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# Crystal structures of ethyl 6-(4-methylphenyl)-4-oxo-4*H*-chromene-2-carboxylate and ethyl 6-(4-fluorophenyl)-4-oxo-4*H*-chromene-2-carboxylate

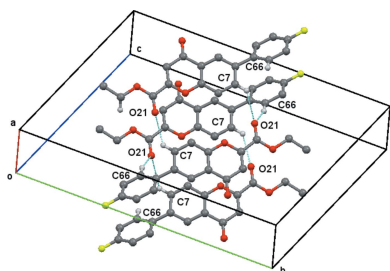
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The crystal structures of two chromone derivatives, *viz.* ethyl 6-(4-methylphenyl)-4-oxo-4*H*-chromene-2-carboxylate, C<sub>19</sub>H<sub>16</sub>O<sub>4</sub>, (**1**), and ethyl 6-(4-fluorophenyl)-4-oxo-4*H*-chromene-2-carboxylate C<sub>18</sub>H<sub>13</sub>FO<sub>4</sub>, (**2**), have been determined: (**1**) crystallizes with two molecules in the asymmetric unit. A comparison of the dihedral angles between the mean planes of the central chromone core with those of the substituents, an ethyl ester moiety at the 2-position and a *para*-substituted phenyl ring at the 6-position shows that each molecule differs significantly from the others, even the two independent molecules (*a* and *b*) of (**1**). In all three molecules, the carbonyl groups of the chromone and the carboxylate are *trans*-related. The supramolecular structure of (**1**) involves only weak C—H··· $\pi$  interactions between H atoms of the substituent phenyl group and the phenyl group, which link molecules into a chain of alternating molecules *a* and *b*, and weak  $\pi$ – $\pi$  stacking interactions between the chromone units. The packing in (**2**) involves C—H···O interactions, which form a network of two intersecting ladders involving the carbonyl atom of the carboxylate group as the acceptor for H atoms at the 7-position of the chromone ring and from an *ortho*-H atom of the exocyclic benzene ring. The carbonyl atom of the chromone acts as an acceptor from a *meta*-H atom of the exocyclic benzene ring.  $\pi$ – $\pi$  interactions stack the molecules by unit translation along the *a* axis.

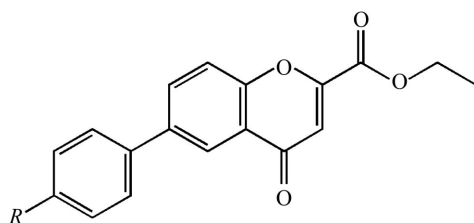
## 1. Chemical context

Benzopyran derivatives represent a large class of natural and synthetic heterocycles that are often linked to a broad array of biological activities, (Gaspar *et al.*, 2014, 2015). Within this vast class of compounds, the chromone core has emerged as a privileged structure for drug discovery and development programs (Welsch *et al.*, 2010). Chemically, the chromone scaffold is a rigid benzoannulated  $\gamma$ -pyrone ring, which can be modulated by diversity-oriented synthesis, (Gaspar *et al.*, 2015; Welsch *et al.*, 2010; Ko *et al.*, 2006; Nicolaou *et al.*, 2000), exhibiting a diversity of pharmacological properties such as anti-inflammatory, antimicrobial and anticancer among others (Gaspar *et al.*, 2015). The application of chromones as a valid scaffold for the development of therapeutic solutions for aging-related diseases is still an emerging field, even though the data acquired indicate their importance in the development of new drug candidates for targets ascribed with respect



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to Alzheimer's and Parkinson's diseases, namely as adenosine receptors ligands (Cagide *et al.*, 2015a) and/or as monoamino oxidase B inhibitors, (Cagide *et al.*, 2015b).

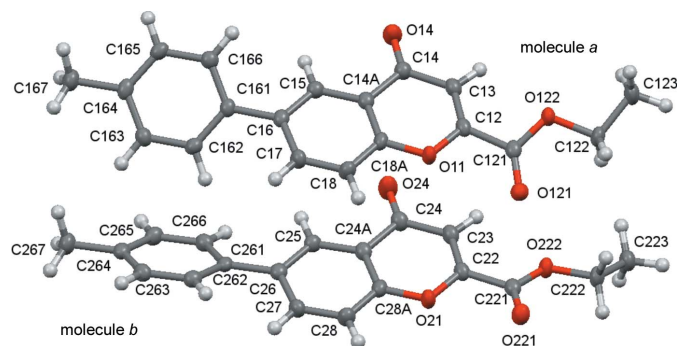


- (1)  $R = -\text{CH}_3$   
 (2)  $R = -\text{F}$

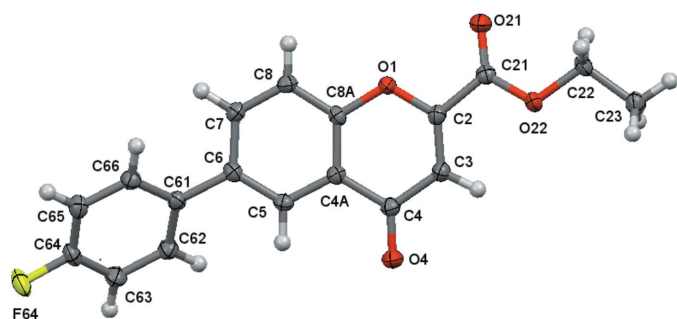
Within this framework, our project has been focused on the discovery of new chemical entities based on a chromone scaffold. Herein we describe the crystal structures of two new chromone derivatives, *viz.* ethyl-6-(4-methylphenyl)-4-oxo-4*H*-chromene-2-carboxylate (**1**) and ethyl-6-(4-fluorophenyl)-4-oxo-4*H*-chromene-2-carboxylate (**2**).

## 2. Molecular Geometry

Ellipsoid plots of the molecules are given in Figs. 1 and 2. Compound (**1**) crystallizes with two molecules (*a* and *b*) in the asymmetric unit.



**Figure 1**  
 A view of the asymmetric unit of (**1**), with displacement ellipsoids drawn at the 70% probability level.



**Figure 2**  
 A view of the asymmetric unit of (**2**), with displacement ellipsoids drawn at the 70% probability level.

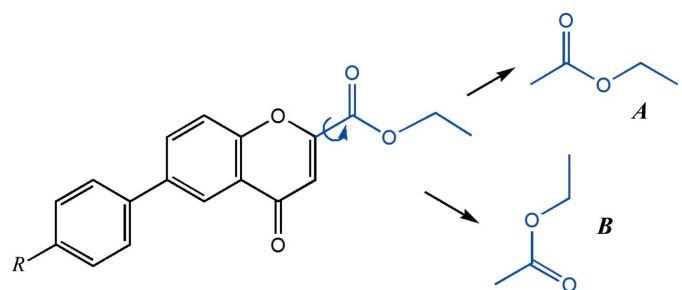
**Table 1**  
 Selected dihedral angles ( $^\circ$ ).

$\theta_{\text{Chr-C3ring}}$  is the dihedral angle between the mean planes of the chromene and the phenyl ring.  $\theta_{\text{Chr-C6ester}}$  is the dihedral angle between the mean planes of the chromone ring and the plane defined by the ester atoms attached to C2 but not including it.  $\theta_{\text{Chr-OCO}}$  is the dihedral angle between the mean planes of the chromone ring and the OCO atoms of the ester.

| Compound                       | $\theta_{\text{Chr-Phe}}$ | $\theta_{\text{Chr-carboxylate}}$ | $\theta_{\text{Chr-OCO}}$ |
|--------------------------------|---------------------------|-----------------------------------|---------------------------|
| ( <b>1</b> ) molecule <i>a</i> | 32.8754                   | 23.23 (7)                         | 21.16 (16)                |
| ( <b>1</b> ) molecule <i>b</i> | 24.14 (5)                 | 14.191 (7)                        | 12.16 (17)                |
| ( <b>2</b> )                   | 36.05 (5)                 | 9.52 (6)                          | 12.97 (13)                |

The molecules consist of a central chromone core with an ethylester substituent at the 2-position and a *p*-substituted phenyl group at the 6-position of the chromone ring system. Those constitutive fragments are essentially planar, therefore the major contribution to the definition of the molecular conformations are the rotations around the C—C bonds that connect the substituents to the chromone ring. As such, the analysis of the molecular geometry will be based on the values for the dihedral angles between the mean planes of the chromone and the phenyl ring ( $\theta_{\text{Chr-Phe}}$ ) and the chromone and the ethyl carboxylate moiety ( $\theta_{\text{Chr-carboxylate}}$ ), Table 1. As can be seen, the dihedral angles for molecules *a* and *b* of (**1**) are significantly different from each other. An overlay fit using the quaternion transformation method (Mackay, 1984) shows that molecule *i* inverts on molecule *ii* where the weighted/unit weight r.m.s. fits are 0.090/0.089 Å for 23 atoms. The largest individual displacement is 0.169 Å (O14/O24 pair). The r.m.s. bond fit is 0.0021 Å and the r.m.s. angle fit is 0.376°. These values show that, in spite of the large differences in the dihedral angles, the molecules are quite similar overall.

Considering the relative position of the ethyl carboxylate residue with respect to the chromone ring as may be seen in Fig. 3, the molecules may have any conformation between two possible extremes: conformation *A* where the carbonyl groups are *trans*-related and conformation *B* where they are *cis*-related. A theoretical calculation made with *Gaussian03* (Frisch *et al.*, 2004) at the B3LYP/631++(d,p) level shows that the energy associated with each of the boundary conformations is similar in adiabatic conditions [see supporting information; the B3LYP model combines the hybrid exchange



**Figure 3**  
 The relative position of the ethyl carboxylate residue with respect to the chromone ring. Molecules may have any conformation between two possible extremes: conformation *A* where the carbonyl groups are *trans*-related and conformation *B* where they are *cis*-related.

