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Crystal structure and Hirshfeld surface analysis of diethyl (3*aS*,3*a1R*,4*S*,5*S*,6*R*,6*aS*,7*R*,9*aS*)-3*a1*,5,6,6*a*-tetrahydro-1*H*,3*H*,4*H*,7*H*-3*a*,6:7,9*a*-diepoxybenzo-*[de]*isochromene-4,5-dicarboxylate

Nurlana D. Sadikhova,^a Zeliha Atioğlu,^b Narmina A. Guliyeva,^c Alexandra G. Podrezova,^d Eugeniya V. Nikitina,^d Mehmet Akkurt^{e*} and Ajaya Bhattarai^{f*}

^aOrganic Chemistry Department, Baku State University, Az 1148 Baku, Azerbaijan, ^bDepartment of Aircraft Electrics and Electronics, School of Applied Sciences, Cappadocia University, Mustafapaşa, 50420 Ürgüp, Nevşehir, Türkiye,

^cDepartment of Organic Substances and Technology of High-Molecular Compounds, SRI "Geotechnological Problems of Oil, Gas and Chemistry", Azerbaijan State Oil and Industry University, Azadlig ave. 20, Az-1010 Baku, Azerbaijan,

^dOrganic Chemistry Department, Faculty of Science, RUDN University, Miklukho-Maklaya St., 6, Moscow 117198, Russian Federation, ^eDepartment of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Türkiye, and

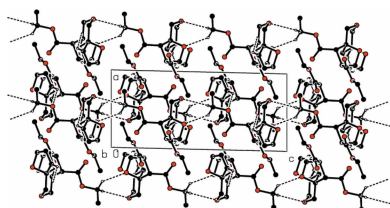
^fDepartment of Chemistry, M.M.A.M.C (Tribhuvan University) Biratnagar, Nepal. *Correspondence e-mail: akkurt@erciyes.edu.tr, ajaya.bhattarai@mmamc.tu.edu.np

akkurt@erciyes.edu.tr, ajaya.bhattarai@mmamc.tu.edu.np

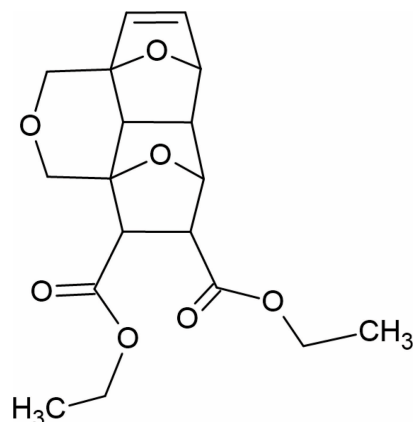
In the title compound, C₁₈H₂₂O₇, two hexane rings and an oxane ring are fused together. The two hexane rings tend toward a distorted boat conformation, while the tetrahydrofuran and dihydrofuran rings adopt envelope conformations. The oxane ring is puckered. The crystal structure features C—H···O hydrogen bonds, which link the molecules into a three-dimensional network. According to a Hirshfeld surface study, H···H (60.3%) and O···H/H···O (35.3%) interactions are the most significant contributors to the crystal packing.

1. Chemical context

The intermolecular Diels–Alder (DA) reaction of furans is a powerful tool in organic and medicinal chemistry, offering a versatile and efficient approach to the synthesis of complex molecules with valuable applications (for reviews and books on the topic, see: Chen *et al.*, 2018; Winkler 1996; Parvatkar *et al.*, 2014; Shi & Wang, 2020; Hopf & Sherburn, 2012; Safavora *et al.*, 2019). The DA reaction of furans is typically carried out under thermal conditions, but the use of high pressure has emerged as a powerful tool for enhancing the reactivity and selectivity of this reaction. High pressure can significantly lower the activation energy of the DA reaction, leading to faster reaction rates and improved yields (see reviews by Rulev & Zubkov, 2022; Schettino & Bini, 2007). On the other hand, by the attachment of functional groups, the DA reaction products can participate in various sorts of intermolecular interactions with interesting coordination, supramolecular, catalytic and solvatochromic properties (Gurbanov *et al.*, 2020*a,b*; Khalilov *et al.*, 2021; Mahmoudi *et al.*, 2017*a,b*; Mahmudov *et al.*, 2015). For example, attachment of carboxylate groups to organic molecules can create coordination sites and interesting supramolecular architectures involving monomeric, oligomeric or polymeric subunits in metal complexes, which affects their catalytic activity (Gurbanov *et al.*, 2022*a,b*; Ma *et al.*, 2017, 2021; Shikhaliyev *et al.*, 2019). The present work showcases a facile methodology for the synthesis of compound **1a** from a simple furan derivative and diethyl fumarate under high-pressure conditions. It is noteworthy that while several methods for the preparation of similar structures



using more reactive dienophiles have been documented in the literature (Borisova *et al.*, 2018*a,b*; Kvyatkovskaya *et al.*, 2021*a,b*), this represents the first instance of such a reaction where thermal activation alone is insufficient to drive the transformation.



