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# β-(3,6,9-Trimethyl-9-xanthenyl)propionic acid

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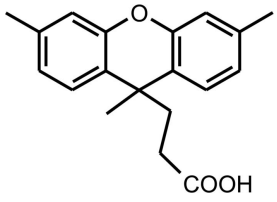
Key indicators: single-crystal X-ray study; $T$ = 85 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.036; $wR$ factor = 0.105; data-to-parameter ratio = 14.6.

The title compound, $C_{19}H_{20}O_3$, was obtained, among other condensation products, from the reaction of *meta*-cresol and levulinic acid. The pyrane ring closure does not alter significantly the environment of the ethereal linkage in comparison with diaryl ethers. The deformations of the endocyclic valence angles in the benzene rings, centred on the C atoms substituted with alkyl groups, is greater than expected. The molecular packing is influenced by O—H···O hydrogen bonds, leading to centrosymmetric dimers.

## Related literature

For related literature, see: Bader & Kontowicz (1954); Blackburn *et al.* (1996); Domenicano (1992); Jacobs *et al.* (2005); Yu & Day (1958); Allen *et al.* (1987).




## Experimental

*Crystal data*

$C_{19}H_{20}O_3$
$M_r$ = 296.35
Monoclinic, $P2_1/c$
$a$ = 10.5042 (9) Å
$b$ = 14.3969 (11) Å
$c$ = 11.2404 (9) Å
$\beta$ = 110.645 (7)°
$V$ = 1590.7 (2) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.08 mm$^{-1}$
$T$ = 85.0 (2) K
0.25 × 0.23 × 0.22 mm

*Data collection*

Oxford Diffraction Xcalibur diffractometer
Absorption correction: none
12735 measured reflections
4411 independent reflections
2929 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.105
$S$ = 1.02
4075 reflections
279 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O24—H24···O25$^{i}$ | 0.935 (18) | 1.732 (19) | 2.6654 (12) | 176.9 (17) |
| C2—H2···O10$^{ii}$ | 0.960 (13) | 2.507 (14) | 3.3989 (14) | 154.6 (10) |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2378).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, o2834 [ **doi:10.1107/S1600536807021332** ]

# β-(3,6,9-Trimethyl-9-xanthenyl)propionic acid

**J. B. Kyziol, E. M. Nowakowska and J. Zaleski**

## Comment

Condensation of phenol with levulinic acid or its ester, in the presence of an acidic catalyst, provides the corresponding bisphenolic acid (DPA) as the only product (Bader & Kontowicz, 1954; Yu & Day, 1958). Xanthene core of the (I) molecule is planar as in other 9,9–disubstituted xanthenes (Jacobs, *et al.*, 2005). A roof–shaped structure, with the fold angle up to 14.2 (1)° was found in xanthene–9–carboxylic acid molecule (Blackburn, *et al.*, 1996). The benzene rings of (I) are almost regular hexagons with the typical aromatic C — C bond lengths (1.395 (8) Å). The internal angles centred on C3, C6, C11 and C14 atoms *i.e.* those, which are bonded to tetrahedral carbons, have lower value (lowest 116.00 (10)° largest 117.99 (10)) than expected 120°. The deformation is greater than expected (Δα = − 1.9°) for any electron releasing substituent (Domenicano, 1992). The O10 and C9 atoms are situated almost exactly in the plane of neighbour benzene rings; the deviations from the plane of four angular atoms are 0.043Å (O10) and 0.029 Å (C9). The geometry of pyrane ring can be described as the flat boat conformation. The internal C11 — C9 — C14 angle (109.65 (9)°) corresponds to the tetrahedral hybridization of C9 atom. The oxygen atom is more flexible member of the ring, the angle centred on O10 (118.48 (8)°) makes the pyrane ring nearly regular. The C — O bond length (1.381 (1) Å) is the same as in open diaryl ethers (Allen *et al.*, 1995). The C26 — C9 — C21 plane is perpendicular to the xanthene system. Four bonds, formed by C9 have the lengths typical for the Ar — C($sp^3$) (1.5268 (14) and 1.5290 (15) Å) and C($sp^3$) – C($sp^3$) (1.5504 (15) and 1.5416 (15) Å). The ethylene C21 — C22 group has *transoid* conformation in crystal network, in part, due to the molecular packing. In solution, rotation along C21 — C22 bond is restricted to some extent because of steric interaction within the molecule (I). It is observed in the proton NMR spectrum as two illegible multiplets, at 2.11 and 1.84 p.p.m., indicating that the environments of vicinal protons are not magnetically equivalent.

