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Crystal structure and Hirshfeld surface analysis of dimethyl 2-oxo-4-(pyridin-2-yl)-6-(thiophen-2-yl)-cyclohex-3-ene-1,3-dicarboxylate

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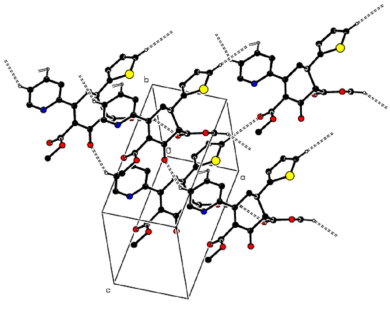
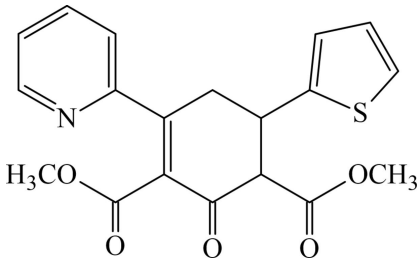
In the title compound, $C_{19}H_{17}NO_5S$, the cyclohexene ring adopts nearly an envelope conformation. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming a three-dimensional network. In addition, C—H···π interactions connect the molecules by forming layers parallel to the (010) plane. According to the Hirshfeld surface analysis, H···H (36.9%), O···H/H···O (31.0%), C···H/H···C (18.9%) and S···H/H···S (7.9%) interactions are the most significant contributors to the crystal packing.

1. Chemical context

The class of molecules known as carbo- and heterocycles, arguably the most important, has a significant impact on the synthesis of various functionalized systems that have found diverse research and commercial applications (Huseynov *et al.*, 2023; Akkurt *et al.*, 2023). Bioactive natural and synthetic compounds frequently incorporate carbocycles and heterocycles as fundamental structural components. Moreover, these compounds may play an important role in organic synthesis as starting materials (Maharramov *et al.*, 2022; Khalilov *et al.*, 2023*a*,*b*). These derivatives have found broad applications in coordination chemistry (Gurbanov *et al.*, 2021; Mahmoudi *et al.*, 2021), medicinal chemistry (Askerova, 2022) and materials chemistry (Velásquez *et al.*, 2019; Afkhami *et al.*, 2019). These ring systems are utilized in various applications, spanning pharmaceuticals, ligands, catalysts, materials and beyond (Maharramov *et al.*, 2021, Sobhi & Faisal, 2023). Functionalized systems incorporating cyclohexanone, pyridine and thiophene motifs have demonstrated diverse biological activities, including molluscicidal, anticancer, antioxidant, cytotoxic, anti-inflammatory, herbicidal, pesticidal, antibacterial, and more (Erenler *et al.*, 2022; Atalay *et al.*, 2022; Donmez & Turkyılmaz, 2022). The broad application of these systems has garnered significant attention toward the efficient and regioselective development of such compounds. In summary, the synthesized compound offers a unique combination of structural features, including heteroatom diversity, conjugation, strategic functional group placement, and potential biological relevance. Analysis of its structure and properties can provide valuable contributions to the broader field of carbo- and heterocyclic chemistry and may have implications for various



applications, including materials science and medicinal chemistry. Hence, within the context of structural studies (Abdinov *et al.*, 2004, 2012, 2014; Naghiyev *et al.*, 2020, 2021*a*, 2022), we present the crystal structure and Hirshfeld surface analysis of the title compound, dimethyl 2-oxo-4-(pyridin-2-yl)-6-(thiophen-2-yl)cyclohex-3-ene-1,3-dicarboxylate.



2. Structural commentary

In the title compound (Fig. 1), the cyclohexene ring (C1–C6) adopts nearly an envelope conformation [puckering parameters (Cremer & Pople, 1975) are Q_T = 0.526 (2) Å, θ = 53.9 (2)° and φ = 117.3 (3)°]. The cyclohexene ring (r.m.s deviation = 0.002 Å) makes dihedral angles of 84.46 (11) and 29.49 (10)° with the thiophene (S1/C9–C12) and pyridine (N1/C13–C17) rings, respectively. The angle between the thiophene and pyridine rings is 77.04 (11)°. The C8—O3—C7—C2, O2—C7—C2—C3, C19—O5—C18—C6 and O4—C18—C6—C5 torsion angles are −169.87 (18), −70.3 (2), 174.97 (15) and 107.7 (2)°, respectively. The geometric properties of the title compound are normal and consistent with those of the related compounds described in the *Database survey* (Section 4).

