

Diethyl 1,4-bis(4-nitrophenyl)-1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate

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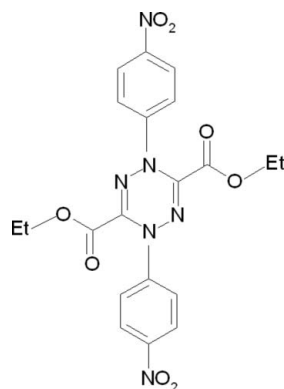
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Key indicators: single-crystal X-ray study; $T = 300$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.053; wR factor = 0.173; data-to-parameter ratio = 15.4.

The complete molecule of the title compound, $\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_8$, is generated by a crystallographic twofold axis. The dihedral angle between the nitrobenzene rings is 43.5 (2)°. The central six-membered ring exhibits a boat conformation. In the crystal structure, weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions are observed.

Related literature

For related literature on diazepine and triazepine derivatives, see: Barltrop *et al.* (1959); Boudina *et al.* (2006); El Hazazi *et al.* (2003); Huisgen & Koch (1955); Nabih *et al.* (2003); Sharp & Hamilton (1946). For related structures, see: Chiaroni *et al.* (1995); El Hazazi *et al.* (2000).



Experimental

Crystal data

$\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_8$	$V = 2197.7$ (9) Å ³
$M_r = 470.40$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 20.739$ (4) Å	$\mu = 0.11$ mm ⁻¹
$b = 7.487$ (2) Å	$T = 300$ K
$c = 14.587$ (3) Å	$0.30 \times 0.15 \times 0.10$ mm
$\beta = 104.00$ (2)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	1352 reflections with $I > 2\sigma(I)$
3158 measured reflections	$R_{\text{int}} = 0.022$
2389 independent reflections	2 standard reflections every 60 min intensity decay: 1.0%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	155 parameters
$wR(F^2) = 0.173$	All H-atom parameters refined
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.27$ e Å ⁻³
2389 reflections	$\Delta\rho_{\text{min}} = -0.26$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C6}-\text{H4}\cdots\text{O2}^{\text{i}}$	0.93	2.57	3.400 (4)	149
$\text{C9}-\text{H6}\cdots\text{O1}^{\text{ii}}$	0.97	2.60	3.294 (4)	129

Symmetry codes: (i) $-x + 1, y, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2514).

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supplementary materials

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Diethyl 1,4-bis(4-nitrophenyl)-1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate

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Comment

In order to prepare a new heterocyclic systems, our research team have been interested in the 1,3-dipolar cycloaddition reaction of nitrile oxides and nitrilimines toward diazepines, benzodiazepines, triazepines and benzotriazepines (El Hazazi *et al.*, 2003; Nabih *et al.*, 2003; Boudina *et al.*, 2006). In this context, we directed our axe of research to examine reactivity of adducts-obtained from the 1,5-benzodiazepine (Barltrop *et al.*, 1959) via 1,3-dipolar cycloaddition reaction of nitrilimines-with *N*-paranitrophenylnitrilimine (Sharp & Hamilton, 1946; Huisgen & Koch, 1955). This reaction provided to bicycloadduct and a new heterocycle (A). The new heterocycle (A) resulted from precursor ethyl paranitrophenylhydrazono- α -bromoglyoxylate by the action of triethylamine in dichloromethane at room temperature (Fig. 1).

The structure of product (A) was determined on the basis of NMR spectral data (^1H and ^{13}C) and studied by single-crystal X-ray diffraction (Fig. 2). The asymmetric unit consists of one independent $[\text{C}_{10}\text{H}_9\text{N}_3\text{O}_4]$ group that form one half of a molecule compound. The main geometric features of this group are in good agreement with those observed in similar compounds (Chiaroni *et al.*, 1995; El Hazazi *et al.*, 2000). The molecule of nominal compound is localized around a twofold rotation axis and exhibit a boat conformation in which N2 and N2a show the maximum deviation (0.3213 Å) from N3/N2/C7/N3ⁱ/N2ⁱ/C7ⁱ plane [symmetry code: (i) $-x + 1, y, -z + 1/2$].

