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Methyl 4-chloro-3,5-di-*p*-tolyl-1*H*-pyrrole-2-carboxylate dichloromethane hemisolvate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.156
Data-to-parameter ratio = 13.4

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

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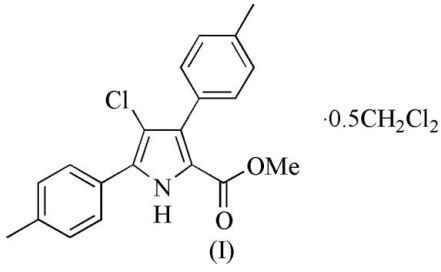
The structure of the title compound, $C_{20}H_{18}ClNO_2\cdot0.5CH_2Cl_2$, at 173 K is described. There is one crystallographically distinct molecule which forms centrosymmetric dimers through N—H···O hydrogen bonding. The dichloromethane solvent molecule is disordered across an inversion centre.

Comment

Recently, we have developed a synthetic procedure that allows the controlled formation of mono- and diarylpyrroles by chemoselective Suzuki–Miyaura coupling (Smith *et al.*, 2006). The key to the method was using chloride as a blocking group which is not very reactive for cross-coupling, and then its removal by catalytic hydrogenation. However, we were unable to complete the synthesis of the 3,5-diaryl-derivatives as catalytic hydrogenation did not remove the chloride. The lack of H atoms on the pyrrole ring made characterization by ^1H and ^{13}C NMR spectroscopy difficult. Therefore, X-ray crystallography was used to confirm the structure of the title compound, (I), and the positions of the aryl rings on the pyrrole core.



(I)

The molecular structure of (I) is depicted in Fig. 1, confirming the disposition of the four substituents of the pyrrole ring. Examination of the molecular geometry has not provided insight into the lack of reactivity of the chloro substituent with respect to the intended hydrogenation of (I) to give the 3,5-diaryl-derivatives of interest to us.

Molecules of (I) form centrosymmetric dimers in the solid state through hydrogen bonding, involving the pyrrole N—H and carbonyl O atom of the ester functionality (Fig. 2 and Table 1).

Experimental

Iodine (1.28 g, 10.02 mmol) was added to a mixture of methyl 4-chloro-1*H*-pyrrole-2-carboxylate (0.80 g, 5.01 mmol) and silver trifluoroacetate (2.21 g, 10.02 mmol) in chloroform (20 ml) at 273 K (ice bath) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 7 h with exclusion of light, before

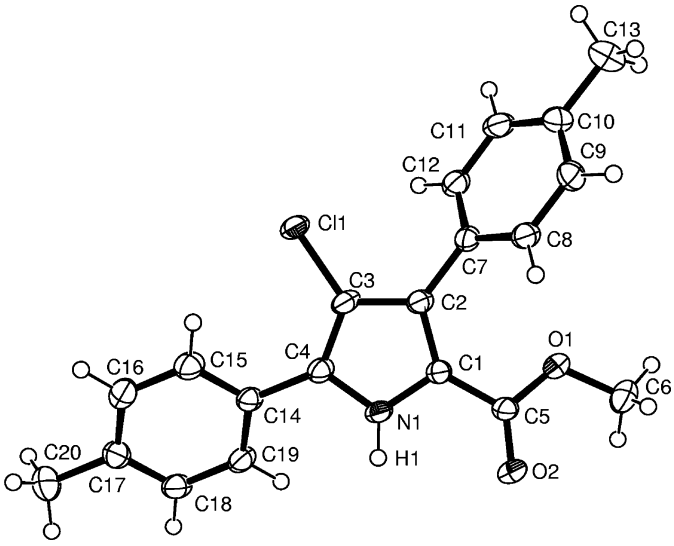


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size and the disordered solvent molecule has been omitted for clarity.

