

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis(4-methoxypyridin-3-yl)diazene

Steffen Thies,^{a*} Christian Näther^b and Rainer Herges^{a*}

^aInstitut für Organische Chemie, Universität Kiel, Otto-Hahn-Platz 4, 24118 Kiel, Germany, and ^bInstitut für Anorganische Chemie, Universität Kiel, Otto-Hahn-Platz 6/7, 24118 Kiel, Germany

Correspondence e-mail: cnaether@ac.uni-kiel.de, rherges@ac.uni-kiel.de

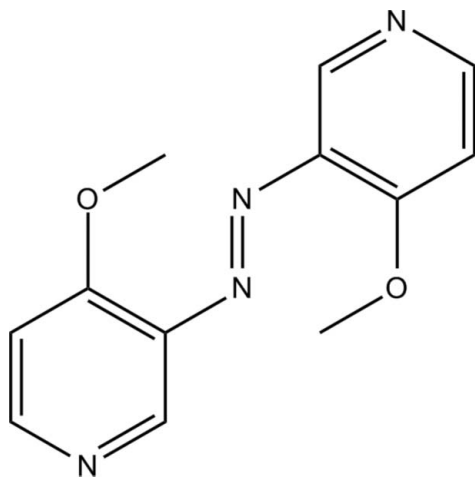
Received 20 April 2012; accepted 24 April 2012

Key indicators: single-crystal X-ray study; $T = 220$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.105; data-to-parameter ratio = 14.7.

The asymmetric unit of the title compound, $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_2$, consists of one half-molecule, which is located on a center of inversion. The molecule has a step-like shape; the azo group adopting a *trans* configuration, with the pyridine rings being parallel-displace.

Related literature

For background to this work, see: Thies *et al.* (2010, 2011); Venkataramani *et al.* (2011).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_2$
 $M_r = 244.26$
 Orthorhombic, *Pbca*
 $a = 13.3976$ (8) Å
 $b = 6.2101$ (6) Å
 $c = 13.6079$ (9) Å

$V = 1132.18$ (15) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 220$ K
 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Stoe IPDS-1 diffractometer
 5829 measured reflections
 1235 independent reflections

1002 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.105$
 $S = 1.04$
 1235 reflections

84 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Data collection: *X-Area* (Stoe & Cie, 2008); cell refinement: *X-Area*; data reduction: *X-RED32*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft *via* SFB 677.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5885).

References

- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Stoe & Cie (2008). *X-Area* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
 Thies, S., Bornholdt, C., Koehler, F., Sönnichsen, F. D., Näther, C., Tuzcek, F. & Herges, R. (2010). *Chem. Eur. J.* **16**, 10074–10083.
 Thies, S., Sell, H., Schütt, C., Bornholdt, C., Näther, C., Tuzcek, F. & Herges, R. (2011). *J. Am. Chem. Soc.* **133**, 16243–16250.
 Venkataramani, S., Jana, U., Dommaschk, M., Sönnichsen, F. D., Tuzcek, F. & Herges, H. (2011). *Science*, **331**, 445–448.

supporting information

Acta Cryst. (2012). E68, o1568 [doi:10.1107/S1600536812018326]

Bis(4-methoxypyridin-3-yl)diazene

Steffen Thies, Christian Näther and Rainer Herges

S1. Comment

We recently reported about a change of the spin state by association/dissociation of photodissociable ligands (PDL's) at square planar Ni(II) porphyrine complexes (Thies *et al.* 2010, Thies *et al.* 2011, Venkataramani *et al.*, 2011). Within this project the title compound was synthesized as potential PDL and its structure was determined by single-crystal X-ray diffraction.

In the crystal structure of the title compound, the azo group is in a *trans* configuration with an torsion angle C2—N2—N2ⁱ—C2ⁱ (*i* = -*x* + 1, -*y* + 2, -*z* + 1) of 180° due to symmetry. The pyridine rings are not coplanar with the central C—N—N—C unit with torsion angles of 32.9 (2)° for C1—C2—N2—N2ⁱ and 151.5 (2)° for C3—C2—N2—N2ⁱ (*i* = -*x* + 1, -*y* + 2, -*z* + 1).