2. Structural commentary

In the title compound, (Fig. 1), the (1*R*,4*S*)-7-oxabicyclo[2.2.1]hept-2-ene (O11/C3*B*/C6*A*/C7–C9/C9*A*), (1*S*,4*S*)-7-oxabicyclo[2.2.1]heptane (O10/C3*A*/C3*B*/C4–C6/C6*A*) and oxane (C1/O2/C3/C3*A*/C3*B*/C9*A*) rings are fused together. The hexane ring (C3*B*/C6*A*/C7–C9/C9*A*) tends towards a distorted boat conformation [the puckering parameters (Cremer & Pople, 1975) are $Q_T = 1.0005$ (15) Å, $\theta = 89.65$ (9)° and $\varphi = 300.58$ (8)°], while the tetrahydrofuran (C3*B*/C6*A*/C7/O11/C9*A*) and dihydrofuran (C7–C9/C9*A*/O11) rings adopt envelope conformations, with puckering parameters $Q(2) = 0.5625$ (13) Å, $\varphi(2) = 1.70$ (14)° and $Q(2) = 0.5143$ (13) Å, $\varphi(2) = 179.57$ (17)°, respectively. The hexane ring (C3*A*/C3*B*/C4–C6/C6*A*) tends towards a distorted boat conformation [puckering parameters $Q_T = 0.9758$ (14) Å, $\theta = 91.04$ (8)° and $\varphi = 2.99$ (8)°], while the tetrahydrofuran rings (C3*A*/C4–C6/

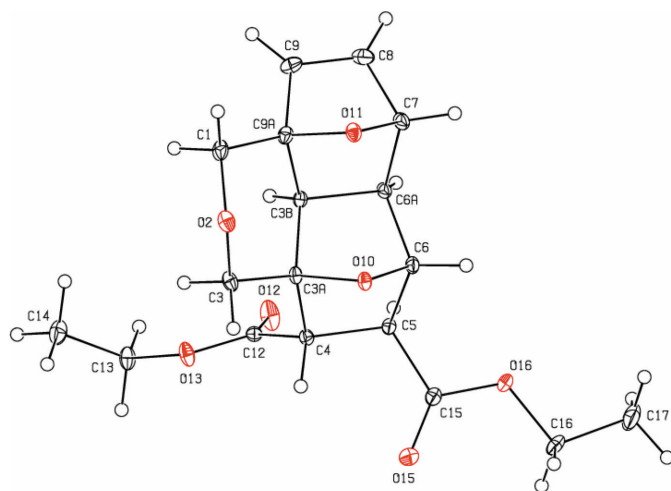


Figure 1
The molecular structure of the title complex with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

Table 1
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>
C3–H3 <i>A</i> ···O13	0.99	2.58	3.1604 (17)	118
C9–H9 <i>A</i> ···O13 ⁱ	0.95	2.47	3.1692 (17)	131
C13–H13 <i>A</i> ···O2 ⁱⁱ	0.99	2.58	3.1905 (17)	120
C13–H13 <i>B</i> ···O10 ⁱⁱ	0.99	2.41	3.2193 (17)	139
C14–H14 <i>C</i> ···O15 ⁱ	0.98	2.64	3.5669 (19)	158

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

O10 and C6/C6*A*/C3*B*/C3*A*/O10) adopt envelope conformations, with puckering parameters $Q(2) = 0.5784$ (13) Å, $\varphi(2) = 185.10$ (14)° and $Q(2) = 0.5235$ (13) Å, $\varphi(2) = 357.36$ (15)°, respectively. The oxane ring (C3*A*/C3*B*/C9*A*/C1/O2/C3) is puckered with puckering parameters $Q_T = 0.5125$ (14) Å, $\theta = 7.89$ (15)° and $\varphi = 3.1$ (12)°. The C3*A*–C4–C12–O12, C3*A*–C4–C12–O13, C4–C12–O13–C13, C6–C5–C15–O15, C6–C5–C15–O16 and C5–C15–O16–C16 torsion angles are 107.12 (15), -72.14 (13), -177.31 (11), 120.28 (15), -60.17 (14) and 178.70 (11)°, respectively. The geometric parameters of the title compound are normal and comparable to those of related compounds listed in the *Database survey* section.

3. Supramolecular features and Hirshfeld surface analysis

The crystal structure of the title compound is stabilized by C–H···O hydrogen bonds, forming a three-dimensional network (Table 1; Figs. 2, 3 and 4). C–H··· π and π – π interactions are not observed in the structure.

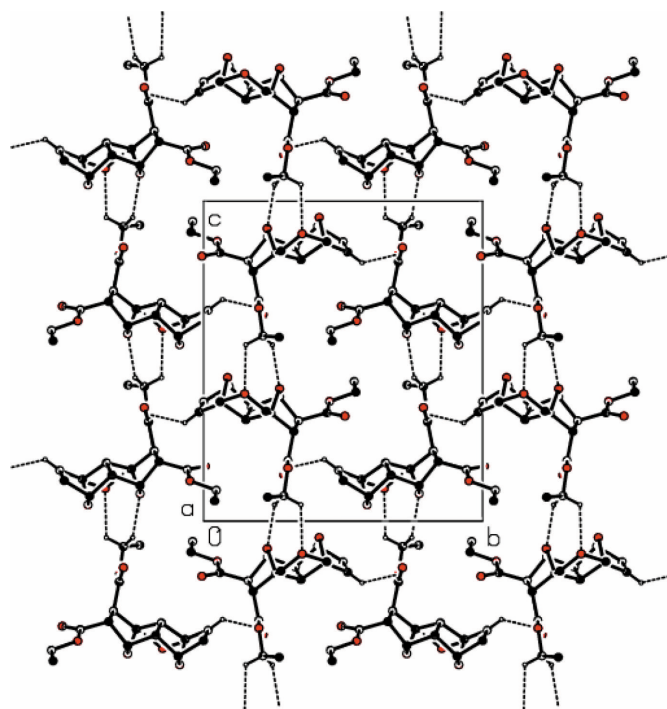


Figure 2
A packing diagram of the title complex, showing the C–H···O interactions along the *a* axis as dashed lines.