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecules are linked by C—H···O hydrogen bonds, forming a three-dimensional network (Table 1; Figs. 2 and 3). In addition, C—H···π interactions connect the molecules, forming layers parallel to the (010) plane, represented by the distances between the same *Cg*1 and the same *Cg*2 centroids (Table 1; Figs. 4 and 5). The lengths of the C—H···π

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

*Cg*1 and *Cg*2 are the centroids of the S1/C9–C12 thiophene and N1/C13–C17 pyridine rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O3^{i}	1.00	2.64	3.625 (2)	168
C8—H8*C*···O2^{ii}	0.98	2.35	3.215 (3)	146
C11—H11···O1^{iii}	0.95	2.62	3.193 (2)	119
C12—H12···O4^{iv}	0.95	2.50	3.446 (2)	180
C14—H14···O2^{v}	0.95	2.61	3.468 (2)	151
C16—H16···O1^{vi}	0.95	2.52	3.305 (3)	140
C19—H19*B*···O2^{vii}	0.98	2.64	3.584 (3)	161
C4—H4*A*···*Cg*2^{ii}	0.99	2.94	3.841 (2)	152
C19—H19*C*···*Cg*1^{viii}	0.98	2.78	3.659 (3)	149

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

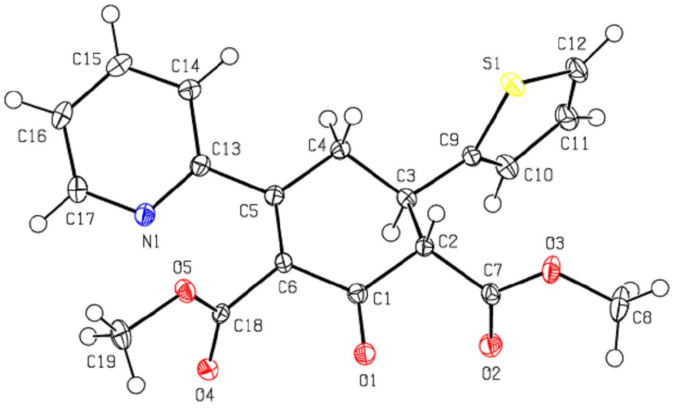


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

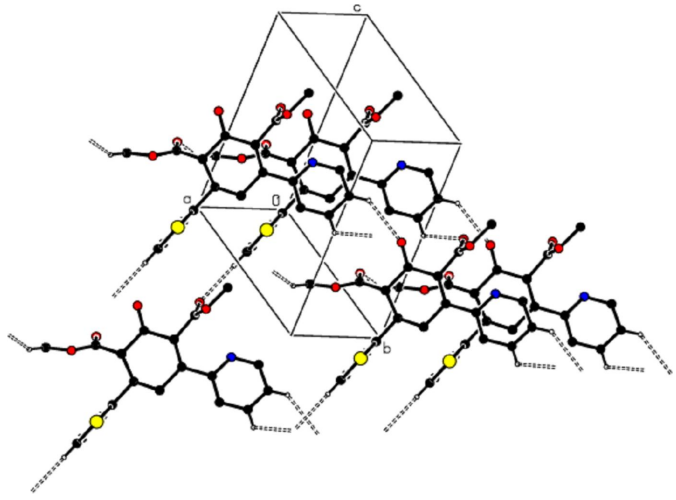


Figure 2
View of partial packing along the *b* axis of the title compound with C—H···O hydrogen bonds shown as dashed lines.

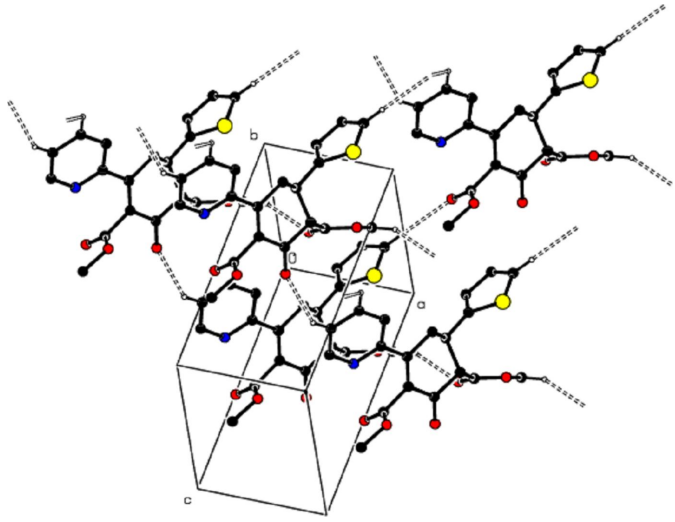


Figure 3
View of partial packing along the *a* axis of the title compound with C—H···O hydrogen bonds shown as dashed lines.

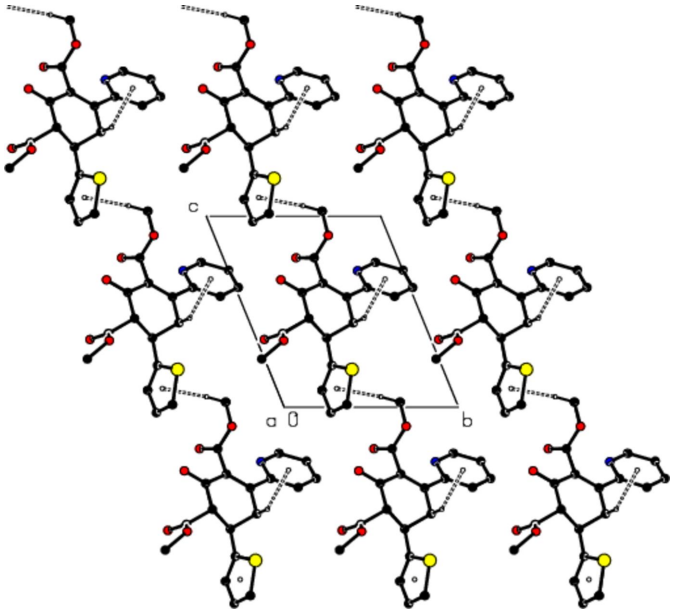


Figure 4
A view of the packing along the *a* axis of the title compound with C—H···π interactions shown as dashed lines.

interactions are similar to the proper hydrogen bonds in the crystal structures. This is reasonable for carbo- and heterocycles (Nishio, 2011).