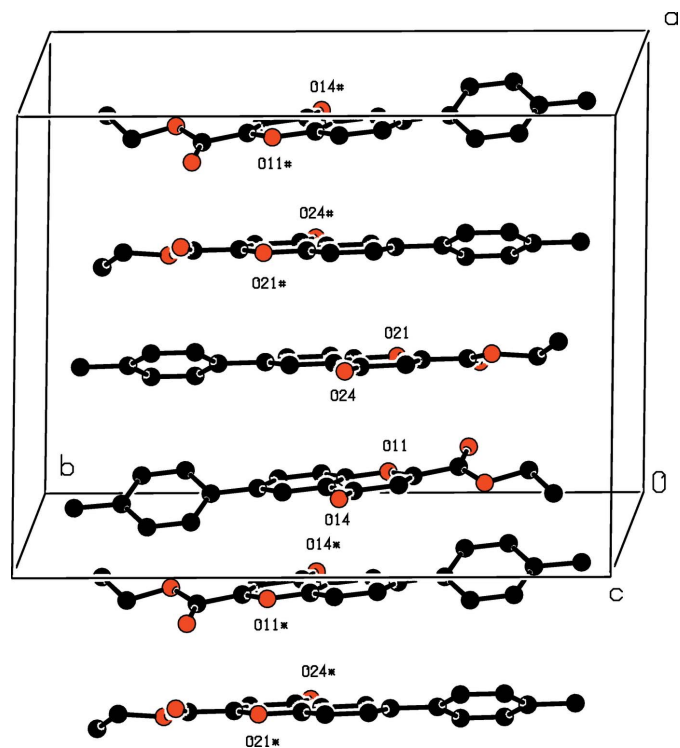
**Table 2**  
Hydrogen-bond geometry (Å, °) for (1).

| <i>D</i> —H··· <i>A</i>           | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|-----------------------------------|-------------|---------------|-----------------------|-------------------------|
| C162—H162···Cg(C261)              | 0.95        | 2.85          | 3.4914 (15)           | 126                     |
| C262—H262···Cg(C161) <sup>i</sup> | 0.95        | 2.84          | 3.5408 (4)            | 131                     |

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

functional of Becke (1997) with the gradient-correlation functional of Lee *et al.* (1988) and the split-valence polarized 6-311+G(d, p) basis set (Hehre *et al.*, 1986)]. Thus the adopted conformation in the solid state, with a geometry closer to *A* where the degree of twist lies between 9 and 21° (as measured by dihedral angles) may be due to packing factors. Preliminary results for the structures of similar compounds such as 6-(phenyl)-4-oxo-4*H*-chromene-2-carboxylate, 6-(4-methoxyphenyl)-4-oxo-4*H*-chromene-2-carboxylate and 6-(4-3,4-dimethoxyphenyl)-4-oxo-4*H*-chromene-2-carboxylate indicate that the major components have the same *trans* conformation as described above. These structures are imprecisely determined (the crystal quality was poor and the structures appeared to be intractably disordered).

The rotation around the C(phenyl)—C(chromone) bond is higher than the rotation around the C(chromone)—C(carboxyethyl) bond for all of the three molecules. This rotation may also contribute to the molecular packing since, in the absence of electronically crowded substituents in the *o*- or



**Figure 4**  
A view showing the stacking of the molecules along the *a* axis. Symmetry codes: (\*)  $-x, -y + 1, -z + 1$ ; (#)  $-x + 1, -y + 1, -z + 1$ . H atoms were omitted.

**Table 3**  
Selected  $\pi$ – $\pi$  contacts and short intermolecular contacts (Å, °).

In compound (1), Cg1, Cg2, Cg5 and Cg6 are the centroids of the rings containing atoms O11, C15, O21 and C25, respectively. In compound (2), Cg1, Cg2 and Cg6 are the centroids of the rings containing atoms O1, C5 and C61. Values marked with an asterisk are average perpendicular distances and angles between the planes.

| Compound | contacts                 | distance   | perp. distance | slippage/angle* |
|----------|--------------------------|------------|----------------|-----------------|
| (1)      | Cg1···Cg2 <sup>i</sup>   | 3.7338 (8) | 3.503*         | 0.45*           |
|          | Cg2···Cg2 <sup>i</sup>   | 3.7226 (8) | 3.5040 (6)     | 1.257           |
|          | Cg5···Cg6 <sup>ii</sup>  | 3.6743 (9) | 3.824*         | 0.98*           |
|          | Cg6···Cg6 <sup>ii</sup>  | 3.9299 (9) | 3.5762 (6)     | 1.630           |
| (2)      | Cg1···Cg1 <sup>iii</sup> | 3.8521 (7) | 3.3989 (4)     | 1.813           |
|          | Cg2···Cg2 <sup>iii</sup> | 3.8521 (7) | 3.3957 (4)     | 1.819           |
|          | Cg3···Cg3 <sup>iii</sup> | 3.8521 (7) | 3.5811 (5)     | 1.419           |

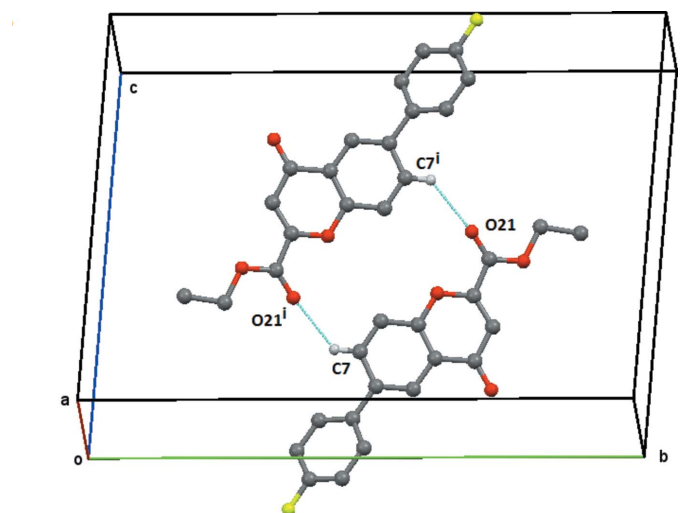
Symmetry codes: (i)  $-x, 1 - y, 1 - z$ ; (ii)  $1 - x, 1 - y, 1 - z$ ; (iii)  $1 + x, y, z$ .

*m*- positions, the phenyl substituent does not impose steric hindrance with respect to the chromone ring.

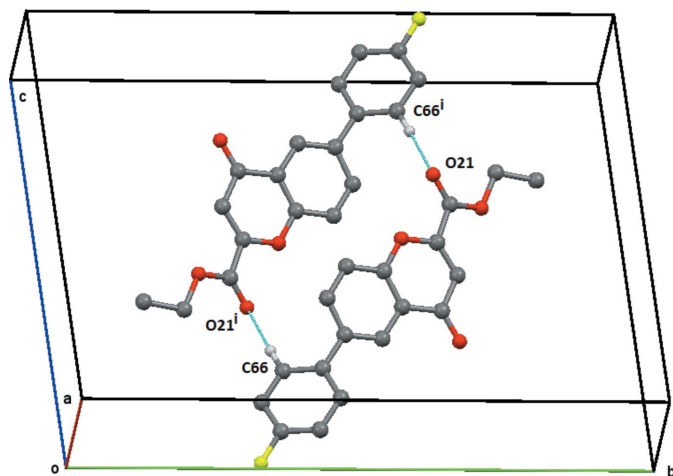
### 3. Supramolecular structures

In the absence of strong hydrogen-bond donors, the supramolecular structures depend on weak C—H···O hydrogen bonds and C—H··· $\pi$  and very weak  $\pi$ – $\pi$  interactions.

In (1) there are no weak C—H···O interactions and aromatic interactions appear to play the major role in the establishment of the packing. There are two T-shaped C—H··· $\pi$  interactions, one between C162 and the centroid of the phenyl ring with pivot atom C261, Cg(C261) within the selected asymmetric unit, and the other between C262 and the centroid of the phenyl ring with pivot atom C161, Cg(C161)( $x, \frac{3}{2} - y, -\frac{1}{2} + z$ ), Table 2. This forms a chain of alternating glide-related asymmetric units which runs parallel to the *c* axis. Within the asymmetric unit, the shortest packing contact is



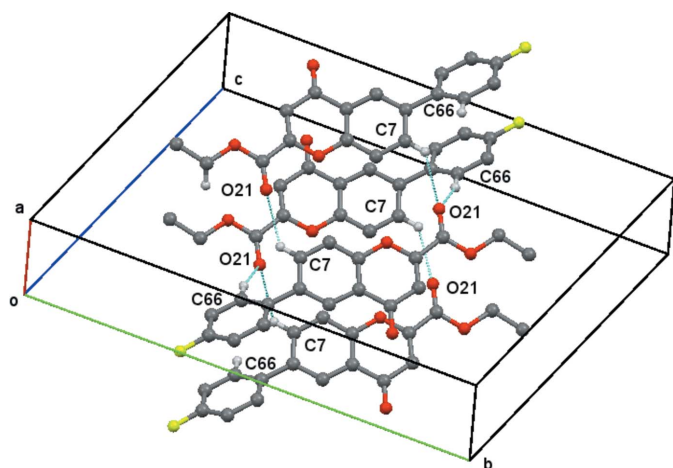
**Figure 5**  
Compound (2), view of the C7—H7···O21 centrosymmetric  $R_2^2(16)$  ring structure centred on  $(0, \frac{1}{2}, \frac{1}{2})$ . Atoms labelled with a postscript, (i), are in molecules at  $(-x, -y + 1, -z + 1)$ . Hydrogen atoms not involved in the hydrogen bonding are omitted.



**Figure 6**  
Compound (2), view of the C66–H66···O21 centrosymmetric  $R_2^2(22)$  ring structure centred on  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ . H atoms not involved in the hydrogen bonding are omitted.

between the rings containing C15 and C25 and has a value of 4.2901 (9) Å, with an average perpendicular distance between the planes of 3.5350 Å and an angle between the planes of 6.46 (7)°, suggesting a possible very weak  $\pi$ – $\pi$  interaction. Centrosymmetrically related pairs of molecule i form  $\pi$ – $\pi$  stacked pairs, as do centrosymmetric pairs of molecule ii, Table 3. These base-paired units form a column of molecule along the  $a$  axis, Fig. 4.

