



Crystal structure and Hirshfeld surface analysis of ethyl (4*R*,4*aS*)-2-methyl-5,8-dioxo-6-phenyl-4*a*,5,6,7,7*a*,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylate

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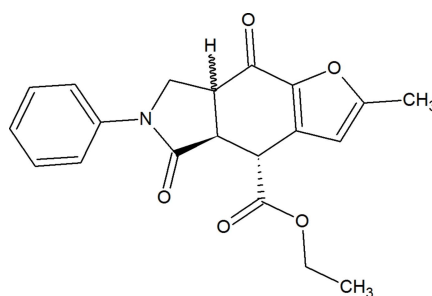
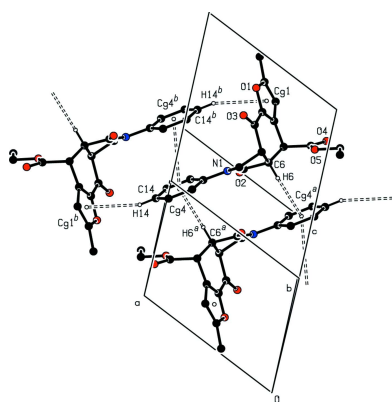
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In the title compound, C₂₀H₁₉NO₅, the central six-membered ring has a slightly distorted half-chair conformation, with puckering parameters of $Q_T = 0.3387(11)$ Å, $\theta = 49.11(19)^\circ$ and $\varphi = 167.3(2)^\circ$. The conformation of the fused pyrrolidine ring is that of an envelope. Molecules are connected by intermolecular C—H···O hydrogen bonds, C—H··· π interactions and π – π stacking interactions [centroid-to-centroid distance = $3.9536(11)$ Å, with a slippage of 2.047 Å], forming a three-dimensional network. The most important contributions to the surface contacts are from H···H (46.3%), O···H/H···O (31.5%) and C···H/H···C (17.3%) interactions, as concluded from a Hirshfeld surface analysis.

1. Chemical context

This work is a continuation of Diels–Alder reaction studies on vinylarene systems, previously carried out for the tandem acylation/[4 + 2] cycloaddition between 3-(aryl)allyl amines and maleic anhydrides or acryloyl chlorides as an example of an IMDAV (the acronym for Intra Molecular Diels–Alder Vinylarene) reaction. An IMDAV reaction is a useful tool for the one-step synthesis of benzofurans, indoles and benzothiophenes annulated with other carbo- and heterocycles (Krishna *et al.*, 2020). Previously, our group carried out a domino-sequence reaction involving acylation/IMDAV/aromatization steps, which led to the target furo- and thieno[2,3-*f*]isoindoles (Zubkov *et al.*, 2016; Horak *et al.*, 2015, 2017; Nadirova *et al.*, 2020).



The present communication is devoted to another IMDAV reaction involving an oxidation step. We report here the first case of a three-component IMDAV/oxidation reaction between 3-(furyl)allylamine (**1**), ethylfumaryl chloride (**2**)



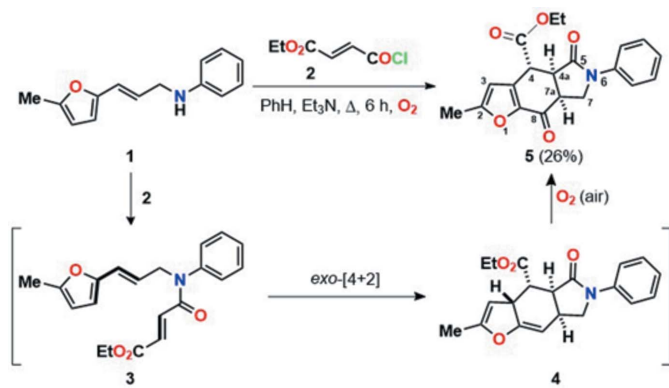


Figure 1
Synthesis scheme of ethyl 2-methyl-5,8-dioxo-6-phenyl-4a,5,6,7,7a,8-hexahydro-4H-furo[2,3-f]isoindole-4-carboxylate (**5**).

and oxygen. Unlike many other reactions, this process does not stop at the furo[2,3-f]isoindole (**4**) formation but is continued by an oxidation step yielding the 8-oxofuro[2,3-f]isoindole (**5**) (Fig. 1). The intramolecular [4 + 2] cycloaddition/oxidation sequence occurs under reflux conditions of the reaction mixture in benzene as a solvent and in ambient atmosphere; after standard purification procedures the title compound (**5**) was isolated in low yield.

Weak intermolecular interactions, *e.g.* hydrogen, halogen, chalcogen, pnictogen, tetrel and triel bonding, as well as agostic, anagostic, π - π stacking, n - π^* , π -cation and π -anion interactions, play an important role in synthesis, catalysis, crystal engineering, or molecular recognition (Afkhami *et al.*, 2017; Asadov *et al.*, 2016; Gurbanov *et al.*, 2017, 2018; Karmakar *et al.*, 2017; Kopylovich *et al.*, 2011*a,b*; Ma *et al.*, 2017*a,b*; Maharramov *et al.*, 2018; Mahmoudi *et al.*, 2017, 2019; Mahmudov *et al.*, 2010, 2020; Mizar *et al.*, 2012; Sutradhar *et al.*, 2015). Herein, we highlight the role of weak interactions in the structural features of **5**.