Crystal Explorer 17.5 (Spackman *et al.*, 2021) was used to generate Hirshfeld surfaces and two-dimensional fingerprint plots in order to quantify the intermolecular interactions in the crystal. The Hirshfeld surfaces were mapped over $d_{\rm norm}$ in the range −0.2536 (red) to +1.2159 (blue) a.u. (Fig. 6). The most important interatomic contact is H···H as it makes the highest contribution to the crystal packing (36.9%, Fig. 7*b*). Other major contributors are O···H/H···O (31.0%, Fig. 7*c*), C···H/H···C (18.9%, Fig. 7*d*) and S···H/H···S (7.9%, Fig. 7*e*) interactions. Other, smaller contributions are made by N···H/H···N (2.6%), O···O (1.1%), O···C/C···O (0.9%), N···C/

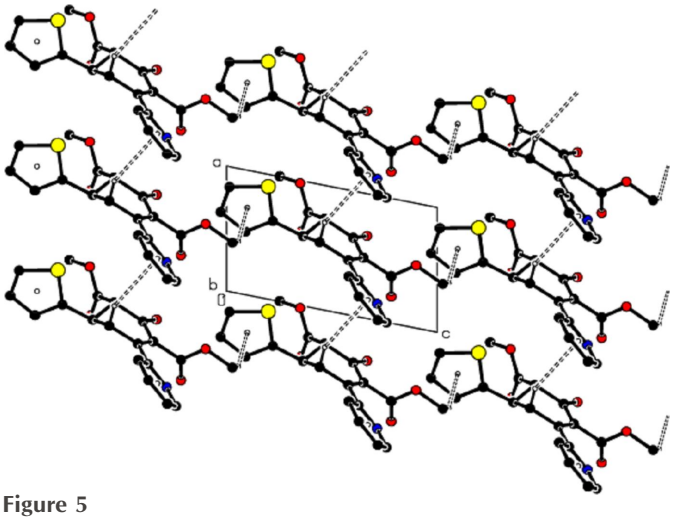


Figure 5
A view of the packing along the *b* axis of the title compound with C—H···π interactions shown as dashed lines.

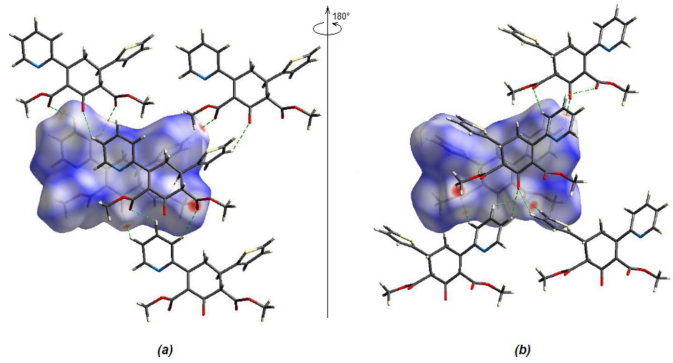


Figure 6
(*a*) Front and (*b*) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over d_{norm}.

C···N (0.4%) and C···C (0.2%) interactions. This distribution is typical for such cyclohexene compounds (Naghiyev *et al.*, 2024).