In contrast, compound (2) has a more intricate supra-molecular structure, based on C–H···O and  $\pi$ – $\pi$  interactions (Tables 3 and 4). Both carboxylic oxygen atoms (O21 and O4) act as acceptors of C–H···O hydrogen bonds. Atom O21 is involved in two centrosymmetrically linked ring structures. In one of these, the C7–H7···O21( $-x, -y + 1, -z + 1$ ) hydrogen bond forms an  $R_2^2(16)$  ring, Fig. 5, and in the other the C66–H66···O21( $-x + 1, -y + 1, -z + 1$ ) hydrogen bond



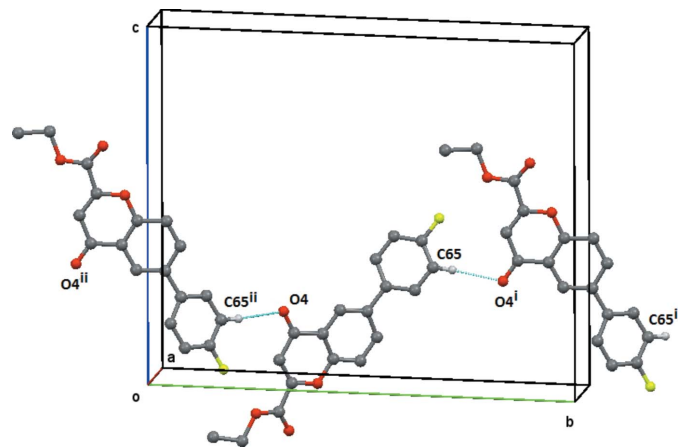
**Figure 7**  
Compound (2), the combined ring structure formed by the combination of the ring structures in Figs. 4 and 5. This chain of rings extends along the  $a$  axis. H atoms not involved in the hydrogen bonding are omitted.

**Table 4**  
Hydrogen-bond geometry (Å, °) for (2).

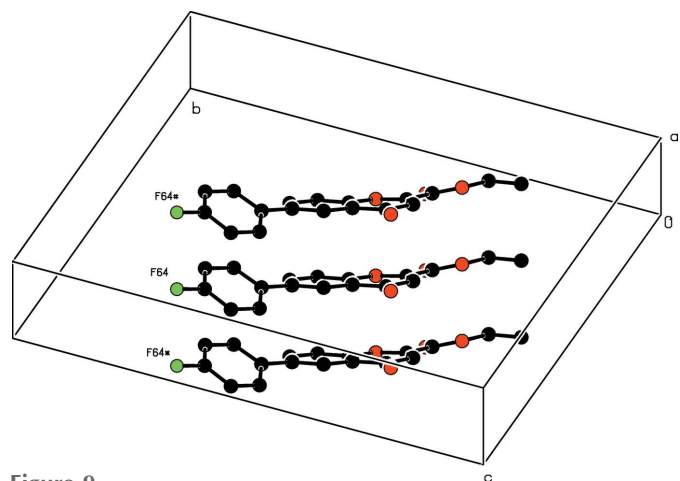
| $D-H\cdots A$                | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------|-------|-------------|-------------|---------------|
| C7–H7···O21 <sup>i</sup>     | 0.95  | 2.47        | 3.1977 (13) | 133           |
| C65–H65···O4 <sup>ii</sup>   | 0.95  | 2.50        | 3.4447 (13) | 175           |
| C66–H66···O21 <sup>iii</sup> | 0.95  | 2.53        | 3.4425 (13) | 162           |

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

forms an  $R_2^2(22)$  ring (Fig. 6). These interactions combine to link the molecules into zigzag chains of rings which run parallel to the  $a$  axis, Fig. 7. These are linked to form a three-dimensional network by the C65–H65···O4( $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$ ) weak hydrogen bond formed by the action of the twofold screw axis at  $(1, y, \frac{3}{4})$ , Fig. 8. The molecules are  $\pi$ – $\pi$  stacked above each other with unit translation along the  $a$  axis, Table 3 and Fig. 9.



**Figure 8**  
Compound (2), the simple C9 chain formed by the C65–H65···O4 weak hydrogen bond. This chain of rings extends along the  $a$  axis and is generated by the twofold screw axis at  $(1, y, \frac{3}{4})$ . Symmetry codes: (i)  $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$ . H atoms not involved in the hydrogen bonding are omitted.



**Figure 9**  
A view showing the stacking of the molecules along the  $a$  axis. Symmetry codes: (\*)  $x - 1, y, z$ ; (#)  $x + 1, y, z + 1$ . H atoms are omitted.

**Table 5**  
Experimental details.

|   | (1)   | (2)   |
|---|---|---|
| <b>Crystal data</b>   |   |   |
| Chemical formula  | C <sub>19</sub> H <sub>16</sub> O <sub>4</sub>              | C <sub>18</sub> H <sub>13</sub> FO <sub>4</sub>           |
| <i>M<sub>r</sub></i>  | 308.32  | 312.28  |
| Crystal system, space group   | Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>   | Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i> |
| Temperature (K)   | 100   | 100   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)  | 14.7129 (11), 18.9613 (13), 11.3031 (6)                     | 3.8521 (2), 20.6970 (15), 17.5478 (11)                    |
| $\beta$ (°)   | 111.632 (7)   | 91.546 (1)  |
| <i>V</i> (Å <sup>3</sup> )  | 2931.2 (4)  | 1398.52 (15)  |
| <i>Z</i>  | 8   | 4   |
| Radiation type  | Mo <i>K</i> $\alpha$  | Mo <i>K</i> $\alpha$                                      |
| $\mu$ (mm <sup>-1</sup> )   | 0.10  | 0.11  |
| Crystal size (mm)   | 0.20 × 0.09 × 0.05  | 0.42 × 0.02 × 0.01  |
| <b>Data collection</b>  |   |   |
| Diffractometer  | Rigaku Saturn724+   | Rigaku Saturn724+   |
| Absorption correction   | Multi-scan ( <i>CrystalClear-SM Expert</i> ; Rigaku, 20112) | Multi-scan <i>CrystalClear-SM Expert</i> (Rigaku, 20112)  |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>   | 0.981, 0.995  | 0.954, 0.999  |
| No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections                             | 22133, 6680, 5311   | 16479, 3177, 2725   |
| <i>R</i> <sub>int</sub>   | 0.033   | 0.035   |
| ( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )   | 0.649   | 0.650   |
| <b>Refinement</b>   |   |   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.038, 0.104, 1.11  | 0.031, 0.087, 0.98  |
| No. of reflections  | 6680  | 3176  |
| No. of parameters   | 419   | 209   |
| H-atom treatment  | H-atom parameters constrained                               | H-atom parameters constrained                             |
| $\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )  | 0.33, -0.23   | 0.31, -0.20   |

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *OSCAIL* (McArdle *et al.*, 2004), *ShelXle* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2009).

The intermolecular interactions probably account for the significant difference (about 36 K) in the melting points for these compounds [411–418 K for (1) and 446–455 K for (2)]. They also may have an influence in the conformations of the molecules since in (2) the atoms in the carboxyethyl group are involved either as donors or acceptors; these interactions may constrain the conformation of the orientation of the carboxyethyl moiety.

#### 4. Synthesis and crystallization

Compounds (1) and (2) were obtained, in moderate yields, by a two-step synthetic procedure. In the first step, the required phenylacetophenone derivatives were obtained from 5'-bromo-2'-hydroxyacetophenone by a Suzuki C–C cross-coupling reaction assisted by microwave (MW) heating (Soares *et al.*, 2015). In the second step, the phenylacetophenone derivatives were converted in the corresponding chromones *via* an intramolecular Claisen condensation reaction accomplished with diethyl oxalate in the presence of ethanolic sodium ethoxide and cyclization under acidic conditions of the intermediate formed *in situ*.

Ethyl 6-(4-methylphenyl)-4-oxo-4*H*-chromene-2-carboxylate (1). Overall yield 50.7%; m.p. 411–418 K. Crystallization: ethyl acetate to form colourless prisms.

Ethyl 6-(4-fluorophenyl)-4-oxo-4*H*-chromene-2-carboxylate (2). Overall yield 55.9%; m.p. 446–455 K. Crystallization: ethyl acetate, to form colourless needles.

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. H atoms were treated as riding atoms with C–H(aromatic) = 0.95 Å, with *U*<sub>iso</sub> = 1.2*U*<sub>eq</sub>(C) and C–H(methyl) = 0.98 Å with *U*<sub>iso</sub> = 1.5*U*<sub>eq</sub>(C).

#### Acknowledgements

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## supporting information

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## Crystal structures of ethyl 6-(4-methylphenyl)-4-oxo-4*H*-chromene-2-carboxylate and ethyl 6-(4-fluorophenyl)-4-oxo-4*H*-chromene-2-carboxylate

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### Computing details

For both compounds, data collection: *CrystalClear-SM Expert* (Rigaku, 2012); cell refinement: *CrystalClear-SM Expert* (Rigaku, 2012); data reduction: *CrystalClear-SM Expert* (Rigaku, 2012); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *OSCAIL* (McArdle *et al.*, 2004), *ShelXle* (Hübschle *et al.*, 2011) and *SHELXL2014* (Sheldrick, 2015b). Molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2009) for (1); *Mercury* (Macrae *et al.*, 2006) for (2). For both compounds, software used to prepare material for publication: *OSCAIL* (McArdle *et al.*, 2004), *SHELXL2014* (Sheldrick, 2015b) and *PLATON* (Spek, 2009).

