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4-[(4-Bromophenyl)diazenyl]-2-ethoxyaniline

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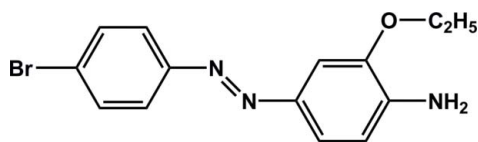
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.008$ Å; R factor = 0.065; wR factor = 0.198; data-to-parameter ratio = 13.5.

The title compound, $C_{14}H_{14}BrN_3O$, exhibits a *trans* geometry about the $-N=N-$ double bond. The dihedral angle between the benzene rings is $24.01(5)^\circ$. An intramolecular $N-H \cdots O$ hydrogen bond occurs. In the crystal, intermolecular $N-H \cdots N$ hydrogen bonds between the amine groups lead to the formation of a $C(8)$ polymeric chain along $[101]$.

Related literature

For the synthesis and crystal structures of similar diazenyl compounds, see: de Wit *et al.* (2008); Yazici *et al.* (2006). For crystal structure of a chloro analogue of the title compound, see: Rofouei *et al.* (2011). For graph-set motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $C_{14}H_{14}BrN_3O$ $M_r = 320.19$ Monoclinic, $P2_1/n$ $a = 13.219(2)$ Å $b = 8.8289(17)$ Å $c = 13.506(2)$ Å $\beta = 118.855(6)^\circ$ $V = 1380.6(4)$ Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 2.97$ mm⁻¹ $T = 200$ K $0.40 \times 0.20 \times 0.10$ mm

Data collection

 Bruker SMART X2S benchtop
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2009)
 $T_{\min} = 0.383$, $T_{\max} = 0.755$

 8299 measured reflections
 2408 independent reflections
 1775 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.065$ $wR(F^2) = 0.198$ $S = 1.00$

2408 reflections

178 parameters

2 restraints

 H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.98$ e Å⁻³ $\Delta\rho_{\text{min}} = -1.11$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3A \cdots N2^i$	0.88 (1)	2.38 (2)	3.228 (6)	163 (5)
$N3-H3B \cdots O1$	0.88 (1)	2.28 (5)	2.628 (5)	103 (4)

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *SMART X2S* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2476).

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supporting information

Acta Cryst. (2011). E67, o3396 [https://doi.org/10.1107/S160053681104877X]

4-[(4-Bromophenyl)diazenyl]-2-ethoxyaniline

Mohammad Reza Melardi, Jafar Attar Gharamaleki, Soheyla Rezabeyk and Mohammad Kazem Rofouei

S1. Comment

We have recently reported the crystal structure of 4-[(4-chlorophenyl)diazenyl]-3-methoxyaniline (Rofouei *et al.*, 2011), a chloro analogue of the title compound. Diazenyl compounds characterized by having a diazo group ($-\text{N}=\text{N}-$) commonly adopt the *trans* configuration in the ground state. In continuation to our work in this field, we now report the crystal structure of the title compound.

The title molecule (Fig. 1) adopts a *trans* configuration about the $-\text{N}_1=\text{N}_2-$ double bond and the $\text{C}_1-\text{N}_1-\text{N}_2-\text{C}_9$ dihedral angle is $177.3(4)^\circ$. The molecular dimensions in the title compound are similar to the corresponding dimensions reported in other azo compounds (Yazici *et al.*, 2006; de Wit *et al.*, 2008; Rofouei *et al.*, 2011).

In the structure of the title compound, the molecules are linked into chain-like polymers along the *c* axis, with C(8) graph set motif (Bernstein *et al.*, 1995), through $\text{N}_3-\text{H}_3\text{A}\cdots\text{N}_2^i$ hydrogen bonds with $\text{D}\cdots\text{A}$ separation of $3.228(6)\text{ \AA}$ (Fig. 2 and Tab. 1). The structure is further consolidated by $\text{N}_3-\text{H}_3\text{A}\cdots\text{O}_1$ intramolecular hydrogen bond with $\text{D}\cdots\text{A}$ separation of $2.628(5)\text{ \AA}$.