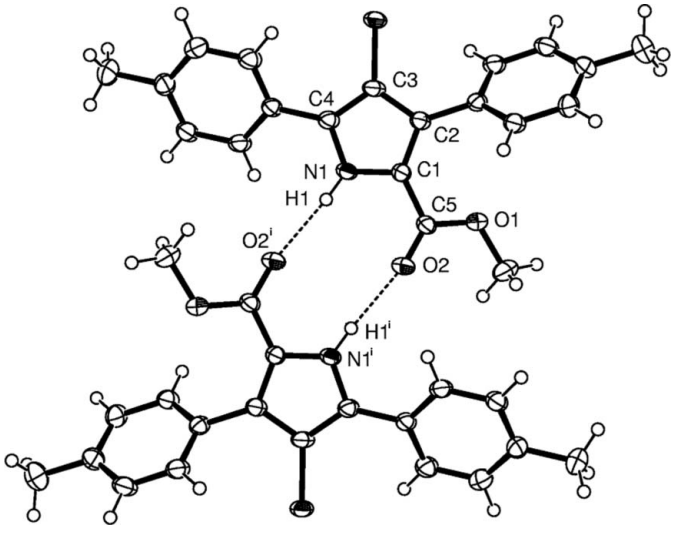


Figure 2
A view of the hydrogen-bonding interactions between molecules of (I), shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size. [Symmetry code: (i) $-x, 2-y, 1-z$.]

quenching with aqueous sodium sulfite and brine. The reaction mixture was extracted with ethyl acetate (3 × 20 ml), and the combined organic extracts were dried and filtered through a small plug of silica gel. The solution was concentrated under reduced pressure to give methyl 4-chloro-3,5-diiodo-1*H*-pyrrole-2-carboxylate (1.85 g, 90%) as a white solid (m.p. 465–470 K).

A solution of the diiodopyrrole from above (0.216 g, 0.525 mmol) in acetone (10 ml), *p*-tolylboronic acid (0.179 g, 1.313 mmol), 2 *M* potassium carbonate (5 ml) and palladium(II) acetate (0.020 g, 0.089 mmol) was refluxed overnight under an atmosphere of nitrogen. The reaction was cooled to room temperature and water (10 ml) was added. The product was then extracted with ethyl acetate (2 × 10 ml). The organic layer was dried and evaporated to give the crude product, which was purified by silica-gel chromatography (eluent 20% ethyl acetate–hexanes). The product was recrystallized from diethyl ether–hexane (1:4 *v*/*v*) to give the title compound, (I), in 78% yield as colourless crystals. Crystals of (I) suitable for X-ray analysis were obtained by recrystallization from dichloromethane (m.p. 452–458 K).

Crystal data

$C_{20}H_{18}ClNO_2\cdot0.5CH_2Cl_2$
$M_r = 382.27$
Triclinic, $P\overline{1}$
$a = 8.456$ (3) Å
$b = 9.902$ (11) Å
$c = 12.316$ (3) Å
$\alpha = 71.61$ (5)°
$\beta = 82.94$ (3)°
$\gamma = 74.33$ (7)°
$V = 941.4$ (11) Å^3
$Z = 2$
$D_x = 1.350$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.36$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.45 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3482 measured reflections
3314 independent reflections
2791 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 25.0°$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.156$
$S = 1.05$
3314 reflections
247 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0933P)^2 + 0.75P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.88	2.06	2.932 (3)	169

Symmetry code: (i) $-x, -y+2, -z+1$.

All H atoms were placed in calculated positions and refined using a riding model, with C—H distances in the range 0.88–0.99 Å and with U_{iso}(H) = 1.2U_{eq}(C), except for methyl H atoms where U_{iso}(H) = 1.5U_{eq}(C). A dichloromethane molecule was located lying on a crystallographic inversion centre, implying disorder; this was modelled with anisotropic refinement of the C and both Cl atoms with all site occupancies fixed at 0.5. This model gave a chemically reasonable geometry for the solvent molecule.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Smith, J. A., Ng, S. & White, J. M. (2006). *Org. Biomol. Chem.* **4**, 2477–2482.