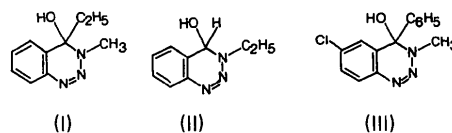
Experimental. Needle crystal $1.04 \times 0.20 \times 0.16$ mm grown from aqueous solution. Density measured by flotation. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions from least-squares analysis of setting angles from 25 reflections with $8.21 \le \theta \le 16.92°$. Intensity data collected by the ω–2θ technique for 1976 unique reflections measured in the range $2 \le \theta \le 25°$, $0 \le h \le 13$, $-10 \le k \le 0$, $-25 \le l \le 0$. Three intensity and three orientation monitor reflections showed no significant variation during the experiment. 760 reflections

were deemed observed ($F_o > 3\sigma$). Lorentz–polarization corrections assuming an ideally imperfect monochromator; no absorption or extinction corrections.

All non-H atoms appeared in an E map with phases determined by the $EEES$ routine in $SHELX$ (Sheldrick, 1976); H atoms subsequently located in difference electron density maps. Final refinement was based on F magnitudes, used the stored scattering factors (Cromer & Mann, 1968; Stewart, Davidson & Simpson, 1965), and adjusted all positional parameters, anisotropic thermal parameters for non-H atoms and isotropic temperature factors for H atoms. Reflections weighted by $w = k/[\sigma^2(F_o) + gF_o^2]$, where g converged to 0·003101. Final $R = 0·066$, $wR = 0·086$, $(\Delta/\sigma)_{max}$ = 0·12. No feature on a final difference electron density map exceeded ±0·20 e Å^{-3}.

Ab initio STO-3G molecular-orbital calculations were carried out by $GAUSSIAN80$ (Binkley *et al.*, 1980; Chandra Singh & Kollman, 1982). The X-ray structures of (I) and (II) were used as input, except that H atoms were adjusted to standard geometry by routines within $CHEM-X$ (Davies, 1986). Atomic charges were obtained from a Mulliken population analysis.

Discussion. The molecular structure and numbering scheme of (I) are depicted in Fig. 1. The packing of molecules within the unit cell is shown in Fig. 2. Table 1 presents coordinates, isotropic and equivalent isotropic temperature factors and net charges, while Table 2

Table 1. *Atom positional parameters for the title compound (fractional coordinates* $\times 10^4$, $\times 10^3$ *for* H *atoms) and isotropic or equivalent isotropic temperature factors* ($\times 10^3$) *with e.s.d.'s in parentheses, together with atomic charges (millielectrons)*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

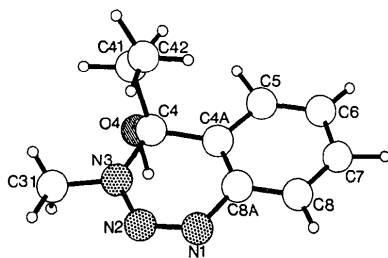|	x	y	z	U/U_{eq}(Å^2)	Charge
N(1)	2688 (5)	1411 (6)	1253 (3)	61 (2)	−190
N(2)	2411 (5)	1930 (6)	706 (3)	59 (2)	−3
N(3)	1397 (5)	2717 (6)	604 (3)	56 (2)	−230
C(4)	478 (5)	3077 (6)	1076 (3)	48 (2)	+248
C(4A)	914 (5)	2568 (6)	1712 (3)	43 (2)	−29
C(5)	272 (6)	2861 (7)	2258 (3)	50 (2)	−65
C(6)	630 (7)	2316 (8)	2834 (4)	61 (3)	−68
C(7)	1669 (7)	1454 (8)	2870 (3)	59 (3)	−64
C(8)	2324 (7)	1161 (8)	2350 (3)	57 (3)	−63
C(8A)	1946 (5)	1717 (7)	1769 (3)	49 (2)	+67
C(31)	1280 (10)	3345 (13)	−22 (4)	71 (3)	−72
O(4)	259 (4)	4709 (4)	1064 (2)	49 (1)	−332
C(41)	−700 (6)	2322 (7)	911 (4)	54 (2)	−105
C(42)	−653 (11)	563 (10)	909 (6)	81 (4)	−181
H(31)	59 (6)	313 (8)	−18 (3)	54 (22)	+81
H(32)	189 (7)	274 (9)	−34 (4)	95 (26)	+96
H(33)	156 (9)	453 (16)	3 (5)	171 (50)	+71
H(4)	104 (9)	543 (11)	117 (4)	123 (32)	+200
H(41A)	−87 (5)	273 (7)	45 (3)	62 (19)	+66
H(41B)	−141 (5)	271 (7)	138 (3)	66 (19)	+71
H(42A)	−145 (6)	12 (7)	66 (3)	63 (19)	+65
H(42B)	−43 (11)	16 (13)	133 (5)	167 (51)	+64
H(42C)	1 (8)	26 (10)	70 (4)	99 (36)	+65
H(5)	−48 (5)	340 (6)	210 (3)	44 (16)	+75
H(6)	25 (7)	250 (9)	321 (4)	85 (25)	+74
H(7)	182 (6)	113 (8)	337 (3)	78 (21)	+73
H(8)	304 (6)	80 (7)	243 (3)	45 (18)	+88

