Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(E)-1,2-Bis(5-chloro-6-methylpyridin-2-yl)diazene

Mustafa Odabaşoğlu,[a]* Figen Arslan,[a] Halis Ölmez[a] and Orhan Büyükgüngör[b]

[a]Department of Chemistry, Faculty of Arts and Science, Ondokuz Mayıs University, TR-55139 Kurupelit Samsun, Turkey, and [b]Department of Physics, Faculty of Arts and Science, Ondokuz Mayıs University, TR-55139 Kurupelit Samsun, Turkey
Correspondence e-mail: muodabas@omu.edu.tr

Received 10 July 2007; accepted 27 July 2007

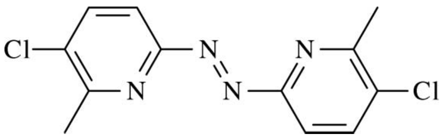
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.053; wR factor = 0.171; data-to-parameter ratio = 18.1.

The structure of the centrosymmetric title compound, $C_{12}H_{10}Cl_2N_4$, is stabilized by C—Cl$\cdots\pi$ and π–π interactions. The C—Cl$\cdots\pi$ interactions result in a zigzag chain. The Cl$\cdots\pi$ chains are connected by π–π interactions and generate Cl$\cdots\pi$ and π–π interacting rings. The π–π interaction occurs between the pyridyl rings of the molecules lying about inversion centres; the centroid–centroid distance is 3.7130 (14) Å and the plane–plane separation is 3.563 Å.

Related literature

For literature on the chemistry of azoaromatic compounds, see: Camalli *et al.* (1990); Hartmann *et al.* (2000); Wong *et al.* (2000); Frantz *et al.* (2003); Baldwin *et al.* (1969). For a recent report on the structures of some pyridyldiazene derivatives, see: Arslan *et al.* (2006).

For related literature, see: Rivarola *et al.* (1985); Sarma & Desiraju (1986).



Experimental

Crystal data

$C_{12}H_{10}Cl_2N_4$
M_r = 281.14
Orthorhombic, *Pbca*
a = 7.9501 (7) Å
b = 11.4298 (9) Å
c = 13.9491 (12) Å
V = 1267.53 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.50 mm^{-1}
T = 296 (1) K
0.65 × 0.37 × 0.18 mm

Data collection

Stoe IPDS2 diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.807, T_{max} = 0.930
7309 measured reflections
1500 independent reflections
1253 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.171
S = 1.09
1500 reflections
83 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—Cl1$\cdots Cg1^{i}$	1.72 (1)	3.46 (1)	4.720 (3)	128 (1)

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDSII diffractometer (purchased under grant No. F279 of the University Research Fund).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2018).

References

Arslan, F., Ölmez, H., Bulut, A., Odabaşoğlu, M. & Büyükgüngör, O. (2006). *Z. Anorg. Allg. Chem.* **632**, 1606–1609.
Baldwin, D. A. P., Lever, A. B. & Parish, R. V. (1969). *Inorg. Chem.* **8**, 107–111.
Camalli, M., Caruso, F., Mattogno, G. & Rivarola, E. (1990). *Inorg. Chim. Acta*, **170**, 225–227.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Frantz, S., Reinhardt, R., Greulich, S., Wanner, M., Fiedler, J., Duboc-Toia, C. & Kaim, W. (2003). *Dalton Trans.* pp. 3370–3375.
Hartmann, H., Scheiring, T., Fiedler, J. & Kaim, W. (2000). *J. Organomet. Chem.* **604**, 267–272.
Rivarola, E., Silvestri, A., Alonzo, G. & Barbieri, R. (1985). *Inorg. Chim. Acta*, **99**, 87–93.
Sarma, J. A. R. P. & Desiraju, G. R. (1986). *Acc. Chem. Res.* **19**, 222–228.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
Wong, W. Y., Cheung, S. H., Lee, S. M. & Leung, S. T. Y. (2000). *J. Organomet. Chem.* **596**, 36–41.

doi:10.1107/S1600536807036793

supplementary materials

Acta Cryst. (2007). E**63**, o3654   [**doi:10.1107/S1600536807036793**]

(*E*)-1,2-Bis(5-chloro-6-methylpyridin-2-yl)diazene

M. Odabasoglu, F. Arslan, H. Ölmez and **O. Büyükgüngör**

Comment

Organic compounds bearing aromatic group Lewis base functionalities are well known to form adducts with halogens (Cl, Br, I). The key interaction involves charge injection from π of electrons of the Lewis base to the σ* orbital of the halogen species, producing a three-centred bond. The Cl atom is a well known steering group in crystal engineering (Sarma & Desiraju, 1986). The motivation for understanding these interactions arises from their potential importance in generating supramolecular architectures for the design of molecular solids with novel properties. Organic molecules with such characteristics provide an excellent means of exploring the roles of nonconventional intermolecular forces in crystal engineering and supramolecular chemistry. Against this background, we report here the crystal structure of (*E*)-1,2-bis(5-chloro-6-methylpyridin-2-yl)diazene, (I).

