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Hydrogen-bonded chains in 3-(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-1-(4-methoxyphenyl)-propenone and 3-(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-1-(3,4,5-trimethoxyphenyl)propenone

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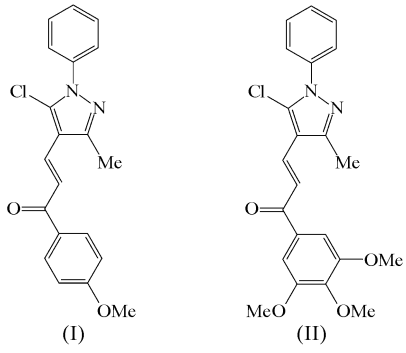
Molecules of 3-(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-1-(4-methoxyphenyl)propenone, $C_{20}H_{17}ClN_2O_2$, (I), are linked into *C*(10) chains and molecules of 3-(5-chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)-1-(3,4,5-trimethoxyphenyl)propenone, $C_{22}H_{21}ClN_2O_4$, (II), are linked into *C*(14) chains, in each case by means of a single C—H···O hydrogen bond.

Comment

We report here the structures of two novel chalcones, prepared by Claisen–Schmidt condensation reactions betweeen 5-chloro-4-formyl-3-methyl-1-phenylpyrazole and methoxy-substituted acetophenones.



With the exception of the unsubstituted phenyl ring C11–C16, the molecular skeleton of compound (I) (Fig. 1) is nearly planar, as shown by the leading torsion angles (Table 1). Similarly, the molecular skeleton of compound (II) (Fig. 2) is nearly planar, apart from the 4-methoxy group at one end of the molecule and the unsubstituted phenyl ring at the other end (Table 3). The 4-methoxy group in (II) has its methyl group twisted well out of the plane of the adjacent aryl ring, presumably for steric reasons, whereas the methyl groups of the 3- and 5-methoxy substituents are essentially coplanar with this ring; the dihedral angle between phenyl ring C11–C16 and the adjacent pyrazole ring is 53.1 (2)° in (I) and 40.0 (2)° in (II). Accordingly, the molecules of (I) and (II) have no internal symmetry and so are chiral, and in the absence of inversion twinning each crystal of (I) thus contains only one enantiomer.

Consistent with the different conformations adopted by the methoxy groups in (II), the pairs of exocyclic C—C—O angles at both C53 and C55 show the difference typical of those found in planar methoxyarenes, including (I), while the two C—C—O angles at C54 have values which are much more similar. Associated with this conformational difference in (II), the C—O—C angles at O53 and O55 are much larger than that at O54, and the C—O distances, particularly those to the methoxy atoms C5*n*1 (*n* = 3, 4 or 5), show significant differences associated with the conformations. The remaining bond lengths and angles show no unusual values. In particular, there is no structural evidence for significant charge polarization.

In each of (I) and (II), the molecules are linked into simple chains by a single C—H···O hydrogen bond (Tables 2 and 4). In compound (I), aryl atom C12 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to carbonyl atom O43 in the molecule at $(1-x, \frac{1}{2}+y, 1-z)$, so forming a *C*(10) chain running parallel to the [010] direction and generated by the 2_1