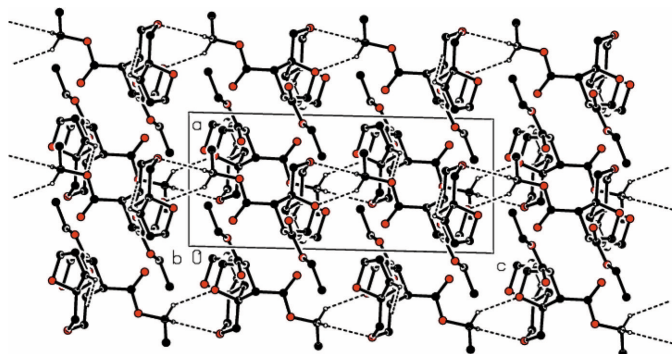


Figure 3
View of the crystal structure of the title complex, along the *b* axis; the same interactions are as in Fig. 2.

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_{norm} (Fig. 5). The interactions listed in Table 2 play a key role in the molecular packing of the title compound. The most important

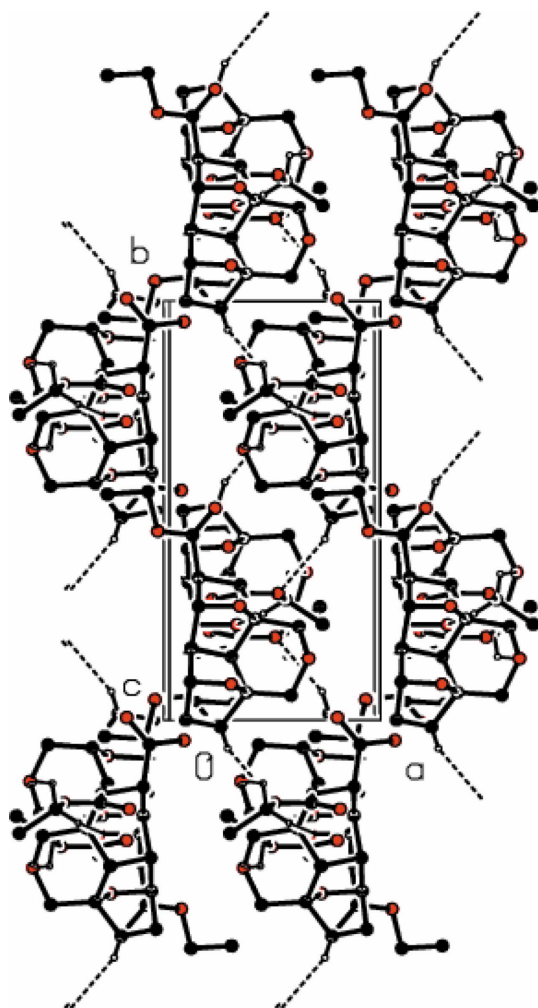


Figure 4
View of the crystal structure of the title complex, along the *c* axis; the same interactions are as in Fig. 2.

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

Contact	Distance	Symmetry operation
H3A...H6AA	2.49	$1 + x, y, z$
O10...H13B	2.41	$x, \frac{1}{2} - y, \frac{1}{2} + z$
H16B...H16B	2.57	$-x, 1 - y, 1 - z$
H1A...O11	2.73	$1 - x, -y, 1 - z$
H17A...H13B	2.29	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
O13...H9A	2.47	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
H7A...C8	3.02	$-x, -y, 1 - z$
H6A...H14A	2.50	$-1 + x, \frac{1}{2} - y, \frac{1}{2} + z$

interatomic contact is H...H as it makes the highest contribution to the crystal packing (60.2%, Fig. 6*b*). The other major contributor is the O...H/H...O (35.4%, Fig. 6*c*) interaction. Other, smaller contributions are made by C...H/H...C (3.9%), O...O (0.3%), C...C (0.2%) and O...C/C...O (0.1%) interactions.

4. Database survey

Four related compounds were found in a search of the Cambridge Structural Database (CSD, version 5.42, update of September 2021; Groom *et al.*, 2016), *viz.* *N*-carbamothioylamino-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (CSD refcode WAFPOK; Li, 2010), {3-hydroxymethyl-1-[2-(3-methoxyphenyl)ethyl]-7-oxabicyclo(2.2.1)hept-5-en-2-yl]methanol (SIMPUA; Wang & Peng, 2007), (1*SR*,2*SR*,4*SR*)-7-oxabicyclo(2.2.1)hept-5-ene-2-carboxylic acid (ETEYEH; Gartenmann Dickson *et al.*, 2004) and (1*S**,2*R**,5*S**,6*S**,7*R**)-5-hydroxy-4-(4-methoxyphenyl)-10-oxa-4-azatricyclo-(5.2.1.02,6)dec-8-en-one (DIWLEB; Gökçe *et al.*, 2008).

