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C—H$\cdots\pi$, π–π and C—H$\cdots$Cl interactions in chloro-substituted Schiff bases and 4-chloro-*N*-[4-(dimethylamino)benzylidene]aniline[1]

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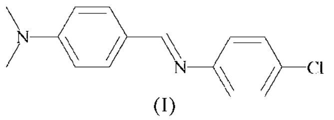
Molecular packing analyses were carried out on 15 crystal data sets of chloro-substituted Schiff bases, including that of the title compound, $C_{15}H_{15}ClN_2$. C—H$\cdots\pi$ and π–π interactions play a major role in the molecular self-assembly in the crystal. The former interactions favor molecules assembling into a screw, with a non-centrosymmetric crystal structure. When the molecular dipole is small, π–π interactions favor a parallel, but not usually antiparallel, mode of packing. Weak C—H$\cdots X$ hydrogen bonds (X = Cl or Br) and $X\cdots X$ interactions seem to be a secondary driving force in packing. The title molecule takes the *trans* form and the two benzene rings are twisted around the central linkage in opposite directions. In the crystal structure, molecules interact through C—H$\cdots\pi$ and π–π interactions, forming a 'dimer' and further forming double chains along [001]. The double chains are extended along [$10\overline{1}$] through C—H$\cdots$Cl hydrogen bonds, forming double layers in (010). In the third direction, there are only ordinary, weaker, van der Waals interactions, which explains the crystal habit (*i.e.* thin plate).

Comment

Benzylideneanilines are an important class of Schiff bases which have been widely used in coordinate, medical and biological chemistry for some time (Metzler *et al.*, 1980; Tarafder *et al.*, 2002). Recently, the thermochromism (Pistolis *et al.*, 1996), photochromism (Jalali-Heravi, 2000) and non-linear optical properties of these compounds have found applications in modern technologies (Sekikawa *et al.*, 1997). In the design of solid materials, one of the key steps is to understand how the constituent molecules are packed, what kinds of interactions play a role in crystal packing and how they interplay (Desiraju, 1989). Since any centrosymmetric crystal has no odd rank tensor property, such as SHG (second harmonic generation) and piezoelecticity, the design of non-centrosymmetric crystals is an important and difficult problem in crystal engineering. As an example, molecular packing analyses were carried out for 14 chloro-substituted Schiff bases retrieved from the Cambridge Structural Database (CSD; Allen, 2002); this class of compounds was chosen because the percentage of non-centrosymmetric space groups within the class is 57.1%, much higher than that for general organic compounds (about 25%). The crystal data of these 14 compounds are listed in Table 3.

These crystals contain no strong-hydrogen-bond-forming groups, such as –COOH, $-NH_2CO-$ or $-NO_2$; various weak interactions, such as C—H$\cdots\pi$ (Dmezawa, 1998), π–π (Sharma, 1993) and weak hydrogen-bonding interactions, and the interplay between these interactions, must therefore play an important role in determining the crystal structures.

Crystal packing analyses were carried out using *OPEC* (Gavezzotti, 1983), which was locally modified with additional calculation routines. Given a reference molecule (FM), and with the distance between interacting molecules limited to within 15 Å, the program calculated approximately 150 surrounding molecules (SM), which form the crystal model.



(I)

The main results are listed in Table 1S (supplementary material). From Table 1S, we can see the following:

(i) C—H$\cdots\pi$ interactions play a major role in controlling the molecular packing. 15 C—H$\cdots\pi$ interactions, out of 18 listed for the most important intermolecular interactions, assemble molecules into a screw, which might explain why the crystals studied are more likely to crystallize in non-centrosymmetric space groups.

(ii) π–π interactions play the same important role as the C—H$\cdots\pi$ interaction. Out of 19 listed, half of the interactions assemble the molecules in a translation-related mode, favoring a non-centrosymmetric crystal. This mode appears to occur when the molecular dipole is relatively small. When the molecular dipole is relatively large, the π–π interactions cause the molecules to pack in an antiparallel fashion into centrosymmetric crystals.

