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2,8-Dichloro-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine

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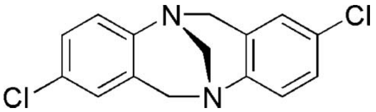
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.077; data-to-parameter ratio = 17.7.

In the molecule of the title compound, $C_{15}H_{12}Cl_2N_2$, the 2,8-dichloro analogue of Tröger's base, the two aryl rings are offset with respect to one another by virtue of the diazocine bridge. The dihedral angle between the two benzene rings is 95.64 (3)°.

Related literature

For general background, see: Prelog & Wieland (1944); Allen *et al.* (1987); Cremer & Pople (1975); Jensen & Wärnmark (2001). For related literature, see: Solano *et al.* (2005); Faroughi *et al.* (2006*a*,*b*).



Experimental

Crystal data

$C_{15}H_{12}Cl_2N_2$
M_r = 291.17
Triclinic, $P\bar{1}$
a = 6.3017 (18) Å
b = 10.203 (3) Å
c = 10.685 (3) Å
α = 83.059 (5)°
β = 77.303 (4)°
γ = 80.297 (5)°
V = 658.1 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 150 (2) K
0.40 × 0.30 × 0.25 mm

Data collection

Siemens SMART 1000 CCD diffractometer
Absorption correction: Gaussian [*GAUSSIAN* (Coppens *et al.*, 1965) and *XPREP* (Siemens, 1995)]
T_{min} = 0.838, T_{max} = 0.887
6481 measured reflections
3041 independent reflections
2845 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.077
S = 1.07
3041 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN for Windows* (Molecular Structure Corporation, 1998), *Xtal*3.6 (Hall *et al.*, 1999), *ORTEPII* (Johnson, 1976) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2235).

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supplementary materials

Acta Cryst. (2007). E**63**, o2695   [**doi:10.1107/S1600536807019496**]

2,8-Dichloro-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine

M. Faroughi, **A. C. Try** and **P. Turner**

Comment

Tröger's base was the first chiral compound to be successfully resolved whose optical activity was the result of stereogenic tertiary nitrogen centres. This resolution was achieved through what may have been the first example of a chiral separation using chromatography with a chiral stationary phase (Prelog & Wieland, 1944). An important feature of this family of molecules is the

diazocine bridge that imparts a twist within the compounds such that the two aryl rings are offset with respect to one another. The angle made by the intersection of two least squares planes (as defined by the aryl rings) is referred to as the dihedral angle. This dihedral angle has been measured across a range of compounds to lie between 82° (Solano *et al.*, 2005) and 108.44 (4)° (Faroughi *et al.*, 2006*b*) for simple dibenzo Tröger's base analogues, and is dependent upon the nature of the substituents on the aromatic rings. We have previously reported that the dihedral angle in 2,8-dibromo Tröger's base is 94.45 (4)° (Faroughi *et al.*, 2006*a*) and now report that the title compound, (I), has a very similar structure.

We were interested in preparing a range of dihalo Tröger's base analogues as precursors for supramolecular recognition elements. The synthesis of (I) in racemic form was achieved by reacting 4-chloroaniline with paraformaldehyde in trifluoroacetic acid (TFA).

In the molecule of the title compound, (I), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Rings B (N1/N2/C1/C6/C7/C15) and C (N1/N2/C8/C13—C15) are not planar, having total puckering amplitudes, Q_T, of 1.376 (3) and 0.741 (3) Å, respectively and twist conformations φ = -115.97 (3)°, θ = 108.20 (2)° and φ = -31.28 (3)°, θ = 48.67 (3)° (Cremer & Pople, 1975). Rings A (C1—C6) and D (C8—C13) are, of course, planar and the dihedral angle between them is 95.64 (3)°.

Experimental

The title compound was prepared according to a literature procedure (Jensen & Wärnmark, 2001) in 87% yield and recrystallized from chloroform solution.

Refinement

H atoms were positioned geometrically, with C—H = 0.95 and 0.99 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

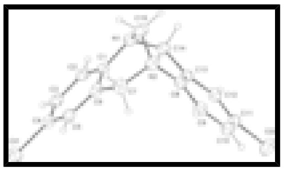


Fig. 1. The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

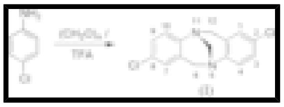


Fig. 2. Reaction scheme.