The compound WAFPOK comprises a racemic mixture of chiral molecules containing four stereogenic centres. The cyclohexane ring tends towards a boat conformation, while the tetrahydrofuran and dihydrofuran rings adopt envelope conformations. The dihedral angle between the thiosemicarbazide fragment and the fused-ring system is 77.20 (10)°. The crystal structure is stabilized by two intermolecular N—H...O hydrogen bonds. SIMPUA is an oxabi-

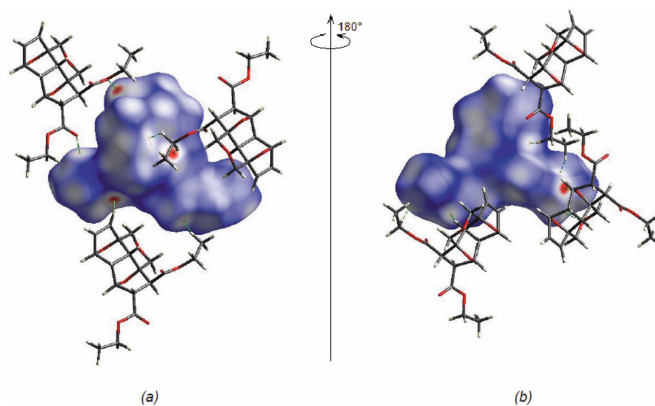
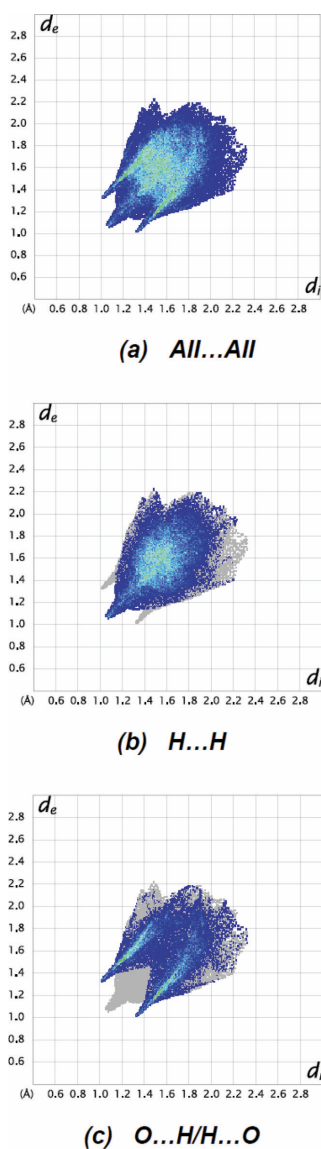


Figure 5
(*a*) Front and (*b*) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over d_{norm} , with a fixed colour scale of -0.1982 to $+1.2419$ a.u.


Figure 6

The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b) H...H and (c) O...H/H...O 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].

cyclo[2.2.1]hept-5-ene with two exo-oriented hydroxymethyl groups, which are not parallel to each other. The molecules are linked to each other by hydrogen bonds, resulting in a supramolecular network. Intermolecular O—H...O hydrogen bonding is observed between the hydroxyl groups. In ETEYEH, the molecules are connected by O—H...O hydrogen bonds, forming centrosymmetric dimers. The structure of DIWLEB comprises a racemic mixture of chiral molecules containing five stereogenic centres. The cyclohexane ring tends towards a boat conformation and the two tetrahydrofuran rings adopt envelope conformations. Molecules are linked into sheets parallel to (100) by a combination of O—H...O, C—H...O and C—H... π interactions, leading to a di-periodic supramolecular structure.


Figure 7
Reaction mechanism.

5. Synthesis and crystallization

A solution of diethyl fumarate (850 mg, 4.95 mmol, 1.1 equiv) and difurfuryl ether (800 mg, 4.5 mmol) in methanol (21 mL) was placed in a Teflon ampoule. The reaction mixture was then held at 15 kbar and r.t. for two days in a piston-cylinder type steel pressure chamber. The obtained methanol solution was concentrated *in vacuo*. The resulting light-yellow oil was solidified in hexane and then recrystallized from ethyl acetate to isolate diastereomer **1a** exclusively (Fig. 7). The residue was filtered off and dried under reduced pressure in a vacuum desiccator to constant weight, yielding the target product as white crystals. White crystals, 0.32 g, 0.94 mmol, yield is 21%, $R_f = 0.7$ ('Sorbfil' plates for thin-layer chromatography, CHCl_3); mp: 418.1–419.1 K. A single-crystal of compound **1a** was obtained by slow evaporation from ethyl acetate at 298 K.