The (I) molecules are arranged in couples joined by the O — H···O hydrogen bond as in the aforementioned xanthene–9–carboxylic acid (Blackburn, *et al.*, 1996). Monomeric carboxylic acids absorb in IR, in diluted carbon tetrachloride solution, at 3500—3550 $cm^{-1}$ due to O — H bond stretching vibrations. In the spectra of (I), registered in the solid state and in solution, this band is shifted to the 2800–3100 $cm^{-1}$ region and overlapped with the C — H stretching vibrations. The absorption enhancement and the shift, exceeding 16% on the 1/ λ scale, indicate a strong character of the hydrogen bond. The interaction is observed in the crystal lattice as short (2.666 Å) distance between two oxygen atoms belonging to neighbour molecules. It is less than the sum of Van der Waals radii (2.80 Å) of atoms participating in the hydrogen bond.

## Experimental

A catalytic amount of dry hydrogen chloride was introduced into the melt of levulinic acid (17.42 g, 0.15 mole) and *meta*-cresol (32.45 g, 0.30 mole). A brownish red mixture was left for 15 days at room temperature and poured on ice. An oily product was collected with ethyl ether and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was distilled in vacuum to remove unreacted substrates. A mixture of non-volatile components was dissolved in benzene and chromatographed on the short column (Kieselgel 60) using the benzene – izooctane 1:1 mixture as the eluent. Compound (III) was eluted first (6.02 g, 19%); m.p. 366–368 K (ethyl ether – n-hexane). The next fraction

provided (I) as colourless prisms, m.p. 468–470 K. Crystallization from ethyl ether – benzene mixture gave crystals (8.03 g, 18%) suitable for X-ray diffraction studies. MS, m/*z* (int.): 296 (1, $M^+$), 281 (4), 223 (100), 208 (4). IR (KBr): 3030 (aromatic protons); 2969, 2869, 2926 (aliphatic C — H stretching); 1706 (carbonyl band in carboxylic acid dimer); 1595*m* 1565, 1501 (skeletal vibrations); 860, 818, 806 (deformations of aromatic protons). $^1$H–NMR ($CDCl_3$): 7.12, d $^3J$ = 8.0 Hz, 2H (H-1, H-8); 6.80, dd $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 2H (H-2, H-7); 6.75, d $^4J$ = 1.2 Hz, 2H (H-4, H-9); 2.24, s, 6H (methyl groups bonded to benzene rings); 2.11, m, 2H and 1.84, m, 2H (ethylene group on C-9); 1.58, s, 3H (methyl group on C-9). $^{13}$C-NMR ($CDCl_3$): 180.0 (carboxyl group); 150.9 (C-12, C-13); 138.0 (C-3, C-6); 126.3 (C-1, C-8); 124.4 (C-2, C-7); 123.3 (C-11, C-14); 116.9 (C-4, C-5); 40.1 (C-6, methyl group); 36.8 (C-9); 32.5, 30.6 (C-1 and C-2, ethylene group); 21.1 (Ar – methyl groups).

From the last fraction small amounts of lactone (II) were isolated (m.p. 452–454 K) and traces of 4,4-bis-(4-hydroxy-2-methylphenyl)- valeric acid (m.p. 448–450 K).

**Figures**

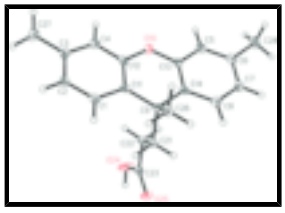

Fig. 1. The molecular structure of (I) with atom labels. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

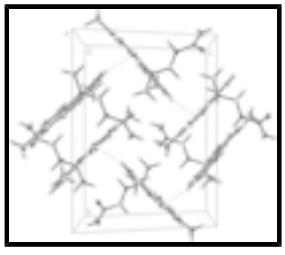

Fig. 2. The packing diagram of (I).