S2. Experimental

3-Nitro-4-methoxypyridine (1.14 g, 7.41 mmol) was dissolved in ethanol (30 ml) and heated to 80°C. Barium hydroxide (3.50 g, 20.8 mmol) dissolved in 20 ml hot water was added. Zinc powder (6.00 g, 91,7 mmol) was added in small portions within 20 min. The reaction mixture was stirred at 80 °C for 3 h and filtered over celite®. 200 ml dichloromethane were added to the filtrate and air was bubbled through the solution for 2 h. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was dissolved in ethanol and two spoons of activated charcoal were added. After stirring at 80°C for 20 min the mixture was filtered over celite® and the product was crystallized from ethyl acetate. An orange solid (120 mg, 0.49 mmol, 13.2%) was afforded (mp: 218.4 °C). ¹H-NMR (500 MHz, 300 K, CDCl₃, TMS): δ = 8.58 (s, 2H, 2-*H*), 8.55 (d, *J* = 5.8 Hz, 2H, 6-*H*), 7.02 (d, *J* = 5.8 Hz, 2H, 5-*H*), 4.08 (s, 6H, OCH₃) p.p.m.. IR (KBr): ν (cm⁻¹) = 2993, 2951, 1562, 1485, 1461, 1442, 1301, 1272, 1014, 817, 762. MS (EI): *m/z* (%) = 244 (100) [*M*]⁺, 136 (66) [*M*-PyrOMe]⁺, 108 (77) [*M*-NNPyrOMe]⁺. MS (CI): *m/z* (%) = 245 (100) [*M*+H]⁺. Anal. Calc.: C₁₂H₁₂N₄O₂ (244.10), ber. C 59.01, H 4.95, N 22.94, gef. C 59.72, H 4.58, N 22.64%.

S3. Refinement

All H atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for aromatic H atoms (1.5 for methyl H atoms) using a riding model.

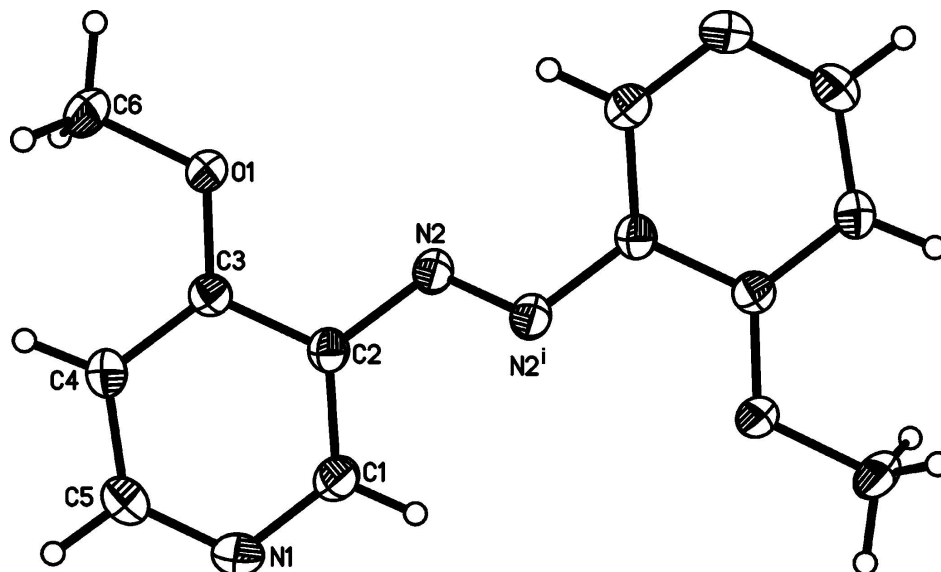


Figure 1

Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: $i = -x + 1, -y + 2, -z + 1$.

Bis(4-methoxyphenyl)diazene

Crystal data

$C_{12}H_{12}N_4O_2$
 $M_r = 244.26$
 Orthorhombic, *Pbca*
 $a = 13.3976$ (8) Å
 $b = 6.2101$ (6) Å
 $c = 13.6079$ (9) Å
 $V = 1132.18$ (15) Å³
 $Z = 4$
 $F(000) = 512$

Data collection

Stoe IPDS-1
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Phi scans
 5829 measured reflections
 1235 independent reflections

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.105$
 $S = 1.04$
 1235 reflections
 84 parameters
 0 restraints

$D_x = 1.433$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 4972 reflections
 $\theta = 4.7$ – 28.8°
 $\mu = 0.10$ mm⁻¹
 $T = 220$ K
 Block, colourless
 $0.3 \times 0.2 \times 0.2$ mm