$^1\text{H NMR}$ (700 MHz, CDCl_3 , 298 K) δ 6.40 (*d*, $J = 5.7$ Hz, 1H, CH=CH), 6.20 (*d*, $J = 5.7$ Hz, 1H, CH=CH), 5.02 (*s*, 1H, CH), 4.83 (*s*, 1H, CH), 4.38 (*d*, $J = 12.8$ Hz, 1H, from CH_2), 4.27 (*d*, $J = 12.9$ Hz, 1H, from CH_2), 4.23–4.13 (*m*, 4H, $2\text{OCH}_2\text{CH}_3$), 4.02 (*d*, $J = 12.9$ Hz, 1H, from CH_2), 3.89 (*d*, $J = 12.8$ Hz, 1H, from CH_2), 3.19 (*d*, $J = 5.2$ Hz, 1H, CH), 3.12 (*d*, $J = 5.2$ Hz, 1H, CH), 2.13 (*d*, $J = 6.4$ Hz, 1H, CH), 1.75 (*d*, $J = 6.3$ Hz, 1H, CH), 1.36–1.14 (*m*, 6H, $2\text{OCH}_2\text{CH}_3$). $^{13}\text{C NMR}$ (175 MHz, CDCl_3 , 298 K) δ 171.69, 170.50, 138.05, 136.58, 84.04, 82.64, 82.26, 81.65, 66.67, 66.29, 61.52 (2C), 53.12, 52.70, 49.90, 43.15, 14.34, 14.25. IR $\nu_{\text{max}}/\text{cm}^{-1}$ (tablet KBr): 3440, 2982, 2950, 2910, 2859, 1728, 1473, 1311, 1211, 1174, 1093, 1029, 973, 912, 856, 697. HRMS (ESI-TOF): calculated for $\text{C}_{18}\text{H}_{23}\text{O}_7$ [$M + \text{H}$] $^+$ 351.1443; found 351.1440.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were included in the refinement using the riding-model approximation with C—H distances of 0.95–1.00 Å, and with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. Two reflections (0 1 1 and 1 1 0), affected by the incident beam-stop, were omitted in the final cycles of refinement.

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Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₈ H ₂₂ O ₇
<i>M_r</i>	350.35
Crystal system, space group	Monoclinic, <i>P</i> ₂ /c
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.1566 (4), 14.1907 (9), 16.2737 (10)
β (°)	91.329 (2)
<i>V</i> (Å ³)	1652.27 (17)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.40 × 0.36 × 0.34
Data collection	
Diffraction	Bruker Kappa APEXII area- detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015).
<i>T_{min}</i> , <i>T_{max}</i>	0.941, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	28552, 4921, 3615
<i>R_{int}</i>	0.051
(sin θ/λ) _{max} (Å ⁻¹)	0.709
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.046, 0.119, 1.03
No. of reflections	4921
No. of parameters	226
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.35, -0.30

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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Crystal structure and Hirshfeld surface analysis of diethyl (3a*S*,3a1*R*,4*S*,5*S*,6*R*,6a*S*,7*R*,9a*S*)-3a1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate

Nurlana D. Sadikhova, Zeliha Atioğlu, Narmina A. Guliyeva, Alexandra G. Podrezova, Eugeniya V. Nikitina, Mehmet Akkurt and Ajaya Bhattarai

Computing details

Diethyl (3a*S*,3a1*R*,4*S*,5*S*,6*R*,6a*S*,7*R*,9a*S*)-3a1,5,6,6a-tetrahydro-1*H*,3*H*,4*H*,7*H*-3a,6:7,9a-diepoxybenzo[*de*]isochromene-4,5-dicarboxylate

Crystal data

C₁₈H₂₂O₇

$M_r = 350.35$

Monoclinic, $P2_1/c$

$a = 7.1566$ (4) Å

$b = 14.1907$ (9) Å

$c = 16.2737$ (10) Å

$\beta = 91.329$ (2)°

$V = 1652.27$ (17) Å³

$Z = 4$

$F(000) = 744$

$D_x = 1.408$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5852 reflections

$\theta = 2.5\text{--}29.9^\circ$

$\mu = 0.11$ mm⁻¹

$T = 100$ K

Bulk, colourless

0.40 × 0.36 × 0.34 mm

Data collection

Bruker KAPPA APEXII area-detector diffractometer

φ and ω scans

Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015).

$T_{\min} = 0.941$, $T_{\max} = 1.000$

28552 measured reflections

4921 independent reflections

3615 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$

$\theta_{\max} = 30.3^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -10 \rightarrow 10$

$k = -20 \rightarrow 18$

$l = -23 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.119$

$S = 1.03$

4921 reflections

226 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.5731P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.35$ e Å⁻³

$\Delta\rho_{\min} = -0.30$ e Å⁻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>	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.65003 (13)	0.14690 (7)	0.39784 (6)	0.0185 (2)
O10	0.32231 (13)	0.27216 (6)	0.41424 (6)	0.01429 (19)
O11	0.28123 (13)	0.08569 (7)	0.44881 (6)	0.0166 (2)
O12	0.20009 (15)	0.28745 (9)	0.14509 (7)	0.0289 (3)
O13	0.51089 (13)	0.30191 (7)	0.16601 (6)	0.0202 (2)
O15	0.20749 (15)	0.50604 (7)	0.32809 (7)	0.0275 (3)
O16	-0.06545 (14)	0.45134 (7)	0.37426 (6)	0.0203 (2)
C1	0.56703 (19)	0.05898 (10)	0.37326 (9)	0.0190 (3)
H1A	0.604785	0.009304	0.412996	0.023*
H1B	0.613288	0.040808	0.318629	0.023*
C3B	0.28585 (17)	0.15148 (9)	0.31737 (8)	0.0127 (2)
H3BA	0.276226	0.137729	0.257158	0.015*
C3A	0.39716 (17)	0.24133 (9)	0.33732 (8)	0.0129 (2)
C3	0.60532 (18)	0.22335 (10)	0.34389 (8)	0.0167 (3)
H3A	0.652818	0.209205	0.288583	0.020*
H3B	0.668881	0.281058	0.364234	0.020*
C4	0.32813 (18)	0.32304 (9)	0.28048 (8)	0.0132 (2)
H4A	0.406592	0.379971	0.292317	0.016*
C5	0.13032 (18)	0.34034 (9)	0.31390 (8)	0.0139 (2)
H5A	0.033387	0.321017	0.271973	0.017*
C6	0.12801 (18)	0.27188 (9)	0.38872 (8)	0.0144 (3)
H6A	0.040849	0.291342	0.432769	0.017*
C6A	0.09390 (18)	0.17152 (9)	0.35618 (8)	0.0141 (2)
H6AA	-0.012435	0.168001	0.315333	0.017*
C7	0.08827 (19)	0.09147 (9)	0.42186 (9)	0.0173 (3)
H7A	-0.003793	0.100706	0.466452	0.021*
C8	0.0674 (2)	0.00021 (10)	0.37333 (10)	0.0224 (3)
H8A	-0.041834	-0.037460	0.367396	0.027*
C9A	0.35656 (18)	0.06594 (9)	0.36921 (8)	0.0155 (3)
C9	0.2335 (2)	-0.01604 (9)	0.34091 (9)	0.0210 (3)
H9A	0.267854	-0.067681	0.307329	0.025*
C12	0.33375 (18)	0.30231 (9)	0.18944 (8)	0.0136 (2)
C13	0.5500 (2)	0.28738 (11)	0.07909 (8)	0.0200 (3)
H13A	0.568211	0.348732	0.051437	0.024*
H13B	0.444317	0.254289	0.051389	0.024*
C14	0.7242 (2)	0.22918 (11)	0.07489 (10)	0.0259 (3)
H14A	0.754364	0.218155	0.017244	0.039*
H14B	0.827848	0.262688	0.102366	0.039*
H14C	0.704464	0.168635	0.102318	0.039*