Experimental

Triethylamine (0.8 mmol) in dichloromethane (2 ml) was added at room temperature to a stirred solution of ethyl paranitrophenylhydrazono- α -bromoglyoxylate (0.65 mmol) in dichloromethane (20 ml). The mixture was stirred at room temperature, washed with water and the aqueous phase was then extracted with ether (3 \times 20 ml). The organic layer was dried over anhydrous sodium sulfate and then concentrated under reduced pressure and recrystallized from ethanol to afford the reaction product (A) (m.p. = 219–220 °C).

Refinement

All H atoms were located in a difference map and refined using a riding model, with $d(\text{C}-\text{H}) = 0.93-0.97$ Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures



Fig. 1. The reaction scheme of the title compound.

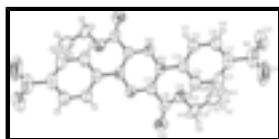


Fig. 2. The molecule structure of the title compound with 50% probability ellipsoids.

Diethyl 1,4-bis(4-nitrophenyl)-1,4-dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate

Crystal data

$C_{20}H_{18}N_6O_8$	$F(000) = 976$
$M_r = 470.40$	$D_x = 1.422 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 25 reflections
$a = 20.739 (4) \text{ \AA}$	$\theta = 10\text{--}15^\circ$
$b = 7.487 (2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 14.587 (3) \text{ \AA}$	$T = 300 \text{ K}$
$\beta = 104.00 (2)^\circ$	Prism, colourless
$V = 2197.7 (9) \text{ \AA}^3$	$0.30 \times 0.15 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.022$
Radiation source: fine-focus sealed tube graphite	$\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 2.0^\circ$
$\omega/2\theta$ scans	$h = -26 \rightarrow 25$
3158 measured reflections	$k = -9 \rightarrow 2$
2389 independent reflections	$l = -1 \rightarrow 18$
1352 reflections with $I > 2\sigma(I)$	2 standard reflections every 60 min intensity decay: 1.0%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.053$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.173$	All H-atom parameters refined
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.080P)^2 + 0.9509P]$
2389 reflections	where $P = (F_o^2 + 2F_c^2)/3$
155 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.32809 (17)	0.4483 (5)	0.63327 (19)	0.1695 (16)
O2	0.41693 (14)	0.3584 (4)	0.72174 (17)	0.1199 (10)
O3	0.32302 (9)	0.0896 (4)	0.16616 (14)	0.1091 (9)
O4	0.37172 (7)	-0.0126 (3)	0.31106 (12)	0.0661 (5)
N1	0.38276 (16)	0.3893 (3)	0.6442 (2)	0.0884 (8)
N2	0.47726 (9)	0.2300 (3)	0.32241 (12)	0.0540 (5)
N3	0.54350 (8)	0.1630 (3)	0.33902 (12)	0.0564 (5)
C1	0.40750 (14)	0.3493 (3)	0.55998 (17)	0.0636 (7)
C2	0.36884 (14)	0.3910 (4)	0.4717 (2)	0.0716 (8)
H1	0.3273	0.4430	0.4653	0.086*
C3	0.39257 (13)	0.3545 (3)	0.39242 (18)	0.0654 (7)
H2	0.3678	0.3856	0.3325	0.078*
C4	0.45413 (11)	0.2706 (3)	0.40419 (15)	0.0520 (5)
C5	0.49295 (12)	0.2332 (3)	0.49362 (16)	0.0590 (6)
H3	0.5346	0.1811	0.5008	0.071*
C6	0.46928 (13)	0.2741 (4)	0.57236 (17)	0.0660 (7)
H4	0.4950	0.2507	0.6328	0.079*
C7	0.43585 (10)	0.1682 (3)	0.23753 (15)	0.0541 (6)
C8	0.36944 (12)	0.0780 (4)	0.23316 (18)	0.0651 (7)
C9	0.30977 (13)	-0.0998 (5)	0.3205 (2)	0.0867 (10)
H5	0.3033	-0.2111	0.2854	0.104*
H6	0.2720	-0.0227	0.2954	0.104*
C10	0.31545 (15)	-0.1344 (5)	0.4218 (2)	0.1016 (12)
H7	0.2749	-0.1864	0.4299	0.122*
H8	0.3236	-0.0241	0.4562	0.122*
H9	0.3516	-0.2153	0.4453	0.122*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.175 (3)	0.249 (4)	0.118 (2)	0.124 (3)	0.100 (2)	0.043 (2)
O2	0.144 (2)	0.165 (3)	0.0653 (13)	0.0037 (18)	0.0534 (14)	-0.0131 (15)
O3	0.0536 (11)	0.199 (3)	0.0711 (12)	-0.0147 (14)	0.0087 (10)	0.0158 (15)
O4	0.0476 (9)	0.0843 (12)	0.0706 (10)	-0.0101 (8)	0.0223 (7)	0.0018 (9)
N1	0.119 (2)	0.0823 (17)	0.0852 (18)	0.0141 (15)	0.0671 (17)	0.0024 (14)
N2	0.0471 (10)	0.0709 (13)	0.0503 (10)	0.0008 (9)	0.0237 (8)	-0.0022 (9)
N3	0.0449 (10)	0.0765 (14)	0.0516 (11)	-0.0025 (9)	0.0187 (8)	-0.0018 (9)
C1	0.0872 (18)	0.0555 (14)	0.0619 (14)	0.0005 (13)	0.0450 (13)	-0.0020 (12)
C2	0.0814 (17)	0.0651 (16)	0.0833 (18)	0.0191 (13)	0.0493 (15)	0.0105 (14)

