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N-(*o*-Chlorophenyl)-2,5-dimethyl-pyrrole-3-carbaldehyde

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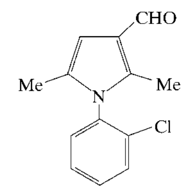
Crystal structure analysis of the title compound, $C_{13}H_{12}ClNO$, reveals three crystallographically independent molecules in the asymmetric unit. The main conformational difference between these molecules is the orientation of the phenyl rings with respect to the pyrrole rings. The coplanar arrangement of the aldehyde groups attached to the pyrrole rings influences the pyrrole-ring geometry. The C2—C3 and N1—C5 bonds are noticeably longer than the C4—C5 and N1—C2 bonds. Two independent molecules of the title compound form dimers *via* intermolecular C—H···O hydrogen bonds [$D\cdots A$ = 3.400 (3) Å and D—H···A = 157°]. The perpendicular orientation of the phenyl and pyrrole rings of one independent molecule and its symmetry-related molecule allows C—H···π interactions, with an H···centroid distance of 2.85 Å and a C—H···π angle of 155°. The distances between the H atom and the pyrrole-ring atoms indicate that the C—H bond points towards one of the bonds in the pyrrole ring.

Comment

The substituted pyrrole ring, which is known to be an important unit in many useful π-electron systems (Evans, 1990; Yanai *et al.*, 2000; Takeda *et al.*, 2001), forms part of our research on substituted heterocyclic compounds (Jukić *et al.*, 1999, 2003). The synthesis of pyrrole rings remains an extremely attractive domain in heterocyclic chemistry, as they constitute the core unit of many natural products (Fürstner *et al.*, 2002) and serve as the building blocks for porphyrin synthesis (Dolušić *et al.*, 2003; Guo *et al.*, 2003; Naik *et al.*, 2003). The present study forms part of our continuing interest in the synthesis, stereochemistry and structural analysis of *N*-aryl- and *N*-heteroaryl-2,5-dimethylpyrrole-3-carbaldehydes (Vorkapić-Furač *et al.*, 1992) and in their use as corrosion inhibitors of iron (Stupnišek-Lisac *et al.*, 1988, 1992) or as synthetic plant-growth factors, cytokinins (Bajrović *et al.*, 1993).

The asymmetric unit of the title compound, (I) (Fig. 1), contains three crystallographically independent molecules, *viz*. *A*, *B* and *C*. The bond lengths in the pyrrole rings and attached aldehyde groups agree within standard uncertainties (Table 1), and the bond lengths in the rest of the molecules differ only slightly. The main conformational difference between these three molecules was observed in the orientation of the phenyl ring with respect to the pyrrole ring, the C2—N1—C9—C10 torsion angles being 92.4 (2), −82.9 (2) and −96.2 (2)° for molecules *A*, *B* and *C*, respectively.



(I)

The aldehyde groups are coplanar with the pyrrole rings to which they are attached; the C4—C3—C6—O1 torsion angles are −4.0 (3), 0.7 (4) and −0.1 (4)° for molecules *A*, *B* and *C*, respectively. A coplanar arrangement of the aldehyde groups allows the extension of the π conjugation of the ring over the carbonyl groups. The π-electron transfer is substantiated by the deviation of the pyrrole-ring geometry. The C2—C3 bond is slightly elongated compared with the average value for a Csp^2═Csp^2 bond distance in 1*H*-pyrroles (1.375 Å; Allen *et al.*, 1987) and noticeably longer than the C4—C5 bond. Because of the C2—C3 and C4—C5 bond-length deviations, the N1—C5 bond is noticeably longer than both the N1—C2 bond and the corresponding Csp^2—N(3) bond distance in 1*H*-pyrroles (1.372 Å; Allen *et al.*, 1987). The fact that the efficient π-system spreads from the pyrrole ring to the carbonyl group is confirmed by the shortening of the C3—C6 bond (conjugated Csp^2—Csp^2 = 1.455 Å; Allen *et al.*, 1987). A survey of the Cambridge Structural Database (Allen, 2002) revealed three structures having an aldehyde group at the 3-position of a pyrrole ring (Conde *et al.*, 1979; de la Figuera Gomez *et al.*, 1985; Lokaj *et al.*, 2001). In these structures, the pyrrole-ring geometry is significantly different from that of (I) because of the influence of the other ring substituents. The structure of (I) is the first example of an *N*-(*o*-chlorophenyl)-substituted pyrrole ring.