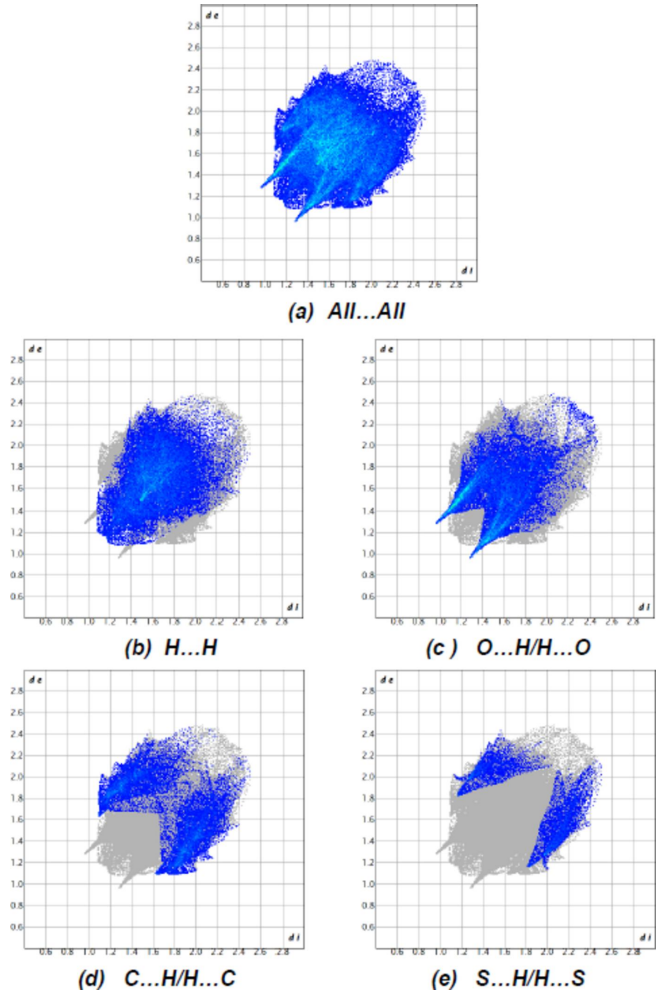


Figure 7
The two-dimensional fingerprint plots, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) O···H/H···O, (*d*) C···H/H···C and (*e*) S···H/H···S interactions [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.43, last update November 2022; Groom *et al.*, 2016) for a central cyclohexene or -hexane ring yielded nine compounds related to the title compound, *viz*. CSD refcodes WOMWUU [(**I**); Naghiyev *et al.*, 2024], UPOMOE [(**II**); Naghiyev *et al.*, 2021*b*], ZOMDUD [(**III**); Gein *et al.*, 2019], PEWJUZ [(**IV**); Fatahpour *et al.*, 2018], OZUKAX [(**V**); Tkachenko *et al.*, 2014], IFUDOD ((**VI**); Gein *et al.*, 2007], IWEVOV [(**VII**); Mohan *et al.*, 2003], IWEVUB [(**VIII**); Mohan *et al.*, 2003] and HALROB [(**IX**); Ravikumar & Mehdi, 1993].

Comparing the title compound and previously published structures, the published structures (Fig. 8) appear to have much higher symmetry space groups. While the title compound crystallizes in the triclinic space group *P*1 with *Z* = 1, (**I**), (**II**) and (**III**) crystallize in the monoclinic space group

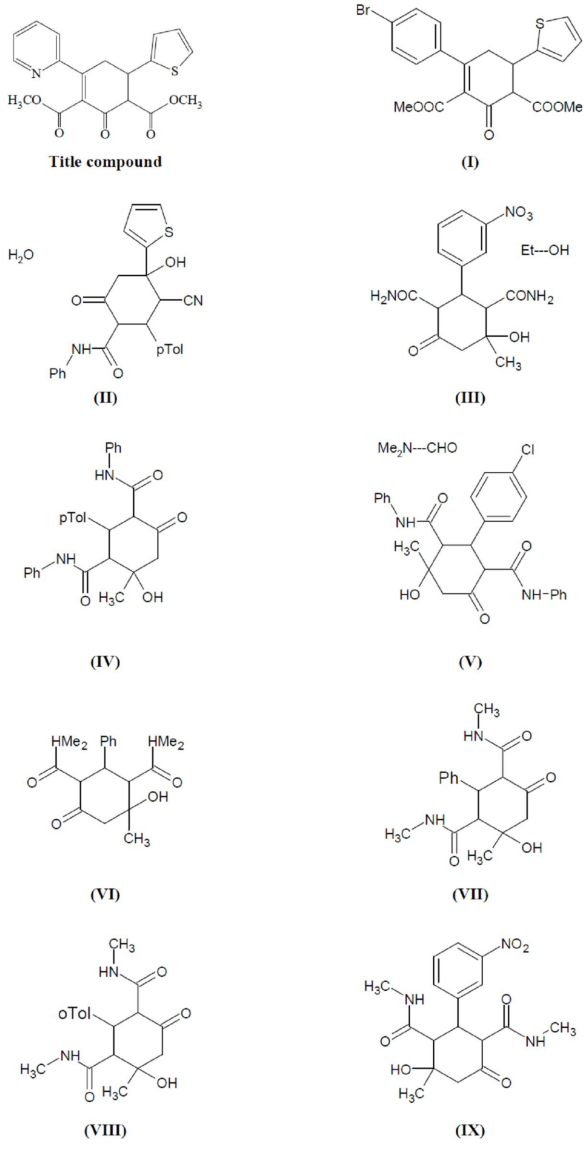


Figure 8
The nine other published cyclohexene/hexane-based structures.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{17}NO_5S$
M_r	371.39
Crystal system, space group	Triclinic, *P*1
Temperature (K)	100
a, *b*, *c* (Å)	5.5260 (1), 8.5012 (1), 10.1076 (2)
α, β, γ (°)	110.910 (2), 98.128 (1), 96.006 (1)
V (Å^3)	432.88 (1)
Z	1
Radiation type	Cu *K*α
μ (mm^{-1})	1.94
Crystal size (mm)	0.25 × 0.23 × 0.09
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2022)
T_{min}, T_{max}	0.647, 0.840
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18199, 3530, 3524
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.634
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.023, 0.059, 1.06
No. of reflections	3530
No. of parameters	238
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.18
Absolute structure	Flack *x* determined using 1675 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.003 (7)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2019/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

$P2_1/c$, with $Z = 4$, (**IV**) in $I2/c$ with $Z = 4$, (**VI**), (**VIII**) and (**IX**) in $P2_1/n$ with $Z = 4$, and (**V**) and (**VII**) in the orthorhombic space group *Pbca* with $Z = 8$.