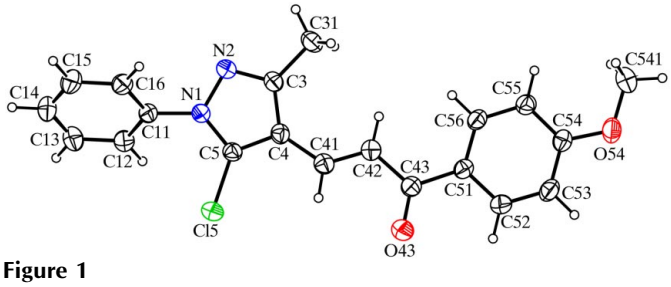


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

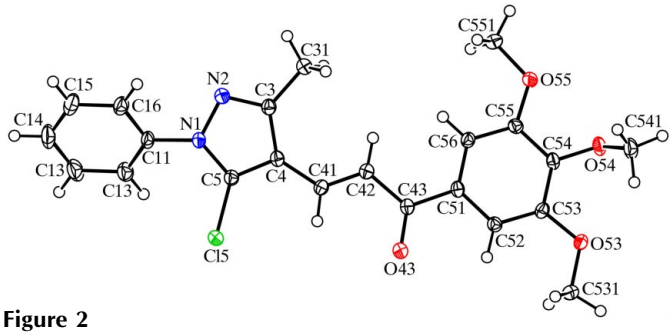


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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screw axis along $(\frac{1}{2}, y, \frac{1}{2})$ (Fig. 3). Just one chain of this type passes through each unit cell, with no significant direction-specific interactions between adjacent chains. In compound (II), atom C13 in the molecule at (x, y, z) acts as donor to methoxy atom O55 in the molecule at $(x, y, 1 + z)$, thereby generating by translation a $C(14)$ chain running parallel to the [001] direction (Fig. 4). Two antiparallel chains of this type pass through each unit cell, but there are no significant direction-specific interactions between adjacent chains.

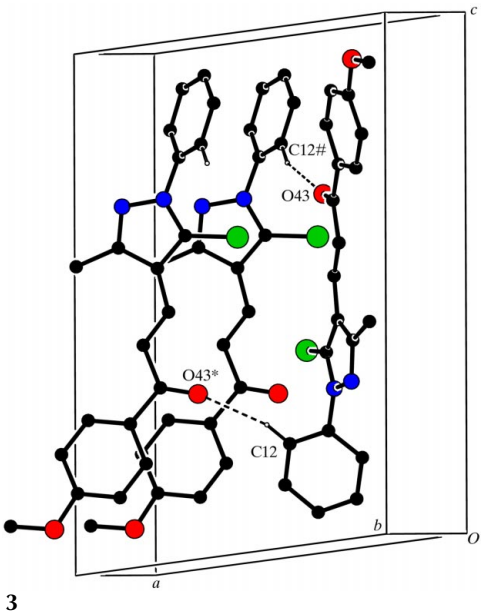

Figure 3
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C(10)$ chain along [010]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 - x, \frac{1}{2} + y, 1 - z)$ and $(1 - x, y - \frac{1}{2}, 1 - z)$, respectively.

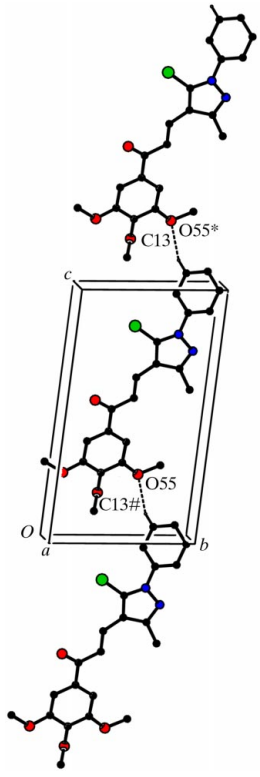

Figure 4
Part of the crystal structure of (II), showing the formation of a hydrogen-bonded $C(14)$ chain along [001]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, y, 1 + z)$ and $(x, y, z - 1)$, respectively.

Experimental

For the syntheses of compounds (I) and (II), a catalytic amount of sodium hydroxide (one pellet) was added to a solution of 5-chloro-4-formyl-3-methyl-1-phenylpyrazole (1 mmol) and either 4-methoxyacetophenone (1 mmol), for (I), or 3,4,5-trimethoxyacetophenone (1 mmol), for (II), in dry ethanol (10 ml). The resulting mixtures were stirred for 2 h at ambient temperature. The precipitates which formed were collected by filtration, washed with ethanol and dried, and then crystallized from ethanol, giving (I) and (II) in yields of 60% [m.p. 372 K for (I) and 413 K for (II)]. For (I), MS IE *m*/*z* (%): 317 (100, M − Cl), 92 (6), 77 (23), 55 (6). For (II), MS IE *m*/*z* (%): 412 (7, M^+), 377 (100, M − Cl), 77 (24), 51 (8). Crystals suitable for single-crystal X-ray diffraction were grown from solutions in dimethylformamide.