The sum of the angles around atom N1 is 360° (Table 1), assuming that the N atoms, whose lone electron pairs are included in the aromatic systems, possess a planar sp^2 arrangement. Consequently, the pyrrole rings are planar, and the largest observed deviation from their mean planes is 0.006 (2) Å for atom C2 in molecule *A*. The phenyl rings are almost perpendicular to the pyrrole rings [the dihedral angles are 86.9 (1), 83.8 (1) and 85.7 (1)° in molecules *A*, *B* and *C*, respectively] and thus are not favourably disposed for inter-ring conjugation. Furthermore, the pyrrole and phenyl rings of

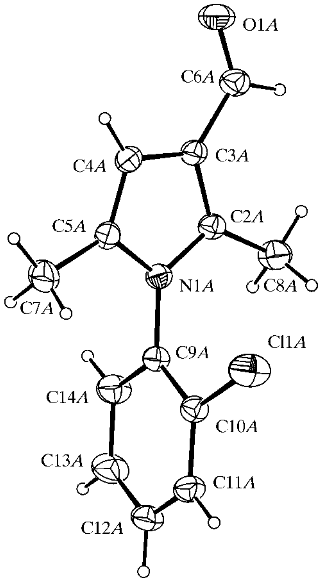


Figure 1
A view of (I), with the atom-numbering scheme. For clarity, only one of the three independent molecules of the asymmetric unit is shown. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level.

molecules *A* and *C* are almost parallel to each other, the dihedral angles being 6.4 (1) and 7.0 (1)°, respectively.

In the crystal structure, two independent molecules of (I) form dimers *via* intermolecular C4*A*—H4*A*···O1*B*[i] hydrogen bonds [symmetry code: (i) $1 - x, -y, 1 - z$]. The *D*···*A* and H···*A* distances are 3.400 (3) and 2.53 Å, and the *D*—H···*A* angle is 157° (Fig. 2). We found molecules linked by such $C_{pyrrole}$—H···O(=CH) hydrogen bonds in only one structure (Adams *et al.*, 1986). Surprisingly, molecule *C* is completely isolated and does not participate in hydrogen bonding. Its shortest intermolecular contacts are H14*C*···O1*B*[ii] and H72*C*···O1*C*[iii] [symmetry codes: (ii) $x, -\frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $x, 1 + y, z$], with distances of 2.62 and 2.63 Å, respectively. The phenyl and pyrrole rings of two neighbouring symmetry-related *A* molecules are perpendicularly oriented. Such molecular packing leads to a C—H···π interaction between phenyl atom H14*A* and the pyrrole ring at $(1 - x, -y, 1 - z)$, with an H···centroid distance of 2.85 Å and a C—H···π angle of 155°. In fact, the H14*A*···C4*A* distance (2.70 Å) is shorter than the distance between the H atom and the pyrrole-ring centroid. The second shortest H···C contact is that to atom C5*A* (2.87 Å), and all other H···C distances are longer than 3.05 Å. According to these observations, the C—H bond points towards the C4*A*—C5*A* bond of the pyrrole ring rather than towards the ring centroid. These C—H···π interactions connect hydrogen-bonded dimers in the *ac* plane.