2,8-Dichloro-6*H*,12*H*-5,11- methanodibenzo[*b*,*f*][1,5]diazocine

Crystal data

$C_{15}H_{12}Cl_2N_2$

$M_r = 291.17$

Triclinic, $P\overline{1}$

Hall symbol: -P 1

$a = 6.3017$ (18) Å

$b = 10.203$ (3) Å

$c = 10.685$ (3) Å

$\alpha = 83.059$ (5)°

$\beta = 77.303$ (4)°

$\gamma = 80.297$ (5)°

$V = 658.1$ (3) Å^3

$Z = 2$

$F_{000} = 300$

$D_x = 1.469$ Mg m^{-3}

Melting point: 402.49 K

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 868 reflections

$\theta = 2.7$–28.3°

$\mu = 0.48$ mm^{-1}

$T = 150$ (2) K

Prism, colorless

0.40 × 0.30 × 0.25 mm

Data collection

Siemens SMART 1000 CCD diffractometer

Radiation source: sealed tube

Monochromator: graphite

$T = 150(2)$ K

ω scans

Absorption correction: gaussian [GAUSSIAN (Coppens *et al.*, 1965) and XPREP (Siemens, 1995)]

$T_{min} = 0.838$, $T_{max} = 0.887$

6481 measured reflections

3041 independent reflections

2845 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$

$\theta_{max} = 28.3$°

$\theta_{min} = 2.0$°

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 13$

$l = -13 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.3P]$
where $P = (F_o^2 + 2F_c^2)/3$

$R[F^2 > 2\sigma(F^2)] = 0.030$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.077$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
$S = 1.07$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
3041 reflections	Extinction correction: none
172 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 > 2sigma(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*	$U_{iso}*/U_{eq}$
Cl1	0.13871 (6)	0.53475 (3)	−0.23138 (3)	0.03051 (10)
Cl2	−0.36576 (6)	0.31732 (4)	0.63832 (3)	0.03694 (11)
N1	0.21497 (17)	0.04929 (10)	0.13464 (10)	0.0225 (2)
N2	0.43312 (17)	0.15300 (11)	0.24498 (10)	0.0237 (2)
C1	0.19385 (19)	0.16949 (12)	0.05035 (11)	0.0202 (2)
C2	0.0451 (2)	0.18494 (12)	−0.03192 (12)	0.0223 (2)
H2	−0.0435	0.1174	−0.0287	0.027*
C3	0.0246 (2)	0.29694 (12)	−0.11795 (12)	0.0235 (2)
H3	−0.0790	0.3076	−0.1723	0.028*
C4	0.1586 (2)	0.39335 (12)	−0.12326 (11)	0.0231 (2)
C5	0.3063 (2)	0.38015 (13)	−0.04268 (12)	0.0244 (2)
H5	0.3972	0.4469	−0.0483	0.029*
C6	0.32302 (19)	0.26959 (12)	0.04676 (11)	0.0216 (2)
C7	0.4719 (2)	0.26153 (14)	0.14220 (12)	0.0257 (3)
H7A	0.6272	0.2467	0.0961	0.031*
H7B	0.4461	0.3475	0.1812	0.031*
C8	0.2378 (2)	0.18853 (12)	0.33978 (11)	0.0210 (2)
C9	0.2439 (2)	0.27932 (13)	0.42655 (12)	0.0247 (3)
H9	0.3760	0.3145	0.4222	0.030*
C10	0.0598 (2)	0.31846 (13)	0.51862 (12)	0.0264 (3)
H10	0.0639	0.3807	0.5770	0.032*
C11	−0.1310 (2)	0.26523 (13)	0.52427 (12)	0.0253 (3)