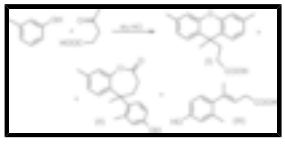

Fig. 3. Reaction scheme.

**β-(3,6,9-Trimethyl-9-xanthenyl)propionic acid**

*Crystal data*

| | |
|---|---|
| $C_{19}H_{20}O_3$ | $F_{000}$ = 632 |
| $M_r$ = 296.35 | $D_x$ = 1.237 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ybc | Cell parameters from 4075 reflections |
| $a$ = 10.5042 (9) Å | θ = 2.7–29.4º |
| $b$ = 14.3969 (11) Å | μ = 0.08 mm$^{-1}$ |
| $c$ = 11.2404 (9) Å | $T$ = 85.0 (2) K |

| | |
|---|---|
| $\beta = 110.645\ (7)^{o}$ | Irregular, colourless |
| $V = 1590.7\ (2)\ Å^3$ | 0.25 × 0.23 × 0.22 mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Oxford Diffraction Xcalibur diffractometer | 2929 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.017$ |
| Monochromator: graphite | $\theta_{max} = 29.4^{o}$ |
| $T = 85.0(2)$ K | $\theta_{min} = 2.7^{o}$ |
| ω–scan | $h = -14 \rightarrow 13$ |
| Absorption correction: NONE | $k = -17 \rightarrow 19$ |
| 12735 measured reflections | $l = -15 \rightarrow 15$ |
| 4411 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | All H-atom parameters refined |
| $wR(F^2) = 0.105$ | $w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 4075 reflections | $\Delta\rho_{max} = 0.32$ e Å$^{-3}$ |
| 279 parameters | $\Delta\rho_{min} = -0.23$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*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.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.54653 (11) | 0.27029 (8) | 0.62341 (10) | 0.0160 (2) |
| H1 | 0.6202 (14) | 0.3115 (9) | 0.6747 (13) | 0.023 (3)* |
| C2 | 0.41988 (11) | 0.27971 (8) | 0.63464 (11) | 0.0166 (2) |

