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Diethyl 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate

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Key indicators

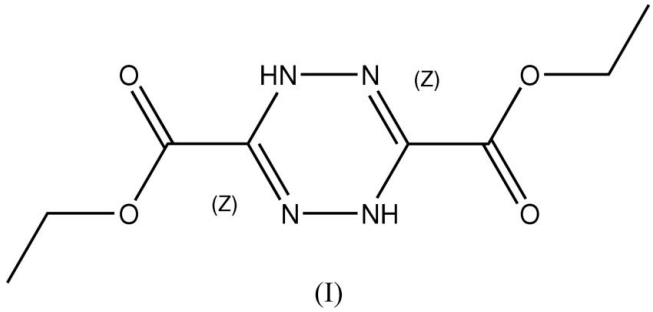
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.050
wR factor = 0.169
Data-to-parameter ratio = 10.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_8H_{12}N_4O_4$, was prepared from ethanol and 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid. The central six-membered ring has a boat conformation.

Comment

s-Tetrazine derivatives have a high potential for biological activity, possessing a wide range of antiviral and antitumor properties, and have been widely used in pesticides and herbicides (Sauer, 1996). In a continuation of our work on the structure–activity relationship of 1,2,4,5-tetrazine derivatives (Hu *et al.*, 2002, 2004), we obtained an orange crystalline compound as the product of the reaction of ethanol and 1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid. The structural identity of our product, (I), was solved using single-crystal X-ray diffraction.



(I)

The molecular structure of (I) is illustrated in Fig. 1. Selected bond lengths and angles are listed in Table 1. Atoms N2, C3, N5 and C6 are coplanar [deviation within 0.0195 (12) Å], and atoms N1 and N4 deviate from the plane by 0.443 (4) and 0.462 (4) Å, respectively, indicating a boat conformation.

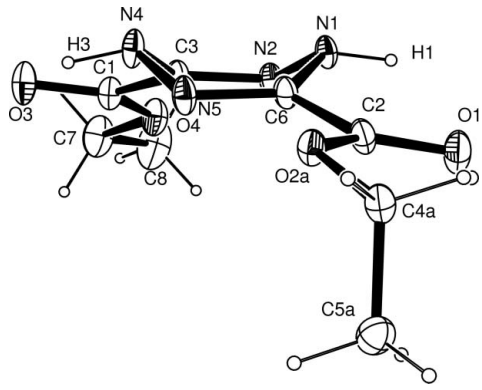


Figure 1
The structure of (I), shown with 30% probability displacement ellipsoids. Only the major component of the disordered ethoxy group is shown.

Experimental

The title compound was prepared according to the procedure of Boger *et al.* (1985). A solution of the compound in ethanol was concentrated gradually at room temperature to afford orange blocks (m.p. 374–375 K).

Crystal data

$C_8H_{12}N_4O_4$
M_r = 228.22
Monoclinic, $P2_1/c$
a = 8.4740 (10) Å
b = 13.4510 (15) Å
c = 10.159 (3) Å
β = 109.090 (17)°
V = 1094.3 (4) Å^3
Z = 4
D_x = 1.385 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.1–12.8°
μ = 0.11 mm^{-1}
T = 298 (2) K
Block, orange
0.35 × 0.30 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.961, T_{max} = 0.983
2262 measured reflections
1954 independent reflections
1165 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 25.2°
$h = -10 \rightarrow 9$
$k = -1 \rightarrow 16$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.169
S = 1.03
1954 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 + 0.3801P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.392 (3)	N4—C3	1.394 (3)
N1—N2	1.408 (3)	N4—N5	1.416 (3)
N2—C3	1.272 (3)	N5—C6	1.277 (3)
C6—N1—N2	113.9 (2)	C6—N5—N4	111.3 (2)
C3—N2—N1	111.5 (2)	N5—C6—N1	121.2 (2)
C3—N4—N5	113.1 (2)	N2—C3—N4	121.3 (2)

During the refinement the atoms of one the ethoxy groups (O2, C4 and C5) gave very large displacement ellipsoids. In the final structure, this group was modeled as disordered over two sites, with occupancy factors in a 0.8:0.2 ratio (the ratio was initially set at 0.5:0.5, but the refinement gave a ratio of 0.8:0.2, which was fixed for the final refinement). To some extent the atoms of the other ethoxy group (O4, C7 and C8) may also be disordered but in this less extreme case the anisotropic refinement proved suitable. H atoms bonded to C atoms were included in calculated positions and refined using a riding model. H atoms except for the H atoms on C4*B* were given isotropic displacement parameters equal to 1.5 times the equivalent isotropic displacement parameters of their parent atoms and C—H distances were restrained to 0.96 Å for those bonded to methyl and 0.97 Å for the remainder. The U_{iso} values of the H atoms bonded to N atoms were refined.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Version 1.05; Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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