Compound (I)

Crystal data

$C_{20}H_{17}ClN_2O_2$
M_r = 352.81
Monoclinic, $P2_1$
a = 12.7985 (10) Å
b = 4.0684 (3) Å
c = 16.6766 (14) Å
β = 95.918 (4)°
V = 863.71 (12) Å^3
Z = 2
D_x = 1.357 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3863 reflections
θ = 3.7–27.7°
μ = 0.24 mm^{-1}
T = 120 (2) K
Needle, colourless
0.80 × 0.18 × 0.01 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.833, T_{max} = 0.998
11 528 measured reflections
3863 independent reflections
2741 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 27.7°
$h = -16 \rightarrow 16$
$k = -4 \rightarrow 5$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.125
S = 1.01
3863 reflections
228 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.0289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), with 1557 Friedel pairs
Flack parameter: 0.06 (7)

Table 1
Selected geometric parameters (Å, °) for (I).

C54—O54	1.367 (3)	O54—C541	1.418 (3)
O54—C54—C53	116.5 (2)	C54—O54—C541	117.9 (2)
O54—C54—C55	124.1 (3)		
C3—C4—C41—C42	−10.0 (5)	C42—C43—C51—C52	−169.7 (3)
C4—C41—C42—C43	−178.5 (3)	C53—C54—O54—C541	178.8 (3)
C41—C42—C43—C51	179.4 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···O43^{i}	0.95	2.50	3.409 (3)	160

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

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O55^{i}	0.95	2.42	3.3203 (17)	158

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

Compound (II)

Crystal data

$C_{22}H_{21}ClN_2O_4$
M_r = 412.86
Triclinic, $P\overline{1}$
a = 7.5118 (2) Å
b = 8.8121 (3) Å
c = 15.6709 (4) Å
α = 81.825 (1)°
β = 82.750 (2)°
γ = 79.459 (2)°
V = 1004.10 (5) Å^3
Z = 2
D_x = 1.366 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4486 reflections
θ = 3.2–27.5°
μ = 0.22 mm^{-1}
T = 120 (2) K
Block, colourless
0.62 × 0.36 × 0.28 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.875, T_{max} = 0.941
19 609 measured reflections
4486 independent reflections
3927 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.5°
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.03
4486 reflections
266 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.3813P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

C53—O53	1.3902 (14)	O53—C531	1.4482 (14)
C54—O54	1.3737 (14)	O54—C541	1.4280 (15)
C55—O55	1.3782 (14)	O55—C551	1.4560 (14)
C52—C53—O53	123.97 (11)	C54—O54—C541	114.74 (9)
C54—C53—O53	116.69 (10)	C54—C55—O55	115.89 (10)
C53—O53—C531	117.36 (9)	C56—C55—O55	123.99 (10)
C53—C54—O54	121.04 (10)	C55—O55—C551	119.21 (9)
C55—C54—O54	118.13 (10)		
C3—C4—C41—C42	−7.7 (2)	C52—C53—O53—C531	−1.42 (16)
C4—C41—C42—C43	−177.93 (10)	C53—C54—O54—C541	−71.19 (15)
C41—C42—C43—C51	175.22 (10)	C56—C55—O55—C551	1.47 (16)
C42—C43—C51—C52	178.79 (10)		

For compound (I), the systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups; $P2_1$ was selected and confirmed by the subsequent structure analysis. The absolute configuration of the molecules in the crystal of (I) selected for study was established (Jones, 1986) by use of the Flack (1983) parameter, but this has no chemical significance. Crystals of compound (II) are triclinic; space group $P\overline{1}$ was selected and confirmed by the subsequent structure analysis. All H atoms in (I) and (II) were located in difference maps, and then treated as riding atoms with C—H distances of 0.95 (CH) or 0.98 Å (CH_3), and with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for the methyl groups. The crystals of both compounds proved to be extremely fragile, and all attempts to cut small fragments from larger crystals resulted in shattering of the parent crystals.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*. Structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997) for (I); *WinGX* (Farrugia, 1999) and *SIR92* (Altomare *et al.*, 1993) for (II). For both compounds, structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); publication software: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1844). Services for accessing these data are described at the back of the journal.

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