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Ethyl 2,6-bis(4-chlorophenyl)-4-hydroxy-5-phenyl-1,2,5,6-tetrahydropyridine-3-carboxylate: supramolecular aggregation through N—H···Cl, C—H···Cl, C—H···S and C—H···π interactions

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Key indicators

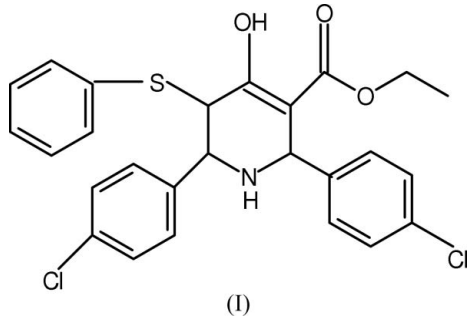
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.082
wR factor = 0.281
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title molecule, $C_{26}H_{23}Cl_2NO_3S$, the tetrahydropyridine ring adopts a half-chair conformation. Intramolecular O—H···O hydrogen bonding generates an $S(6)$ ring motif. Intermolecular N—H···Cl, C—H···Cl and C—H···S hydrogen bonding generates primary graph-set motifs $C(8)$, $C(11)$ and $C(6)$, respectively. No significant π–π interactions exist in the crystal structure.

Comment

Piperidines belong to an important class of heterocycles which are found to possess a variety of biological activities, including cytotoxic and anticancer properties (Dimmock *et al.*, 1990, 2001). Piperidone derivatives have also attracted wide attention from chemists and biologists due to their predicted mode of interaction with cellular thiols, with little or no affinity for the hydroxy and amine groups found in nucleic acids (Baluja *et al.*, 1964; Mutus *et al.*, 1989). This prompted us to perform the synthesis of polysubstituted piperidones. We report here the crystal structure of the title compound, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The tetrahydropyridine ring adopts a half-chair conformation with atoms N1 and C6 deviating by −0.314 (13) and 0.479 (13) Å, respectively, from the least-squares plane defined by atoms C2/C3/C4/C5. The dihedral angle between the phenylsulfanyl ring (C51–C56) and the adjacent chlorophenyl ring (C61–C66) is 11.0 (5)°, and that between the ethoxycarbonyl (O2/O3/C7–C9) group and the adjacent chlorophenyl ring (C21–C26) is 86.3 (4)°.

The crystal structure of (I) is stabilized by N—H···Cl, C—H···Cl and C—H···S interactions. The N1—H1···Cl1^{i}, C62—H62···Cl1^{ii} and C66—H66···S1^{iii} interactions generate $C(8)$, $C(11)$ and $C(6)$ chains, respectively (Table 1 and Fig. 2). Two of these interactions, C62—H62···Cl1^{ii} and N1—H1···Cl1^{i}, together generate a secondary graph-set motif $R_2^2(19)$ (Fig. 2). Two weak C—H···π interactions *viz.* C53—H53···$Cg1^{iv}$ and C25—H25···$Cg2^{ii}$ [$Cg1$ and $Cg2$ are the C61–C66 and C21–

C26 ring centroids, respectively; symmetry codes as in Table 2] are observed. No π–π interactions are observed.

Experimental

To a solution of ammonium acetate (0.162 g, 2 mmol) in ethanol (20 ml), was added a mixture of ethyl 4-[(4-methylphenyl)sulfanyl]-3-oxobutanoate (0.5 g, 2 mmol) and freshly distilled 4-chlorobenzaldehyde (0.591 g, 4 mmol); the resulting mixture was warmed on a water bath for 5 min and the reaction mixture was then set aside at room temperature. The product precipitated as a solid; it was filtered and recrystallized from ethanol (yield: 0.567 g, 54%; m.p. 431–432 K).