(iii) Weak interactions, such as C—H$\cdots$Cl (Thallapally & Nangia, 2001), also favor the assembling of molecules with the first kind of symmetric operators (screw 10 and translation 13 in the 27 important interactions listed), but the percentage of packing energy is relatively small.

(iv) To our surprise, the role played by X atoms (X = Cl or Br) through so-called $X\cdots X$ interactions (Desiraju, 1994) seems to be only a secondary one, perhaps because the atomic fractions are not large enough. However, the replacement of substituents like NO_2 by X atoms can also modify the properties of crystals designed for similar purposes.

During our study of the design of organic functional materials, the title compound, (I) (Fig. 1), was obtained, and

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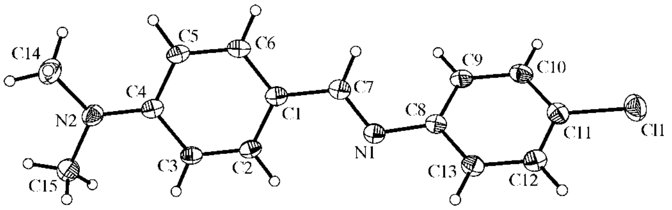

Figure 1
A view of the title molecule, showing 30% probability displacement ellipsoids.

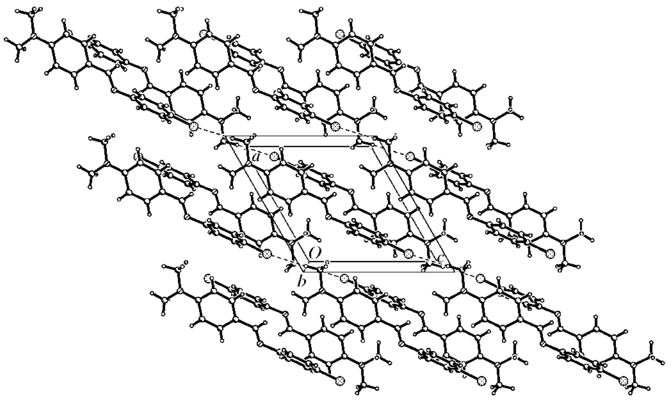

Figure 2
A packing diagram, viewed down the *b* axis.

its crystal structure is reported here. Selected geometric parameters are listed in Table 1.

The title molecule has a *trans* configuration and the C1—C7—N1—C8 (plane 3) torsion angle is 179.93 (13)°. A dihedral angle of 50.4° exists between planes 1 and 2 (plane 1 is the ring plane directly attached to atom C7 and plane 2 is the ring plane directly attached to atom N1), which are twisted in opposite directions around the central linkage, by 9.6 and 41.3° for planes 1 and 2, respectively. There are no strong-hydrogen-bond-forming groups, such as –COOH, $-NH_2CO-$, –OH or $-NO_2$, in (I), so weak interactions must play determining roles in the crystal packing (Fig. 2). The molecules that interact strongly with the FM are listed in Tables 2 and 4. As shown by these tables, molecules interact through $C-H\cdots\pi$ and π–π interactions, forming a 'dimer' and further double chains along [001]. The double chains are connected by a $C14-H14B\cdots Cl1$ hydrogen bond [3.729 (3) Å and 175°], extending along $[10\overline{1}]$, forming (010) double layers. In the third direction, there are only ordinary, weaker, van der Waals interactions, consistent with the formation of thin plates.

Experimental

To a solution of 4-(*N*,*N*-dimethylamino)benzaldehyde (10 mmol) in ethanol (10 ml), 4-chloroaniline (11 mmol) was added. The solution was refluxed for 30 min at 363 K and then cooled to ambient temperature, yielding a pale-yellow product. The product was recrystallized three times from 85% ethanol, and colorless plate-like crystals were obtained from an acetone solution by slow evaporation at ambient temperature over a period of a week. Analysis calculated for $C_{15}H_{15}ClN_2$: C 69.63, H 5.84, N 10.82%; found: C 69.73, H 5.79, N 10.84%. IR (KBr pellets, cm^{-1}): 1649, 1582, 1519, 1420, 765, 726; ^1H NMR ($CDCl_3$, 399.97 MHz): δ 3.08 [*s*, 6H, $-N(CH_3)_2$], 6.73–6.75 (*d*, 2H, Ph), 7.15 (*s*, 2H, Ph), 7.32–7.34 (*d*, 2H, Ph), 7.76 (*s*, 2H, Ph), 8.28 (*s*, 1H, –CH=N–).