| | | | | |
|---|---|---|---|---|
| H2 | 0.4057 (13) | 0.3257 (9) | 0.6905 (13) | 0.021 (3)* |
| C3 | 0.31129 (11) | 0.22389 (7) | 0.56366 (10) | 0.0153 (2) |
| C4 | 0.33408 (11) | 0.15899 (7) | 0.48222 (11) | 0.0159 (2) |
| H4 | 0.2591 (13) | 0.1191 (9) | 0.4271 (12) | 0.019 (3)* |
| C5 | 0.58806 (12) | 0.00426 (8) | 0.27792 (10) | 0.0160 (2) |
| H5 | 0.5021 (13) | −0.0277 (8) | 0.2353 (12) | 0.018 (3)* |
| C6 | 0.70170 (12) | −0.01383 (8) | 0.24647 (11) | 0.0174 (2) |
| C7 | 0.82073 (12) | 0.03521 (8) | 0.31188 (11) | 0.0198 (3) |
| H7 | 0.9041 (14) | 0.0249 (9) | 0.2919 (13) | 0.022 (3)* |
| C8 | 0.82337 (12) | 0.10053 (8) | 0.40325 (11) | 0.0184 (2) |
| H8 | 0.9108 (15) | 0.1358 (9) | 0.4460 (13) | 0.026 (4)* |
| C9 | 0.71229 (11) | 0.19491 (7) | 0.53293 (10) | 0.0125 (2) |
| O10 | 0.47112 (8) | 0.08046 (5) | 0.39100 (7) | 0.01616 (18) |
| C11 | 0.57152 (11) | 0.20465 (7) | 0.54259 (10) | 0.0124 (2) |
| C12 | 0.46221 (11) | 0.14936 (7) | 0.47324 (10) | 0.0131 (2) |
| C13 | 0.59229 (11) | 0.06962 (7) | 0.37053 (10) | 0.0134 (2) |
| C14 | 0.70842 (11) | 0.12055 (7) | 0.43461 (10) | 0.0132 (2) |
| C21 | 0.81734 (11) | 0.16763 (7) | 0.66432 (10) | 0.0131 (2) |
| H21A | 0.8232 (12) | 0.2171 (9) | 0.7274 (12) | 0.016 (3)* |
| H21B | 0.9093 (13) | 0.1643 (9) | 0.6583 (12) | 0.020 (3)* |
| C22 | 0.78051 (12) | 0.07679 (8) | 0.71238 (11) | 0.0176 (2) |
| H22A | 0.6909 (15) | 0.0772 (10) | 0.7165 (14) | 0.030 (4)* |
| H22B | 0.7760 (15) | 0.0259 (10) | 0.6524 (15) | 0.034 (4)* |
| C23 | 0.87758 (11) | 0.04535 (7) | 0.83856 (10) | 0.0142 (2) |
| O24 | 0.82955 (9) | −0.02352 (6) | 0.88773 (9) | 0.0309 (2) |
| H24 | 0.8952 (18) | −0.0415 (12) | 0.9649 (18) | 0.051 (5)* |
| O25 | 0.98967 (8) | 0.07885 (6) | 0.89079 (8) | 0.0206 (2) |
| C26 | 0.75498 (12) | 0.28876 (8) | 0.49252 (11) | 0.0172 (2) |
| H26A | 0.8466 (14) | 0.2862 (9) | 0.4846 (12) | 0.023 (3)* |
| H26B | 0.7580 (12) | 0.3375 (9) | 0.5566 (12) | 0.019 (3)* |
| H26C | 0.6906 (15) | 0.3085 (9) | 0.4072 (14) | 0.025 (4)* |