Crystal data

$C_{26}H_{23}Cl_2NO_3S$
M_r = 500.41
Monoclinic, $P2_1/c$
a = 18.8708 (4) Å
b = 5.7702 (2) Å
c = 22.4409 (6) Å
β = 95.135 (8)°
V = 2433.74 (12) Å^3
Z = 4
D_x = 1.366 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.38 mm^{-1}
T = 293 (2) K
Block, colourless
0.25 × 0.18 × 0.14 mm

Data collection

Enraf–Nonius MACH3 four-circle diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.921, T_{max} = 0.948
5339 measured reflections
4262 independent reflections
1936 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 25.0°
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.082
$wR(F^2)$ = 0.281
S = 1.03
4262 reflections
303 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1151P)^2 + 8.2382P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1^{i}	0.83 (9)	2.69 (9)	3.503 (7)	171 (8)
C62—H62···Cl1^{ii}	0.93	2.77	3.673 (8)	164
C66—H66···S1^{iii}	0.93	2.85	3.748 (8)	163
O1—H1*A*···O2	0.82	2.03	2.699 (9)	138
C25—H25···*Cg*2^{ii}	0.93	2.92	3.603 (8)	131
C53—H53···*Cg*1^{iv}	0.93	2.96	3.765 (10)	145

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

The N-bound H atom was located in a difference Fourier map and its positional parameters were refined. O- and C-bound H atoms were placed in calculated positions, with O—H = 0.82 and C—H = 0.93–0.98 Å, and allowed to ride on their carrier atoms, with U_{iso}(H) = 1.2U_{eq}(C,N) for CH_2, CH and NH groups, and 1.5U_{eq}(C,O) for the –OH and –CH_3 groups.

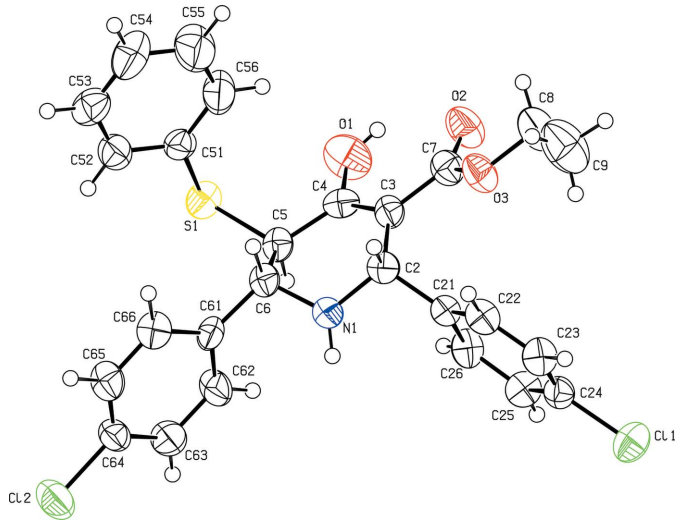


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

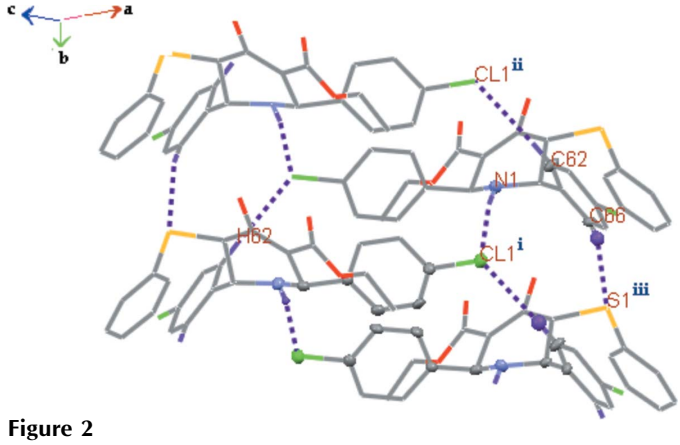


Figure 2
Part of the hydrogen-bonded (dashed lines) network in (I). H atoms not involved in hydrogen bonding have been omitted for clarity. Symmetry codes are given in Table 1.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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