4,4′-Bis(2,6-dichlorobenzylideneamino)biphenyl

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The title molecule, $C_{26}H_{16}Cl_4N_2$, lies on a crystallographic inversion centre and is disordered. The dihedral angle between the two benzene rings of the central biphenyl unit is 34.4 (3)°. The unique benzene ring of the biphenyl group is essentially coplanar with the –C(H)=N– unit, whereas the 2,6-dichlorophenyl substituent is twisted with respect to it. The reason for the twisted conformation is attributed to steric crowding by the Cl atoms.

Comment

Primary amines condense with an abundance of aldehydes and ketones to form Schiff bases. Of the large number of derivatives of diamines whose crystal structures have been determined to date, as noted from the Cambridge Structural Database (Version 5.27; Allen, 2002), those of 4,4′-diaminobiphenyl are limited to 3,3′-dimethoxy-4,4′-(2-hydroxybenzylideneamino)biphenyl (Aygun et al., 2004) 2,2′-dibromo-4,4′-bis(4-methoxybenzylideneamino)biphenyl (Lesser et al., 1975) and 4,4′-bis(2-hydroxybenzylideneamino)biphenyl (Mishra et al., 2002). The condensation of 4,4′-diaminobiphenyl with 2,6-dichlorobenzaldehyde affords the expected title compound, (I). However, owing to the steric crowding by the Cl substituents, the crystal structure of (I) exhibits disorder (Fig. 1). The biphenyl entity assumes two orientations, as does the aromatic ring of the 2,6-dichlorobenzaldehyde group [dihedral angle between unprimed ring and the N1/C7/C8 fragment = 54.2 (4)° and that between the primed ring and the N1/C7′/C8′ fragment = 64.5 (7)°; the unprimed and primed C atoms refer to the disordered atoms of the ring]. Crowding by the Cl atoms probably contributes to the large dihedral angles in this unit (and, consequently, to a loss of delocalization). There is a centre of symmetry at the mid-point of the central C—C bond.

(I)
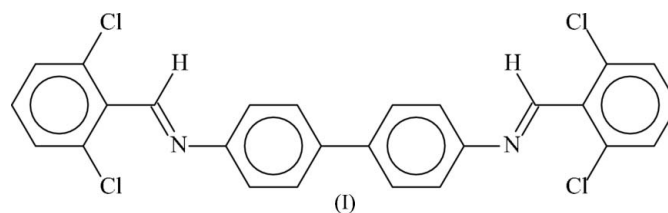
In other Schiff bases that are derived from 2,6-dichlorobenzaldehyde, the aromatic ring of the aldehydic unit is similarly twisted with respect to the –C=N– unit; this feature is observed in the camphordiamine (Busacca et al., 2000) and 6,6′-dimethylbiphenyl-2,2′-diamine (Gillespie et al., 2002) derivatives.
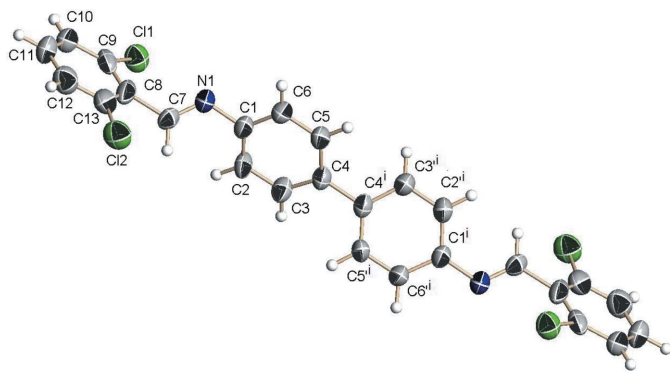
Figure 1
A plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. One of the two disordered components is shown. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

Experimental

Benzidine (1 mmol, 0.184 g) dissolved in a small volume of methanol was reacted with 2,6-dichlorobenzaldehyde (2 mmol, 0.35g) which was also dissolved in methanol. The solution was stirred for 2 h, and the colourless product that separated was collected and recrystallized from dichloromethane.

Crystal data

$C_{26}H_{16}Cl_4N_2$	$Z = 2$
$M_r = 498.21$	$D_x = 1.449$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.7801$ (3) Å	$\mu = 0.54$ mm^{-1}
$b = 10.9874$ (6) Å	$T = 291$ (2) K
$c = 21.778$ (1) Å	Block, colourless
$\beta = 93.230$ (1)°	$0.36 \times 0.25 \times 0.13$ mm
$V = 1142.0$ (1) Å^3	

Data collection

Bruker APEX area-detector diffractometer	2623 independent reflections
	1932 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.017$
Absorption correction: none	$\theta_{max} = 27.5°$
9739 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$+ 0.4894P]$
$wR(F^2) = 0.167$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2623 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
229 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	

The structure of (I) is disordered in the aromatic rings of the biphenylene and 2,6-dichlorosalicylidene systems. For the biphenylene unit, which lies on a centre of inversion, the ring is disordered over two positions about the 1,4-axis. Atoms C1 and C4 are ordered. The C—C distances were restrained to 1.39 (1) Å. Additionally, the pair of C1–C6 and C1/C2′–C6′ rings were restrained to be approximately planar. The ring in the 2,6-dichlorosalicylidene unit was refined as two regular hexagons with sides of 1.39 Å. The two C atoms were restrained in a nearly isotropic manner, and the four C—Cl distances were restrained to within 0.005 Å of each other. A tighter restraint was used to prevent a wide spread of distances. The disorder affected other atoms: the bond pair N1—C7/N1—C7′ was also similarly restrained, as was the C7—C8/C7′—C8′ bond pair. Additionally, the displacement parameters of atoms C8 and C8′ were made equal, as these atoms appeared to be most affected by the disorder. As the disorder refined to nearly 0.50:0.50, as expected for a static disorder model, it was fixed at exactly 0.50:0.50. The crystal did not appear to be twinned.

H atoms were placed in calculated positions, with C—H 0.93 Å, and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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