| C27 | 0.17292 (12) | 0.23341 (9) | 0.57411 (13) | 0.0213 (3) |
| H27A | 0.1353 (14) | 0.1730 (11) | 0.5853 (13) | 0.026 (4)* |
| H27B | 0.1723 (16) | 0.2743 (11) | 0.6474 (15) | 0.039 (4)* |
| H27C | 0.1077 (17) | 0.2583 (11) | 0.4953 (16) | 0.042 (4)* |
| C28 | 0.69469 (15) | −0.08295 (10) | 0.14359 (13) | 0.0252 (3) |
| H28A | 0.6348 (17) | −0.1350 (12) | 0.1440 (16) | 0.049 (5)* |
| H28B | 0.6580 (18) | −0.0541 (12) | 0.0595 (18) | 0.053 (5)* |
| H28C | 0.7874 (17) | −0.1085 (11) | 0.1545 (15) | 0.042 (4)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0167 (5) | 0.0160 (5) | 0.0134 (5) | −0.0013 (4) | 0.0029 (4) | −0.0016 (4) |
| C2 | 0.0186 (6) | 0.0163 (6) | 0.0148 (5) | 0.0017 (4) | 0.0057 (5) | −0.0017 (4) |
| C3 | 0.0146 (5) | 0.0143 (5) | 0.0173 (5) | 0.0016 (4) | 0.0062 (4) | 0.0032 (4) |
| C4 | 0.0150 (5) | 0.0135 (5) | 0.0179 (6) | −0.0024 (4) | 0.0043 (4) | −0.0001 (4) |
| C5 | 0.0180 (6) | 0.0147 (5) | 0.0144 (5) | −0.0031 (4) | 0.0047 (5) | −0.0005 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C6 | 0.0210 (6) | 0.0172 (6) | 0.0150 (5) | 0.0002 (4) | 0.0074 (5) | −0.0002 (4) |
| C7 | 0.0171 (6) | 0.0246 (6) | 0.0194 (6) | 0.0010 (5) | 0.0086 (5) | −0.0027 (5) |
| C8 | 0.0143 (5) | 0.0229 (6) | 0.0167 (6) | −0.0013 (4) | 0.0040 (5) | −0.0015 (5) |
| C9 | 0.0116 (5) | 0.0139 (5) | 0.0107 (5) | −0.0004 (4) | 0.0023 (4) | 0.0006 (4) |
| O10 | 0.0148 (4) | 0.0163 (4) | 0.0191 (4) | −0.0040 (3) | 0.0080 (3) | −0.0060 (3) |
| C11 | 0.0128 (5) | 0.0131 (5) | 0.0099 (5) | 0.0004 (4) | 0.0023 (4) | 0.0026 (4) |
| C12 | 0.0167 (5) | 0.0112 (5) | 0.0111 (5) | 0.0000 (4) | 0.0047 (4) | 0.0001 (4) |
| C13 | 0.0141 (5) | 0.0143 (5) | 0.0124 (5) | 0.0003 (4) | 0.0054 (4) | 0.0024 (4) |
| C14 | 0.0141 (5) | 0.0144 (5) | 0.0105 (5) | 0.0004 (4) | 0.0037 (4) | 0.0019 (4) |
| C21 | 0.0126 (5) | 0.0139 (5) | 0.0114 (5) | −0.0014 (4) | 0.0024 (4) | 0.0000 (4) |
| C22 | 0.0173 (6) | 0.0174 (6) | 0.0140 (5) | −0.0044 (4) | 0.0003 (5) | 0.0017 (4) |