C15	0.10027 (19)	0.44187 (9)	0.33870 (8)	0.0159 (3)
C16	-0.1128 (2)	0.54538 (10)	0.40327 (9)	0.0216 (3)
H16A	-0.109745	0.591211	0.357452	0.026*
H16B	-0.022582	0.565926	0.446699	0.026*
C17	-0.3058 (2)	0.53933 (13)	0.43679 (13)	0.0369 (4)
H17A	-0.343372	0.601375	0.457067	0.055*
H17B	-0.393486	0.518921	0.393188	0.055*
H17C	-0.306732	0.493754	0.482017	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0118 (4)	0.0270 (5)	0.0167 (5)	0.0022 (4)	-0.0019 (4)	0.0041 (4)
O10	0.0130 (4)	0.0189 (4)	0.0110 (4)	0.0006 (3)	0.0019 (3)	-0.0018 (3)
O11	0.0142 (4)	0.0204 (5)	0.0150 (5)	0.0032 (4)	0.0017 (4)	0.0033 (4)
O12	0.0162 (5)	0.0536 (7)	0.0168 (5)	0.0001 (5)	-0.0023 (4)	-0.0039 (5)
O13	0.0136 (5)	0.0351 (6)	0.0121 (5)	-0.0026 (4)	0.0021 (4)	-0.0042 (4)
O15	0.0267 (6)	0.0169 (5)	0.0394 (7)	-0.0021 (4)	0.0097 (5)	-0.0038 (4)
O16	0.0207 (5)	0.0145 (4)	0.0260 (6)	0.0047 (4)	0.0069 (4)	-0.0019 (4)
C1	0.0142 (6)	0.0225 (7)	0.0204 (7)	0.0070 (5)	0.0014 (5)	0.0027 (5)
C3B	0.0105 (5)	0.0150 (6)	0.0126 (6)	0.0016 (4)	0.0000 (5)	-0.0006 (4)
C3A	0.0113 (6)	0.0171 (6)	0.0102 (6)	0.0008 (4)	0.0015 (5)	-0.0012 (4)
C3	0.0108 (6)	0.0244 (7)	0.0148 (6)	0.0006 (5)	0.0006 (5)	0.0034 (5)
C4	0.0129 (6)	0.0148 (6)	0.0120 (6)	-0.0005 (4)	0.0017 (5)	-0.0005 (4)
C5	0.0125 (6)	0.0143 (6)	0.0149 (6)	0.0014 (5)	0.0019 (5)	-0.0010 (5)
C6	0.0115 (6)	0.0164 (6)	0.0153 (6)	0.0024 (5)	0.0028 (5)	0.0006 (5)
C6A	0.0103 (6)	0.0147 (6)	0.0175 (6)	0.0011 (4)	0.0016 (5)	0.0027 (5)
C7	0.0117 (6)	0.0178 (6)	0.0224 (7)	0.0011 (5)	0.0023 (5)	0.0043 (5)
C8	0.0204 (7)	0.0155 (6)	0.0310 (8)	-0.0027 (5)	-0.0031 (6)	0.0049 (6)
C9A	0.0143 (6)	0.0164 (6)	0.0158 (6)	0.0037 (5)	0.0005 (5)	0.0003 (5)
C9	0.0245 (7)	0.0132 (6)	0.0251 (7)	0.0030 (5)	-0.0033 (6)	0.0009 (5)
C12	0.0146 (6)	0.0126 (6)	0.0134 (6)	0.0008 (4)	0.0007 (5)	0.0022 (4)
C13	0.0203 (7)	0.0295 (7)	0.0103 (6)	0.0035 (6)	0.0025 (5)	-0.0019 (5)
C14	0.0276 (8)	0.0308 (8)	0.0194 (7)	0.0090 (6)	0.0048 (6)	-0.0007 (6)
C15	0.0180 (6)	0.0166 (6)	0.0132 (6)	0.0035 (5)	0.0008 (5)	0.0006 (5)
C16	0.0267 (7)	0.0154 (6)	0.0226 (7)	0.0093 (5)	0.0013 (6)	-0.0026 (5)
C17	0.0280 (9)	0.0320 (9)	0.0512 (12)	0.0115 (7)	0.0102 (8)	-0.0112 (8)