Fig. 1 shows the structure of the title compound, with the atom-numbering scheme. The molecules of (I) are linked to each other by C—Cl···π and π–π interactions (Fig. 2); C—Cl···π interactions [Cl···(pyridyl centroid) = 3.460 (3) Å and 127.91 (3)°] resulting in a zigzag chain. The Cl···π chains are connected by π–π interactions and generate C—Cl···π and π–π interactions rings. The π–π interaction occurs between the pyridyl rings of the molecules related by inversion centers; details have been provided in Table 1.

Experimental

(*E*)-1,2-bis(5-chloro-6-methylpyridin-2-yl)diazene was prepared according to the method of Rivarola *et al.* (1985). The product was crystallized from n-hexane: n-heptane mixture (1:1/v:v) to obtain well shaped crystals (yield 17%; m.p. 387–391 K).

Refinement

All C-bound H atoms were refined using the riding model approximation with d(C—H) = 0.93 for aromatic and d(C—H) = 0.96 for methyl C—H [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom)].

Figures

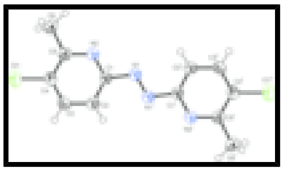


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) −*x*, −*y*, −*z*].

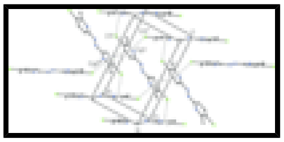


Fig. 2. Part of the crystal structure of (I), showing the formation of C—Cl···π and π–π interactions rings. H atoms not involved in intermolecular interactions have been ommited for clarity. [Symmetry codes: (i) *x* + 1/2, *y*, 3/2 − *z*; (ii) 2 − *x*, 1 − *y*, 1 − *z*].

(*E*)-1,2-Bis(5-chloro-6-methylpyridin-2-yl)diazene

Crystal data

$C_{12}H_{10}Cl_2N_4$

M_r = 281.14

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

a = 7.9501 (7) Å

b = 11.4298 (9) Å

c = 13.9491 (12) Å

V = 1267.53 (19) Å^3

Z = 4

F_{000} = 576

D_x = 1.473 Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 7309 reflections

θ = 2.3–28.0°

μ = 0.50 mm^{-1}

T = 296 (1) K

Prism, orange

0.65 × 0.37 × 0.18 mm

Data collection

Stoe IPDS2
diffractometer

Monochromator: plane graphite

Detector resolution: 6.67 pixels mm^{-1}

T = 296(1) K

ω scans

Absorption correction: integration
(X-RED; Stoe & Cie, 2002)

T_{min} = 0.807, T_{max} = 0.930

7309 measured reflections

1500 independent reflections

1253 reflections with $I > 2\sigma(I)$

R_{int} = 0.039

θ_{max} = 27.9°

θ_{min} = 2.9°

h = −10→10

k = −13→14

l = −15→18

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.053

$wR(F^2)$ = 0.171

S = 1.09

1500 reflections

83 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.1012P)^2 + 0.5449P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max}$ = 0.31 e Å^{-3}

$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N2	0.7882 (2)	0.42313 (17)	0.60026 (15)	0.0398 (5)
C4	0.9971 (3)	0.5649 (2)	0.63185 (17)	0.0389 (5)
N1	0.5405 (2)	0.46417 (17)	0.52351 (16)	0.0417 (5)
C1	0.6977 (3)	0.5070 (2)	0.55861 (17)	0.0366 (5)
C5	0.9378 (3)	0.4508 (2)	0.63723 (18)	0.0396 (5)
C2	0.7482 (3)	0.6226 (2)	0.55239 (19)	0.0426 (5)
H2	0.6800	0.6787	0.5238	0.051*
C3	0.9029 (3)	0.6515 (2)	0.59006 (19)	0.0433 (6)
H3	0.9424	0.7280	0.5872	0.052*
C6	1.0332 (4)	0.3545 (3)	0.6847 (2)	0.0609 (8)
H6A	0.9765	0.2815	0.6741	0.091*
H6B	1.0400	0.3695	0.7523	0.091*
H6C	1.1446	0.3505	0.6583	0.091*
Cl1	1.19168 (9)	0.59937 (7)	0.67861 (6)	0.0629 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0387 (9)	0.0335 (9)	0.0471 (11)	−0.0002 (7)	−0.0045 (8)	0.0049 (8)
C4	0.0348 (10)	0.0412 (12)	0.0407 (12)	−0.0024 (8)	0.0011 (8)	−0.0029 (9)
N1	0.0361 (9)	0.0356 (9)	0.0533 (12)	−0.0005 (7)	−0.0045 (8)	0.0044 (8)
C1	0.0340 (10)	0.0337 (11)	0.0421 (11)	0.0009 (8)	0.0002 (8)	0.0023 (9)
C5	0.0394 (11)	0.0372 (11)	0.0424 (12)	0.0036 (9)	−0.0028 (9)	0.0007 (9)
C2	0.0415 (11)	0.0325 (10)	0.0538 (13)	0.0026 (9)	−0.0040 (10)	0.0055 (10)
C3	0.0426 (11)	0.0342 (11)	0.0530 (14)	−0.0054 (9)	0.0008 (10)	0.0005 (10)
C6	0.0608 (16)	0.0467 (15)	0.075 (2)	0.0043 (12)	−0.0245 (14)	0.0109 (14)
Cl1	0.0486 (4)	0.0658 (5)	0.0744 (6)	−0.0092 (3)	−0.0149 (3)	−0.0042 (4)

