organic compounds

3-(5-Chloro-3-methyl-1-phenyl-pyrazol-4-yl)-1,5-diphenylpentane-1,5-dione: sheets built from C—H···O and C—H···π(arene) hydrogen bonds

Jorge Trilleras,[a] Jairo Quiroga,[a] José M. de la Torre,[b] Justo Cobo,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

Molecules of the title compound, $C_{27}H_{23}ClN_2O_2$, are linked into sheets of alternating large and small rings by a combination of C—H···O and C—H···π(arene) hydrogen bonds.

Comment

The title compound, (I), has been obtained from the base-catalysed condensation of 5-chloro-3-methyl-1-phenyl-pyrazole-4-carbaldehyde with acetophenone. Evidently, the intended target 3-(5-chloro-3-methyl-1-phenylpyrazol-4-yl)-1-phenylpropenone, (II), required as an intermediate for the synthesis of novel fused heterocyclic systems, has undergone a Michael-type reaction with a further molecule of aceto-phenone to form the observed product, (I).

Compound (I) and the analogous 3-(5-chloro-3-methyl-1-phenylpyrazol-4-yl)-1,5-di-2-thienylpentane-1,5-dione, (III) (Trilleras et al., 2005), both crystallize in the space group Pbca, with dimensions which are fairly similar, bearing in mind the different temperatures for the two determinations [293 (2) K for (I) and 120 (2) K for (III)], and hence the two compounds are isomorphous. In addition, the corresponding atom coor-dinates are very similar, as are the molecular conformations, with an all-trans and nearly planar aliphatic chain exhibiting approximate local mirror symmetry (Table 1). Indeed, with the exception of the N-bound phenyl ring (C11–C16), which makes a dihedral angle of 42.7 (2)° with the pyrazole ring, the entire molecule has approximate mirror symmetry. However, there are some significant differences between the supra-molecular structures of (I) and (III), so that these compounds are not strictly isostructural.

The supramolecular aggregation in compound (I) is deter-mined by a combination of C—H···O and C—H···π(arene)
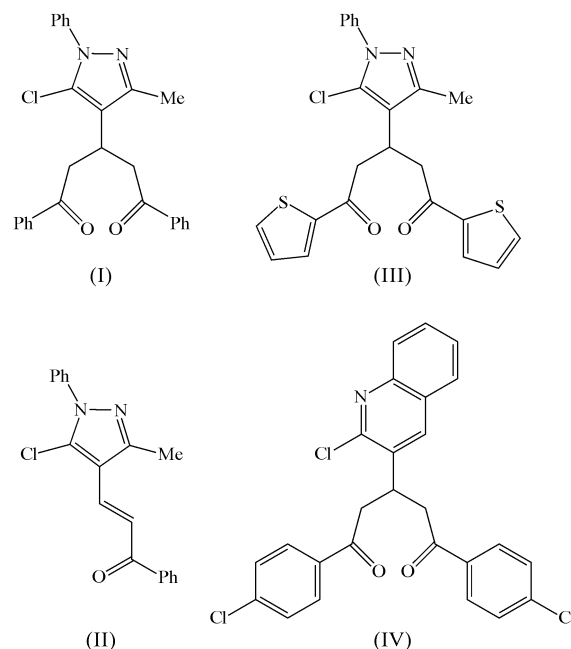
hydrogen bonds (Table 1). Atom C8 in the molecule at (x, y, z) acts as hydrogen-bond donor to the C91–C96 ring in the molecule at $(1 - x, 1 - y, 1 - z)$, so forming by inversion a centrosymmetric dimer, centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). This behaviour thus mimics that of compound (III), where one of the thiophene rings acts as the hydrogen-bond acceptor. However, while the dimers in (III) are not further linked by any direction-specific intermolecular forces, those in (I) are linked into sheets by a single C—H···O hydrogen bond, whose action in isolation is to link the molecules into chains.
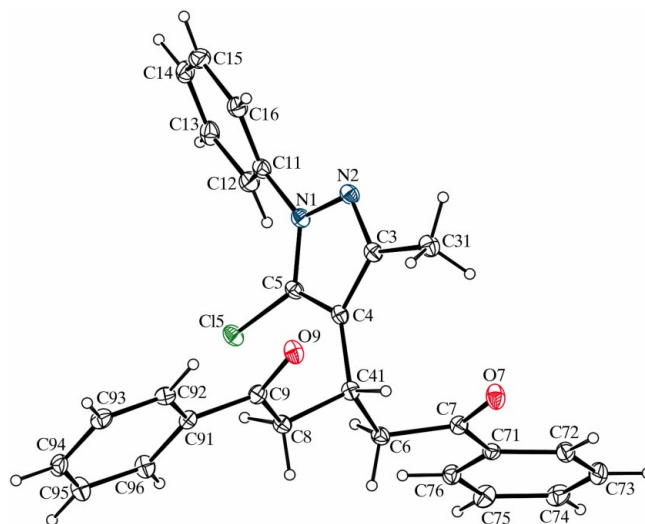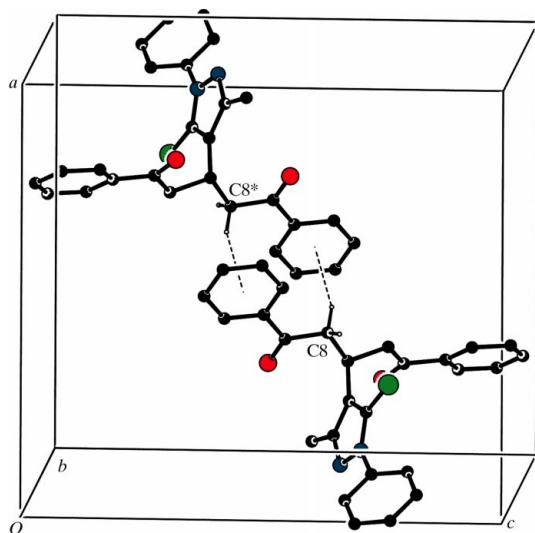