5. Synthesis and crystallization

For a novel synthesis of the title compound, a solution of 1-(pyridin-2-yl)-3-(thiophen-2-yl)prop-2-en-1-one (7 mmol) and dimethyl-1,3-acetonedicarboxylate (5.2 mmol) in methanol (30 mL) was stirred for 10 min. Then *N*-methylpiperazine (3 drops) was added to the reaction mixture, which was stirred for 48 h at room temperature. Then 20 mL of methanol were removed from the reaction mixture, which was left overnight. The precipitated crystals were separated by filtration and recrystallized from an ethanol/water (1:1) solution (m.p. = 480 K, yield 69%).

^{1}H NMR (300 MHz, DMSO-d_6, ppm.): 3.30 (*dd*, 2H, CH_2, $^2J_{H-H}$ = 16.3 and $^3J_{H-H}$ = 8.3); 3.65 (*s*, 6H, 2OCH_3); 4.02 (*dd*, 1H, CH, $^3J_{H-H}$ = 8.3, $^3J_{H-H}$ = 13.3); 4.20 (*d*, 1H, CH, $^3J_{H-H}$ = 13.3); 7.00 (*t*, 1H, $CH_{thien.}$, $^3J_{H-H}$ = 5.1); 7.09 (*d*, 1H, $CH_{thien.}$, $^3J_{H-H}$ = 3.5); 7.41 (*d*, 1H, $CH_{thien.}$, $^3J_{H-H}$ = 5.1); 7.46 (*t*, 1H, $CH_{pyrid.}$, $^3J_{H-H}$ = 7.4); 7.76 (*d*, 1H, $CH_{pyrid.}$, $^3J_{H-H}$ = 7.4); 7.91 (*t*, 1H, $CH_{pyrid.}$, $^3J_{H-H}$ = 5.7); 8.63 (*d*, 1H, $CH_{pyrid.}$, $^3J_{H-H}$ = 5.7). ^{13}C NMR (75 MHz, DMSO-d_6, ppm.): 35.47 (CH_2), 38.23 (CH), 52.24 (OCH_3), 52.43 (OCH_3), 60.45 (CH), 123.58

($CH_{pyrid.}$), 125.20 ($CH_{pyrid.}$), 125.61 ($CH_{pyrid.}$), 125.77 ($CH_{pyrid.}$), 127.47 ($CH_{thien.}$), 131.43 ($C_{quat.}$), 137.93 ($CH_{thien.}$), 144.28 ($C_{thien.}$), 149.49 ($CH_{thien.}$), 153.21 ($C_{quat.}$), 155.14 ($C_{quat.}$), 166.83 (CO), 169.52 (CO), 191.68 (C═O).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound H atoms were placed in calculated positions (C—H = 0.95 −1.00 Å) and refined as riding with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

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Authors' contributions are as follows. Conceptualization, IGM, ANK and FNN; methodology, IGM and MA; investigation, VNK and FNN; writing (original draft), MA, AB and ANK, writing (review and editing of the manuscript), İGM and ANK; visualization, MA, EZH and FNN; funding acquisition, VNK, AB and FNN; resources, AB, VNK and MA; supervision, MA and ANK.

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supporting information

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Crystal structure and Hirshfeld surface analysis of dimethyl 2-oxo-4-(pyridin-2-yl)-6-(thiophen-2-yl)cyclohex-3-ene-1,3-dicarboxylate

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Computing details

Dimethyl 2-oxo-4-(pyridin-2-yl)-6-(thiophen-2-yl)cyclohex-3-ene-1,3-dicarboxylate