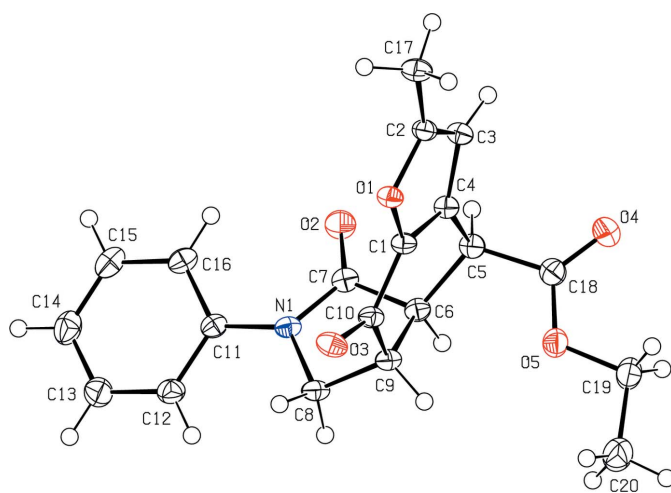


Figure 2
The molecular structure of **5** with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

2. Structural commentary

In the molecule of the title compound **5** (Fig. 2), the central six-membered ring (C1/C4–C6/C9–C10) has a slightly distorted half-chair conformation, with puckering parameters (Cremer & Pople, 1975) of $Q_T = 0.3387$ (11) Å, $\theta = 49.11$ (19)° and $\varphi = 167.3$ (2)°. The fused pyrrolidine ring (N1/C6–C9) adopts an envelope conformation with the C9 atom as the flap [the puckering parameters are $Q(2) = 0.3634$ (11) Å and $\varphi(2) = 289.63$ (17)°], while the fused furan ring (O1/C1–C4) is essentially planar [r.m.s. deviation = 0.001 Å]. All bond lengths and angles in the title compound (**5**) are comparable to the closely related compound (3*aR*,4*R*,4*aS*,9*aR*)-4-hydroxy-perhydrofuro(2,3-*f*)indolizin-7(2*H*)-one (CSD refcode SIBJET; Švorc *et al.*, 2007).

3. Supramolecular features

In the crystal structure of **5**, molecules are linked by two kinds of C–H... π interactions (Table 1). The first one is between an aromatic H atom (H14) of the phenyl group (C11–C16) and the centroid of the O1/C1–C4 furan ring ($Cg1$) of an adjacent molecule, and the second one is between the methine H atom (H6) of the fused pyrrolidine ring (N1/C6–C9) and the centroid of the C11–C16 phenyl ring ($Cg4$) of another adjacent molecule (Fig. 3).

In addition, there is a π - π stacking interaction [$Cg4 \cdots Cg4^i = 3.9536$ (11) Å; symmetry code: (i) $2 - x, 1 - y, 1 - z$], with a rather large slippage of 2.047 Å (Fig. 3).

The final three-dimensional network structure is completed by C–H...O hydrogen bonding (Fig. 4) between a phenyl H

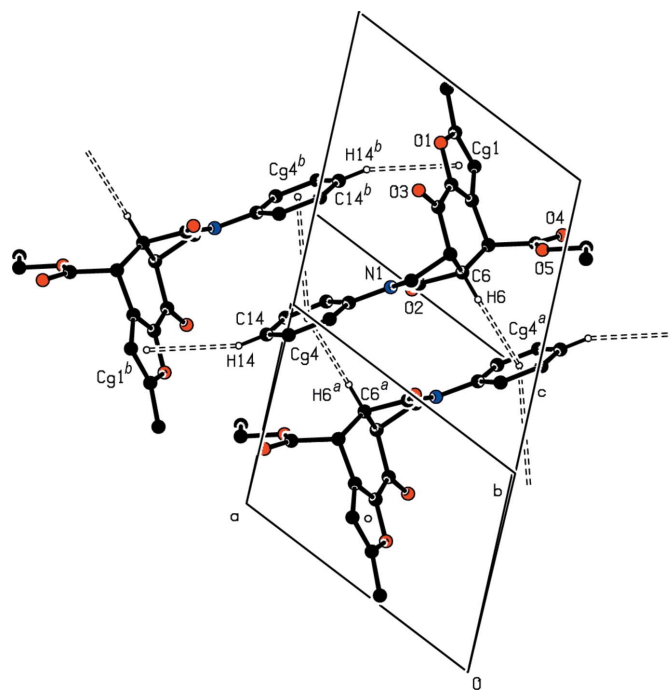


Figure 3
A view of the C–H... π interactions and π - π stacking interactions in the crystal structure of **5**. [Symmetry codes: (a) $1 - x, 1 - y, 1 - z$; (b) $2 - x, 1 - y, 1 - z$.]

Table 1

Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*4 are the centroids of the furan (O1/C1–C4) and phenyl (C11–C16) rings, respectively.