| C23 | 0.0170 (5) | 0.0118 (5) | 0.0142 (5) | 0.0012 (4) | 0.0059 (4) | −0.0005 (4) |
| O24 | 0.0235 (5) | 0.0328 (5) | 0.0244 (5) | −0.0119 (4) | −0.0062 (4) | 0.0162 (4) |
| O25 | 0.0147 (4) | 0.0245 (4) | 0.0177 (4) | −0.0034 (3) | −0.0003 (3) | 0.0067 (3) |
| C26 | 0.0198 (6) | 0.0157 (6) | 0.0165 (6) | −0.0024 (4) | 0.0071 (5) | 0.0018 (4) |
| C27 | 0.0161 (6) | 0.0208 (6) | 0.0282 (7) | 0.0006 (5) | 0.0092 (5) | −0.0022 (5) |
| C28 | 0.0283 (7) | 0.0269 (7) | 0.0239 (7) | −0.0040 (5) | 0.0135 (6) | −0.0098 (5) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.3865 (15) | O10—C13 | 1.3799 (13) |
| C1—C11 | 1.3984 (15) | O10—C12 | 1.3813 (12) |
| C1—H1 | 0.984 (14) | C11—C12 | 1.3887 (14) |
| C2—C3 | 1.3935 (15) | C13—C14 | 1.3874 (15) |
| C2—H2 | 0.960 (13) | C21—C22 | 1.5164 (15) |
| C3—C4 | 1.3867 (16) | C21—H21A | 0.991 (12) |
| C3—C27 | 1.5052 (16) | C21—H21B | 0.993 (13) |
| C4—C12 | 1.3916 (15) | C22—C23 | 1.4954 (15) |
| C4—H4 | 0.995 (13) | C22—H22A | 0.958 (15) |
| C5—C6 | 1.3840 (16) | C22—H22B | 0.986 (15) |
| C5—C13 | 1.3922 (15) | C23—O25 | 1.2150 (13) |
| C5—H5 | 0.976 (13) | C23—O24 | 1.3190 (14) |
| C6—C7 | 1.3978 (16) | O24—H24 | 0.935 (18) |
| C6—C28 | 1.5076 (16) | C26—H26A | 0.998 (13) |
| C7—C8 | 1.3855 (16) | C26—H26B | 0.998 (14) |
| C7—H7 | 0.989 (14) | C26—H26C | 1.001 (14) |
| C8—C14 | 1.4020 (15) | C27—H27A | 0.981 (15) |
| C8—H8 | 1.010 (14) | C27—H27B | 1.015 (16) |
| C9—C11 | 1.5268 (14) | C27—H27C | 0.977 (17) |
| C9—C14 | 1.5289 (15) | C28—H28A | 0.979 (18) |
| C9—C26 | 1.5416 (15) | C28—H28B | 0.978 (19) |
| C9—C21 | 1.5504 (15) | C28—H28C | 1.007 (17) |
| C2—C1—C11 | 122.08 (10) | C14—C13—C5 | 122.40 (10) |
| C2—C1—H1 | 118.0 (8) | C13—C14—C8 | 116.00 (10) |
| C11—C1—H1 | 119.9 (8) | C13—C14—C9 | 122.67 (9) |
| C1—C2—C3 | 120.63 (10) | C8—C14—C9 | 121.33 (10) |
| C1—C2—H2 | 120.2 (8) | C22—C21—C9 | 111.88 (9) |
| C3—C2—H2 | 119.2 (8) | C22—C21—H21A | 108.9 (7) |
| C4—C3—C2 | 118.01 (10) | C9—C21—H21A | 110.1 (7) |