Crystal data

$C_{15}H_{15}ClN_2$
$M_r = 258.74$
Monoclinic, $P2_1/c$
$a = 9.852\ (6)$ Å
$b = 16.268\ (9)$ Å
$c = 9.512\ (6)$ Å
$\beta = 119.904\ (6)^\circ$
$V = 1321.5\ (14)$ Å^3
$Z = 4$

$D_x = 1.301$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3935 reflections
$\theta = 3.5$–27.5°
$\mu = 0.27$ mm^{-1}
$T = 193\ (2)$ K
Thin plate, colorless
0.70 × 0.70 × 0.30 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.832$, $T_{max} = 0.923$
10 180 measured reflections

2956 independent reflections
2773 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5^\circ$
$h = -12 \rightarrow 12$
$k = -21 \rightarrow 17$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.143$
$S = 1.16$
2956 reflections
166 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2 + 0.3993P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C11	1.744 (2)	N2—C14	1.445 (3)
N1—C7	1.280 (2)	N2—C15	1.445 (3)
N1—C8	1.415 (2)	C1—C7	1.452 (2)
N2—C4	1.366 (2)		
C7—N1—C8	119.36 (14)	C5—C4—C3	116.90 (16)
C4—N2—C14	120.87 (16)	N1—C7—C1	122.31 (15)
C4—N2—C15	121.45 (15)	C13—C8—C9	118.75 (16)
C14—N2—C15	116.13 (17)	C13—C8—N1	117.70 (14)
C6—C1—C2	117.26 (16)	C9—C8—N1	123.46 (14)
C6—C1—C7	120.36 (15)	C10—C11—C12	121.24 (17)
C2—C1—C7	122.33 (15)	C10—C11—Cl1	119.74 (14)
N2—C4—C5	121.90 (15)	C12—C11—Cl1	119.01 (14)
N2—C4—C3	121.19 (15)		
C7—C1—C2—C3	176.70 (14)	C8—N1—C7—C1	179.93 (13)
C14—N2—C4—C5	−15.4 (3)	C6—C1—C7—N1	170.00 (16)
C15—N2—C4—C5	179.36 (18)	C2—C1—C7—N1	−7.4 (2)
C14—N2—C4—C3	165.29 (18)	C7—N1—C8—C13	140.53 (16)
C15—N2—C4—C3	0.1 (3)	C7—N1—C8—C9	−43.0 (2)
C7—C1—C6—C5	−175.78 (15)	N1—C8—C9—C10	−176.86 (15)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C14-H14B\cdots Cl1^{i}$	0.98	2.75	3.729 (3)	175
$C2-H2\cdots Cl1^{ii}$	0.95	3.11	3.812 (3)	132
$C6-H6\cdots N2^{iii}$	0.95	2.83	3.481 (3)	127
$C14-H14A\cdots N1^{iv}$	0.98	3.08	3.602 (4)	115
$C10-H10\cdots N1^{iii}$	0.95	2.87	3.728 (3)	152

Symmetry codes: (i) $x-1, y, 1+z$; (ii) $x, y, 1+z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $x-1, y, z$.

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Table 3
The chloro-substituted Schiff bases in this study.

Plane 1 is the plane directly attached to atom C7; plane 2 is the plane directly attached to atom N1; *S* and *S′* refer to the substituent groups in planes 1 and 2, respectively; μ is the molecular dipole moment calculated by *MOPAC* (Stewart, 1989).