C12	−0.1417 (2)	0.17465 (12)	0.44002 (12)	0.0236 (2)
H12	−0.2736	0.1387	0.4463	0.028*
C13	0.0435 (2)	0.13667 (11)	0.34567 (11)	0.0206 (2)
C14	0.0297 (2)	0.04557 (12)	0.24619 (12)	0.0227 (2)
H14A	0.0304	−0.0471	0.2865	0.027*
H14B	−0.1104	0.0735	0.2163	0.027*
C15	0.4179 (2)	0.03436 (13)	0.18434 (13)	0.0266 (3)
H15A	0.4225	−0.0444	0.2482	0.032*
H15B	0.5462	0.0184	0.1127	0.032*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.04063 (19)	0.02569 (16)	0.02488 (16)	−0.00416 (13)	−0.00813 (13)	0.00082 (12)
Cl2	0.03147 (19)	0.0498 (2)	0.02675 (17)	0.00243 (15)	−0.00157 (13)	−0.01223 (14)
N1	0.0245 (5)	0.0207 (5)	0.0233 (5)	−0.0005 (4)	−0.0072 (4)	−0.0045 (4)
N2	0.0211 (5)	0.0275 (5)	0.0236 (5)	−0.0012 (4)	−0.0071 (4)	−0.0048 (4)
C1	0.0206 (6)	0.0204 (5)	0.0190 (5)	−0.0002 (4)	−0.0023 (4)	−0.0065 (4)
C2	0.0230 (6)	0.0226 (6)	0.0226 (6)	−0.0032 (4)	−0.0047 (4)	−0.0075 (4)
C3	0.0236 (6)	0.0270 (6)	0.0209 (6)	−0.0010 (5)	−0.0062 (5)	−0.0064 (5)
C4	0.0274 (6)	0.0223 (6)	0.0180 (5)	−0.0013 (5)	−0.0027 (4)	−0.0029 (4)
C5	0.0255 (6)	0.0268 (6)	0.0222 (6)	−0.0080 (5)	−0.0027 (5)	−0.0046 (5)
C6	0.0185 (5)	0.0270 (6)	0.0198 (5)	−0.0032 (4)	−0.0023 (4)	−0.0065 (4)
C7	0.0213 (6)	0.0340 (7)	0.0236 (6)	−0.0078 (5)	−0.0051 (5)	−0.0029 (5)
C8	0.0222 (6)	0.0218 (5)	0.0198 (5)	−0.0011 (4)	−0.0079 (4)	−0.0007 (4)
C9	0.0278 (6)	0.0259 (6)	0.0232 (6)	−0.0051 (5)	−0.0106 (5)	−0.0017 (5)
C10	0.0350 (7)	0.0252 (6)	0.0207 (6)	−0.0014 (5)	−0.0101 (5)	−0.0045 (5)
C11	0.0278 (6)	0.0278 (6)	0.0179 (5)	0.0018 (5)	−0.0044 (5)	−0.0016 (5)
C12	0.0242 (6)	0.0250 (6)	0.0216 (6)	−0.0041 (5)	−0.0066 (5)	0.0016 (5)
C13	0.0246 (6)	0.0187 (5)	0.0194 (5)	−0.0024 (4)	−0.0079 (4)	−0.0001 (4)
C14	0.0266 (6)	0.0205 (5)	0.0229 (6)	−0.0055 (5)	−0.0072 (5)	−0.0026 (4)
C15	0.0251 (6)	0.0259 (6)	0.0291 (6)	0.0038 (5)	−0.0094 (5)	−0.0072 (5)

Geometric parameters (Å, °)

Cl1—C4	1.7411 (13)	C6—C7	1.5170 (17)
Cl2—C11	1.7477 (13)	C7—H7A	0.9900
N1—C1	1.4366 (16)	C7—H7B	0.9900
N1—C15	1.4678 (17)	C8—C9	1.3981 (17)
N1—C14	1.4754 (16)	C8—C13	1.3997 (17)
N2—C8	1.4362 (16)	C9—C10	1.3821 (19)
N2—C15	1.4663 (16)	C9—H9	0.9500
N2—C7	1.4736 (17)	C10—C11	1.388 (2)
C1—C2	1.3983 (17)	C10—H10	0.9500
C1—C6	1.4014 (17)	C11—C12	1.3847 (18)
C2—C3	1.3841 (18)	C12—C13	1.3975 (17)
C2—H2	0.9500	C12—H12	0.9500
C3—C4	1.3888 (18)	C13—C14	1.5191 (16)
C3—H3	0.9500	C14—H14A	0.9900