Crystal data

$C_{19}H_{17}NO_5S$
$M_r = 371.39$
Triclinic, $P\overline{1}$
$a = 5.5260$ (1) Å
$b = 8.5012$ (1) Å
$c = 10.1076$ (2) Å
$\alpha = 110.910$ (2)°
$\beta = 98.128$ (1)°
$\gamma = 96.006$ (1)°
$V = 432.88$ (1) Å^3
$Z = 1$
$F(000) = 194$
$D_x = 1.425$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 16321 reflections
$\theta = 4.8$–$77.4°$
$\mu = 1.94$ mm^{-1}
$T = 100$ K
Prism, colourless
0.25 × 0.23 × 0.09 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube
φ and ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2022)
$T_{min} = 0.647$, $T_{max} = 0.840$
18199 measured reflections
3530 independent reflections
3524 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 77.8°$, $\theta_{min} = 4.8°$
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.059$
$S = 1.06$
3530 reflections
238 parameters
3 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.097P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL2019/2* (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0131 (14)
Absolute structure: Flack *x* determined using 1675 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.003 (7)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6259 (4)	0.3716 (2)	0.6011 (2)	0.0132 (4)
C2	0.7320 (4)	0.3495 (2)	0.46536 (19)	0.0127 (4)
H2	0.898999	0.422837	0.493270	0.015*
C3	0.5592 (4)	0.4059 (2)	0.36259 (19)	0.0136 (4)
H3	0.390686	0.337398	0.343691	0.016*
C4	0.5382 (4)	0.5930 (2)	0.4416 (2)	0.0146 (4)
H4A	0.703452	0.664844	0.465810	0.017*
H4B	0.425908	0.630379	0.377470	0.017*
C5	0.4396 (3)	0.6170 (2)	0.5780 (2)	0.0134 (4)
C6	0.4809 (4)	0.5121 (2)	0.64983 (19)	0.0129 (4)
C7	0.7580 (4)	0.1653 (2)	0.3869 (2)	0.0142 (4)
C8	1.0028 (4)	−0.0161 (3)	0.2524 (3)	0.0281 (5)
H8A	0.894696	−0.044480	0.158603	0.042*
H8B	0.954145	−0.100288	0.293541	0.042*
H8C	1.175204	−0.017674	0.239795	0.042*
C9	0.6332 (4)	0.3713 (2)	0.2190 (2)	0.0144 (4)
C10	0.5052 (4)	0.2567 (3)	0.0887 (2)	0.0188 (4)
H10	0.352786	0.185818	0.077251	0.023*
C11	0.6230 (4)	0.2541 (3)	−0.0286 (2)	0.0211 (4)
H11	0.557058	0.181613	−0.126180	0.025*
C12	0.8386 (4)	0.3654 (3)	0.0135 (2)	0.0198 (4)
H12	0.941797	0.380424	−0.050162	0.024*
C13	0.2915 (4)	0.7557 (2)	0.6266 (2)	0.0138 (4)
C14	0.3097 (4)	0.8926 (2)	0.5803 (2)	0.0170 (4)
H14	0.419867	0.900060	0.517866	0.020*
C15	0.1640 (4)	1.0168 (2)	0.6273 (2)	0.0193 (4)
H15	0.173481	1.111309	0.597847	0.023*
C16	0.0042 (4)	1.0017 (3)	0.7177 (2)	0.0192 (4)
H16	−0.098664	1.084695	0.750789	0.023*
C17	−0.0018 (4)	0.8619 (3)	0.7589 (2)	0.0182 (4)
H17	−0.109760	0.852595	0.822018	0.022*
C18	0.3784 (4)	0.5217 (2)	0.7826 (2)	0.0132 (4)
C19	0.3964 (4)	0.6765 (3)	1.0269 (2)	0.0222 (4)
H19A	0.220812	0.685154	1.005687	0.033*
H19B	0.484406	0.781046	1.106272	0.033*
H19C	0.411825	0.578189	1.054703	0.033*
N1	0.1361 (3)	0.7402 (2)	0.71452 (18)	0.0161 (3)
O1	0.6615 (3)	0.27874 (17)	0.66693 (15)	0.0178 (3)
O2	0.5944 (3)	0.04488 (18)	0.35502 (15)	0.0196 (3)

O3	0.9794 (3)	0.15282 (18)	0.34916 (15)	0.0188 (3)
O4	0.2142 (3)	0.41766 (17)	0.78248 (15)	0.0175 (3)
O5	0.5031 (3)	0.65445 (18)	0.89989 (14)	0.0168 (3)
S1	0.90193 (7)	0.47674 (5)	0.19781 (5)	0.01854 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0118 (9)	0.0139 (8)	0.0134 (8)	0.0017 (7)	0.0025 (7)	0.0047 (7)
C2	0.0131 (9)	0.0131 (8)	0.0128 (8)	0.0041 (7)	0.0039 (7)	0.0049 (7)
C3	0.0140 (9)	0.0149 (9)	0.0123 (8)	0.0022 (7)	0.0033 (7)	0.0056 (7)
C4	0.0166 (10)	0.0143 (8)	0.0152 (9)	0.0053 (7)	0.0044 (7)	0.0072 (7)
C5	0.0122 (9)	0.0125 (8)	0.0144 (8)	0.0016 (7)	0.0026 (7)	0.0039 (7)
C6	0.0133 (9)	0.0129 (8)	0.0125 (9)	0.0028 (7)	0.0048 (7)	0.0039 (7)
C7	0.0157 (10)	0.0173 (9)	0.0114 (8)	0.0058 (7)	0.0039 (7)	0.0065 (7)
C8	0.0193 (11)	0.0212 (11)	0.0342 (12)	0.0067 (8)	0.0092 (9)	−0.0032 (9)
C9	0.0153 (10)	0.0160 (8)	0.0149 (9)	0.0054 (7)	0.0059 (7)	0.0075 (7)
C10	0.0185 (10)	0.0228 (10)	0.0153 (9)	0.0030 (8)	0.0048 (8)	0.0071 (8)
C11	0.0245 (11)	0.0256 (10)	0.0137 (9)	0.0051 (9)	0.0059 (8)	0.0071 (8)
C12	0.0226 (11)	0.0253 (10)	0.0147 (9)	0.0066 (8)	0.0083 (8)	0.0088 (8)
C13	0.0136 (10)	0.0125 (8)	0.0137 (8)	0.0024 (7)	0.0019 (7)	0.0033 (7)
C14	0.0189 (11)	0.0157 (9)	0.0179 (9)	0.0036 (8)	0.0040 (8)	0.0078 (8)
C15	0.0211 (11)	0.0135 (9)	0.0223 (10)	0.0032 (8)	0.0002 (8)	0.0067 (8)
C16	0.0182 (10)	0.0152 (9)	0.0204 (9)	0.0068 (7)	0.0016 (8)	0.0019 (7)
C17	0.0167 (10)	0.0201 (9)	0.0173 (9)	0.0064 (8)	0.0054 (7)	0.0046 (8)
C18	0.0166 (10)	0.0119 (8)	0.0129 (8)	0.0061 (7)	0.0048 (7)	0.0049 (7)
C19	0.0245 (11)	0.0264 (10)	0.0127 (9)	0.0052 (9)	0.0070 (8)	0.0023 (8)
N1	0.0166 (9)	0.0159 (8)	0.0165 (8)	0.0055 (6)	0.0050 (6)	0.0057 (6)
O1	0.0222 (8)	0.0200 (7)	0.0170 (6)	0.0095 (6)	0.0071 (6)	0.0107 (5)
O2	0.0192 (8)	0.0158 (7)	0.0218 (7)	0.0010 (6)	0.0061 (6)	0.0045 (5)
O3	0.0150 (7)	0.0166 (7)	0.0222 (7)	0.0055 (5)	0.0065 (6)	0.0023 (6)
O4	0.0219 (8)	0.0150 (6)	0.0170 (6)	0.0035 (6)	0.0083 (6)	0.0059 (5)
O5	0.0183 (7)	0.0181 (7)	0.0128 (6)	0.0020 (5)	0.0049 (5)	0.0039 (5)
S1	0.0179 (2)	0.0223 (2)	0.0148 (2)	−0.00028 (18)	0.00576 (16)	0.00623 (17)