### (1) Ethyl 6-(4-methylphenyl)-4-oxo-4*H*-chromene-2-carboxylate

#### Crystal data

|                                |   |
|--------------------------------|---|
| $C_{19}H_{16}O_4$              | $F(000) = 1296$   |
| $M_r = 308.32$                 | $D_x = 1.397 \text{ Mg m}^{-3}$                         |
| Monoclinic, $P2_1/c$           | Mo $K\alpha$ radiation, $\lambda = 0.71075 \text{ \AA}$ |
| $a = 14.7129 (11) \text{ \AA}$ | Cell parameters from 18061 reflections                  |
| $b = 18.9613 (13) \text{ \AA}$ | $\theta = 3.0\text{--}27.5^\circ$                       |
| $c = 11.3031 (6) \text{ \AA}$  | $\mu = 0.10 \text{ mm}^{-1}$                            |
| $\beta = 111.632 (7)^\circ$    | $T = 100 \text{ K}$                                     |
| $V = 2931.2 (4) \text{ \AA}^3$ | Prism, colourless                                       |
| $Z = 8$                        | $0.20 \times 0.09 \times 0.05 \text{ mm}$               |

#### Data collection

|   |  |
|---|--|
| Rigaku Saturn724+ (2x2 bin mode) diffractometer       | 22133 measured reflections   |
| Radiation source: Rotating Anode                      | 6680 independent reflections   |
| Confocal monochromator                                | 5311 reflections with $I > 2\sigma(I)$                                 |
| Detector resolution: $28.5714 \text{ pixels mm}^{-1}$ | $R_{\text{int}} = 0.033$   |
| profile data from $\omega$ -scans                     | $\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 3.0^\circ$ |
| Absorption correction: multi-scan                     | $h = -17 \rightarrow 19$   |
| ( <i>CrystalClear-SM Expert</i> ; Rigaku, 20112)      | $k = -17 \rightarrow 24$   |
| $T_{\text{min}} = 0.981$ , $T_{\text{max}} = 0.995$   | $l = -14 \rightarrow 14$   |

#### Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | 419 parameters   |
| Least-squares matrix: full      | 0 restraints   |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.104$               | H-atom parameters constrained                            |
| $S = 1.11$                      |  |
| 6680 reflections                |  |

$$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.4579P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|      | x            | y           | z            | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|-------------|--------------|----------------------------------|
| O11  | 0.13984 (7)  | 0.39931 (4) | 0.51267 (8)  | 0.0167 (2)                       |
| O14  | 0.14523 (8)  | 0.46234 (5) | 0.86202 (8)  | 0.0239 (2)                       |
| O121 | 0.18698 (7)  | 0.26721 (4) | 0.47772 (8)  | 0.0186 (2)                       |
| O122 | 0.13729 (7)  | 0.23141 (4) | 0.63468 (8)  | 0.0162 (2)                       |
| C12  | 0.14765 (9)  | 0.35255 (6) | 0.60658 (11) | 0.0153 (3)                       |
| C13  | 0.14901 (9)  | 0.37041 (6) | 0.72208 (11) | 0.0161 (3)                       |
| H13  | 0.1540       | 0.3344      | 0.7827       | 0.019*                           |
| C14  | 0.14293 (10) | 0.44401 (6) | 0.75658 (11) | 0.0166 (3)                       |
| C14A | 0.13289 (9)  | 0.49463 (6) | 0.65301 (11) | 0.0150 (2)                       |
| C15  | 0.12422 (9)  | 0.56769 (6) | 0.66738 (11) | 0.0156 (3)                       |
| H15  | 0.1247       | 0.5855      | 0.7462       | 0.019*                           |
| C16  | 0.11494 (9)  | 0.61435 (6) | 0.56912 (11) | 0.0147 (2)                       |
| C17  | 0.11434 (10) | 0.58625 (6) | 0.45309 (11) | 0.0171 (3)                       |
| H17  | 0.1084       | 0.6175      | 0.3849       | 0.021*                           |
| C18  | 0.12206 (10) | 0.51512 (7) | 0.43612 (11) | 0.0176 (3)                       |
| H18  | 0.1209       | 0.4972      | 0.3571       | 0.021*                           |
| C18A | 0.13157 (9)  | 0.46978 (6) | 0.53635 (11) | 0.0150 (3)                       |
| C121 | 0.15961 (9)  | 0.27911 (6) | 0.56400 (11) | 0.0152 (3)                       |
| C122 | 0.16128 (10) | 0.15886 (6) | 0.61422 (11) | 0.0173 (3)                       |
| H12A | 0.2328       | 0.1535      | 0.6384       | 0.021*                           |
| H12B | 0.1288       | 0.1457      | 0.5235       | 0.021*                           |
| C123 | 0.12554 (11) | 0.11295 (6) | 0.69613 (12) | 0.0222 (3)                       |
| H12C | 0.1445       | 0.0639      | 0.6900       | 0.033*                           |
| H12D | 0.0542       | 0.1162      | 0.6671       | 0.033*                           |
| H12E | 0.1546       | 0.1287      | 0.7848       | 0.033*                           |
| C161 | 0.10558 (9)  | 0.69191 (6) | 0.58084 (11) | 0.0141 (2)                       |
| C162 | 0.14423 (9)  | 0.73832 (6) | 0.51543 (11) | 0.0160 (3)                       |
| H162 | 0.1776       | 0.7200      | 0.4645       | 0.019*                           |
| C163 | 0.13461 (9)  | 0.81085 (6) | 0.52375 (11) | 0.0168 (3)                       |
| H163 | 0.1612       | 0.8412      | 0.4779       | 0.020*                           |
| C164 | 0.08671 (9)  | 0.83989 (6) | 0.59792 (11) | 0.0162 (3)                       |
| C165 | 0.04831 (9)  | 0.79352 (6) | 0.66303 (11) | 0.0164 (3)                       |
| H165 | 0.0150       | 0.8120      | 0.7140       | 0.020*                           |
| C166 | 0.05741 (9)  | 0.72085 (6) | 0.65533 (11) | 0.0157 (3)                       |
| H166 | 0.0306       | 0.6906      | 0.7011       | 0.019*                           |
| C167 | 0.07977 (10) | 0.91884 (6) | 0.60848 (12) | 0.0208 (3)                       |



|      |              |             |              |            |
|------|--------------|-------------|--------------|------------|
| H16A | 0.0176       | 0.9310      | 0.6167       | 0.031*     |
| H16B | 0.0831       | 0.9412      | 0.5320       | 0.031*     |
| H16C | 0.1341       | 0.9356      | 0.6836       | 0.031*     |
| O21  | 0.36690 (7)  | 0.39338 (4) | 0.38688 (8)  | 0.0173 (2) |
| O24  | 0.39990 (8)  | 0.46146 (5) | 0.74405 (8)  | 0.0256 (2) |
| O221 | 0.34285 (7)  | 0.25860 (4) | 0.32365 (8)  | 0.0197 (2) |
| O222 | 0.39836 (7)  | 0.22764 (4) | 0.53103 (8)  | 0.0170 (2) |
| C22  | 0.37715 (9)  | 0.34766 (6) | 0.48321 (11) | 0.0151 (3) |
| C23  | 0.38783 (9)  | 0.36726 (6) | 0.60153 (11) | 0.0166 (3) |
| H23  | 0.3942       | 0.3321      | 0.6639       | 0.020*     |
| C24  | 0.38986 (10) | 0.44161 (6) | 0.63652 (11) | 0.0170 (3) |
| C24A | 0.37849 (9)  | 0.49097 (6) | 0.53085 (11) | 0.0152 (3) |
| C25  | 0.37738 (9)  | 0.56447 (6) | 0.54600 (11) | 0.0155 (3) |
| H25  | 0.3850       | 0.5832      | 0.6270       | 0.019*     |
| C26  | 0.36546 (9)  | 0.61053 (6) | 0.44566 (11) | 0.0154 (3) |
| C27  | 0.35322 (10) | 0.58073 (6) | 0.32652 (12) | 0.0182 (3) |
| H27  | 0.3446       | 0.6111      | 0.2564       | 0.022*     |
| C28  | 0.35334 (10) | 0.50898 (7) | 0.30850 (12) | 0.0190 (3) |
| H28  | 0.3444       | 0.4901      | 0.2271       | 0.023*     |
| C28A | 0.36677 (9)  | 0.46452 (6) | 0.41131 (11) | 0.0159 (3) |
| C221 | 0.37034 (9)  | 0.27309 (6) | 0.43493 (11) | 0.0156 (3) |
| C222 | 0.38561 (10) | 0.15314 (6) | 0.49520 (11) | 0.0187 (3) |
| H22A | 0.4129       | 0.1431      | 0.4289       | 0.022*     |
| H22B | 0.3154       | 0.1405      | 0.4615       | 0.022*     |
| C223 | 0.43928 (11) | 0.11188 (7) | 0.61367 (12) | 0.0211 (3) |
| H22C | 0.4313       | 0.0613      | 0.5947       | 0.032*     |
| H22D | 0.4127       | 0.1233      | 0.6791       | 0.032*     |
| H22E | 0.5089       | 0.1240      | 0.6446       | 0.032*     |
| C261 | 0.36521 (9)  | 0.68856 (6) | 0.46004 (11) | 0.0146 (3) |
| C262 | 0.31923 (9)  | 0.73240 (6) | 0.35536 (11) | 0.0163 (3) |
| H262 | 0.2869       | 0.7120      | 0.2738       | 0.020*     |
| C263 | 0.31995 (9)  | 0.80523 (6) | 0.36846 (11) | 0.0167 (3) |
| H263 | 0.2885       | 0.8336      | 0.2955       | 0.020*     |
| C264 | 0.36574 (9)  | 0.83778 (6) | 0.48628 (11) | 0.0165 (3) |
| C265 | 0.41121 (10) | 0.79387 (6) | 0.59067 (11) | 0.0175 (3) |
| H265 | 0.4428       | 0.8144      | 0.6723       | 0.021*     |
| C266 | 0.41138 (9)  | 0.72107 (7) | 0.57822 (11) | 0.0166 (3) |
| H266 | 0.4434       | 0.6928      | 0.6512       | 0.020*     |
| C267 | 0.36524 (11) | 0.91687 (6) | 0.49995 (12) | 0.0211 (3) |
| H26A | 0.3662       | 0.9391      | 0.4221       | 0.032*     |
| H26B | 0.4231       | 0.9316      | 0.5725       | 0.032*     |
| H26C | 0.3061       | 0.9313      | 0.5141       | 0.032*     |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$   | $U^{23}$    |
|-----|------------|------------|------------|-------------|------------|-------------|
| O11 | 0.0239 (5) | 0.0110 (4) | 0.0160 (4) | 0.0018 (4)  | 0.0083 (4) | 0.0015 (3)  |
| O14 | 0.0381 (6) | 0.0187 (5) | 0.0180 (4) | -0.0004 (4) | 0.0138 (4) | -0.0006 (4) |