S2. Experimental

To a 100 ml flask in an ice bath, was added (0.349 g, 2 mmol) *p*-boromoaniline and (3.65 g, 0.1 mol) of HCl ($d = 1.18\text{ g.ml}^{-1}$). To the obtained solution, was added dropwise a solution of sodium nitrite (0.14 g in 5 ml H_2O). Then, a diluted solution of *o*-ethoxyaniline (0.244 g, 2 mmol) in methanol (5 ml) was added to the above solution. The pH of the solution was adjusted at about 6–7 by adding a solution of 10% of sodium acetate. The solution was stirred for about an hour, giving an orange precipitate. It was then filtered off and dried in vacuum. After dissolving in diethylether and recrystallization, red crystals of the title compound were obtained. *M.p.* 373–376 K.

S3. Refinement

Hydrogen atoms bonded to carbon were included at geometrically idealized positions and refined in riding mode with distances $\text{H}-\text{C} = 0.95, 0.98$ and 0.99 \AA for aryl, methyl and methylene type H-atoms, respectively with $U_{\text{iso}}(\text{H})$ set to $1.2(1.5\text{ for methyl})U_{\text{eq}}(\text{C})$. Hydrogen atoms bonded to N were located from a difference Fourier map and refined with the $\text{N}-\text{H}$ distances restrained to $0.88(1)\text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

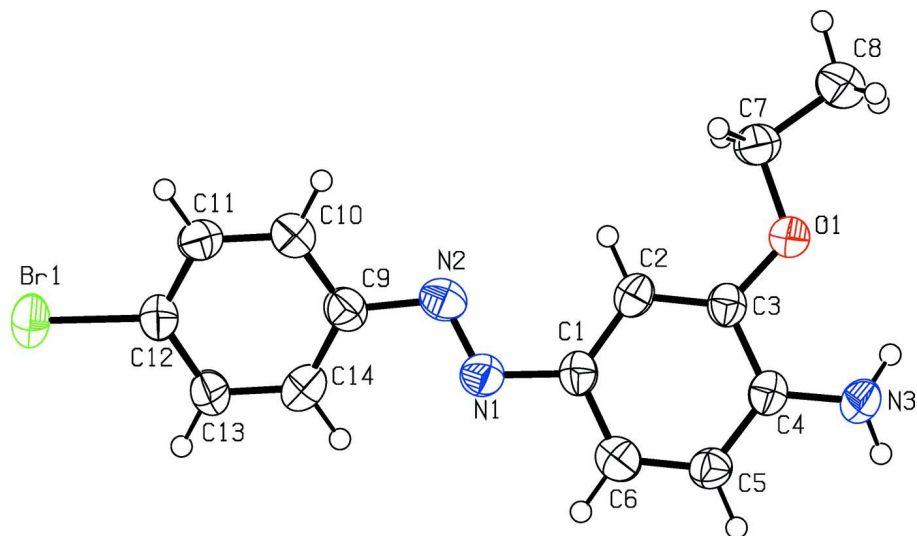


Figure 1

The molecular structure of the title compound, displacement ellipsoids are drawn at 50% probability level.

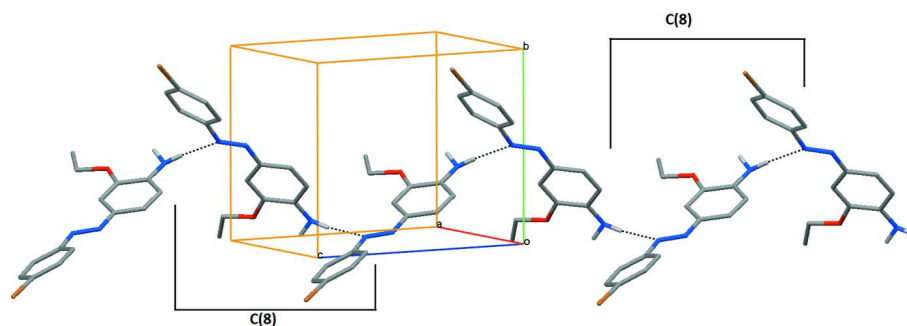


Figure 2

A part of the unit cell showing N3—H3A...N2 hydrogen bonds, to produce polymeric chain of the title molecules along the *c* axis.