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule projected onto its least-squares plane, showing the atom-numbering scheme.
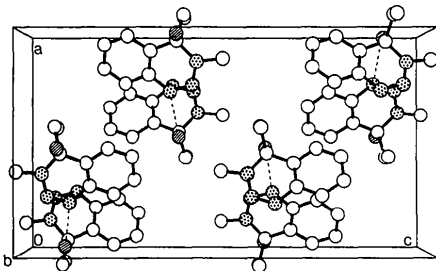

Fig. 2. The contents of one unit cell in perspective projection down the *b* axis. N atoms are stippled, O atoms hatched, and H atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

contains bond lengths, bond angles and selected torsion angles.*

Bond distances and angles in (I) are not strikingly different from those in the related benzotriazines (II) and (III). Within the N$_3$ unit the N(1)–N(2) distance is *ca* 0·07 Å shorter than N(2)–N(3), but both show multiple-bond character. Bond angles at N(1) and N(2) are close to 120°, while C(4)–N(3)–N(2) is significantly larger. These molecules suffer steric interference between the 3-substituent, the 4-substituent(s) and H(5). Crowding is relieved by bending the 3-substituent towards N(2) so that C(31)–N(3)–C(4) > C(31)–N(3)–N(2) and by bending the 4-hydroxyl group away from C(4A) and towards N(3). The C(31)···O(4) and C(31)···C(41) contacts are 2·816 (9) and 3·102 (9) Å respectively. As in (III), the angle subtended at C(4) by its two substituents O(4) and C(41) is less than tetrahedral; the resulting close contact is manifested in the O(4)···C(41) distance of 2·332 (8) Å.

An indication of the degree of ring puckering is given by the torsion angles N(1)–N(2)–N(3)–C(4), N(2)–N(3)–C(4)–C(4A) and N(3)–C(4)–C(4A)–C(8A). In

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* Lists of structure factors, anisotropic thermal parameters and least-squares-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44182 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles* (°), *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

N(1)–N(2)	1·275 (7)	C(8)–C(8A)	1·382 (9)
N(2)–N(3)	1·343 (7)	C(4A)–C(8A)	1·377 (8)
N(3)–C(4)	1·469 (8)	N(1)–C(8A)	1·398 (8)
C(4)–C(4A)	1·494 (8)	N(3)–C(31)	1·432 (9)
C(4A)–C(5)	1·382 (8)	C(4)–C(41)	1·516 (8)
C(5)–C(6)	1·363 (10)	C(41)–C(42)	1·505 (10)
C(6)–C(7)	1·385 (10)	C(4)–O(4)	1·418 (7)
C(7)–C(8)	1·346 (10)		