C4—C5	1.3813 (18)	C14—H14B	0.9900
C5—C6	1.3930 (18)	C15—H15A	0.9900
C5—H5	0.9500	C15—H15B	0.9900

C1—N1—C15	110.57 (10)	C9—C8—C13	119.88 (11)
C1—N1—C14	112.99 (9)	C9—C8—N2	118.21 (11)
C15—N1—C14	107.69 (10)	C13—C8—N2	121.90 (11)
C8—N2—C15	111.00 (10)	C10—C9—C8	120.66 (12)
C8—N2—C7	111.85 (10)	C10—C9—H9	119.7
C15—N2—C7	107.72 (10)	C8—C9—H9	119.7
C2—C1—C6	119.56 (11)	C9—C10—C11	118.88 (12)
C2—C1—N1	119.08 (11)	C9—C10—H10	120.6
C6—C1—N1	121.34 (11)	C11—C10—H10	120.6
C3—C2—C1	121.12 (11)	C12—C11—C10	121.75 (12)
C3—C2—H2	119.4	C12—C11—Cl2	119.29 (10)
C1—C2—H2	119.4	C10—C11—Cl2	118.95 (10)
C2—C3—C4	118.68 (12)	C11—C12—C13	119.36 (12)
C2—C3—H3	120.7	C11—C12—H12	120.3
C4—C3—H3	120.7	C13—C12—H12	120.3
C5—C4—C3	121.10 (12)	C12—C13—C8	119.47 (11)
C5—C4—Cl1	119.04 (10)	C12—C13—C14	120.04 (11)
C3—C4—Cl1	119.85 (10)	C8—C13—C14	120.41 (11)
C4—C5—C6	120.48 (12)	N1—C14—C13	111.62 (10)
C4—C5—H5	119.8	N1—C14—H14A	109.3
C6—C5—H5	119.8	C13—C14—H14A	109.3
C5—C6—C1	118.99 (11)	N1—C14—H14B	109.3
C5—C6—C7	120.05 (11)	C13—C14—H14B	109.3
C1—C6—C7	120.90 (11)	H14A—C14—H14B	108.0
N2—C7—C6	111.91 (10)	N2—C15—N1	111.81 (10)
N2—C7—H7A	109.2	N2—C15—H15A	109.3
C6—C7—H7A	109.2	N1—C15—H15A	109.3
N2—C7—H7B	109.2	N2—C15—H15B	109.3
C6—C7—H7B	109.2	N1—C15—H15B	109.3
H7A—C7—H7B	107.9	H15A—C15—H15B	107.9

C15—N1—C1—C2	163.66 (10)	C15—N2—C8—C13	−15.32 (15)
C14—N1—C1—C2	−75.55 (13)	C7—N2—C8—C13	105.03 (13)
C15—N1—C1—C6	−14.71 (15)	C13—C8—C9—C10	0.13 (18)
C14—N1—C1—C6	106.08 (12)	N2—C8—C9—C10	179.10 (11)
C6—C1—C2—C3	0.66 (17)	C8—C9—C10—C11	0.54 (19)
N1—C1—C2—C3	−177.73 (10)	C9—C10—C11—C12	−0.22 (19)
C1—C2—C3—C4	1.33 (18)	C9—C10—C11—Cl2	−178.62 (10)
C2—C3—C4—C5	−1.45 (18)	C10—C11—C12—C13	−0.75 (19)
C2—C3—C4—Cl1	179.45 (9)	Cl2—C11—C12—C13	177.65 (9)
C3—C4—C5—C6	−0.44 (19)	C11—C12—C13—C8	1.40 (18)
Cl1—C4—C5—C6	178.66 (9)	C11—C12—C13—C14	−175.40 (11)
C4—C5—C6—C1	2.44 (18)	C9—C8—C13—C12	−1.10 (17)
C4—C5—C6—C7	−174.95 (11)	N2—C8—C13—C12	179.97 (11)
C2—C1—C6—C5	−2.54 (17)	C9—C8—C13—C14	175.69 (11)
N1—C1—C6—C5	175.82 (10)	N2—C8—C13—C14	−3.24 (17)