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C3	0.0725 (15)	0.0698 (17)	0.0634 (14)	0.0164 (13)	0.0354 (12)	0.0112 (12)
C4	0.0581 (13)	0.0524 (13)	0.0528 (12)	-0.0049 (10)	0.0276 (10)	-0.0017 (10)
C5	0.0563 (13)	0.0717 (16)	0.0537 (13)	-0.0029 (12)	0.0225 (10)	-0.0057 (12)
C6	0.0762 (17)	0.0738 (17)	0.0533 (13)	-0.0050 (14)	0.0258 (12)	-0.0059 (12)
C7	0.0455 (11)	0.0700 (15)	0.0510 (12)	0.0068 (11)	0.0200 (10)	0.0026 (11)
C8	0.0433 (12)	0.099 (2)	0.0579 (14)	0.0004 (12)	0.0217 (11)	-0.0058 (14)
C9	0.0569 (15)	0.121 (3)	0.092 (2)	-0.0301 (16)	0.0365 (14)	-0.0204 (18)
C10	0.0654 (17)	0.130 (3)	0.110 (2)	-0.0187 (18)	0.0216 (17)	0.046 (2)

Geometric parameters (\AA , $^\circ$)

O1—N1	1.191 (3)	C3—C4	1.396 (3)
O2—N1	1.202 (3)	C3—H2	0.9300
O3—C8	1.198 (3)	C4—C5	1.386 (3)
O4—C8	1.314 (3)	C5—C6	1.388 (3)
O4—C9	1.477 (3)	C5—H3	0.9300
N1—C1	1.473 (3)	C6—H4	0.9300
N2—C7	1.403 (3)	C7—N3 ⁱ	1.290 (3)
N2—C4	1.422 (3)	C7—C8	1.522 (3)
N2—N3	1.427 (3)	C9—C10	1.478 (4)
N3—C7 ⁱ	1.290 (3)	C9—H5	0.9700
C1—C6	1.371 (4)	C9—H6	0.9700
C1—C2	1.378 (4)	C10—H7	0.9600
C2—C3	1.389 (3)	C10—H8	0.9600
C2—H1	0.9300	C10—H9	0.9600
C8—O4—C9	117.3 (2)	C6—C5—H3	120.2
O1—N1—O2	121.5 (3)	C1—C6—C5	119.2 (2)
O1—N1—C1	118.4 (3)	C1—C6—H4	120.4
O2—N1—C1	120.0 (3)	C5—C6—H4	120.4
C7—N2—C4	123.50 (18)	N3 ⁱ —C7—N2	120.89 (19)
C7—N2—N3	113.10 (17)	N3 ⁱ —C7—C8	115.9 (2)
C4—N2—N3	116.03 (18)	N2—C7—C8	122.52 (19)
C7 ⁱ —N3—N2	110.49 (18)	O3—C8—O4	126.6 (2)