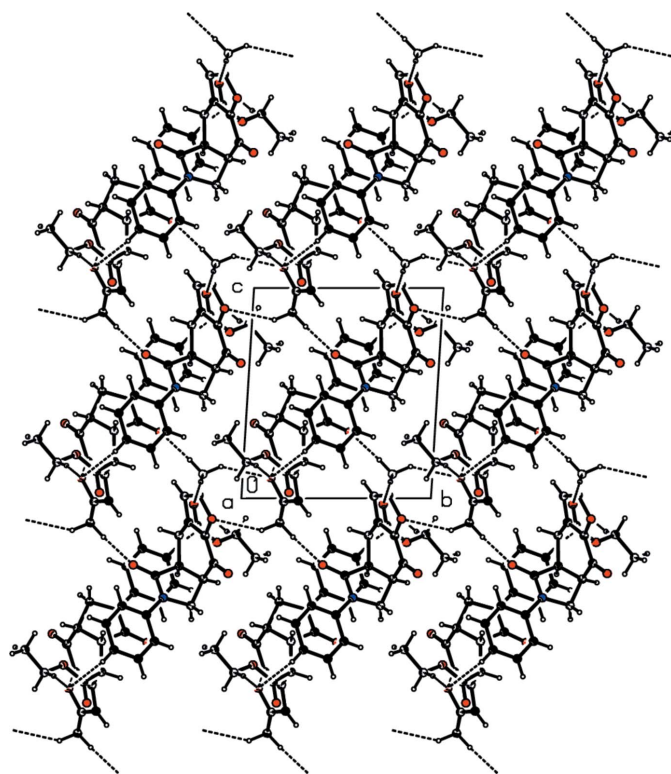
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C14–H14···O1 ⁱ	0.95	2.53	3.4766 (16)	172
C17–H17A···O4 ⁱⁱ	0.98	2.51	3.4913 (18)	176
C17–H17B···O2 ⁱⁱⁱ	0.98	2.31	3.2441 (15)	159
C17–H17C···O1 ^{iv}	0.98	2.57	3.4232 (14)	145
C19–H19B···O1 ^v	0.99	2.54	3.5181 (17)	168
C6–H6··· <i>Cg</i> 4 ^{vi}	1.00	2.71	3.5892 (14)	146
C14–H14··· <i>Cg</i> 1 ⁱ	0.95	2.93	3.8320 (16)	159

 Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, -y+2, -z+2$; (v) $x-1, y, z$; (vi) $-x+1, -y+1, -z+1$.

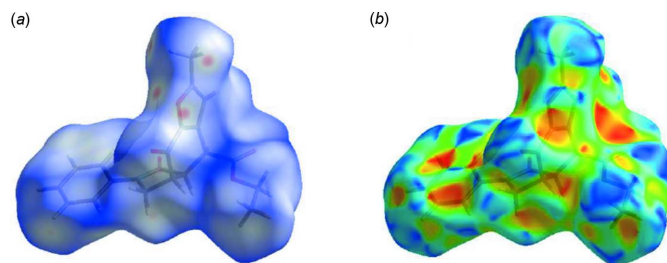
atom and the furan O atom (C14–H14···O1ⁱ), between a methyl H atom and the carbonyl O atom (C17–H17A···O4ⁱⁱ and C17–H17B···O2ⁱⁱⁱ), and between a methyl H atom and a methylene H atom and the furan O atom (C17–H17C···O1^{iv} and C19–H19B···O1^v). Numerical details of the hydrogen-bonding interactions as well as symmetry codes are given in Table 1.

4. Hirshfeld surface analysis

Hirshfeld surfaces and their associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were used to quantify

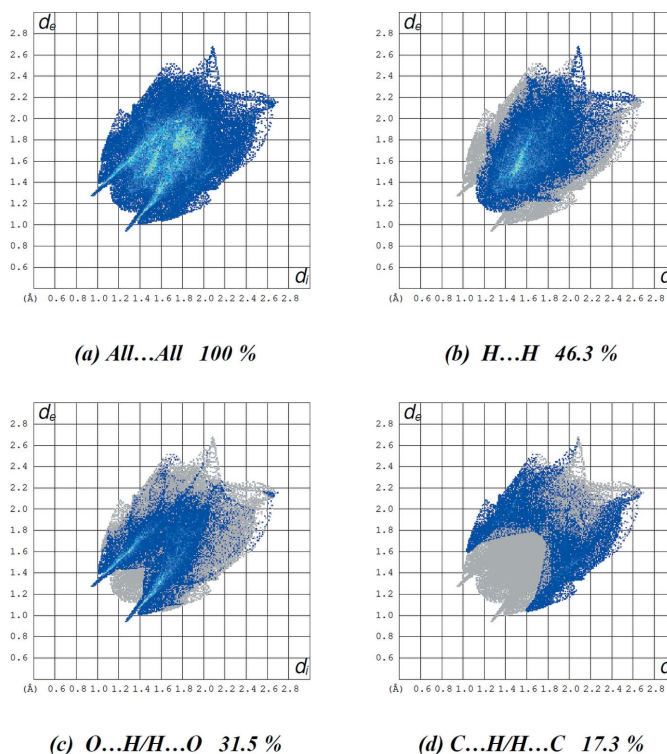

Figure 4

A view of the intermolecular C–H···O interactions in the crystal structure of **5**.


Figure 5

(A) A view of the three-dimensional Hirshfeld surface for **5**, plotted over d_{norm} in the range -0.2980 to 1.4527 a.u.; (B) Hirshfeld surface of the title compound **5** plotted over shape-index.

the various intermolecular interactions, and were generated using *CrystalExplorer17* (Turner *et al.*, 2017). The shorter and longer contacts are indicated as red and blue spots on the Hirshfeld surfaces, and contacts with distances equal to the sum of the van der Waals radii are represented as white spots. Hirshfeld surfaces of the title compound **5** mapped over the normalized distance, d_{norm} , using a standard surface resolution with a fixed colour scale of -0.2980 (red) to 1.4527 a.u. (blue) are illustrated in Fig. 5a. The shape-index of the Hirshfeld surface is a tool for visualizing the π – π stacking by the presence of adjacent red and blue triangles. The plot of the Hirshfeld surface mapped over shape-index shown in Fig. 5b clearly suggests that π – π interactions in (**5**) are significant.


Figure 6

A view of the two-dimensional fingerprint plots for **5**, showing (a) all interactions, and delineated into (b) H···H, (c) O···H/H···O and (d) C···H/H···C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

Table 2
Summary of short interatomic contacts (Å) in the title compound **5**.

