1-[(2,4-Dichlorobenzoyl)methyl]-4-(N,N-dimethyl-amino)pyridinium bromide

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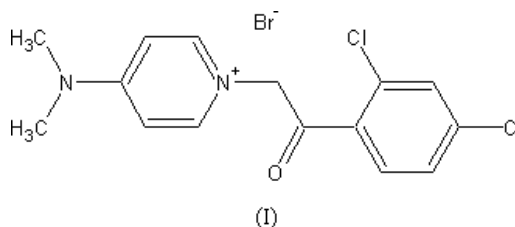
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In the title compound, $C_{15}H_{15}Cl_2N_2O^+\cdot Br^-$, the angle between the least-squares planes of the dichlorophenyl moiety and the pyridine ring is 20.23 (9)°. The molecular packing is mainly influenced by intermolecular C—H$\cdots$Br hydrogen-bond interactions. The molecules form an extended chain along the b axis, through C—H$\cdots$Br hydrogen bonds.

Comment

4-Dimethylaminopyridine (DMAP) is an excellent catalyst for a variety of synthetic transformations under mild conditions (Prabakaran et al., 2001, and references therein; Sundar et al., 2004). In continuation of our work, the structure determination of the title compound, (I), was undertaken.

(I)

A perspective view of the molecule of (I), with the atomic numbering scheme, is shown in Fig. 1. The bond lengths and angles in (I) are comparable to those reported in related structures (Sundar et al., 2004). The angle between the least-squares planes of the dimethylamine moiety and the pyridine ring is 7.37 (13)°. The angle between the least-squares planes of the dichlorophenyl moiety and the pyridine ring is 20.23 (9)°, a value that is much less than those [81.01 (11) and 78.64 (13)°] observed in the related structures (Sundar et al., 2004). This drastic conformational change may be due to the additional substitution of a Cl atom at the meta position of the phenyl ring.

An interesting feature of the pyridinium systems is that they have a substantial degree of quinoidal character, since the bond lengths C2—C3 [1.348 (3) Å] and C5—C6 [1.356 (3) Å] are significantly shorter than those observed for C3—C4 [1.422 (3) Å] and C4—C5 [1.411 (3) Å]. The bond length C4—N2 [1.340 (3) Å] is intermediate between typical C—N single- and double-bond distances (1.465 and 1.239 Å; Allen et al., 1987), indicating significant conjugation. The sums of the bond angles around N1 and N2 are equal to 360.0°. Hence, there is no evidence for an sp^3 lone pair.

The molecules are linked by C—H$\cdots$Br hydrogen bonds into continuous infinite chains running along the b axis (Fig. 2). Atoms C1 and C15 act as hydrogen-bond donors and form C—H$\cdots$Br interactions (Table 1). The relatively short

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C8···Cl2[iv] contact of 3.843 (3) Å [symmetry code: (iv) 1 + x, y, z] may indicate a weak intermolecular C—H···Cl hydrogen bond, the H8C···Cl2[iv] distance being 2.94 Å.

Experimental

A solution of 2,4-dichlorophenacyl bromide (2.0 g, 4 mmol) and DMAP (0.5 g, 4 mmol) in dry acetone was refluxed for 30 min. After cooling to room temperature (303 K), the solid that separated was filtered off and washed with dry acetone to give the stable salt (I) (m.p. 534 K), which was recrystallized from ethanol.

Crystal data

$C_{15}H_{15}Cl_2N_2O^+ \cdot Br^-$	$D_x = 1.572$ Mg m^{-3}
$M_r = 390.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 938
$a = 9.6148$ (16) Å	reflections
$b = 8.9986$ (16) Å	$\theta = 2.5$–29.1°
$c = 19.437$ (3) Å	$\mu = 2.82$ mm^{-1}
$\beta = 101.399$ (5)°	$T = 298$ (2) K
$V = 1648.5$ (5) Å^3	Block, colourless
$Z = 4$	$0.60 \times 0.40 \times 0.30$ mm

Data collection

Bruker SMART CCD 1K	3638 independent reflections
diffractometer	3067 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan	$\theta_{max} = 27.1°$
(SADABS; Siemens, 1996)	$h = -12 \rightarrow 12$
$T_{min} = 0.250$, $T_{max} = 0.430$	$k = 0 \rightarrow 11$
30507 measured reflections	$l = 0 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 0.6372P]$
$wR(F^2) = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
3638 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
190 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···Br	0.97	2.88	3.832 (2)	168
C15—H15···Br	0.93	2.84	3.687 (2)	151
C1—H1B···Br^i	0.97	2.78	3.620 (2)	145
C5—H5···Br^{ii}	0.93	2.87	3.753 (2)	158
C12—H12···Br^{iii}	0.93	2.80	3.691 (2)	160

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

All H atoms were treated as riding, with C—H = 0.93–0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H and $1.2U_{eq}(C)$ for all other H atoms.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP3 (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PARST (Nardelli, 1995).
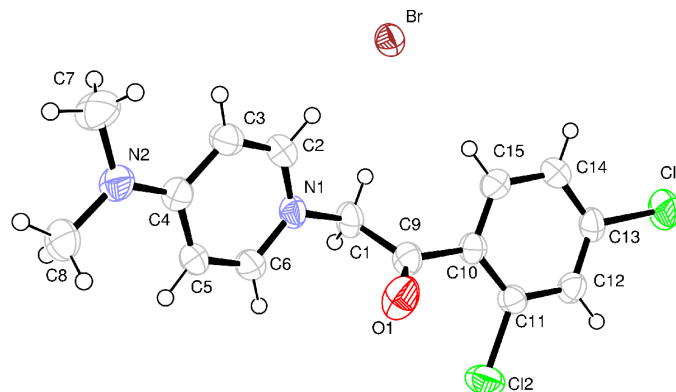
Figure 1
A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii.
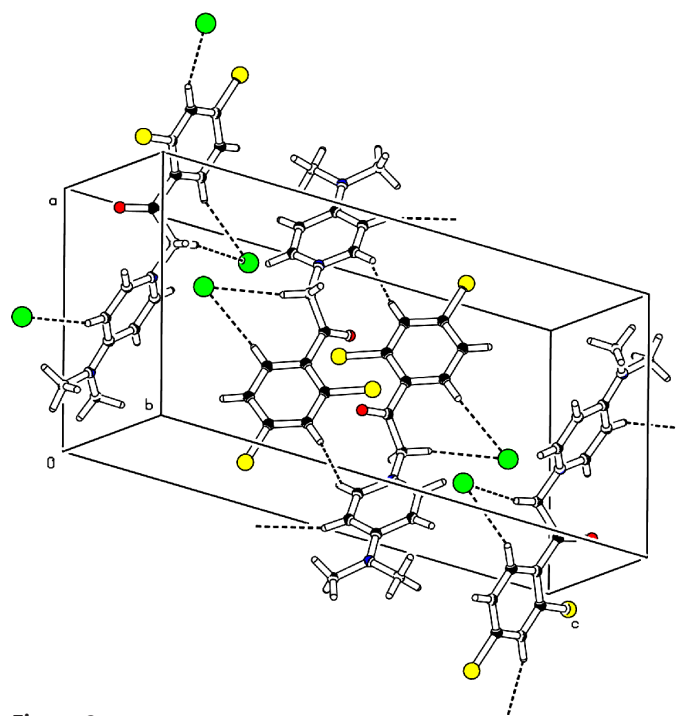
Figure 2
The crystal packing for (I), showing the linkage of ions by C—H···Br hydrogen bonds (dashed lines).

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