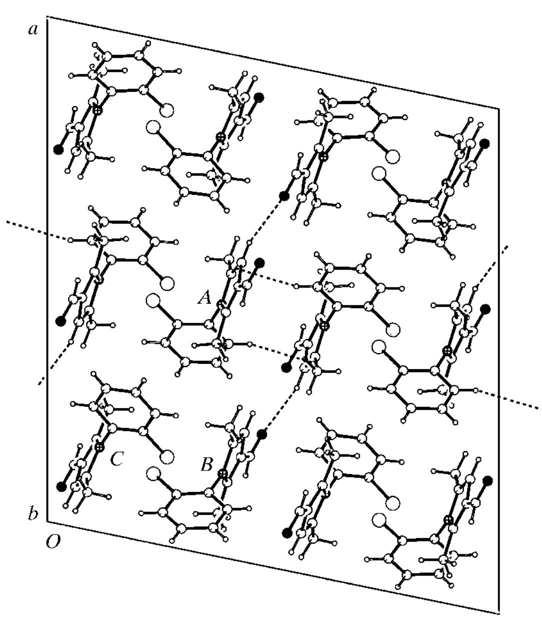


Figure 2
The crystal packing, viewed along the *b* axis. The three independent molecules are designated *A*, *B* and *C*. Intermolecular hydrogen bonds and C—H···π interactions are shown by dashed lines.

Experimental

The title compound was prepared by condensation of hexane-2,5-dione with 2-chloroaniline and subsequent Vilsmeier–Haack formylation of the pyrrole ring (Vorkapić-Furač *et al.*, 1989), according to the modified procedure given for the preparation of pyrrole-2-carbaldehyde and *N*-methylpyrrole-2-carbaldehyde by Silverstein *et al.* (1955). Compound (I) was recrystallized twice from a methanol–water (50:50, *v*/*v*) mixture and obtained as yellow crystals (yield 89%, m.p. 333 K). The structure of the compound was confirmed by elemental analysis and IR, UV, NMR and electron-impact spectra (Vorkapić-Furač *et al.*, 1989). A single crystal was obtained by slow evaporation at room temperature from a methanol–water solution (50:50, *v*/*v*).

Crystal data

$C_{13}H_{12}ClNO$
$M_r = 233.69$
Monoclinic, $P2_1/c$
$a = 21.6815$ (3) Å
$b = 8.61270$ (10) Å
$c = 19.7231$ (2) Å
$\beta = 101.6257$ (5)°
$V = 3607.46$ (8) Å^3
$Z = 12$
$D_x = 1.291$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8586 reflections
$\theta = 2.6$–27.5°
$\mu = 0.30$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.35 × 0.35 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*DENZO–SMN*, Otwinowski & Minor, 1997)
$T_{min} = 0.902$, $T_{max} = 0.957$
43 063 measured reflections
8109 independent reflections
5495 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 27.4°$
$h = -28 \rightarrow 27$
$k = -11 \rightarrow 10$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.159$
$S = 1.02$
8109 reflections
451 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 1.2178P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1*A*—C2*A*	1.366 (2)	C3*B*—C4*B*	1.426 (3)
N1*A*—C5*A*	1.400 (2)	C3*B*—C6*B*	1.440 (3)
O1*A*—C6*A*	1.214 (3)	C4*B*—C5*B*	1.351 (3)
C2*A*—C3*A*	1.384 (3)	N1*C*—C2*C*	1.372 (2)
C3*A*—C4*A*	1.419 (3)	N1*C*—C5*C*	1.399 (2)
C3*A*—C6*A*	1.442 (3)	O1*C*—C6*C*	1.217 (3)
C4*A*—C5*A*	1.353 (3)	C2*C*—C3*C*	1.384 (3)
N1*B*—C2*B*	1.368 (2)	C3*C*—C4*C*	1.423 (3)
N1*B*—C5*B*	1.400 (2)	C3*C*—C6*C*	1.441 (3)
O1*B*—C6*B*	1.214 (3)	C4*C*—C5*C*	1.352 (3)
C2*B*—C3*B*	1.382 (3)		
C2*A*—N1*A*—C5*A*	110.13 (16)	C5*B*—N1*B*—C9*B*	124.51 (15)
C2*A*—N1*A*—C9*A*	125.66 (16)	C2*C*—N1*C*—C5*C*	109.75 (16)
C5*A*—N1*A*—C9*A*	124.20 (16)	C2*C*—N1*C*—C9*C*	125.83 (16)
C2*B*—N1*B*—C5*B*	110.12 (15)	C5*C*—N1*C*—C9*C*	124.36 (15)
C2*B*—N1*B*—C9*B*	125.34 (15)		