Geometric parameters (Å, °)

O2—C3	1.4274 (16)	C5—C15	1.5130 (18)
O2—C1	1.4347 (17)	C5—C6	1.5580 (18)
O10—C3A	1.4410 (15)	C5—H5A	1.0000
O10—C6	1.4420 (15)	C6—C6A	1.5370 (18)
O11—C7	1.4414 (16)	C6—H6A	1.0000
O11—C9A	1.4420 (16)	C6A—C7	1.5609 (18)
O12—C12	1.2035 (16)	C6A—H6AA	1.0000
O13—C12	1.3323 (16)	C7—C8	1.522 (2)

O13—C13	1.4630 (16)	C7—H7A	1.0000
O15—C15	1.2058 (17)	C8—C9	1.332 (2)
O16—C15	1.3384 (16)	C8—H8A	0.9500
O16—C16	1.4581 (16)	C9A—C9	1.5241 (19)
C1—C9A	1.5094 (18)	C9—H9A	0.9500
C1—H1A	0.9900	C13—C14	1.498 (2)
C1—H1B	0.9900	C13—H13A	0.9900
C3B—C3A	1.5341 (18)	C13—H13B	0.9900
C3B—C6A	1.5515 (17)	C14—H14A	0.9800
C3B—C9A	1.5561 (18)	C14—H14B	0.9800
C3B—H3BA	1.0000	C14—H14C	0.9800
C3A—C3	1.5127 (17)	C16—C17	1.499 (2)
C3A—C4	1.5565 (18)	C16—H16A	0.9900
C3—H3A	0.9900	C16—H16B	0.9900
C3—H3B	0.9900	C17—H17A	0.9800
C4—C12	1.5120 (18)	C17—H17B	0.9800
C4—C5	1.5478 (18)	C17—H17C	0.9800
C4—H4A	1.0000		
C3—O2—C1	113.82 (10)	C3B—C6A—H6AA	112.8
C3A—O10—C6	97.15 (9)	C7—C6A—H6AA	112.8
C7—O11—C9A	96.51 (10)	O11—C7—C8	101.02 (10)
C12—O13—C13	118.82 (11)	O11—C7—C6A	102.12 (10)
C15—O16—C16	116.54 (11)	C8—C7—C6A	105.52 (11)
O2—C1—C9A	111.20 (10)	O11—C7—H7A	115.4
O2—C1—H1A	109.4	C8—C7—H7A	115.4
C9A—C1—H1A	109.4	C6A—C7—H7A	115.4
O2—C1—H1B	109.4	C9—C8—C7	105.96 (12)
C9A—C1—H1B	109.4	C9—C8—H8A	127.0
H1A—C1—H1B	108.0	C7—C8—H8A	127.0
C3A—C3B—C6A	102.82 (10)	O11—C9A—C1	111.53 (11)
C3A—C3B—C9A	111.90 (10)	O11—C9A—C9	101.20 (11)
C6A—C3B—C9A	101.66 (10)	C1—C9A—C9	122.17 (11)
C3A—C3B—H3BA	113.2	O11—C9A—C3B	102.22 (10)
C6A—C3B—H3BA	113.1	C1—C9A—C3B	112.73 (11)
C9A—C3B—H3BA	113.1	C9—C9A—C3B	104.67 (11)
O10—C3A—C3	112.03 (10)	C8—C9—C9A	105.25 (12)
O10—C3A—C3B	103.56 (10)	C8—C9—H9A	127.4
C3—C3A—C3B	112.36 (10)	C9A—C9—H9A	127.4
O10—C3A—C4	99.83 (9)	O12—C12—O13	125.17 (12)
C3—C3A—C4	117.78 (11)	O12—C12—C4	125.66 (12)
C3B—C3A—C4	109.72 (10)	O13—C12—C4	109.17 (11)
O2—C3—C3A	112.21 (11)	O13—C13—C14	107.45 (12)
O2—C3—H3A	109.2	O13—C13—H13A	110.2
C3A—C3—H3A	109.2	C14—C13—H13A	110.2
O2—C3—H3B	109.2	O13—C13—H13B	110.2
C3A—C3—H3B	109.2	C14—C13—H13B	110.2
H3A—C3—H3B	107.9	H13A—C13—H13B	108.5