Figure 1
A view of the molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Atom C14 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O7 in the molecule at $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$, so forming a $C(12)$ (Bernstein *et al.*, 1995) chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(0, y, \frac{3}{4})$ (Fig. 3). The combined action of the two hydrogen bonds generates a sheet.

The C14 atoms in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, which form the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as
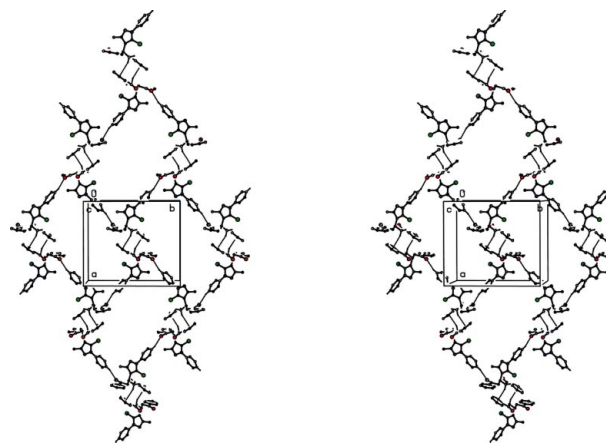

Figure 2
Part of the crystal structure of compound (I), showing the formation of a centrosymmetric dimer formed by paired C—H···π(arene) hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. The atom marked with an asterisk (*) is at the symmetry position $(1 - x, 1 - y, 1 - z)$.
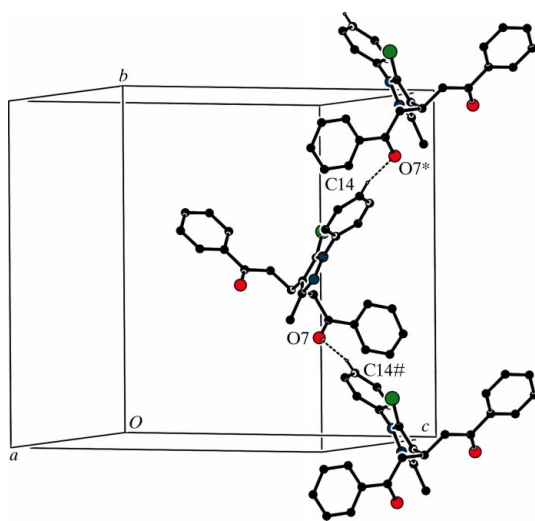
Figure 3
Part of the crystal structure of compound (I), showing the formation of a $C(12)$ chain along [010] formed by C—H···O hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a (102) sheet by the combined action of C—H···O and C—H···π(arene) hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