Geometric parameters (Å, º)

C1—O1	1.215 (2)	C10—C11	1.426 (3)
C1—C6	1.484 (3)	C10—H10	0.9500
C1—C2	1.526 (2)	C11—C12	1.353 (3)
C2—C7	1.515 (3)	C11—H11	0.9500
C2—C3	1.546 (3)	C12—S1	1.725 (2)
C2—H2	1.0000	C12—H12	0.9500
C3—C9	1.499 (2)	C13—N1	1.349 (2)
C3—C4	1.529 (2)	C13—C14	1.400 (3)
C3—H3	1.0000	C14—C15	1.384 (3)
C4—C5	1.509 (3)	C14—H14	0.9500
C4—H4A	0.9900	C15—C16	1.386 (3)

C4—H4B	0.9900	C15—H15	0.9500
C5—C6	1.353 (3)	C16—C17	1.391 (3)
C5—C13	1.485 (3)	C16—H16	0.9500
C6—C18	1.508 (2)	C17—N1	1.335 (3)
C7—O2	1.207 (2)	C17—H17	0.9500
C7—O3	1.335 (2)	C18—O4	1.199 (2)
C8—O3	1.452 (2)	C18—O5	1.344 (2)
C8—H8A	0.9800	C19—O5	1.448 (2)
C8—H8B	0.9800	C19—H19A	0.9800
C8—H8C	0.9800	C19—H19B	0.9800
C9—C10	1.364 (3)	C19—H19C	0.9800
C9—S1	1.733 (2)		

O1—C1—C6	121.66 (16)	C3—C9—S1	123.13 (14)
O1—C1—C2	121.05 (17)	C9—C10—C11	113.26 (19)
C6—C1—C2	117.28 (15)	C9—C10—H10	123.4
C7—C2—C1	111.28 (15)	C11—C10—H10	123.4
C7—C2—C3	108.90 (15)	C12—C11—C10	112.96 (18)
C1—C2—C3	109.64 (15)	C12—C11—H11	123.5
C7—C2—H2	109.0	C10—C11—H11	123.5
C1—C2—H2	109.0	C11—C12—S1	111.23 (15)
C3—C2—H2	109.0	C11—C12—H12	124.4
C9—C3—C4	113.33 (15)	S1—C12—H12	124.4
C9—C3—C2	113.64 (16)	N1—C13—C14	122.33 (18)
C4—C3—C2	108.56 (15)	N1—C13—C5	116.34 (17)
C9—C3—H3	107.0	C14—C13—C5	121.32 (17)
C4—C3—H3	107.0	C15—C14—C13	118.75 (18)
C2—C3—H3	107.0	C15—C14—H14	120.6
C5—C4—C3	110.93 (15)	C13—C14—H14	120.6
C5—C4—H4A	109.5	C14—C15—C16	119.19 (19)
C3—C4—H4A	109.5	C14—C15—H15	120.4
C5—C4—H4B	109.5	C16—C15—H15	120.4
C3—C4—H4B	109.5	C15—C16—C17	118.38 (19)
H4A—C4—H4B	108.0	C15—C16—H16	120.8
C6—C5—C13	122.14 (17)	C17—C16—H16	120.8
C6—C5—C4	120.52 (17)	N1—C17—C16	123.48 (19)
C13—C5—C4	117.32 (16)	N1—C17—H17	118.3
C5—C6—C1	122.52 (16)	C16—C17—H17	118.3
C5—C6—C18	123.87 (17)	O4—C18—O5	125.11 (17)
C1—C6—C18	113.58 (15)	O4—C18—C6	123.28 (18)
O2—C7—O3	123.86 (18)	O5—C18—C6	111.52 (16)
O2—C7—C2	124.32 (18)	O5—C19—H19A	109.5
O3—C7—C2	111.70 (16)	O5—C19—H19B	109.5
O3—C8—H8A	109.5	H19A—C19—H19B	109.5
O3—C8—H8B	109.5	O5—C19—H19C	109.5
H8A—C8—H8B	109.5	H19A—C19—H19C	109.5
O3—C8—H8C	109.5	H19B—C19—H19C	109.5
H8A—C8—H8C	109.5	C17—N1—C13	117.88 (17)