	CSD refcode	Space group	*S*	*S′*	μ (D)
1	BADDAL10	$P2_1/c$	2-OH	4′-Cl	2.20
2	BEYQEB	$P2_12_12_1$	2-OH	5′-Cl, 2′-Me	3.03
3	CBZYAN	$P2_12_12_1$	2,4-Cl		1.10
4	CHLSAN	$P2_12_12_1$	2-OH	2′-Cl	3.73
5	CSALAN02	$Pca2_1$	2-OH, 5-Cl		2.35
6	FAKDIE	$P2_1/n$	4-Cl	2′-OH	2.76
7	RONKEK	$P2_1$	4-Cl	3′-Cl	0.52
8	RONKOU	$P2_1$	4-Br	3′-Cl	0.57
9	RONKUA	$P2_1$	4-Cl	2′-Br	0.48
10	RONLAH	$P2_1/c$	3-Cl	4′-Br	2.78
11	WEMJIH	$P2_12_12_1$	3-Br	3′-Cl	1.46
12	YICNON	$P2_1/c$	3,5-Cl, 2-OH	4′-NEt_2	6.22
13	YICPAB	$P2_1/c$	3,5-Cl, 2-OH	4′-NMe_2	6.16
14	ZAMMEF	$P2_1/c$	2,3-OH	2′-Cl	3.73
15	(I)	$P2_1/c$	4-NMe_2	4′-Cl	6.20

Table 4
C—H···π and π–π interactions (Å, °) in (I).

Plane 3–3 denotes the π–π interaction between the two planes 3 in the interacting molecules; the parameters following are the distances between the planes and between their centers, respectively. ESM% is the percentage interaction energy between the two interacting molecules in the total packing energy, calculated by *OPEC* (Gavezzotti, 1983).

ESM%	Interaction	H···P	C—H···P	Symmetry code
15.3	C—H12···P1	3.47	126.9	$-x+1, -y+1, -z+1$
15.3	C—H13···P3	3.65	121.7	$-x+1, -y+1, -z+1$
15.3	Plane 3–3	4.24	4.66	$-x+1, -y+1, -z+1$
12.6	C—H10···P3	3.63	138.8	$x, -y+\frac{1}{2}, z+\frac{1}{2}$

H atoms were positioned geometrically and treated as riding, with C—H distances of 0.98 (methyl H atoms) and 0.95 Å (other H atoms), and with $U_{\rm iso}$(H) values of 1.5$U_{\rm eq}$(C) (methyl) and 1.2$U_{\rm eq}$(C) (other H atoms).

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1245). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*, ch. 5. Amsterdam: Elsevier.

Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 2353–2360.

Dmezawa, Y. (1998). *Bull. Chem. Soc. Jpn*, **71**, 1207–1213.

Gavezzotti, A. (1983). *J. Am. Chem. Soc.* **105**, 5520–5525.

Jacobson, R. (1998). Private communication.

Jalali-Heravi, M. (2000). *Spectrochim. Acta Part A*, **56**, 1575–1581.

Metzler, C. M., Cahill, A. & Metzler, D E. (1980). *J. Am. Chem. Soc.* **102**, 6075–6082.

Pistolis, G., Gegiou, D. & Hadjoudis, D. (1996). *J. Photochem. Photobiol. A*, **93**, 179–184.

Rigaku/MSC (2001). *CrystalClear.* Version 1.3. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Rigaku/MSC & Rigaku (2001). *CrystalStructure.* Version 3.00. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Sekikawa, T., Kobayashi, T. & Inabe, T. (1997). *J. Phys. Chem. A*, **101**, 644–649.

Sharma, C. V. K. (1993). *J. Chem. Soc. Perkin Trans.* 2, pp. 2209–2216.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Stewart, J. P. (1989). *MOPAC.* Version 6.0. Quantum Chemistry Program Exchange 581, Indiana University, USA.

Tarafder, M. T. H., Jin, K. T., Crouse, K. A., Ali, A. M., Yamin, B. M. & Fun, H.-K. (2002). *Polyhedron*, **21**, 2547–2554.

Thallapally, P. K. & Nangia, A. (2001). *CrystEngComm*, article No. 27, pp. 114–119.