1002 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.045$
 $\theta_{max} = 27.1^\circ$, $\theta_{min} = 3.0^\circ$
 $h = -17 \rightarrow 12$
 $k = -7 \rightarrow 7$
 $l = -17 \rightarrow 17$

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.204P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.030 (8)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.66974 (9)	0.6358 (2)	0.34371 (9)	0.0314 (3)
C1	0.62249 (10)	0.7907 (2)	0.39360 (9)	0.0263 (3)
H1	0.6591	0.9134	0.4119	0.032*
C2	0.52211 (9)	0.7811 (2)	0.42010 (8)	0.0211 (3)
C3	0.46546 (10)	0.60269 (19)	0.38987 (8)	0.0205 (3)
C4	0.51423 (10)	0.4414 (2)	0.33786 (9)	0.0250 (3)
H4	0.4794	0.3190	0.3161	0.030*
C5	0.61506 (11)	0.4644 (2)	0.31870 (10)	0.0301 (3)
H5	0.6475	0.3513	0.2857	0.036*
N2	0.47208 (8)	0.94965 (17)	0.47068 (7)	0.0228 (3)
O1	0.36924 (7)	0.60036 (15)	0.41627 (7)	0.0277 (3)
C6	0.30947 (11)	0.4230 (2)	0.38338 (11)	0.0321 (4)
H6A	0.3032	0.4284	0.3124	0.048*
H6B	0.2438	0.4320	0.4130	0.048*
H6C	0.3410	0.2888	0.4024	0.048*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0230 (6)	0.0348 (6)	0.0364 (7)	−0.0008 (5)	0.0067 (5)	−0.0042 (5)
C1	0.0237 (7)	0.0271 (7)	0.0280 (6)	−0.0044 (5)	0.0010 (5)	−0.0020 (5)
C2	0.0227 (6)	0.0202 (6)	0.0203 (5)	0.0000 (5)	−0.0014 (4)	−0.0006 (4)
C3	0.0200 (6)	0.0208 (6)	0.0205 (6)	0.0011 (5)	−0.0014 (4)	0.0011 (4)
C4	0.0273 (7)	0.0216 (6)	0.0261 (6)	−0.0009 (5)	−0.0004 (5)	−0.0045 (5)
C5	0.0292 (7)	0.0283 (7)	0.0329 (7)	0.0039 (6)	0.0052 (5)	−0.0058 (5)
N2	0.0231 (5)	0.0202 (5)	0.0251 (5)	−0.0017 (4)	−0.0012 (4)	−0.0022 (4)
O1	0.0193 (5)	0.0241 (5)	0.0396 (6)	−0.0030 (4)	0.0020 (4)	−0.0086 (4)
C6	0.0230 (7)	0.0288 (7)	0.0444 (8)	−0.0068 (6)	−0.0037 (6)	−0.0068 (6)

Geometric parameters (Å, °)

N1—C5	1.3360 (19)	C4—C5	1.3832 (19)
N1—C1	1.3369 (18)	C4—H4	0.9400
C1—C2	1.3936 (18)	C5—H5	0.9400
C1—H1	0.9400	N2—N2 ⁱ	1.260 (2)
C2—C3	1.4044 (17)	O1—C6	1.4333 (16)
C2—N2	1.4209 (16)	C6—H6A	0.9700
C3—O1	1.3384 (16)	C6—H6B	0.9700
C3—C4	1.3897 (17)	C6—H6C	0.9700
C5—N1—C1	116.29 (12)	C3—C4—H4	120.6
N1—C1—C2	123.89 (12)	N1—C5—C4	124.74 (13)
N1—C1—H1	118.1	N1—C5—H5	117.6
C2—C1—H1	118.1	C4—C5—H5	117.6
C1—C2—C3	118.65 (11)	N2 ⁱ —N2—C2	113.10 (14)
C1—C2—N2	123.30 (11)	C3—O1—C6	117.56 (10)
C3—C2—N2	117.91 (11)	O1—C6—H6A	109.5
O1—C3—C4	125.58 (11)	O1—C6—H6B	109.5
O1—C3—C2	116.77 (11)	H6A—C6—H6B	109.5
C4—C3—C2	117.62 (12)	O1—C6—H6C	109.5
C5—C4—C3	118.73 (12)	H6A—C6—H6C	109.5
C5—C4—H4	120.6	H6B—C6—H6C	109.5

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