| | | | |
|---|---|---|---|
| C4—C3—C27 | 120.60 (10) | C22—C21—H21B | 111.0 (7) |
| C2—C3—C27 | 121.39 (10) | C9—C21—H21B | 109.3 (7) |
| C3—C4—C12 | 120.76 (10) | H21A—C21—H21B | 105.5 (10) |
| C3—C4—H4 | 121.2 (7) | C23—C22—C21 | 115.13 (9) |
| C12—C4—H4 | 118.1 (7) | C23—C22—H22A | 108.0 (9) |
| C6—C5—C13 | 121.01 (10) | C21—C22—H22A | 113.0 (8) |
| C6—C5—H5 | 121.2 (7) | C23—C22—H22B | 106.0 (9) |
| C13—C5—H5 | 117.8 (7) | C21—C22—H22B | 110.8 (9) |
| C5—C6—C7 | 117.56 (10) | H22A—C22—H22B | 103.1 (12) |
| C5—C6—C28 | 120.46 (11) | O25—C23—O24 | 122.99 (10) |
| C7—C6—C28 | 121.97 (11) | O25—C23—C22 | 123.97 (10) |
| C8—C7—C6 | 120.87 (11) | O24—C23—C22 | 113.04 (9) |
| C8—C7—H7 | 118.9 (8) | C23—O24—H24 | 109.4 (11) |
| C6—C7—H7 | 120.2 (8) | C9—C26—H26A | 112.5 (8) |
| C7—C8—C14 | 122.13 (11) | C9—C26—H26B | 110.0 (7) |
| C7—C8—H8 | 118.1 (8) | H26A—C26—H26B | 107.7 (10) |
| C14—C8—H8 | 119.7 (8) | C9—C26—H26C | 111.3 (8) |
| C11—C9—C14 | 109.64 (8) | H26A—C26—H26C | 105.8 (10) |
| C11—C9—C26 | 109.27 (9) | H26B—C26—H26C | 109.3 (10) |
| C14—C9—C26 | 109.70 (9) | C3—C27—H27A | 111.9 (8) |
| C11—C9—C21 | 109.72 (8) | C3—C27—H27B | 113.5 (9) |
| C14—C9—C21 | 109.86 (8) | H27A—C27—H27B | 107.0 (12) |
| C26—C9—C21 | 108.63 (9) | C3—C27—H27C | 110.5 (9) |
| C13—O10—C12 | 118.49 (8) | H27A—C27—H27C | 104.8 (13) |
| C12—C11—C1 | 116.40 (10) | H27B—C27—H27C | 108.7 (12) |
| C12—C11—C9 | 122.50 (9) | C6—C28—H28A | 111.0 (10) |
| C1—C11—C9 | 121.11 (9) | C6—C28—H28B | 110.9 (10) |
| O10—C12—C11 | 123.34 (9) | H28A—C28—H28B | 107.1 (14) |
| O10—C12—C4 | 114.55 (9) | C6—C28—H28C | 111.4 (9) |
| C11—C12—C4 | 122.11 (10) | H28A—C28—H28C | 108.3 (13) |
| O10—C13—C14 | 123.20 (10) | H28B—C28—H28C | 107.9 (13) |
| O10—C13—C5 | 114.39 (9) | | |
| C11—C1—C2—C3 | −0.69 (17) | C3—C4—C12—O10 | 178.37 (9) |
| C1—C2—C3—C4 | 0.11 (16) | C3—C4—C12—C11 | −1.23 (16) |
| C1—C2—C3—C27 | −179.71 (11) | C12—O10—C13—C14 | 4.26 (15) |
| C2—C3—C4—C12 | 0.82 (16) | C12—O10—C13—C5 | −174.54 (9) |
| C27—C3—C4—C12 | −179.36 (10) | C6—C5—C13—O10 | 179.65 (9) |
| C13—C5—C6—C7 | 0.60 (16) | C6—C5—C13—C14 | 0.84 (17) |
| C13—C5—C6—C28 | −178.39 (11) | O10—C13—C14—C8 | 179.55 (9) |
| C5—C6—C7—C8 | −1.04 (17) | C5—C13—C14—C8 | −1.75 (16) |
| C28—C6—C7—C8 | 177.93 (11) | O10—C13—C14—C9 | −0.99 (16) |
| C6—C7—C8—C14 | 0.08 (18) | C5—C13—C14—C9 | 177.72 (10) |
| C2—C1—C11—C12 | 0.31 (16) | C7—C8—C14—C13 | 1.29 (16) |
| C2—C1—C11—C9 | −179.34 (10) | C7—C8—C14—C9 | −178.18 (10) |
| C14—C9—C11—C12 | 2.30 (13) | C11—C9—C14—C13 | −2.18 (14) |
| C26—C9—C11—C12 | 122.56 (11) | C26—C9—C14—C13 | −122.18 (11) |
| C21—C9—C11—C12 | −118.44 (10) | C21—C9—C14—C13 | 118.47 (11) |
| C14—C9—C11—C1 | −178.06 (9) | C11—C9—C14—C8 | 177.26 (9) |
| C26—C9—C11—C1 | −57.80 (13) | C26—C9—C14—C8 | 57.25 (13) |