C2—C1—C6—C7	174.83 (11)	C1—N1—C14—C13	−74.78 (13)
N1—C1—C6—C7	−6.81 (17)	C15—N1—C14—C13	47.63 (13)
C8—N2—C7—C6	−77.31 (13)	C12—C13—C14—N1	162.98 (10)
C15—N2—C7—C6	44.93 (13)	C8—C13—C14—N1	−13.79 (15)
C5—C6—C7—N2	168.04 (11)	C8—N2—C15—N1	52.32 (14)
C1—C6—C7—N2	−9.29 (16)	C7—N2—C15—N1	−70.44 (13)
C15—N2—C8—C9	165.73 (11)	C1—N1—C15—N2	53.76 (14)
C7—N2—C8—C9	−73.93 (14)	C14—N1—C15—N2	−70.13 (13)

Fig. 1

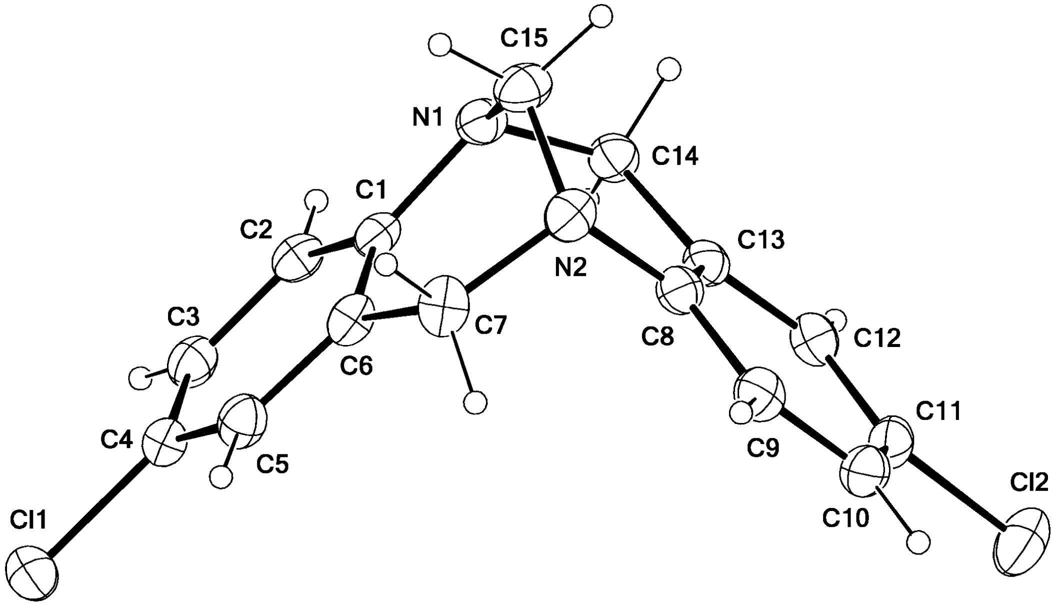
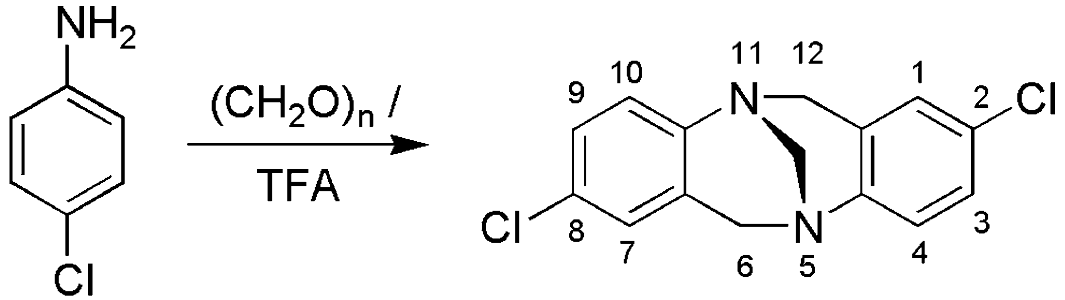


Fig. 2



(I)