H atoms attached to C6*A*/*B*/*C* were found in a difference Fourier map and the coordinates and isotropic displacement parameters were refined freely. All other H atoms were included in calculated positions as riding atoms, with C—H distances of 0.96 Å for methyl H atoms and 0.93 Å for the remaining H atoms.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1632). Services for accessing these data are described at the back of the journal.

References

Adams, H., Bailey, N. A., Fenton, D. E., Moss, S., Rodriguez de Barbarin, C. O. & Jones, G. (1986). *J. Chem. Soc. Dalton Trans.* pp. 693–699.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bajrović, K., Kniewald, Z. & Vorkapić-Furač, J. (1993). *Pharmazie*, **48**, 787–788.
Conde, A., López Castro, A., Márquez, R., Declercq, J. P. & Germain, G. (1979). *Acta Cryst.* B**35**, 2228–2229.
Dolušić, E., Toppet, S., Van Meervelt, L., Tinant, B. & Dehaen, W. (2003). *Tetrahedron*, **59**, 395–400.
Evans, G. P. (1990). *Advances in Electrochemical Science and Engineering*, Vol. 1, edited by H. Gerisher & C. W. Tobias, pp. 1–37. New York: Wiley.
Figuera Gomez, T. H. de la, Arques, J. S., Jones, R. A., Dawes, H. M. & Hursthouse, M. B. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 899–902.
Fürstner, A., Krause, H. & Thiel, O. R. (2002). *Tetrahedron*, **58**, 6373–6380.
Guo, C.-C., Li, H.-P. & Zhang, X.-B. (2003). *Bioorg. Med. Chem.* **11**, 1–7.
Jukić, M., Cetina, M., Pavlović, G. & Rapić, V. (1999). *Struct. Chem.* **10**, 85–90.
Jukić, M., Hergold-Brundić, A., Cetina, M., Nagl, A. & Vorkapić-Furač, J. (2003). *Struct. Chem.* In the press.
Lokaj, J., Kettmann, V., Milata, V., Štetinová, J. & Petrov, O. (2001). *Acta Cryst.* E**57**, o404–o405.
Naik, R., Joshi, P., Kaiwar, S. P. & Deshpande, R. K. (2003). *Tetrahedron*, **59**, 2207–2213.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Silverstein, R. M., Ryskiewicz, E. E., Willard, C. & Koehler, R. C. (1955). *J. Org. Chem.* **20**, 668–672.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stupnišek-Lisac, E., Berković-Salajster, K. & Vorkapić-Furač, J. (1988). *Corrosion* (*Houston*), **28**, 1189–1202.
Stupnišek-Lisac, E., Metikoš-Huković, M., Lenčić, D., Vorkapić-Furač, J. & Berković, K. (1992). *Corrosion* (*Houston*), **48**, 924–930.
Takeda, M., Matsumoto, S. & Ogura, K. (2001). *Heterocycles*, **55**, 231–235.
Vorkapić-Furač, J., Mintas, M., Burgemeister, T. & Mannschreck, A. (1989). *J. Chem. Soc. Perkin Trans.* 2, pp. 713–717.
Vorkapić-Furač, J., Mintas, M., Kastner, F. & Mannschreck, A. (1992). *J. Heterocycl. Chem.* **29**, 327–333.
Yanai, H., Yoshizawa, D., Tanaka, S., Fukuda, T., Akazome, M. & Ogura, K. (2000). *Chem. Lett.* pp. 238–239.