C12—C4—C5	114.86 (11)	C13—C14—H14A	109.5
C12—C4—C3A	114.96 (10)	C13—C14—H14B	109.5
C5—C4—C3A	100.93 (10)	H14A—C14—H14B	109.5
C12—C4—H4A	108.6	C13—C14—H14C	109.5
C5—C4—H4A	108.6	H14A—C14—H14C	109.5
C3A—C4—H4A	108.6	H14B—C14—H14C	109.5
C15—C5—C4	112.43 (11)	O15—C15—O16	124.01 (12)
C15—C5—C6	112.40 (11)	O15—C15—C5	125.88 (12)
C4—C5—C6	101.66 (10)	O16—C15—C5	110.11 (11)
C15—C5—H5A	110.0	O16—C16—C17	106.76 (12)
C4—C5—H5A	110.0	O16—C16—H16A	110.4
C6—C5—H5A	110.0	C17—C16—H16A	110.4
O10—C6—C6A	104.25 (10)	O16—C16—H16B	110.4
O10—C6—C5	101.29 (10)	C17—C16—H16B	110.4
C6A—C6—C5	108.24 (11)	H16A—C16—H16B	108.6
O10—C6—H6A	114.0	C16—C17—H17A	109.5
C6A—C6—H6A	114.0	C16—C17—H17B	109.5
C5—C6—H6A	114.0	H17A—C17—H17B	109.5
C6—C6A—C3B	100.08 (10)	C16—C17—H17C	109.5
C6—C6A—C7	116.41 (11)	H17A—C17—H17C	109.5
C3B—C6A—C7	100.52 (10)	H17B—C17—H17C	109.5
C6—C6A—H6AA	112.8		
C3—O2—C1—C9A	-59.58 (14)	C9A—O11—C7—C8	50.63 (11)
C6—O10—C3A—C3	-173.99 (10)	C9A—O11—C7—C6A	-58.08 (11)
C6—O10—C3A—C3B	-52.67 (11)	C6—C6A—C7—O11	-70.74 (13)
C6—O10—C3A—C4	60.53 (10)	C3B—C6A—C7—O11	36.17 (12)
C6A—C3B—C3A—O10	31.09 (12)	C6—C6A—C7—C8	-175.97 (11)
C9A—C3B—C3A—O10	-77.27 (12)	C3B—C6A—C7—C8	-69.05 (12)
C6A—C3B—C3A—C3	152.18 (11)	O11—C7—C8—C9	-32.10 (14)
C9A—C3B—C3A—C3	43.82 (14)	C6A—C7—C8—C9	73.94 (14)
C6A—C3B—C3A—C4	-74.76 (12)	C7—O11—C9A—C1	177.58 (10)
C9A—C3B—C3A—C4	176.89 (10)	C7—O11—C9A—C9	-51.00 (11)
C1—O2—C3—C3A	59.76 (14)	C7—O11—C9A—C3B	56.88 (11)
O10—C3A—C3—O2	64.99 (14)	O2—C1—C9A—O11	-63.19 (14)
C3B—C3A—C3—O2	-51.11 (15)	O2—C1—C9A—C9	177.15 (12)
C4—C3A—C3—O2	179.91 (11)	O2—C1—C9A—C3B	51.15 (15)
O10—C3A—C4—C12	-163.65 (10)	C3A—C3B—C9A—O11	75.48 (12)
C3—C3A—C4—C12	74.92 (15)	C6A—C3B—C9A—O11	-33.62 (12)
C3B—C3A—C4—C12	-55.30 (14)	C3A—C3B—C9A—C1	-44.38 (15)
O10—C3A—C4—C5	-39.44 (11)	C6A—C3B—C9A—C1	-153.48 (11)
C3—C3A—C4—C5	-160.87 (11)	C3A—C3B—C9A—C9	-179.32 (11)
C3B—C3A—C4—C5	68.91 (12)	C6A—C3B—C9A—C9	71.58 (12)
C12—C4—C5—C15	-110.49 (13)	C7—C8—C9—C9A	-0.35 (15)
C3A—C4—C5—C15	125.24 (11)	O11—C9A—C9—C8	32.70 (14)
C12—C4—C5—C6	129.10 (11)	C1—C9A—C9—C8	157.22 (13)
C3A—C4—C5—C6	4.83 (12)	C3B—C9A—C9—C8	-73.26 (14)
C3A—O10—C6—C6A	54.98 (11)	C13—O13—C12—O12	3.4 (2)

C3A—O10—C6—C5	-57.36 (10)	C13—O13—C12—C4	-177.31 (11)
C15—C5—C6—O10	-89.24 (12)	C5—C4—C12—O12	-9.39 (19)
C4—C5—C6—O10	31.18 (12)	C3A—C4—C12—O12	107.12 (15)
C15—C5—C6—C6A	161.48 (10)	C5—C4—C12—O13	171.36 (10)
C4—C5—C6—C6A	-78.09 (12)	C3A—C4—C12—O13	-72.14 (13)
O10—C6—C6A—C3B	-34.93 (12)	C12—O13—C13—C14	-143.18 (13)
C5—C6—C6A—C3B	72.31 (12)	C16—O16—C15—O15	-1.7 (2)
O10—C6—C6A—C7	72.24 (13)	C16—O16—C15—C5	178.70 (11)
C5—C6—C6A—C7	179.48 (10)	C4—C5—C15—O15	6.3 (2)
C3A—C3B—C6A—C6	2.12 (12)	C6—C5—C15—O15	120.28 (15)
C9A—C3B—C6A—C6	118.07 (10)	C4—C5—C15—O16	-174.16 (11)
C3A—C3B—C6A—C7	-117.38 (11)	C6—C5—C15—O16	-60.17 (14)
C9A—C3B—C6A—C7	-1.44 (12)	C15—O16—C16—C17	177.50 (13)

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>
C3—H3A...O13	0.99	2.58	3.1604 (17)	118
C9—H9A...O13 ⁱ	0.95	2.47	3.1692 (17)	131
C13—H13A...O2 ⁱⁱ	0.99	2.58	3.1905 (17)	120
C13—H13B...O10 ⁱⁱ	0.99	2.41	3.2193 (17)	139
C14—H14C...O15 ⁱ	0.98	2.64	3.5669 (19)	158

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