4-[(4-Bromophenyl)diazenyl]-2-ethoxyaniline

Crystal data

$C_{14}H_{14}BrN_3O$

$M_r = 320.19$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 13.219\ (2)\ \text{\AA}$

$b = 8.8289\ (17)\ \text{\AA}$

$c = 13.506\ (2)\ \text{\AA}$

$\beta = 118.855\ (6)^\circ$

$V = 1380.6\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 648$

$D_x = 1.540\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2935 reflections

$\theta = 2.9\text{--}24.8^\circ$

$\mu = 2.97\ \text{mm}^{-1}$

$T = 200\ \text{K}$

Block, yellow

$0.40 \times 0.20 \times 0.10\ \text{mm}$

Data collection

Bruker SMART X2S benchtop
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $8.33\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

 $T_{\min} = 0.383$, $T_{\max} = 0.755$

8299 measured reflections

2408 independent reflections

1775 reflections with $I > 2\Sigma(I)$ $R_{\text{int}} = 0.075$ $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.8^\circ$ $h = -15 \rightarrow 13$ $k = -10 \rightarrow 10$ $l = -16 \rightarrow 16$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.065$ $wR(F^2) = 0.198$ $S = 1.00$

2408 reflections

178 parameters

2 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.1373P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.98 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -1.11 \text{ e } \text{\AA}^{-3}$ *Special details*

Experimental. ^1H NMR (300 MHz, d^6 -DMSO): 1.31 (3H, CH₃), 4.10 (2H, OCH₂), 6.72–7.68 (7H, aromatic ring) and 5.87 (2H, NH₂ groups). ^{13}C NMR (100 MHz, DMSO): 14.63 (CH₃), 63.44 (OCH₂), 101.60–151.34 (C atoms of aromatic rings).

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.62107 (6)	0.84573 (8)	0.08362 (5)	0.0740 (4)
O1	-0.1368 (3)	0.1305 (4)	-0.0555 (3)	0.0469 (9)
N1	0.1207 (4)	0.4681 (5)	-0.1255 (3)	0.0441 (10)
N2	0.1867 (4)	0.4891 (4)	-0.0227 (3)	0.0444 (10)
N3	-0.2711 (4)	0.1068 (5)	-0.2750 (4)	0.0477 (11)
H3A	-0.296 (5)	0.071 (6)	-0.343 (2)	0.057*
H3B	-0.270 (5)	0.039 (5)	-0.227 (3)	0.057*
C1	0.0220 (4)	0.3782 (5)	-0.1537 (4)	0.0380 (11)
C2	-0.0054 (4)	0.3036 (5)	-0.0774 (4)	0.0396 (11)
H2	0.0424	0.3161	0.0018	0.047*
C3	-0.1012 (4)	0.2134 (5)	-0.1179 (4)	0.0364 (11)
C4	-0.1750 (4)	0.1953 (5)	-0.2364 (4)	0.0368 (11)
C5	-0.1446 (4)	0.2697 (5)	-0.3088 (4)	0.0399 (11)
H5	-0.1917	0.2580	-0.3881	0.048*
C6	-0.0488 (5)	0.3591 (5)	-0.2688 (4)	0.0438 (13)
H6	-0.0305	0.4089	-0.3205	0.053*