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|      |            |            |            |             |            |             |
|------|------------|------------|------------|-------------|------------|-------------|
| O121 | 0.0209 (5) | 0.0164 (4) | 0.0209 (4) | 0.0001 (4)  | 0.0103 (4) | -0.0004 (3) |
| O122 | 0.0215 (5) | 0.0103 (4) | 0.0174 (4) | 0.0006 (3)  | 0.0079 (4) | 0.0009 (3)  |
| C12  | 0.0135 (6) | 0.0129 (6) | 0.0182 (6) | -0.0002 (5) | 0.0044 (5) | 0.0023 (4)  |
| C13  | 0.0154 (7) | 0.0149 (6) | 0.0175 (6) | -0.0010 (5) | 0.0053 (5) | 0.0023 (5)  |
| C14  | 0.0173 (7) | 0.0157 (6) | 0.0168 (6) | -0.0006 (5) | 0.0063 (5) | -0.0002 (5) |
| C14A | 0.0131 (6) | 0.0145 (6) | 0.0167 (6) | 0.0002 (5)  | 0.0047 (5) | 0.0006 (5)  |
| C15  | 0.0155 (6) | 0.0157 (6) | 0.0155 (6) | -0.0011 (5) | 0.0058 (5) | -0.0015 (5) |
| C16  | 0.0123 (6) | 0.0138 (6) | 0.0170 (6) | -0.0001 (5) | 0.0042 (5) | -0.0010 (4) |
| C17  | 0.0210 (7) | 0.0138 (6) | 0.0163 (6) | 0.0017 (5)  | 0.0065 (5) | 0.0023 (4)  |
| C18  | 0.0228 (7) | 0.0158 (6) | 0.0149 (6) | 0.0022 (5)  | 0.0076 (5) | -0.0006 (5) |
| C18A | 0.0145 (7) | 0.0111 (6) | 0.0190 (6) | 0.0008 (5)  | 0.0059 (5) | -0.0011 (4) |
| C121 | 0.0123 (6) | 0.0139 (6) | 0.0175 (6) | 0.0001 (5)  | 0.0033 (5) | 0.0005 (5)  |
| C122 | 0.0224 (7) | 0.0106 (6) | 0.0186 (6) | 0.0017 (5)  | 0.0071 (5) | -0.0009 (4) |
| C123 | 0.0317 (8) | 0.0125 (6) | 0.0231 (6) | 0.0001 (6)  | 0.0109 (6) | 0.0015 (5)  |
| C161 | 0.0136 (6) | 0.0125 (6) | 0.0140 (5) | 0.0001 (5)  | 0.0024 (5) | -0.0006 (4) |
| C162 | 0.0161 (7) | 0.0165 (6) | 0.0159 (6) | 0.0015 (5)  | 0.0065 (5) | -0.0012 (5) |
| C163 | 0.0180 (7) | 0.0146 (6) | 0.0172 (6) | -0.0015 (5) | 0.0059 (5) | 0.0008 (5)  |
| C164 | 0.0152 (7) | 0.0136 (6) | 0.0155 (6) | 0.0007 (5)  | 0.0005 (5) | -0.0020 (4) |
| C165 | 0.0155 (7) | 0.0177 (6) | 0.0151 (6) | 0.0014 (5)  | 0.0047 (5) | -0.0032 (5) |
| C166 | 0.0155 (7) | 0.0164 (6) | 0.0140 (5) | -0.0009 (5) | 0.0042 (5) | -0.0003 (4) |
| C167 | 0.0241 (8) | 0.0141 (6) | 0.0237 (6) | 0.0007 (5)  | 0.0084 (6) | -0.0017 (5) |
| O21  | 0.0246 (5) | 0.0114 (4) | 0.0164 (4) | 0.0006 (4)  | 0.0082 (4) | 0.0010 (3)  |
| O24  | 0.0415 (7) | 0.0190 (5) | 0.0152 (4) | -0.0008 (4) | 0.0091 (4) | -0.0007 (3) |
| O221 | 0.0232 (5) | 0.0172 (5) | 0.0163 (4) | 0.0007 (4)  | 0.0046 (4) | -0.0006 (3) |
| O222 | 0.0224 (5) | 0.0109 (4) | 0.0163 (4) | 0.0013 (4)  | 0.0053 (4) | 0.0008 (3)  |
| C22  | 0.0137 (6) | 0.0134 (6) | 0.0167 (6) | 0.0003 (5)  | 0.0040 (5) | 0.0025 (4)  |
| C23  | 0.0160 (7) | 0.0151 (6) | 0.0166 (6) | 0.0000 (5)  | 0.0037 (5) | 0.0028 (5)  |
| C24  | 0.0169 (7) | 0.0168 (6) | 0.0154 (6) | -0.0008 (5) | 0.0036 (5) | 0.0012 (5)  |
| C24A | 0.0130 (6) | 0.0152 (6) | 0.0156 (6) | 0.0000 (5)  | 0.0031 (5) | 0.0011 (4)  |
| C25  | 0.0155 (7) | 0.0155 (6) | 0.0147 (5) | -0.0011 (5) | 0.0047 (5) | -0.0018 (4) |
| C26  | 0.0126 (6) | 0.0162 (6) | 0.0174 (6) | -0.0004 (5) | 0.0055 (5) | -0.0008 (5) |
| C27  | 0.0226 (7) | 0.0149 (6) | 0.0188 (6) | 0.0012 (5)  | 0.0096 (5) | 0.0028 (5)  |
| C28  | 0.0257 (7) | 0.0165 (6) | 0.0161 (6) | 0.0003 (5)  | 0.0092 (5) | -0.0010 (5) |
| C28A | 0.0154 (7) | 0.0130 (6) | 0.0196 (6) | 0.0008 (5)  | 0.0068 (5) | -0.0006 (5) |
| C221 | 0.0130 (6) | 0.0151 (6) | 0.0186 (6) | 0.0004 (5)  | 0.0055 (5) | 0.0014 (5)  |
| C222 | 0.0235 (7) | 0.0114 (6) | 0.0202 (6) | -0.0015 (5) | 0.0070 (5) | -0.0021 (5) |
| C223 | 0.0280 (8) | 0.0142 (6) | 0.0222 (6) | 0.0005 (5)  | 0.0107 (6) | 0.0024 (5)  |
| C261 | 0.0139 (6) | 0.0138 (6) | 0.0179 (6) | 0.0006 (5)  | 0.0082 (5) | -0.0001 (4) |
| C262 | 0.0149 (7) | 0.0181 (6) | 0.0157 (6) | -0.0011 (5) | 0.0056 (5) | -0.0021 (5) |
| C263 | 0.0158 (7) | 0.0170 (6) | 0.0168 (6) | 0.0019 (5)  | 0.0056 (5) | 0.0029 (5)  |
| C264 | 0.0151 (7) | 0.0158 (6) | 0.0207 (6) | -0.0004 (5) | 0.0090 (5) | -0.0013 (5) |
| C265 | 0.0174 (7) | 0.0175 (6) | 0.0171 (6) | -0.0009 (5) | 0.0057 (5) | -0.0039 (5) |
| C266 | 0.0157 (7) | 0.0179 (6) | 0.0159 (6) | 0.0014 (5)  | 0.0054 (5) | 0.0020 (5)  |
| C267 | 0.0253 (8) | 0.0148 (6) | 0.0228 (6) | 0.0002 (5)  | 0.0085 (6) | -0.0023 (5) |

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*Geometric parameters (Å, °)*

|                |             |                |             |
|----------------|-------------|----------------|-------------|
| O11—C12        | 1.3551 (14) | O21—C22        | 1.3561 (14) |
| O11—C18A       | 1.3769 (14) | O21—C28A       | 1.3770 (14) |
| O14—C14        | 1.2299 (14) | O24—C24        | 1.2282 (14) |
| O121—C121      | 1.2057 (14) | O221—C221      | 1.2025 (14) |
| O122—C121      | 1.3258 (14) | O222—C221      | 1.3274 (14) |
| O122—C122      | 1.4597 (14) | O222—C222      | 1.4625 (14) |
| C12—C13        | 1.3418 (16) | C22—C23        | 1.3403 (16) |
| C12—C121       | 1.5046 (17) | C22—C221       | 1.5056 (17) |
| C13—C14        | 1.4606 (17) | C23—C24        | 1.4615 (17) |
| C13—H13        | 0.9500      | C23—H23        | 0.9500      |
| C14—C14A       | 1.4785 (16) | C24—C24A       | 1.4777 (16) |
| C14A—C18A      | 1.3936 (16) | C24A—C28A      | 1.3911 (16) |
| C14A—C15       | 1.4061 (16) | C24A—C25       | 1.4049 (17) |
| C15—C16        | 1.3869 (16) | C25—C26        | 1.3904 (17) |
| C15—H15        | 0.9500      | C25—H25        | 0.9500      |
| C16—C17        | 1.4126 (16) | C26—C27        | 1.4095 (16) |
| C16—C161       | 1.4875 (16) | C26—C261       | 1.4885 (16) |
| C17—C18        | 1.3729 (17) | C27—C28        | 1.3757 (17) |
| C17—H17        | 0.9500      | C27—H27        | 0.9500      |
| C18—C18A       | 1.3877 (16) | C28—C28A       | 1.3895 (17) |
| C18—H18        | 0.9500      | C28—H28        | 0.9500      |
| C122—C123      | 1.5001 (17) | C222—C223      | 1.4998 (17) |
| C122—H12A      | 0.9900      | C222—H22A      | 0.9900      |
| C122—H12B      | 0.9900      | C222—H22B      | 0.9900      |
| C123—H12C      | 0.9800      | C223—H22C      | 0.9800      |
| C123—H12D      | 0.9800      | C223—H22D      | 0.9800      |
| C123—H12E      | 0.9800      | C223—H22E      | 0.9800      |
| C161—C166      | 1.3973 (17) | C261—C266      | 1.3989 (16) |
| C161—C162      | 1.3979 (17) | C261—C262      | 1.3995 (16) |
| C162—C163      | 1.3893 (17) | C262—C263      | 1.3885 (17) |
| C162—H162      | 0.9500      | C262—H262      | 0.9500      |
| C163—C164      | 1.3924 (17) | C263—C264      | 1.3952 (17) |
| C163—H163      | 0.9500      | C263—H263      | 0.9500      |
| C164—C165      | 1.3930 (17) | C264—C265      | 1.3968 (17) |
| C164—C167      | 1.5083 (16) | C264—C267      | 1.5079 (17) |
| C165—C166      | 1.3901 (17) | C265—C266      | 1.3875 (17) |
| C165—H165      | 0.9500      | C265—H265      | 0.9500      |
| C166—H166      | 0.9500      | C266—H266      | 0.9500      |
| C167—H16A      | 0.9800      | C267—H26A      | 0.9800      |
| C167—H16B      | 0.9800      | C267—H26B      | 0.9800      |
| C167—H16C      | 0.9800      | C267—H26C      | 0.9800      |
|                |             |                |             |
| C12—O11—C18A   | 118.08 (9)  | C22—O21—C28A   | 118.25 (9)  |
| C121—O122—C122 | 114.80 (9)  | C221—O222—C222 | 115.53 (9)  |
| C13—C12—O11    | 124.30 (11) | C23—C22—O21    | 124.14 (11) |
| C13—C12—C121   | 125.68 (11) | C23—C22—C221   | 126.14 (11) |