Contact	Distance	Symmetry operation
H17A...O4	2.51	1 + x, y, z;
H14...O1	2.53	2 - x, 1 - y, 1 - z;
H17C...O1	2.57	1 - x, 2 - y, 2 - z;
H17B...O2	2.31	1 - x, 1 - y, 2 - z;
H8A...O3	2.69	1 - x, 2 - y, 1 - z;
O4...H13	2.67	-1 + x, y, 1 + z;
H20C...C3	3.09	-x, 2 - y, 2 - z;
H6...C16	2.72	1 - x, 1 - y, 1 - z;
H17B...H12	2.47	x, y, 1 + z;
H20C...H16	2.56	-1 + x, 1 + y, z.

Various intermolecular contacts are collated in Table 2. Associated two-dimensional fingerprint plots together with their percentage contributions are shown in Fig. 6. The crystal packing is dominated by H...H contacts, representing van der Waals interactions (46.3% contribution to the overall surface), followed by O...H/H...O and C...H/H...C interactions, which contribute 31.5% and 17.3%, respectively. All other contacts have a minor contribution to the crystal packing.

5. Database survey

A search of the Cambridge Crystallographic Database (CSD version 5.40, update of September 2019; Groom *et al.*, 2016) yielded five entries closely related to **5**, *viz.* 2,4,6-triphenyl-7a,8-dihydro-4*H*-furo[2,3-*f*]isoindole-5,7(4*aH*,6*H*)-dione (CSD refcode JOGYIP; Zhou *et al.*, 2014), (4*R**,4*aR**,7*aS**)-5-oxo-6-phenyl-4a,5,6,7,7a,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylic acid (LESXIS; Horak *et al.*, 2013), 6-benzyl-2,4,4a-trimethyl-5-oxo-4a,5,6,7,7a,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylic acid (QAFSUO; Zubkov *et al.*, 2016), 6-benzyl-4-methyl-5-oxo-4a,5,6,7,7a,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylic acid (QAFTAV; Zubkov *et al.*, 2016) and 6-allyl-5-oxo-4a,5,6,7,7a,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylic acid (QUKPAP; Horak *et al.*, 2015).

In the crystal structure of JOGYIP (space group $P\bar{1}$), the packing is stabilized by C—H...O intermolecular contacts, C—H... π interactions and π – π stacking interactions, forming a three-dimensional network.

In the crystal structure of LESXIS (*Pbca*), the asymmetric unit contains two molecules with similar bond lengths and angles. In both molecules, the conformation of the cyclohexene ring is that of a half-chair, while the pyrrolidinone ring adopts an envelope conformation with the γ -carbon atom of the α -pyrrolidinone ring as the flap. In the crystal, O—H...O hydrogen bonds between the carboxylic and carbonyl groups link alternate independent molecules into chains propagating parallel to the *b*-axis direction. The crystal packing also features weak C—H... π interactions.

In the crystal structures of QAFSUO ($P2_1/c$) and QAFTAV ($P2_1/n$), the three-dimensional packings are stabilized by O—H...O intermolecular bonds, C—H...O intermolecular contacts and C—H... π interactions.

The asymmetric unit of QUKPAP ($P2_1/c$) comprises two similar molecules, *A* and *B*, of the same chirality. The only

considerable difference concerns the conformation of the allyl group. The five-membered isoindole rings adopt envelope conformations, whereas the six-membered rings are half-chair-puckered. The carboxyl hydrogen atoms are involved in strong hydrogen-bond formation with the carbonyl atoms of neighboring molecules, giving rise to $(A...B...)_n$ chains.

In the five structures, the different groups bonded to the central twelve-membered ring systems account for the distinct intermolecular interactions in the crystals.

6. Synthesis and crystallization

Ethyl 2-methyl-5,8-dioxo-6-phenyl-4a,5,6,7,7a,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylate (**5**) was synthesized according to a previously reported method (Zubkov *et al.*, 2016; Nadirova *et al.*, 2020): A solution of ethyl fumaroyl chloride (**2**; 3.6 g, 22.5 mmol) in benzene (25 ml) was added dropwise to a mixture of *N*-[(2*E*)-3-(5-methylfuran-2-yl)prop-2-en-1-yl]aniline (**1**; 3.2 g, 15.0 mmol) with triethylamine (4.2 ml, 30 mmol) in benzene (25 ml). The mixture was heated under reflux for 6 h. The mixture was then cooled to r.t. and poured into water (200 ml). The organic layer was separated, the aqueous layer was extracted with AcOEt (3 \times 50 ml). The organic layers were combined and dried over anhydrous MgSO₄. The extract was evaporated under reduced pressure, and the residue was crystallized at 279 K within a few days. The resulting light-beige crystals were filtered off and washed with diethyl ether (3 \times 10 ml). Yield 1.4 g (26%). M.p. = 437–439 K. IR (KBr), ν (cm⁻¹): 1736, 1704, 1665. ¹H NMR (CDCl₃, 600.2 MHz, 301 K): δ = 7.55 (*dd*, 2H, HAr, *J* = 7.6, *J* = 2.0), 7.34 (*td*, 2H, HAr, *J* = 7.6, *J* = 2.0), 7.14 (*td*, 1H, HAr, *J* = 7.6, *J* = 2.0), 6.32 (*s*, 1H, H3), 4.56 (*s*, 1H, H4), 4.43 (*dd*, 1H, H-7a, *J* = 8.5, *J* = 2.0), 4.27–4.17 (*m*, 2H, OCH₂), 4.05 (*ddd*, 1H, H-7B, *J* = 2.0, *J* = 6.5), 3.76 (*dd*, 1H, H-4a, *J* = 1.7, *J* = 8.5), 3.51 (*td*, 1H, H-7A, *J* = 2.0, *J* = 6.5), 2.39 (*d*, 3H, CH₃, *J* = 1.5), 1.30 (*td*, 3H, CH₂CH₃, *J* = 2.2, *J* = 7.2). ¹³C NMR (CDCl₃, 150.9 MHz, 301 K): δ = 181.4, 170.9, 170.5 (CO, CO₂, NCO), 160.9, 145.3, 138.7, 136.9, 128.8 (2C), 124.9, 119.8 (2C), 109.8, 62.0, 49.4, 45.4, 41.8, 38.7, 14.1 (CH₃), 14.0 (CH₃). MS (APCI): *m/z* = 354 [*M* + H]⁺.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms bound to C atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95–1.00 Å and $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$.