C7	-0.0682 (5)	0.1345 (6)	0.0658 (4)	0.0454 (13)
H7A	-0.0598	0.2399	0.0937	0.054*
H7B	0.0096	0.0923	0.0900	0.054*
C8	-0.1313 (5)	0.0403 (7)	0.1108 (4)	0.0601 (15)
H8A	-0.0876	0.0388	0.1936	0.090*
H8B	-0.1396	-0.0633	0.0818	0.090*
H8C	-0.2079	0.0839	0.0864	0.090*
C9	0.2870 (4)	0.5761 (5)	-0.0032 (4)	0.0429 (12)
C10	0.3484 (5)	0.6451 (5)	0.0999 (4)	0.0472 (13)
H10	0.3240	0.6346	0.1552	0.057*
C11	0.4442 (4)	0.7285 (6)	0.1237 (4)	0.0461 (12)
H11	0.4841	0.7798	0.1940	0.055*
C12	0.4832 (4)	0.7385 (6)	0.0462 (4)	0.0479 (13)
C13	0.4241 (6)	0.6680 (7)	-0.0578 (5)	0.0611 (17)
H13	0.4510	0.6746	-0.1115	0.073*
C14	0.3252 (5)	0.5878 (7)	-0.0819 (4)	0.0566 (15)
H14	0.2829	0.5401	-0.1534	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0634 (5)	0.0968 (6)	0.0643 (5)	-0.0445 (4)	0.0328 (4)	-0.0213 (3)
O1	0.043 (2)	0.060 (2)	0.0371 (17)	-0.0123 (17)	0.0188 (17)	-0.0022 (15)
N1	0.046 (3)	0.043 (2)	0.040 (2)	-0.0016 (19)	0.018 (2)	0.0031 (17)
N2	0.049 (3)	0.043 (2)	0.043 (2)	0.0051 (19)	0.024 (2)	0.0064 (18)
N3	0.045 (3)	0.055 (3)	0.041 (2)	-0.014 (2)	0.019 (2)	-0.0120 (19)
C1	0.034 (3)	0.037 (2)	0.044 (3)	-0.002 (2)	0.020 (2)	-0.0029 (19)
C2	0.031 (3)	0.043 (2)	0.039 (2)	0.000 (2)	0.012 (2)	-0.001 (2)
C3	0.031 (3)	0.038 (2)	0.042 (3)	0.001 (2)	0.019 (2)	-0.002 (2)
C4	0.032 (3)	0.035 (2)	0.043 (3)	0.001 (2)	0.018 (2)	-0.0042 (19)
C5	0.041 (3)	0.043 (3)	0.037 (3)	-0.001 (2)	0.020 (2)	-0.005 (2)
C6	0.055 (3)	0.036 (2)	0.049 (3)	0.000 (2)	0.031 (3)	-0.002 (2)
C7	0.049 (3)	0.049 (3)	0.037 (3)	-0.001 (2)	0.019 (2)	-0.001 (2)
C8	0.068 (4)	0.060 (3)	0.050 (3)	-0.010 (3)	0.028 (3)	0.005 (3)
C9	0.044 (3)	0.043 (3)	0.045 (3)	0.000 (2)	0.023 (2)	0.005 (2)
C10	0.050 (3)	0.049 (3)	0.046 (3)	-0.004 (2)	0.025 (3)	0.002 (2)
C11	0.049 (3)	0.047 (3)	0.036 (3)	-0.004 (2)	0.017 (2)	0.000 (2)
C12	0.040 (3)	0.054 (3)	0.046 (3)	-0.012 (2)	0.018 (2)	0.001 (2)
C13	0.062 (4)	0.081 (4)	0.050 (3)	-0.034 (3)	0.035 (3)	-0.016 (3)
C14	0.050 (3)	0.068 (4)	0.043 (3)	-0.014 (3)	0.015 (3)	-0.010 (3)

Geometric parameters (Å, °)

Br1—C12	1.893 (5)	C6—H6	0.9500
O1—C3	1.361 (6)	C7—C8	1.498 (8)
O1—C7	1.439 (6)	C7—H7A	0.9900
N1—N2	1.246 (5)	C7—H7B	0.9900
N1—C1	1.412 (6)	C8—H8A	0.9800