|                |             |                |             |
|----------------|-------------|----------------|-------------|
| O11—C12—C121   | 109.95 (10) | O21—C22—C221   | 109.67 (9)  |
| C12—C13—C14    | 121.37 (11) | C22—C23—C24    | 121.38 (11) |
| C12—C13—H13    | 119.3       | C22—C23—H23    | 119.3       |
| C14—C13—H13    | 119.3       | C24—C23—H23    | 119.3       |
| O14—C14—C13    | 123.11 (11) | O24—C24—C23    | 123.13 (11) |
| O14—C14—C14A   | 122.88 (11) | O24—C24—C24A   | 122.83 (11) |
| C13—C14—C14A   | 114.01 (10) | C23—C24—C24A   | 114.04 (10) |
| C18A—C14A—C15  | 118.18 (11) | C28A—C24A—C25  | 118.24 (11) |
| C18A—C14A—C14  | 119.48 (11) | C28A—C24A—C24  | 119.56 (11) |
| C15—C14A—C14   | 122.34 (10) | C25—C24A—C24   | 122.19 (11) |
| C16—C15—C14A   | 121.49 (11) | C26—C25—C24A   | 121.82 (11) |
| C16—C15—H15    | 119.3       | C26—C25—H25    | 119.1       |
| C14A—C15—H15   | 119.3       | C24A—C25—H25   | 119.1       |
| C15—C16—C17    | 117.90 (11) | C25—C26—C27    | 117.43 (11) |
| C15—C16—C161   | 122.99 (10) | C25—C26—C261   | 122.68 (11) |
| C17—C16—C161   | 119.11 (10) | C27—C26—C261   | 119.89 (10) |
| C18—C17—C16    | 121.85 (11) | C28—C27—C26    | 122.09 (11) |
| C18—C17—H17    | 119.1       | C28—C27—H27    | 119.0       |
| C16—C17—H17    | 119.1       | C26—C27—H27    | 119.0       |
| C17—C18—C18A   | 118.90 (11) | C27—C28—C28A   | 118.93 (11) |
| C17—C18—H18    | 120.6       | C27—C28—H28    | 120.5       |
| C18A—C18—H18   | 120.6       | C28A—C28—H28   | 120.5       |
| O11—C18A—C18   | 115.60 (10) | O21—C28A—C28   | 115.91 (10) |
| O11—C18A—C14A  | 122.73 (10) | O21—C28A—C24A  | 122.62 (10) |
| C18—C18A—C14A  | 121.67 (11) | C28—C28A—C24A  | 121.47 (11) |
| O121—C121—O122 | 126.18 (11) | O221—C221—O222 | 126.22 (11) |
| O121—C121—C12  | 123.04 (11) | O221—C221—C22  | 123.05 (11) |
| O122—C121—C12  | 110.77 (10) | O222—C221—C22  | 110.73 (10) |
| O122—C122—C123 | 106.78 (10) | O222—C222—C223 | 106.56 (10) |
| O122—C122—H12A | 110.4       | O222—C222—H22A | 110.4       |
| C123—C122—H12A | 110.4       | C223—C222—H22A | 110.4       |
| O122—C122—H12B | 110.4       | O222—C222—H22B | 110.4       |
| C123—C122—H12B | 110.4       | C223—C222—H22B | 110.4       |
| H12A—C122—H12B | 108.6       | H22A—C222—H22B | 108.6       |
| C122—C123—H12C | 109.5       | C222—C223—H22C | 109.5       |
| C122—C123—H12D | 109.5       | C222—C223—H22D | 109.5       |
| H12C—C123—H12D | 109.5       | H22C—C223—H22D | 109.5       |
| C122—C123—H12E | 109.5       | C222—C223—H22E | 109.5       |
| H12C—C123—H12E | 109.5       | H22C—C223—H22E | 109.5       |
| H12D—C123—H12E | 109.5       | H22D—C223—H22E | 109.5       |
| C166—C161—C162 | 117.85 (11) | C266—C261—C262 | 117.31 (11) |
| C166—C161—C16  | 121.74 (11) | C266—C261—C26  | 121.49 (11) |
| C162—C161—C16  | 120.40 (11) | C262—C261—C26  | 121.20 (11) |
| C163—C162—C161 | 121.06 (11) | C263—C262—C261 | 121.22 (11) |
| C163—C162—H162 | 119.5       | C263—C262—H262 | 119.4       |
| C161—C162—H162 | 119.5       | C261—C262—H262 | 119.4       |
| C162—C163—C164 | 121.27 (11) | C262—C263—C264 | 121.58 (11) |
| C162—C163—H163 | 119.4       | C262—C263—H263 | 119.2       |

|                     |              |                     |              |
|---------------------|--------------|---------------------|--------------|
| C164—C163—H163      | 119.4        | C264—C263—H263      | 119.2        |
| C163—C164—C165      | 117.54 (11)  | C263—C264—C265      | 117.07 (11)  |
| C163—C164—C167      | 120.28 (11)  | C263—C264—C267      | 121.25 (11)  |
| C165—C164—C167      | 122.16 (11)  | C265—C264—C267      | 121.68 (11)  |
| C166—C165—C164      | 121.70 (11)  | C266—C265—C264      | 121.70 (11)  |
| C166—C165—H165      | 119.2        | C266—C265—H265      | 119.1        |
| C164—C165—H165      | 119.2        | C264—C265—H265      | 119.1        |
| C165—C166—C161      | 120.59 (11)  | C265—C266—C261      | 121.12 (11)  |
| C165—C166—H166      | 119.7        | C265—C266—H266      | 119.4        |
| C161—C166—H166      | 119.7        | C261—C266—H266      | 119.4        |
| C164—C167—H16A      | 109.5        | C264—C267—H26A      | 109.5        |
| C164—C167—H16B      | 109.5        | C264—C267—H26B      | 109.5        |
| H16A—C167—H16B      | 109.5        | H26A—C267—H26B      | 109.5        |
| C164—C167—H16C      | 109.5        | C264—C267—H26C      | 109.5        |
| H16A—C167—H16C      | 109.5        | H26A—C267—H26C      | 109.5        |
| H16B—C167—H16C      | 109.5        | H26B—C267—H26C      | 109.5        |
|                     |              |                     |              |
| C18A—O11—C12—C13    | -0.81 (19)   | C28A—O21—C22—C23    | -0.43 (19)   |
| C18A—O11—C12—C121   | -177.93 (10) | C28A—O21—C22—C221   | 177.20 (10)  |
| O11—C12—C13—C14     | -0.6 (2)     | O21—C22—C23—C24     | -0.4 (2)     |
| C121—C12—C13—C14    | 176.04 (12)  | C221—C22—C23—C24    | -177.63 (12) |
| C12—C13—C14—O14     | -179.03 (13) | C22—C23—C24—O24     | -179.71 (13) |
| C12—C13—C14—C14A    | 1.46 (18)    | C22—C23—C24—C24A    | 0.44 (18)    |
| O14—C14—C14A—C18A   | 179.54 (12)  | O24—C24—C24A—C28A   | -179.56 (13) |
| C13—C14—C14A—C18A   | -0.96 (17)   | C23—C24—C24A—C28A   | 0.29 (18)    |
| O14—C14—C14A—C15    | -0.7 (2)     | O24—C24—C24A—C25    | -0.7 (2)     |
| C13—C14—C14A—C15    | 178.85 (12)  | C23—C24—C24A—C25    | 179.18 (12)  |
| C18A—C14A—C15—C16   | -0.24 (19)   | C28A—C24A—C25—C26   | -0.31 (19)   |
| C14—C14A—C15—C16    | 179.95 (12)  | C24—C24A—C25—C26    | -179.21 (12) |
| C14A—C15—C16—C17    | 0.05 (19)    | C24A—C25—C26—C27    | 0.75 (19)    |
| C14A—C15—C16—C161   | 179.98 (12)  | C24A—C25—C26—C261   | -179.29 (12) |
| C15—C16—C17—C18     | 0.36 (19)    | C25—C26—C27—C28     | -0.3 (2)     |
| C161—C16—C17—C18    | -179.57 (12) | C261—C26—C27—C28    | 179.72 (12)  |
| C16—C17—C18—C18A    | -0.6 (2)     | C26—C27—C28—C28A    | -0.5 (2)     |
| C12—O11—C18A—C18    | -178.91 (11) | C22—O21—C28A—C28    | -178.28 (11) |
| C12—O11—C18A—C14A   | 1.31 (18)    | C22—O21—C28A—C24A   | 1.20 (18)    |
| C17—C18—C18A—O11    | -179.42 (11) | C27—C28—C28A—O21    | -179.49 (12) |
| C17—C18—C18A—C14A   | 0.4 (2)      | C27—C28—C28A—C24A   | 1.0 (2)      |
| C15—C14A—C18A—O11   | 179.80 (11)  | C25—C24A—C28A—O21   | 179.94 (11)  |
| C14—C14A—C18A—O11   | -0.39 (19)   | C24—C24A—C28A—O21   | -1.13 (19)   |
| C15—C14A—C18A—C18   | 0.03 (19)    | C25—C24A—C28A—C28   | -0.60 (19)   |
| C14—C14A—C18A—C18   | 179.84 (12)  | C24—C24A—C28A—C28   | 178.33 (12)  |
| C122—O122—C121—O121 | 8.49 (18)    | C222—O222—C221—O221 | -5.78 (19)   |
| C122—O122—C121—C12  | -170.74 (10) | C222—O222—C221—C22  | 174.17 (10)  |
| C13—C12—C121—O121   | -156.97 (13) | C23—C22—C221—O221   | 165.68 (13)  |
| O11—C12—C121—O121   | 20.10 (17)   | O21—C22—C221—O221   | -11.89 (17)  |
| C13—C12—C121—O122   | 22.30 (18)   | C23—C22—C221—O222   | -14.27 (18)  |
| O11—C12—C121—O122   | -160.63 (10) | O21—C22—C221—O222   | 168.16 (10)  |