H8B—C8—H8C	109.5	C7—O3—C8	114.76 (16)
C10—C9—C3	126.53 (18)	C18—O5—C19	113.04 (15)
C10—C9—S1	110.34 (15)	C12—S1—C9	92.21 (10)
O1—C1—C2—C7	29.2 (3)	C3—C9—C10—C11	179.62 (19)
C6—C1—C2—C7	−151.60 (17)	S1—C9—C10—C11	−0.2 (2)
O1—C1—C2—C3	149.70 (18)	C9—C10—C11—C12	0.2 (3)
C6—C1—C2—C3	−31.1 (2)	C10—C11—C12—S1	−0.2 (2)
C7—C2—C3—C9	−51.8 (2)	C6—C5—C13—N1	−20.6 (3)
C1—C2—C3—C9	−173.75 (15)	C4—C5—C13—N1	157.70 (17)
C7—C2—C3—C4	−178.86 (15)	C6—C5—C13—C14	160.74 (19)
C1—C2—C3—C4	59.17 (19)	C4—C5—C13—C14	−20.9 (3)
C9—C3—C4—C5	174.49 (16)	N1—C13—C14—C15	0.4 (3)
C2—C3—C4—C5	−58.3 (2)	C5—C13—C14—C15	178.96 (17)
C3—C4—C5—C6	28.6 (3)	C13—C14—C15—C16	−0.3 (3)
C3—C4—C5—C13	−149.71 (17)	C14—C15—C16—C17	0.5 (3)
C13—C5—C6—C1	179.18 (17)	C15—C16—C17—N1	−0.9 (3)
C4—C5—C6—C1	0.9 (3)	C5—C6—C18—O4	107.7 (2)
C13—C5—C6—C18	1.4 (3)	C1—C6—C18—O4	−70.2 (2)
C4—C5—C6—C18	−176.85 (18)	C5—C6—C18—O5	−75.7 (2)
O1—C1—C6—C5	179.91 (19)	C1—C6—C18—O5	106.35 (19)
C2—C1—C6—C5	0.7 (3)	C16—C17—N1—C13	0.9 (3)
O1—C1—C6—C18	−2.1 (3)	C14—C13—N1—C17	−0.7 (3)
C2—C1—C6—C18	178.65 (16)	C5—C13—N1—C17	−179.31 (17)
C1—C2—C7—O2	50.6 (3)	O2—C7—O3—C8	6.2 (3)
C3—C2—C7—O2	−70.3 (2)	C2—C7—O3—C8	−169.87 (18)
C1—C2—C7—O3	−133.27 (17)	O4—C18—O5—C19	−8.5 (3)
C3—C2—C7—O3	105.76 (18)	C6—C18—O5—C19	174.97 (15)
C4—C3—C9—C10	−122.9 (2)	C11—C12—S1—C9	0.08 (18)
C2—C3—C9—C10	112.5 (2)	C10—C9—S1—C12	0.06 (16)
C4—C3—C9—S1	56.8 (2)	C3—C9—S1—C12	−179.74 (17)
C2—C3—C9—S1	−67.7 (2)		

Hydrogen-bond geometry (Å, º)

*Cg*1 and *Cg*2 are the centroids of the S1/C9–C12 thiophene and N1/C13–C17 pyridine rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O3^{i}	1.00	2.64	3.625 (2)	168
C8—H8*C*···O2^{ii}	0.98	2.35	3.215 (3)	146
C11—H11···O1^{iii}	0.95	2.62	3.193 (2)	119
C12—H12···O4^{iv}	0.95	2.50	3.446 (2)	180
C14—H14···O2^{v}	0.95	2.61	3.468 (2)	151
C16—H16···O1^{vi}	0.95	2.52	3.305 (3)	140
C19—H19*B*···O2^{vii}	0.98	2.64	3.584 (3)	161
C4—H4*A*···*Cg*2^{ii}	0.99	2.94	3.841 (2)	152
C19—H19*C*···*Cg*1^{viii}	0.98	2.78	3.659 (3)	149

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*, *y*, *z*−1; (iv) *x*+1, *y*, *z*−1; (v) *x*, *y*+1, *z*; (vi) *x*−1, *y*+1, *z*; (vii) *x*, *y*+1, *z*+1; (viii) *x*, *y*, *z*+1.