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Table 3

Experimental details.

Crystal data	
Chemical formula	C ₂₀ H ₁₉ NO ₅
<i>M_r</i>	353.36
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8100 (18), 9.9182 (16), 11.165 (2)
α , β , γ (°)	81.205 (7), 70.657 (6), 72.642 (4)
<i>V</i> (Å ³)	877.0 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.10
Crystal size (mm)	0.2 × 0.2 × 0.2
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.659, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	19857, 5332, 4669
<i>R_{int}</i>	0.019
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.716
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 0.125, 1.04
No. of reflections	5332
No. of parameters	237
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.53, -0.18

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

References

Afkhami, F. A., Khandar, A. A., Mahmoudi, G., Maniukiewicz, W., Gurbanov, A. V., Zubkov, F. I., Şahin, O., Yesilel, O. Z. & Frontera, A. (2017). *CrystEngComm*, **19**, 1389–1399.

Asadov, Z. H., Rahimov, R. A., Ahmadova, G. A., Mammadova, K. A. & Gurbanov, A. V. (2016). *J. Surfact. Deterg.* **19**, 145–153.

Bruker (2014). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.

Gurbanov, A. V., Mahmoudi, G., Guedes da Silva, M. F. C., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2018). *Inorg. Chim. Acta*, **471**, 130–136.

Gurbanov, A. V., Mahmudov, K. T., Sutradhar, M., Guedes da Silva, M. F. C., Mahmudov, T. A., Guseinov, F. I., Zubkov, F. I., Maharramov, A. M. & Pombeiro, A. J. L. (2017). *J. Organomet. Chem.* **834**, 22–27.

Horak, Y. I., Lytvyn, R. Z., Homza, Y. V., Zaytsev, V. P., Mertsalov, D. F., Babkina, M. N., Nikitina, E. V., Lis, T., Kinzhybalov, V., Matiyuchuk, V. S., Zubkov, F. I., Varlamov, A. V. & Obushak, M. D. (2015). *Tetrahedron Lett.* **56**, 4499–4501.

Horak, Y. I., Lytvyn, R. Z., Laba, Y.-O. V., Homza, Y. V., Zaytsev, V. P., Nadirova, M. A., Nikanorova, T. V., Zubkov, F. I., Varlamov, A. V. & Obushak, M. D. (2017). *Tetrahedron Lett.* **58**, 4103–4106.

Horak, Y. I., Lytvyn, R. Z., Zubkov, F. I., Nikitina, E. V., Homza, Y. V., Lis, T., Kinzhybalov, V. & Obushak, M. D. (2013). *Acta Cryst.* **E69**, o273–o274.

Karmakar, A., Rúbio, G. M. D. M., Paul, A., Guedes da Silva, M. F. C., Mahmudov, K. T., Guseinov, F. I., Carabineiro, S. A. C. & Pombeiro, A. J. L. (2017). *Dalton Trans.* **46**, 8649–8657.

Kopylovich, M. N., Mahmudov, K. T., Haukka, M., Luzyanin, K. V. & Pombeiro, A. J. L. (2011a). *Inorg. Chim. Acta*, **374**, 175–180.

Kopylovich, M. N., Mahmudov, K. T., Mizar, A. & Pombeiro, A. J. L. (2011b). *Chem. Commun.* **47**, 7248–7250.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Krishna, G., Grudinina, D. G., Nikitina, E. V. & Zubkov, F. I. (2020). *Synthesis* (submitted).

Ma, Z., Gurbanov, A. V., Maharramov, A. M., Guseinov, F. I., Kopylovich, M. N., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2017a). *J. Mol. Catal. A Chem.* **426**, 526–533.

Ma, Z., Gurbanov, A. V., Sutradhar, M., Kopylovich, M. N., Mahmudov, K. T., Maharramov, A. M., Guseinov, F. I., Zubkov, F. I. & Pombeiro, A. J. L. (2017b). *Mol. Catal.* **428**, 17–23.

Maharramov, A. M., Shikhaliyev, N. Q., Suleymanova, G. T., Gurbanov, A. V., Babayeva, G. V., Mammadova, G. Z., Zubkov, F. I., Nenajdenko, V. G., Mahmudov, K. T. & Pombeiro, A. J. L. (2018). *Dyes Pigm.* **159**, 135–141.

Mahmoudi, G., Dey, L., Chowdhury, H., Bauza, A., Ghosh, B. K., Kirillov, A. M., Seth, S. K., Gurbanov, A. V. & Frontera, A. (2017). *Inorg. Chim. Acta*, **461**, 192–205.

Mahmoudi, G., Khandar, A. A., Afkhami, F. A., Mirslaw, B., Gurbanov, A. V., Zubkov, F. I., Kennedy, A., Franconetti, A. & Frontera, A. (2019). *CrystEngComm*, **21**, 108–117.

Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Resnati, G. & Pombeiro, A. J. L. (2020). *Coord. Chem. Rev.* **418**, 213381.