C6—C1—C2	122.0 (2)	O3—C8—C7	122.9 (2)
C6—C1—N1	118.5 (2)	O4—C8—C7	110.5 (2)
C2—C1—N1	119.5 (2)	O4—C9—C10	108.1 (2)
C1—C2—C3	119.4 (2)	O4—C9—H5	110.1
C1—C2—H1	120.3	C10—C9—H5	110.1
C3—C2—H1	120.3	O4—C9—H6	110.1
C2—C3—C4	118.9 (2)	C10—C9—H6	110.1
C2—C3—H2	120.5	H5—C9—H6	108.4
C4—C3—H2	120.5	C9—C10—H7	109.5
C5—C4—C3	120.8 (2)	C9—C10—H8	109.5
C5—C4—N2	120.6 (2)	H7—C10—H8	109.5
C3—C4—N2	118.5 (2)	C9—C10—H9	109.5
C4—C5—C6	119.6 (2)	H7—C10—H9	109.5
C4—C5—H3	120.2	H8—C10—H9	109.5

C7—N2—N3—C7 ⁱ	42.9 (2)	N2—C4—C5—C6	180.0 (2)
C4—N2—N3—C7 ⁱ	-165.9 (2)	C2—C1—C6—C5	-2.1 (4)
O1—N1—C1—C6	-177.2 (3)	N1—C1—C6—C5	179.1 (2)
O2—N1—C1—C6	1.1 (4)	C4—C5—C6—C1	0.6 (4)
O1—N1—C1—C2	3.9 (4)	C4—N2—C7—N3 ⁱ	167.8 (2)
O2—N1—C1—C2	-177.7 (3)	N3—N2—C7—N3 ⁱ	-43.5 (3)
C6—C1—C2—C3	0.6 (4)	C4—N2—C7—C8	-21.9 (4)
N1—C1—C2—C3	179.4 (2)	N3—N2—C7—C8	126.8 (2)
C1—C2—C3—C4	2.3 (4)	C9—O4—C8—O3	-4.4 (4)
C2—C3—C4—C5	-3.7 (4)	C9—O4—C8—C7	176.5 (2)
C2—C3—C4—N2	178.5 (2)	N3 ⁱ —C7—C8—O3	-40.8 (4)
C7—N2—C4—C5	143.2 (2)	N2—C7—C8—O3	148.5 (3)
N3—N2—C4—C5	-4.6 (3)	N3 ⁱ —C7—C8—O4	138.4 (2)
C7—N2—C4—C3	-39.0 (3)	N2—C7—C8—O4	-32.3 (3)
N3—N2—C4—C3	173.1 (2)	C8—O4—C9—C10	-159.4 (3)
C3—C4—C5—C6	2.3 (4)		

Symmetry codes: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C6—H4 \cdots O2 ⁱⁱ	0.93	2.57	3.400 (4)	149.
C9—H6 \cdots O1 ⁱⁱⁱ	0.97	2.60	3.294 (4)	129.

Symmetry codes: (ii) $-x+1, y, -z+3/2$; (iii) $-x+1/2, -y+1/2, -z+1$.

Fig. 1

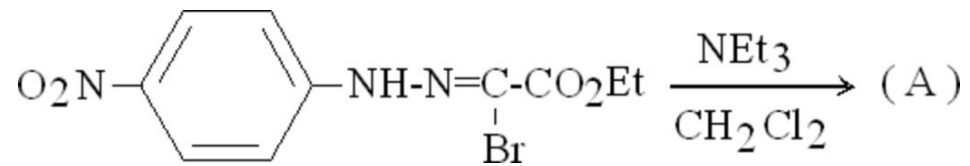


Fig. 2