N(2)–N(1)–C(8A)	119·6 (5)	N(1)–C(8A)–C(8)	116·3 (6)
N(3)–N(2)–N(1)	121·8 (5)	N(1)–C(8A)–C(4A)	122·4 (6)
C(4)–N(3)–N(2)	126·6 (5)	C(4A)–C(8A)–C(8)	121·3 (7)
C(4A)–C(4)–N(3)	108·5 (5)	C(31)–N(3)–N(2)	114·4 (6)
C(5)–C(4A)–C(4)	121·6 (6)	C(31)–N(3)–C(4)	118·8 (6)
C(8A)–C(4A)–C(4)	120·7 (6)	O(4)–C(4)–N(3)	108·4 (5)
C(8A)–C(4A)–C(5)	117·7 (6)	O(4)–C(4)–C(4A)	111·2 (5)
C(6)–C(5)–C(4A)	121·7 (7)	C(41)–C(4)–N(3)	111·8 (5)
C(7)–C(6)–C(5)	118·7 (7)	C(41)–C(4)–C(4A)	111·7 (5)
C(8)–C(7)–C(6)	121·2 (7)	C(41)–C(4)–O(4)	105·2 (5)
C(8A)–C(8)–C(7)	119·3 (7)	C(42)–C(41)–C(4)	113·3 (7)

C(8A)–N(1)–N(2)–N(3)	−2·7 (1)	N(3)–C(4)–C(41)–C(42)	63·3 (1)
N(1)–N(2)–N(3)–C(4)	−0·8 (1)	C(31)–N(3)–C(4)–O(4)	−48·1 (1)
N(1)–N(2)–N(3)–C(31)	174·3 (1)	C(31)–N(3)–C(4)–C(41)	67·4 (1)
N(2)–N(3)–C(4)–C(4A)	6·0 (1)	N(3)–C(4)–C(4A)–C(8A)	−8·1 (1)
N(2)–N(3)–C(4)–O(4)	126·8 (1)	C(4)–C(4A)–C(8A)–N(1)	5·9 (1)
N(2)–N(3)–C(4)–C(41)	−117·7 (1)	C(4A)–C(8A)–N(1)–N(2)	0·1 (1)

the strongly puckered ring of (II) these torsion angles are −21·7, 35·0 and −26·4° respectively, while in the relatively flat (III) they are only −1·5, −2·1 and 3·7°. The title compound resembles (III) more closely than (II) with values of −0·8 (1), 6·0 (1) and −8·1 (1)°. The distortion of (II) is accompanied by some pyramidalization of its N(3), but this atom in (I) is not so affected, the sum of its bond angles at N(3) being 359·8 (10)°. The whole bicyclic system of (I) is virtually planar with deviations ranging from −0·075 to +0·045 Å. Geometry optimization of isolated molecules of (I) and (II) with GAUSSIAN80 tends to increase the degree of puckering: the relevant torsion angles become 18·8, −13·4 and 0·4° for (I) and −40·2, 50·2 and −28·9° for (II).

All three 4-hydroxybenzotriazines are linked by intermolecular O(4)–H(4)···N(1) hydrogen bonds. In (I) the OH···N distance of 2·762 (7) Å and OH···N angle of 173 (2)° are similar to those in the other structures. The charge-density calculation (Table 1) rules out N(2) as the proton acceptor in a hydrogen bond since it is nearly neutral. The other three heteroatoms are all candidates since they bear appreciable negative charges. However, the space around N(3) is congested with substituents, and the production of satisfactory OH···O hydrogen bonds may be incompatible with good packing of the heterocycles. Therefore N(1) appears to offer the best combination of negative charge and accessibility.

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Structure of 2β-Methyl-3-oxolupane-28-nitrile

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Abstract. $C_{31}H_{49}NO$, $M_r = 451·75$, monoclinic, $P2_1$, $a = 15·073$ (2), $b = 23·318$ (6), $c = 7·991$ (1) Å, $\beta = 104·77$ (1)°, $V = 2716·0$ (8) Å³, $Z = 4$, $D_m = 1·098$ (5), $D_x = 1·104$ Mg m⁻³, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·456$ mm⁻¹, $F(000) = 1000$, $T = 296$ K, $R = 0·041$ for 4290 unique observed reflections. The