Geometric parameters (Å, °)

N2—C1	1.331 (3)	C5—C6	1.492 (3)
N2—C5	1.334 (3)	C2—C3	1.378 (3)
C4—C3	1.372 (3)	C2—H2	0.9300
C4—C5	1.389 (3)	C3—H3	0.9300
C4—Cl1	1.724 (2)	C6—H6A	0.9600
N1—N1^{i}	1.231 (4)	C6—H6B	0.9600
N1—C1	1.429 (3)	C6—H6C	0.9600

C1—C2	1.383 (3)

C1—N2—C5	118.6 (2)	C3—C2—H2	121.2
C3—C4—C5	121.0 (2)	C1—C2—H2	121.2
C3—C4—Cl1	119.07 (19)	C4—C3—C2	118.4 (2)
C5—C4—Cl1	119.92 (19)	C4—C3—H3	120.8
N1^{i}—N1—C1	114.4 (2)	C2—C3—H3	120.8
N2—C1—C2	123.9 (2)	C5—C6—H6A	109.5
N2—C1—N1	112.04 (19)	C5—C6—H6B	109.5
C2—C1—N1	124.0 (2)	H6A—C6—H6B	109.5
N2—C5—C4	120.3 (2)	C5—C6—H6C	109.5
N2—C5—C6	116.8 (2)	H6A—C6—H6C	109.5
C4—C5—C6	122.9 (2)	H6B—C6—H6C	109.5
C3—C2—C1	117.7 (2)		

C5—N2—C1—C2	−1.0 (4)	C3—C4—C5—C6	−178.0 (3)
C5—N2—C1—N1	−179.4 (2)	Cl1—C4—C5—C6	1.8 (4)
N1^{i}—N1—C1—N2	−173.5 (3)	N2—C1—C2—C3	1.3 (4)
N1^{i}—N1—C1—C2	8.1 (4)	N1—C1—C2—C3	179.5 (2)
C1—N2—C5—C4	−0.1 (4)	C5—C4—C3—C2	−0.7 (4)
C1—N2—C5—C6	178.9 (2)	Cl1—C4—C3—C2	179.5 (2)
C3—C4—C5—N2	1.0 (4)	C1—C2—C3—C4	−0.4 (4)
Cl1—C4—C5—N2	−179.26 (19)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—Cl1···Cg1^{ii}	1.724 (2)	3.460 (3)	4.720 (3)	127.91 (3)

Symmetry codes: (ii) −*x*+1/2, *y*−3/2, *z*.

Fig. 1

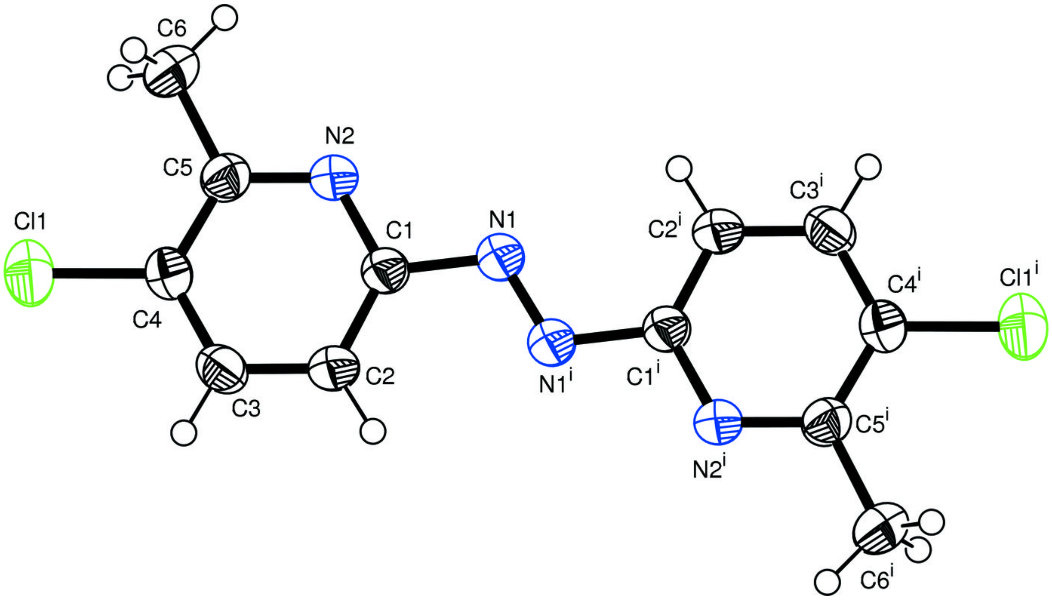


Fig. 2