| | | | |
|---|---|---|---|
| C21—C9—C11—C1 | 61.20 (12) | C21—C9—C14—C8 | −62.09 (13) |
| C13—O10—C12—C11 | −4.13 (14) | C11—C9—C21—C22 | 59.23 (12) |
| C13—O10—C12—C4 | 176.28 (9) | C14—C9—C21—C22 | −61.37 (12) |
| C1—C11—C12—O10 | −178.93 (9) | C26—C9—C21—C22 | 178.62 (9) |
| C9—C11—C12—O10 | 0.72 (15) | C9—C21—C22—C23 | 179.65 (9) |
| C1—C11—C12—C4 | 0.64 (15) | C21—C22—C23—O25 | −12.54 (17) |
| C9—C11—C12—C4 | −179.71 (9) | C21—C22—C23—O24 | 167.94 (10) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O24—H24···O25$^{i}$ | 0.935 (18) | 1.732 (19) | 2.6654 (12) | 176.9 (17) |
| C2—H2···O10$^{ii}$ | 0.960 (13) | 2.507 (14) | 3.3989 (14) | 154.6 (10) |

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

**Fig. 1**

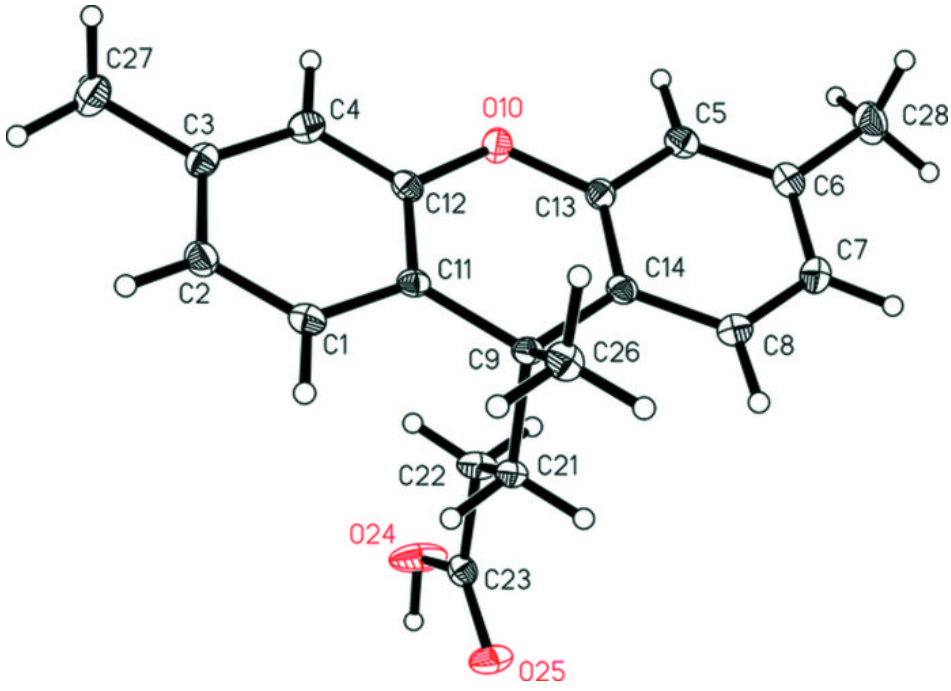
C27
C3
C4
O10
C5
C28
C6
C12
C13
C7
C11
C14
C2
C1
C9
C26
C8
C22
C21
O24
C23
O25

**Fig. 2**

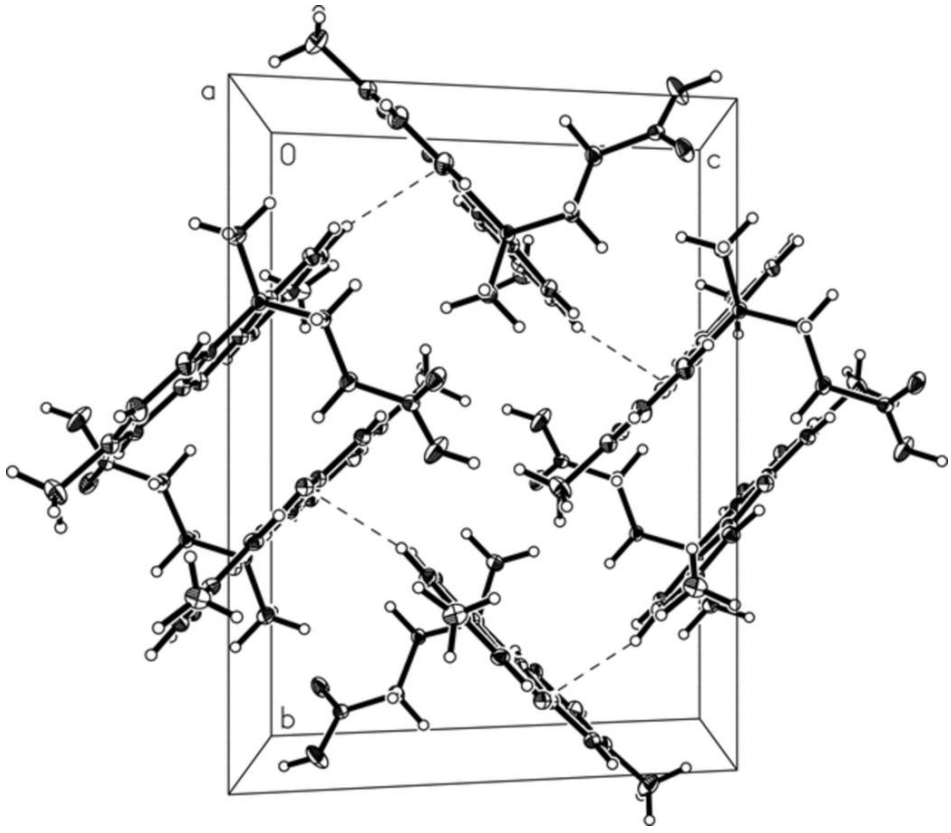

**Fig. 3**