|                     |              |                     |              |
|---------------------|--------------|---------------------|--------------|
| C121—O122—C122—C123 | -176.76 (10) | C221—O222—C222—C223 | 168.94 (11)  |
| C15—C16—C161—C166   | -33.27 (18)  | C25—C26—C261—C266   | 24.15 (19)   |
| C17—C16—C161—C166   | 146.65 (12)  | C27—C26—C261—C266   | -155.89 (12) |
| C15—C16—C161—C162   | 147.55 (12)  | C25—C26—C261—C262   | -156.33 (12) |
| C17—C16—C161—C162   | -32.53 (18)  | C27—C26—C261—C262   | 23.63 (18)   |
| C166—C161—C162—C163 | -0.31 (18)   | C266—C261—C262—C263 | 0.30 (18)    |
| C16—C161—C162—C163  | 178.90 (11)  | C26—C261—C262—C263  | -179.24 (11) |
| C161—C162—C163—C164 | 0.36 (19)    | C261—C262—C263—C264 | -0.47 (19)   |
| C162—C163—C164—C165 | -0.32 (18)   | C262—C263—C264—C265 | 0.19 (18)    |
| C162—C163—C164—C167 | 178.21 (12)  | C262—C263—C264—C267 | -179.32 (12) |
| C163—C164—C165—C166 | 0.26 (18)    | C263—C264—C265—C266 | 0.26 (19)    |
| C167—C164—C165—C166 | -178.24 (11) | C267—C264—C265—C266 | 179.76 (12)  |
| C164—C165—C166—C161 | -0.23 (19)   | C264—C265—C266—C261 | -0.4 (2)     |
| C162—C161—C166—C165 | 0.25 (18)    | C262—C261—C266—C265 | 0.14 (19)    |
| C16—C161—C166—C165  | -178.95 (11) | C26—C261—C266—C265  | 179.68 (12)  |

## Hydrogen-bond geometry (Å, °)

| D—H...A                           | D—H  | H...A | D...A       | D—H...A |
|-----------------------------------|------|-------|-------------|---------|
| C162—H162...Cg(C261)              | 0.95 | 2.85  | 3.4914 (15) | 126     |
| C262—H262...Cg(C161) <sup>i</sup> | 0.95 | 2.84  | 3.5408 (4)  | 131     |

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

## (2) Ethyl 6-(4-fluorophenyl)-4-oxo-4H-chromene-2-carboxylate

## Crystal data

C<sub>18</sub>H<sub>13</sub>FO<sub>4</sub>  
*M<sub>r</sub>* = 312.28  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 3.8521 (2) Å  
*b* = 20.6970 (15) Å  
*c* = 17.5478 (11) Å  
 $\beta$  = 91.546 (1)°  
*V* = 1398.52 (15) Å<sup>3</sup>  
*Z* = 4

*F*(000) = 648  
*D<sub>x</sub>* = 1.483 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71075 Å  
 Cell parameters from 15331 reflections  
 $\theta$  = 2.3–27.5°  
 $\mu$  = 0.11 mm<sup>-1</sup>  
*T* = 100 K  
 Needle, colourless  
 0.42 × 0.02 × 0.01 mm

## Data collection

Rigaku Saturn724+ (2x2 bin mode)  
 diffractometer  
 Radiation source: Sealed Tube  
 Graphite Monochromator monochromator  
 Detector resolution: 28.5714 pixels mm<sup>-1</sup>  
 profile data from  $\omega$ -scans  
 Absorption correction: multi-scan  
*CrystalClear-SM Expert* (Rigaku, 20112)  
*T<sub>min</sub>* = 0.954, *T<sub>max</sub>* = 0.999

16479 measured reflections  
 3177 independent reflections  
 2725 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.035  
 $\theta_{\max}$  = 27.5°,  $\theta_{\min}$  = 2.3°  
*h* = -4→4  
*k* = -26→26  
*l* = -22→22

## Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.031

*wR*(*F*<sup>2</sup>) = 0.087  
*S* = 0.98  
 3176 reflections

209 parameters  
 0 restraints  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.4787P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{Å}^{-3}$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

|      | x            | y           | z           | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|-------------|-------------|----------------------------------|
| C2   | 0.3562 (3)   | 0.34130 (5) | 0.52749 (6) | 0.0141 (2)                       |
| C3   | 0.5254 (3)   | 0.30718 (5) | 0.58218 (6) | 0.0155 (2)                       |
| H3   | 0.5714       | 0.2626      | 0.5741      | 0.019*                           |
| C4   | 0.6397 (3)   | 0.33746 (5) | 0.65381 (6) | 0.0149 (2)                       |
| C5   | 0.6674 (3)   | 0.44460 (5) | 0.72144 (6) | 0.0138 (2)                       |
| H5   | 0.7882       | 0.4245      | 0.7630      | 0.017*                           |
| C4A  | 0.5615 (3)   | 0.40718 (5) | 0.65824 (6) | 0.0135 (2)                       |
| C6   | 0.5990 (3)   | 0.51041 (5) | 0.72442 (6) | 0.0137 (2)                       |
| C7   | 0.4184 (3)   | 0.53915 (5) | 0.66195 (6) | 0.0145 (2)                       |
| H7   | 0.3699       | 0.5841      | 0.6633      | 0.017*                           |
| C8   | 0.3108 (3)   | 0.50362 (5) | 0.59912 (6) | 0.0147 (2)                       |
| H8   | 0.1891       | 0.5237      | 0.5577      | 0.018*                           |
| C8A  | 0.3843 (3)   | 0.43766 (5) | 0.59763 (6) | 0.0134 (2)                       |
| C21  | 0.2302 (3)   | 0.31555 (5) | 0.45161 (6) | 0.0143 (2)                       |
| C22  | 0.2530 (3)   | 0.22857 (5) | 0.36482 (6) | 0.0175 (2)                       |
| H22A | 0.3781       | 0.2496      | 0.3230      | 0.021*                           |
| H22B | 0.0005       | 0.2343      | 0.3553      | 0.021*                           |
| C23  | 0.3417 (3)   | 0.15775 (5) | 0.36840 (6) | 0.0193 (2)                       |
| H23A | 0.2795       | 0.1373      | 0.3195      | 0.029*                           |
| H23B | 0.2120       | 0.1372      | 0.4091      | 0.029*                           |
| H23C | 0.5914       | 0.1526      | 0.3789      | 0.029*                           |
| C61  | 0.7187 (3)   | 0.55070 (5) | 0.79004 (6) | 0.0142 (2)                       |
| C62  | 0.7275 (3)   | 0.52672 (5) | 0.86460 (6) | 0.0169 (2)                       |
| H62  | 0.6491       | 0.4840      | 0.8740      | 0.020*                           |
| C63  | 0.8493 (3)   | 0.56456 (5) | 0.92520 (6) | 0.0193 (2)                       |
| H63  | 0.8535       | 0.5483      | 0.9759      | 0.023*                           |
| C64  | 0.9640 (3)   | 0.62638 (5) | 0.90974 (6) | 0.0182 (2)                       |
| C65  | 0.9542 (3)   | 0.65260 (5) | 0.83766 (6) | 0.0179 (2)                       |
| H65  | 1.0299       | 0.6956      | 0.8290      | 0.021*                           |
| C66  | 0.8302 (3)   | 0.61423 (5) | 0.77786 (6) | 0.0161 (2)                       |
| H66  | 0.8207       | 0.6315      | 0.7277      | 0.019*                           |
| F64  | 1.0940 (2)   | 0.66280 (3) | 0.96871 (4) | 0.02586 (17)                     |
| O1   | 0.27388 (19) | 0.40483 (3) | 0.53315 (4) | 0.01485 (17)                     |
| O4   | 0.7946 (2)   | 0.30785 (4) | 0.70522 (4) | 0.02071 (19)                     |