Mahmudov, K. T., Maharramov, A. M., Aliyeva, R. A., Aliyev, I. A., Kopylovich, M. N. & Pombeiro, A. J. L. (2010). *Anal. Lett.* **43**, 2923–2938.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

Mizar, A., Guedes da Silva, M. F. C., Kopylovich, M. N., Mukherjee, S., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *Eur. J. Inorg. Chem.* pp. 2305–2313.

Nadirova, M. A., Laba, Y.-O. V., Zaytsev, V. P., Sokolova, J. S., Pokazeev, K. M., Anokhina, V. A., Khrustalev, V. N., Horak, Y. I., Lytvyn, R. Z., Siczek, M., Kinzhybalov, V., Zubavichus, Y. V., Kuznetsov, M. L., Obushak, M. D. & Zubkov, F. I. (2020). *Synthesis*, **52**, 2196–2223.

Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.

Spek, A. L. (2020). *Acta Cryst.* **E76**, 1–11.

Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, M. F. C., Mahmudov, K. T., Liu, C.-M. & Pombeiro, A. J. L. (2015). *Eur. J. Inorg. Chem.* pp. 3959–3969.

Švorc, L., Vrábek, V., Kožíšek, J., Marchalín, Š. & Žúžiová, J. (2007). *Acta Cryst.* **E63**, o1452–o1454.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.

Zhou, L., Zhang, M., Li, W. & Zhang, J. (2014). *Angew. Chem. Int. Ed.* **53**, 6542–6545.

Zubkov, F. I., Zaytsev, V. P., Mertsalov, D. F., Nikitina, E. V., Horak, Y. I., Lytvyn, R. Z., Homza, Y. V., Obushak, M. D., Dorovatovskii, P. V., Khrustalev, V. N. & Varlamov, A. V. (2016). *Tetrahedron*, **72**, 2239–2253.

supporting information

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Crystal structure and Hirshfeld surface analysis of ethyl (4*R*,4*aS*)-2-methyl-5,8-dioxo-6-phenyl-4*a*,5,6,7,7*a*,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylate

Vladimir P. Zaytsev, Lala V. Chervyakova, Elena A. Sorokina, Kirill A. Vasilyev, Sevim Türktekin Çelikesir, Mehmet Akkurt and Ajaya Bhattarai

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *S SAINT* (Bruker, 2014); data reduction: *S SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

Ethyl (4*R*,4*aS*)-2-methyl-5,8-dioxo-6-phenyl-4*a*,5,6,7,7*a*,8-hexahydro-4*H*-furo[2,3-*f*]isoindole-4-carboxylate

Crystal data

C₂₀H₁₉NO₅

M_r = 353.36

Triclinic, *P* $\bar{1}$

a = 8.8100 (18) Å

b = 9.9182 (16) Å

c = 11.165 (2) Å

α = 81.205 (7)°

β = 70.657 (6)°

γ = 72.642 (4)°

V = 877.0 (3) Å³

Z = 2

F(000) = 372

D_x = 1.338 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 9941 reflections

θ = 2.6–30.6°

μ = 0.10 mm⁻¹

T = 120 K

Prism, light beige

0.2 × 0.2 × 0.2 mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan

(*SADABS*; Krause *et al.*, 2015)

T_{min} = 0.659, *T_{max}* = 0.746

19857 measured reflections

5332 independent reflections

4669 reflections with *I* > 2 σ (*I*)

R_{int} = 0.019

θ_{\max} = 30.6°, θ_{\min} = 2.2°

h = -12→12

k = -14→14

l = -15→15

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.044

wR(*F*²) = 0.125

S = 1.04

5332 reflections

237 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.2272P]$$

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

$$\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.49262 (11)	0.82060 (9)	0.82393 (8)	0.01800 (17)
C2	0.52219 (12)	0.77526 (10)	1.01557 (9)	0.01914 (18)
C3	0.41740 (12)	0.69939 (10)	1.01089 (9)	0.02056 (18)
H3	0.367401	0.639266	1.077116	0.025*
C4	0.39835 (11)	0.72876 (9)	0.88651 (9)	0.01857 (17)
C5	0.29588 (12)	0.68264 (10)	0.82451 (9)	0.02036 (18)
H5	0.297539	0.581687	0.852768	0.024*
C6	0.37337 (12)	0.69298 (10)	0.67917 (9)	0.01928 (17)
H6	0.289113	0.686876	0.639739	0.023*
C7	0.52879 (12)	0.57073 (10)	0.63456 (9)	0.02000 (18)
C8	0.56409 (13)	0.76769 (10)	0.49121 (9)	0.02031 (18)
H8A	0.508910	0.774189	0.425593	0.024*
H8B	0.650611	0.820227	0.458834	0.024*
C9	0.43715 (12)	0.82351 (9)	0.61653 (9)	0.01886 (17)
H9	0.343898	0.902634	0.599506	0.023*
C10	0.52459 (12)	0.87442 (9)	0.69242 (9)	0.01830 (17)
C11	0.78337 (12)	0.53580 (10)	0.44672 (9)	0.01931 (18)
C12	0.84407 (13)	0.58679 (11)	0.32111 (10)	0.0241 (2)
H12	0.786842	0.676487	0.292163	0.029*
C13	0.98773 (14)	0.50692 (13)	0.23836 (11)	0.0308 (2)
H13	1.028278	0.541994	0.153099	0.037*
C14	1.07198 (14)	0.37572 (13)	0.28046 (12)	0.0321 (2)
H14	1.169324	0.320347	0.223866	0.039*
C15	1.01305 (14)	0.32603 (11)	0.40575 (11)	0.0283 (2)
H15	1.071538	0.236753	0.434436	0.034*
C16	0.87003 (13)	0.40465 (10)	0.48986 (10)	0.02336 (19)
H16	0.831446	0.369962	0.575521	0.028*
C17	0.59178 (14)	0.78967 (11)	1.11582 (10)	0.0247 (2)
H17A	0.711689	0.780661	1.078853	0.037*
H17B	0.573698	0.715273	1.183471	0.037*
H17C	0.535888	0.882592	1.151301	0.037*
C18	0.11631 (12)	0.77419 (11)	0.87182 (10)	0.02347 (19)
C19	-0.08020 (14)	0.98413 (12)	0.82766 (12)	0.0312 (2)
H19A	-0.098723	1.029690	0.906094	0.037*
H19B	-0.166938	0.933475	0.843495	0.037*
C20	-0.08800 (16)	1.09358 (14)	0.71871 (14)	0.0416 (3)