N2—C9	1.442 (7)	C8—H8B	0.9800
N3—C4	1.363 (7)	C8—H8C	0.9800
N3—H3A	0.876 (10)	C9—C10	1.371 (7)
N3—H3B	0.879 (10)	C9—C14	1.383 (8)
C1—C6	1.384 (7)	C10—C11	1.363 (7)
C1—C2	1.410 (7)	C10—H10	0.9500
C2—C3	1.367 (7)	C11—C12	1.375 (7)
C2—H2	0.9500	C11—H11	0.9500
C3—C4	1.424 (7)	C12—C13	1.383 (7)
C4—C5	1.388 (7)	C13—C14	1.380 (9)
C5—C6	1.363 (7)	C13—H13	0.9500
C5—H5	0.9500	C14—H14	0.9500
C3—O1—C7	118.4 (4)	O1—C7—H7B	110.5
N2—N1—C1	116.3 (4)	C8—C7—H7B	110.5
N1—N2—C9	111.8 (4)	H7A—C7—H7B	108.7
C4—N3—H3A	114 (4)	C7—C8—H8A	109.5
C4—N3—H3B	116 (4)	C7—C8—H8B	109.5
H3A—N3—H3B	113 (5)	H8A—C8—H8B	109.5
C6—C1—C2	119.4 (4)	C7—C8—H8C	109.5
C6—C1—N1	114.1 (4)	H8A—C8—H8C	109.5
C2—C1—N1	126.5 (4)	H8B—C8—H8C	109.5
C3—C2—C1	119.6 (4)	C10—C9—C14	119.4 (5)
C3—C2—H2	120.2	C10—C9—N2	117.6 (5)
C1—C2—H2	120.2	C14—C9—N2	123.0 (5)
O1—C3—C2	126.5 (4)	C11—C10—C9	120.4 (5)
O1—C3—C4	112.5 (4)	C11—C10—H10	119.8
C2—C3—C4	121.0 (4)	C9—C10—H10	119.8
N3—C4—C5	122.3 (4)	C10—C11—C12	120.2 (5)
N3—C4—C3	120.0 (4)	C10—C11—H11	119.9
C5—C4—C3	117.7 (4)	C12—C11—H11	119.9
C6—C5—C4	121.6 (4)	C11—C12—C13	120.6 (5)
C6—C5—H5	119.2	C11—C12—Br1	119.7 (4)
C4—C5—H5	119.2	C13—C12—Br1	119.7 (4)
C5—C6—C1	120.8 (5)	C14—C13—C12	118.4 (5)
C5—C6—H6	119.6	C14—C13—H13	120.8
C1—C6—H6	119.6	C12—C13—H13	120.8
O1—C7—C8	106.3 (4)	C13—C14—C9	120.9 (5)
O1—C7—H7A	110.5	C13—C14—H14	119.6
C8—C7—H7A	110.5	C9—C14—H14	119.6
C1—N1—N2—C9	177.3 (4)	C2—C1—C6—C5	0.2 (7)
N2—N1—C1—C6	179.6 (4)	N1—C1—C6—C5	177.1 (4)
N2—N1—C1—C2	-3.8 (7)	C3—O1—C7—C8	177.1 (5)
C6—C1—C2—C3	0.2 (7)	N1—N2—C9—C10	161.2 (5)
N1—C1—C2—C3	-176.3 (5)	N1—N2—C9—C14	-21.2 (7)
C7—O1—C3—C2	-0.6 (7)	C14—C9—C10—C11	2.1 (8)
C7—O1—C3—C4	178.2 (4)	N2—C9—C10—C11	179.8 (4)

C1—C2—C3—O1	177.6 (5)	C9—C10—C11—C12	-3.0 (8)
C1—C2—C3—C4	-1.0 (7)	C10—C11—C12—C13	1.9 (9)
O1—C3—C4—N3	2.2 (6)	C10—C11—C12—Br1	-176.6 (4)
C2—C3—C4—N3	-178.9 (5)	C11—C12—C13—C14	0.1 (10)
O1—C3—C4—C5	-177.4 (4)	Br1—C12—C13—C14	178.6 (5)
C2—C3—C4—C5	1.5 (7)	C12—C13—C14—C9	-1.0 (10)
N3—C4—C5—C6	179.3 (5)	C10—C9—C14—C13	-0.1 (9)
C3—C4—C5—C6	-1.1 (7)	N2—C9—C14—C13	-177.6 (6)
C4—C5—C6—C1	0.3 (8)		

Hydrogen-bond geometry (Å, °)

<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>
N3—H3 <i>A</i> \cdots N2 ⁱ	0.88 (1)	2.38 (2)	3.228 (6)	163 (5)
N3—H3 <i>B</i> \cdots O1	0.88 (1)	2.28 (5)	2.628 (5)	103 (4)

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