|     |            |             |             |              |
|-----|------------|-------------|-------------|--------------|
| O21 | 0.0372 (2) | 0.34557 (4) | 0.40948 (4) | 0.02041 (18) |
| O22 | 0.3576 (2) | 0.25727 (4) | 0.43820 (4) | 0.01680 (17) |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|------------|------------|------------|-------------|-------------|-------------|
| C2  | 0.0153 (5) | 0.0131 (5) | 0.0141 (5) | -0.0001 (4) | 0.0014 (4)  | -0.0013 (4) |
| C3  | 0.0180 (5) | 0.0132 (5) | 0.0151 (5) | 0.0016 (4)  | -0.0001 (4) | -0.0010 (4) |
| C4  | 0.0163 (5) | 0.0143 (5) | 0.0141 (5) | 0.0011 (4)  | 0.0001 (4)  | 0.0009 (4)  |
| C5  | 0.0141 (5) | 0.0151 (5) | 0.0121 (5) | -0.0001 (4) | -0.0001 (4) | 0.0018 (4)  |
| C4A | 0.0134 (5) | 0.0139 (5) | 0.0132 (5) | 0.0004 (4)  | 0.0012 (4)  | 0.0005 (4)  |
| C6  | 0.0130 (5) | 0.0155 (5) | 0.0126 (5) | -0.0014 (4) | 0.0011 (4)  | -0.0006 (4) |
| C7  | 0.0151 (5) | 0.0126 (4) | 0.0157 (5) | 0.0002 (4)  | 0.0012 (4)  | 0.0006 (4)  |
| C8  | 0.0154 (5) | 0.0150 (5) | 0.0138 (5) | 0.0013 (4)  | -0.0005 (4) | 0.0020 (4)  |
| C8A | 0.0140 (5) | 0.0149 (5) | 0.0113 (4) | -0.0014 (4) | 0.0005 (4)  | -0.0011 (4) |
| C21 | 0.0154 (5) | 0.0144 (5) | 0.0133 (5) | -0.0012 (4) | 0.0014 (4)  | 0.0006 (4)  |
| C22 | 0.0198 (5) | 0.0194 (5) | 0.0130 (5) | 0.0002 (4)  | -0.0033 (4) | -0.0046 (4) |
| C23 | 0.0193 (6) | 0.0183 (5) | 0.0203 (5) | 0.0004 (4)  | -0.0002 (4) | -0.0050 (4) |
| C61 | 0.0135 (5) | 0.0152 (5) | 0.0139 (5) | 0.0013 (4)  | 0.0001 (4)  | -0.0015 (4) |
| C62 | 0.0201 (5) | 0.0143 (5) | 0.0161 (5) | -0.0008 (4) | 0.0006 (4)  | 0.0004 (4)  |
| C63 | 0.0250 (6) | 0.0199 (5) | 0.0130 (5) | 0.0004 (4)  | -0.0004 (4) | 0.0007 (4)  |
| C64 | 0.0197 (5) | 0.0198 (5) | 0.0149 (5) | -0.0013 (4) | -0.0010 (4) | -0.0065 (4) |
| C65 | 0.0199 (5) | 0.0149 (5) | 0.0190 (5) | -0.0019 (4) | 0.0020 (4)  | -0.0017 (4) |
| C66 | 0.0180 (5) | 0.0159 (5) | 0.0144 (5) | 0.0004 (4)  | 0.0009 (4)  | 0.0005 (4)  |
| F64 | 0.0363 (4) | 0.0244 (3) | 0.0167 (3) | -0.0080 (3) | -0.0025 (3) | -0.0070 (3) |
| O1  | 0.0197 (4) | 0.0123 (3) | 0.0123 (3) | 0.0017 (3)  | -0.0030 (3) | -0.0008 (3) |
| O4  | 0.0290 (5) | 0.0163 (4) | 0.0165 (4) | 0.0055 (3)  | -0.0062 (3) | 0.0002 (3)  |
| O21 | 0.0265 (4) | 0.0183 (4) | 0.0161 (4) | 0.0045 (3)  | -0.0046 (3) | 0.0003 (3)  |
| O22 | 0.0204 (4) | 0.0154 (4) | 0.0143 (4) | 0.0026 (3)  | -0.0039 (3) | -0.0039 (3) |

*Geometric parameters (Å, °)*

|         |             |          |             |
|---------|-------------|----------|-------------|
| C2—C3   | 1.3457 (14) | C21—O22  | 1.3257 (12) |
| C2—O1   | 1.3568 (12) | C22—O22  | 1.4647 (12) |
| C2—C21  | 1.5025 (14) | C22—C23  | 1.5059 (15) |
| C3—C4   | 1.4617 (14) | C22—H22A | 0.9900      |
| C3—H3   | 0.9500      | C22—H22B | 0.9900      |
| C4—O4   | 1.2315 (13) | C23—H23A | 0.9800      |
| C4—C4A  | 1.4766 (14) | C23—H23B | 0.9800      |
| C5—C6   | 1.3886 (14) | C23—H23C | 0.9800      |
| C5—C4A  | 1.4042 (14) | C61—C62  | 1.3989 (14) |
| C5—H5   | 0.9500      | C61—C66  | 1.4015 (14) |
| C4A—C8A | 1.3984 (14) | C62—C63  | 1.3920 (15) |
| C6—C7   | 1.4135 (14) | C62—H62  | 0.9500      |
| C6—C61  | 1.4851 (14) | C63—C64  | 1.3829 (16) |
| C7—C8   | 1.3797 (14) | C63—H63  | 0.9500      |
| C7—H7   | 0.9500      | C64—F64  | 1.3646 (12) |
| C8—C8A  | 1.3948 (14) | C64—C65  | 1.3759 (15) |



|               |              |                 |              |
|---------------|--------------|-----------------|--------------|
| C8—H8         | 0.9500       | C65—C66         | 1.3903 (14)  |
| C8A—O1        | 1.3774 (12)  | C65—H65         | 0.9500       |
| C21—O21       | 1.2065 (13)  | C66—H66         | 0.9500       |
| C3—C2—O1      | 124.47 (9)   | O22—C22—H22A    | 110.2        |
| C3—C2—C21     | 125.77 (9)   | C23—C22—H22A    | 110.2        |
| O1—C2—C21     | 109.76 (8)   | O22—C22—H22B    | 110.2        |
| C2—C3—C4      | 121.14 (9)   | C23—C22—H22B    | 110.2        |
| C2—C3—H3      | 119.4        | H22A—C22—H22B   | 108.5        |
| C4—C3—H3      | 119.4        | C22—C23—H23A    | 109.5        |
| O4—C4—C3      | 123.05 (9)   | C22—C23—H23B    | 109.5        |
| O4—C4—C4A     | 122.91 (9)   | H23A—C23—H23B   | 109.5        |
| C3—C4—C4A     | 114.03 (9)   | C22—C23—H23C    | 109.5        |
| C6—C5—C4A     | 121.29 (9)   | H23A—C23—H23C   | 109.5        |
| C6—C5—H5      | 119.4        | H23B—C23—H23C   | 109.5        |
| C4A—C5—H5     | 119.4        | C62—C61—C66     | 118.41 (9)   |
| C8A—C4A—C5    | 118.51 (9)   | C62—C61—C6      | 121.68 (9)   |
| C8A—C4A—C4    | 119.79 (9)   | C66—C61—C6      | 119.91 (9)   |
| C5—C4A—C4     | 121.69 (9)   | C63—C62—C61     | 120.93 (10)  |
| C5—C6—C7      | 118.26 (9)   | C63—C62—H62     | 119.5        |
| C5—C6—C61     | 121.65 (9)   | C61—C62—H62     | 119.5        |
| C7—C6—C61     | 120.07 (9)   | C64—C63—C62     | 118.27 (10)  |
| C8—C7—C6      | 121.77 (9)   | C64—C63—H63     | 120.9        |
| C8—C7—H7      | 119.1        | C62—C63—H63     | 120.9        |
| C6—C7—H7      | 119.1        | F64—C64—C65     | 118.67 (10)  |
| C7—C8—C8A     | 118.68 (9)   | F64—C64—C63     | 118.35 (10)  |
| C7—C8—H8      | 120.7        | C65—C64—C63     | 122.98 (10)  |
| C8A—C8—H8     | 120.7        | C64—C65—C66     | 117.97 (10)  |
| O1—C8A—C8     | 116.10 (9)   | C64—C65—H65     | 121.0        |
| O1—C8A—C4A    | 122.40 (9)   | C66—C65—H65     | 121.0        |
| C8—C8A—C4A    | 121.50 (9)   | C65—C66—C61     | 121.41 (10)  |
| O21—C21—O22   | 125.79 (10)  | C65—C66—H66     | 119.3        |
| O21—C21—C2    | 122.64 (9)   | C61—C66—H66     | 119.3        |
| O22—C21—C2    | 111.57 (9)   | C2—O1—C8A       | 118.08 (8)   |
| O22—C22—C23   | 107.55 (8)   | C21—O22—C22     | 115.51 (8)   |
| O1—C2—C3—C4   | -0.66 (17)   | C3—C2—C21—O22   | -11.10 (15)  |
| C21—C2—C3—C4  | 179.33 (10)  | O1—C2—C21—O22   | 168.89 (8)   |
| C2—C3—C4—O4   | 179.88 (11)  | C5—C6—C61—C62   | -35.73 (15)  |
| C2—C3—C4—C4A  | -1.71 (15)   | C7—C6—C61—C62   | 145.98 (11)  |
| C6—C5—C4A—C8A | 0.07 (15)    | C5—C6—C61—C66   | 143.58 (11)  |
| C6—C5—C4A—C4  | 178.64 (10)  | C7—C6—C61—C66   | -34.71 (15)  |
| O4—C4—C4A—C8A | -179.98 (10) | C66—C61—C62—C63 | -1.07 (16)   |
| C3—C4—C4A—C8A | 1.60 (14)    | C6—C61—C62—C63  | 178.25 (10)  |
| O4—C4—C4A—C5  | 1.48 (16)    | C61—C62—C63—C64 | -0.46 (17)   |
| C3—C4—C4A—C5  | -176.94 (9)  | C62—C63—C64—F64 | -177.91 (10) |
| C4A—C5—C6—C7  | 0.08 (15)    | C62—C63—C64—C65 | 1.81 (18)    |
| C4A—C5—C6—C61 | -178.24 (9)  | F64—C64—C65—C66 | 178.21 (10)  |

|               |              |                 |              |
|---------------|--------------|-----------------|--------------|
| C5—C6—C7—C8   | -0.02 (16)   | C63—C64—C65—C66 | -1.50 (17)   |
| C61—C6—C7—C8  | 178.33 (10)  | C64—C65—C66—C61 | -0.15 (16)   |
| C6—C7—C8—C8A  | -0.20 (16)   | C62—C61—C66—C65 | 1.39 (16)    |
| C7—C8—C8A—O1  | -179.34 (9)  | C6—C61—C66—C65  | -177.94 (10) |
| C7—C8—C8A—C4A | 0.36 (16)    | C3—C2—O1—C8A    | 3.16 (15)    |
| C5—C4A—C8A—O1 | 179.38 (9)   | C21—C2—O1—C8A   | -176.84 (8)  |
| C4—C4A—C8A—O1 | 0.79 (15)    | C8—C8A—O1—C2    | 176.53 (9)   |
| C5—C4A—C8A—C8 | -0.30 (15)   | C4A—C8A—O1—C2   | -3.17 (14)   |
| C4—C4A—C8A—C8 | -178.89 (10) | O21—C21—O22—C22 | 0.82 (15)    |
| C3—C2—C21—O21 | 168.95 (11)  | C2—C21—O22—C22  | -179.12 (8)  |
| O1—C2—C21—O21 | -11.05 (14)  | C23—C22—O22—C21 | -165.47 (9)  |

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H... <i>A</i>      | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C7—H7...O21 <sup>i</sup>     | 0.95        | 2.47          | 3.1977 (13)           | 133                     |
| C65—H65...O4 <sup>ii</sup>   | 0.95        | 2.50          | 3.4447 (13)           | 175                     |
| C66—H66...O21 <sup>iii</sup> | 0.95        | 2.53          | 3.4425 (13)           | 162                     |

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