H20A	-0.064035	1.046628	0.640874	0.062*
H20B	-0.005259	1.146023	0.706811	0.062*
H20C	-0.199768	1.159291	0.737594	0.062*
N1	0.63587 (10)	0.61915 (8)	0.52807 (8)	0.01870 (16)
O1	0.56926 (8)	0.85082 (7)	0.90205 (6)	0.01874 (14)
O2	0.55020 (10)	0.45051 (8)	0.68426 (8)	0.02855 (17)
O3	0.61486 (10)	0.95404 (8)	0.64330 (7)	0.02436 (16)
O4	0.01858 (11)	0.75061 (11)	0.97188 (8)	0.0372 (2)
O5	0.08563 (9)	0.88584 (8)	0.79139 (8)	0.02685 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0213 (4)	0.0180 (4)	0.0169 (4)	-0.0062 (3)	-0.0084 (3)	0.0004 (3)
C2	0.0218 (4)	0.0193 (4)	0.0156 (4)	-0.0045 (3)	-0.0065 (3)	0.0010 (3)
C3	0.0240 (4)	0.0211 (4)	0.0172 (4)	-0.0079 (3)	-0.0070 (3)	0.0024 (3)
C4	0.0204 (4)	0.0182 (4)	0.0183 (4)	-0.0059 (3)	-0.0071 (3)	-0.0001 (3)
C5	0.0216 (4)	0.0207 (4)	0.0210 (4)	-0.0082 (3)	-0.0077 (3)	0.0001 (3)
C6	0.0212 (4)	0.0191 (4)	0.0201 (4)	-0.0062 (3)	-0.0088 (3)	-0.0009 (3)
C7	0.0228 (4)	0.0182 (4)	0.0220 (4)	-0.0068 (3)	-0.0095 (3)	-0.0008 (3)
C8	0.0277 (4)	0.0163 (4)	0.0171 (4)	-0.0030 (3)	-0.0101 (3)	0.0005 (3)
C9	0.0232 (4)	0.0170 (4)	0.0176 (4)	-0.0040 (3)	-0.0093 (3)	0.0000 (3)
C10	0.0229 (4)	0.0151 (4)	0.0170 (4)	-0.0041 (3)	-0.0075 (3)	0.0000 (3)
C11	0.0215 (4)	0.0192 (4)	0.0208 (4)	-0.0050 (3)	-0.0105 (3)	-0.0031 (3)
C12	0.0258 (5)	0.0264 (5)	0.0212 (4)	-0.0049 (4)	-0.0105 (4)	-0.0015 (3)
C13	0.0279 (5)	0.0398 (6)	0.0237 (5)	-0.0050 (4)	-0.0082 (4)	-0.0059 (4)
C14	0.0254 (5)	0.0362 (6)	0.0333 (6)	-0.0004 (4)	-0.0091 (4)	-0.0128 (5)
C15	0.0256 (5)	0.0238 (5)	0.0377 (6)	-0.0007 (4)	-0.0156 (4)	-0.0073 (4)
C16	0.0258 (5)	0.0203 (4)	0.0273 (5)	-0.0041 (3)	-0.0140 (4)	-0.0019 (3)
C17	0.0318 (5)	0.0269 (5)	0.0200 (4)	-0.0102 (4)	-0.0133 (4)	0.0021 (3)
C18	0.0220 (4)	0.0282 (5)	0.0236 (4)	-0.0104 (4)	-0.0081 (3)	-0.0012 (4)
C19	0.0214 (5)	0.0308 (5)	0.0354 (6)	-0.0035 (4)	-0.0043 (4)	-0.0008 (4)
C20	0.0310 (6)	0.0337 (6)	0.0474 (7)	-0.0021 (5)	-0.0057 (5)	0.0073 (5)
N1	0.0232 (4)	0.0154 (3)	0.0183 (3)	-0.0037 (3)	-0.0092 (3)	0.0003 (3)
O1	0.0228 (3)	0.0200 (3)	0.0160 (3)	-0.0080 (2)	-0.0081 (2)	0.0012 (2)
O2	0.0321 (4)	0.0176 (3)	0.0336 (4)	-0.0080 (3)	-0.0081 (3)	0.0041 (3)
O3	0.0334 (4)	0.0215 (3)	0.0213 (3)	-0.0130 (3)	-0.0090 (3)	0.0028 (3)
O4	0.0260 (4)	0.0512 (5)	0.0276 (4)	-0.0097 (4)	-0.0042 (3)	0.0070 (4)
O5	0.0211 (3)	0.0244 (4)	0.0303 (4)	-0.0051 (3)	-0.0040 (3)	0.0017 (3)

Geometric parameters (Å, °)