hydrogen-bond donors to O7 atoms in the molecules at $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively, which form parts of the dimers centred at $(-\frac{1}{2}, 1, 1)$ and $(\frac{3}{2}, 0, 0)$, respectively. Similarly, the O7 atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ accept hydrogen bonds from the C14 atoms in the molecules at $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and $(1 + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, respectively, which themselves lie in the dimers centred at $(-\frac{1}{2}, 0, 1)$ and $(\frac{3}{2}, 1, 0)$. Thus, each dimer is linked to four adjacent dimers, and propagation of these intermolecular interactions by the space-group symmetry operations links the molecules into a (102) sheet containing large and small rings alternating in chessboard fashion (Fig. 4).

The only direction-specific contact between adjacent sheets is a rather long C—H···O contact with aryl atom C73 as the donor (Table 2), but whose H···O distance is close to the van der Waals limit. This interaction is, therefore, probably of little or no structural significance.

In closely analogous 1,5-bis(4-chlorophenyl)-3-(2-chloro-quinolin-3-yl)pentane-1,5-dione, (IV) (Insuasty *et al.*, 2006), which also crystallizes in the space group *Pbca*, although with unit-cell dimensions markedly different from those of (I) and (III), a combination of one C—H···N hydrogen bond and one C—H···O hydrogen bond links the molecules into sheets of $R_4^4(26)$ rings, but C—H···π(arene) hydrogen bonds are absent.

Experimental

To a solution of acetophenone (1 mmol) and 5-chloro-4-formyl-3-methyl-1-phenylpyrazole (0.5 mmol) in absolute ethanol (10 ml), a catalytic amount of sodium hydroxide (1 pellet) was added and the reaction mixture was stirred at room temperature for 1 h. The precipitate which formed was isolated by filtration, washed with ethanol, dried and finally recrystallized from dimethylformamide to give colourless crystals suitable for single-crystal X-ray diffraction (m.p. 390 K, yield 65%). MS (70 eV) *m/z* (%): 442 (1, M^+), 323 (30), 287 (16), 105 (100), 77 (58), 51 (10).

organic compounds

Table 1
Selected torsion angles (°).

C72—C71—C7—C6	−169.29 (18)	C92—C91—C9—C8	177.01 (17)
C71—C7—C6—C41	−165.78 (16)	C91—C9—C8—C41	174.85 (16)
C7—C6—C41—C8	−157.20 (16)	C9—C8—C41—C6	166.61 (16)
C3—C4—C41—C6	−116.5 (2)	C3—C4—C41—C8	119.4 (2)

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

Cg is the centroid of the C91–C96 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8B···Cg[i]	0.97	2.79	3.673 (2)	152
C14—H14···O7[ii]	0.93	2.50	3.402 (3)	165
C73—H73···O9[iii]	0.93	2.59	3.449 (3)	154

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

The space group *Pbca* was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.93 (aromatic), 0.96 (CH$_3$), 0.97 (CH$_2$) or 0.98 Å (aliphatic CH), and with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for the methyl group.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Insuasty, B., Torres, H., Cobo, J., Low, J. N. & Glidewell, C. (2006). *Acta Cryst.* **C62**, o39–o41.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Nonius (1999). *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). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Trilleras, J., Quiroga, J., Cobo, J., Low, J. N. & Glidewell, C. (2005). *Acta Cryst.* **E61**, o1892–o1894.