C1—C4	1.3712 (12)	C11—C12	1.3987 (14)
C1—O1	1.3775 (11)	C11—C16	1.4023 (13)
C1—C10	1.4478 (12)	C11—N1	1.4156 (12)
C2—C3	1.3712 (13)	C12—C13	1.3906 (15)
C2—O1	1.3736 (11)	C12—H12	0.9500
C2—C17	1.4849 (13)	C13—C14	1.3904 (17)

C3—C4	1.4294 (13)	C13—H13	0.9500
C3—H3	0.9500	C14—C15	1.3893 (18)
C4—C5	1.5035 (13)	C14—H14	0.9500
C5—C18	1.5305 (14)	C15—C16	1.3897 (15)
C5—C6	1.5385 (14)	C15—H15	0.9500
C5—H5	1.0000	C16—H16	0.9500
C6—C7	1.5282 (14)	C17—H17A	0.9800
C6—C9	1.5420 (13)	C17—H17B	0.9800
C6—H6	1.0000	C17—H17C	0.9800
C7—O2	1.2239 (12)	C18—O4	1.2031 (13)
C7—N1	1.3737 (12)	C18—O5	1.3356 (13)
C8—N1	1.4734 (12)	C19—O5	1.4587 (13)
C8—C9	1.5316 (13)	C19—C20	1.5066 (18)
C8—H8A	0.9900	C19—H19A	0.9900
C8—H8B	0.9900	C19—H19B	0.9900
C9—C10	1.5369 (13)	C20—H20A	0.9800
C9—H9	1.0000	C20—H20B	0.9800
C10—O3	1.2289 (12)	C20—H20C	0.9800
C4—C1—O1	110.30 (8)	C12—C11—N1	118.92 (8)
C4—C1—C10	128.08 (8)	C16—C11—N1	121.42 (9)
O1—C1—C10	121.47 (8)	C13—C12—C11	120.37 (10)
C3—C2—O1	110.50 (8)	C13—C12—H12	119.8
C3—C2—C17	133.13 (9)	C11—C12—H12	119.8
O1—C2—C17	116.36 (8)	C14—C13—C12	119.97 (11)
C2—C3—C4	106.32 (8)	C14—C13—H13	120.0
C2—C3—H3	126.8	C12—C13—H13	120.0
C4—C3—H3	126.8	C15—C14—C13	119.64 (10)
C1—C4—C3	106.46 (8)	C15—C14—H14	120.2
C1—C4—C5	121.28 (8)	C13—C14—H14	120.2
C3—C4—C5	132.22 (8)	C14—C15—C16	121.15 (10)
C4—C5—C18	107.45 (8)	C14—C15—H15	119.4
C4—C5—C6	109.46 (8)	C16—C15—H15	119.4
C18—C5—C6	113.92 (8)	C15—C16—C11	119.18 (10)
C4—C5—H5	108.6	C15—C16—H16	120.4
C18—C5—H5	108.6	C11—C16—H16	120.4
C6—C5—H5	108.6	C2—C17—H17A	109.5
C7—C6—C5	111.40 (8)	C2—C17—H17B	109.5
C7—C6—C9	102.38 (7)	H17A—C17—H17B	109.5
C5—C6—C9	118.72 (8)	C2—C17—H17C	109.5
C7—C6—H6	107.9	H17A—C17—H17C	109.5
C5—C6—H6	107.9	H17B—C17—H17C	109.5
C9—C6—H6	107.9	O4—C18—O5	124.84 (10)
O2—C7—N1	126.77 (9)	O4—C18—C5	123.54 (10)
O2—C7—C6	125.30 (9)	O5—C18—C5	111.55 (8)
N1—C7—C6	107.91 (8)	O5—C19—C20	106.88 (9)
N1—C8—C9	102.56 (7)	O5—C19—H19A	110.3
N1—C8—H8A	111.3	C20—C19—H19A	110.3

C9—C8—H8A	111.3	O5—C19—H19B	110.3
N1—C8—H8B	111.3	C20—C19—H19B	110.3
C9—C8—H8B	111.3	H19A—C19—H19B	108.6
H8A—C8—H8B	109.2	C19—C20—H20A	109.5
C8—C9—C10	109.49 (8)	C19—C20—H20B	109.5
C8—C9—C6	102.03 (7)	H20A—C20—H20B	109.5
C10—C9—C6	114.13 (7)	C19—C20—H20C	109.5
C8—C9—H9	110.3	H20A—C20—H20C	109.5
C10—C9—H9	110.3	H20B—C20—H20C	109.5
C6—C9—H9	110.3	C7—N1—C11	126.27 (8)
O3—C10—C1	123.57 (9)	C7—N1—C8	111.65 (8)
O3—C10—C9	121.65 (8)	C11—N1—C8	121.13 (8)
C1—C10—C9	114.77 (8)	C2—O1—C1	106.42 (7)
C12—C11—C16	119.66 (9)	C18—O5—C19	116.94 (8)

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 and Cg4 are the centroids of the furan (O1/C1–C4) and phenyl (C11–C16) rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C14—H14 \cdots O1 ⁱ	0.95	2.53	3.4766 (16)	172
C17—H17A \cdots O4 ⁱⁱ	0.98	2.51	3.4913 (18)	176
C17—H17B \cdots O2 ⁱⁱⁱ	0.98	2.31	3.2441 (15)	159
C17—H17C \cdots O1 ^{iv}	0.98	2.57	3.4232 (14)	145
C19—H19B \cdots O1 ^v	0.99	2.54	3.5181 (17)	168
C6—H6 \cdots Cg4 ^{vi}	1.00	2.71	3.5892 (14)	146
C14—H14 \cdots Cg1 ⁱ	0.95	2.93	3.8320 (16)	159

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, -y+2, -z+2$; (v) $x-1, y, z$; (vi) $-x+1, -y+1, -z+1$.