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2,3,5′,6,6′,7-Hexamethoxy-3′*H*,10*H*-spiro[anthracene-9,1′-isobenzofuran]-3′,10-dione

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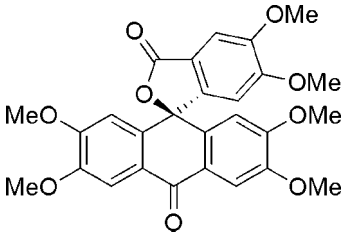
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.056; wR factor = 0.179; data-to-parameter ratio = 20.8.

The title molecule, $C_{27}H_{24}O_9$, was formed *via* a transannular electrophilic addition of a putative cyclotriveratrylene triketone and is made up of an anthrone and an isobenzofuranone ring that are connected *via* one C atom to form a spiro compound. The anthracene and isobenzofuranone ring systems of the spiro compound are both essentially planar and perpendicular to each other, with an angle of 89.90 (2)° between them. The rigid molecule crystallizes with large voids of 598.7 Å^3, or 21.5% of the unit-cell volume, that are partially filled with unmodelled disordered solvent molecules. The voids stretch as infinite channels along the [101] direction. The packing of the structure is partially stabilized by a range of weak C—H···O hydrogen bonds and also by C—H···π interactions. No significant π–π interactions are present in the crystal structure.

Related literature

Cookson *et al.* (1968) described the first synthesis of the title molecule. Baldwin & Kelly (1968) subsequently reported its correct identification as a spiro compound by UV and NMR methods. Lutz, French *et al.* (2007) and Lutz, Zeller & Becker (2007) give background information on other compounds derived from cyclotriveratrylene. *PLATON* (Spek, 2003, 2007) was used to correct the data set for disordered solvent effects. For related literature, see Herbstein (2000).



Experimental

Crystal data

$C_{27}H_{24}O_9$
M_r = 492.46
Monoclinic, $P2/n$
a = 13.1371 (7) Å
b = 13.3281 (7) Å
c = 16.6587 (9) Å
β = 107.043 (1)°
V = 2788.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 298 (2) K
0.48 × 0.42 × 0.27 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.950, T_{max} = 0.976
28518 measured reflections
6913 independent reflections
5390 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.179
S = 1.08
6913 reflections
333 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

*Cg*1 and *Cg*2 are the centroids of the O9/C14/C19/C24/C25 and C8–C13 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C23—H23···O8^{i}	0.93	2.50	3.3892 (17)	161
C20—H20···O3^{ii}	0.93	2.37	3.2965 (16)	175
C17—H17*B*···O2^{iii}	0.96	2.56	3.513 (2)	171
C15—H15*B*···O5^{iv}	0.96	2.48	3.411 (2)	165
C2—H2···*Cg*1	0.93	2.56	2.8621 (17)	100
C12—H12···*Cg*1	0.93	2.62	2.9142 (16)	99
C28—H28*B*···*Cg*2^{v}	0.96	2.88	3.671 (2)	141

Symmetry codes: (i) $-x+\frac{1}{2}, y, -z+\frac{5}{2}$; (ii) $-x+\frac{1}{2}, y, -z+\frac{3}{2}$; (iii) $x, y+1, z$; (iv) $x, y-1, z$; (v) $-x, -y+2, -z+2$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2373).

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supplementary materials

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2,3,5',6,6',7-Hexamethoxy-3'*H*,10*H*-spiro[anthracene-9,1'-isobenzofuran]-3',10-dione

M. R. Lutz Jr, M. Zeller and D. P. Becker

Comment

We are interested in apex-modified cyclotriveratrylene (CTV) derivatives and recently reported the isolation and conformational crown/saddle dynamics of CTV mono-oxime (Lutz, French *et al.*, 2007). In the course of studying the Beckmann rearrangement of the CTV oxime, we isolated and reported the structure of a helical pentacycle formed *via* a tandem Beckmann and subsequent electrophilic addition sequence (Lutz, Zeller *et al.*, 2007).

Cookson *et al.* (1968) reported the isolation of a CTV derivative from oxidation of CTV with sodium dichromate in acetic acid that they thought was the CTV triketone. The triketone, however, has in fact never been isolated, but the compound isolated by Cookson was shortly thereafter identified using UV– and NMR-spectroscopic methods (Baldwin & Kelly, 1968) to have a spiro structure, produced *via* acid-catalyzed electrophilic addition and rearrangement of the putative triketone under the acidic conditions Fig. 1. Both this spiro compound, the crystal structure of which will be descibed here, and the tandem Beckman/electrophilic addition products (Lutz, Zeller & Becker, 2007) are formed *via trans*-annular electrophilic addition to somehow related cationic intermediates. Interestingly, the spiro derivative is a structural analogue to the cyclized lactone form of the exceedingly useful fluorescent spirolactone fluorescein. The title compound contains a diaryl ketone rather than the diaryl ether of fluorescein.

The title compound crystallizes with large regions filled with heavily disordered solvent molecules. The voids make up 598.7 Å^3 or 21.5% of the unit cell volume and stretch as infinite channels along the direction [101] with y = 0.5 (Fig. 4). ^{1}H NMR spectra of dissolved crystals indicated the presence of both methylene chloride and ethyl acetate, the solvents the crystals were grown from. However, with the data collected at room temperature, no obvious solvent model was discernible from difference maps, and data collection at 100 K did not improve the data quality: even at a slow cooling rates the crystal quality suffered upon cooling resulting in significantely larger R values, and the disorder of the diffuse solvent molecules persists even at 100 K. Thus a correction for the diffuse solvent was applied using the Squeeze algorithm implemented in *PLATON* (Spek, 2003, 2007). The number of electrons within the voids was estimated by *PLATON* to be 52, indicating that the voids are only partially filled with solvent.

The anthrone and isobenzofuranone ring systems, Fig. 2, are both essentially planar with r.m.s. deviations from the mean square planes of only 0.12 and 0.01 Å, respectively, and they are basically perpendicular to each other with an angle of 89.90 (2)° between them. Also the methoxy groups are in plane with the ring systems they are bonded to. The largest deviation is observed for C17 which is located 0.321 (3) Å outside of the plane of the anthrone ring sytem.

The packing of the structure is partially stabilized by a range of weak C—H···O hydrogen bonds formed by methyl H atoms C15B and C17*b* and by the aromatic hydrogen atoms H20 and H23 to both keto and methoxy oxygen atoms. There are also three C—H···$C_{\pi\text{-arom}}$ interactions with H···centroid distances that could be interpreted as stabilizing, but two of these are intramolecular interactions forced by the spiro-geometry of the molecule (C2—H2···*Cg*1 and C12—H12···*Cg*1), and only the interaction C28—H28B···*Cg*2 may be seen as truely positively contributing to the packing interactions (*Cg*1 and *Cg*2 define the ring centroids of O9 C14 C19 C24 C25 and C8 C9 C10 C11 C12 C13, respectively) Fig. 3 & 4. See the

hydrogen bonding table for metric parameters of the C—H···O and C—H···π interactions. No significant π–π interactions are present in the structure of the title compound.

Experimental

A 500-ml round bottom flask was charged with cyclotriveratrylene (13.52 g, 30 mmol), sodium dichromate dihydrate (16.1 g, 54.0 mmol), glacial acetic acid (91 ml), and deionized water (107 ml). The orange reaction mixture was brought to reflux in a hot oil bath (408–413 K, 135–140 °C). Within one hour the reaction mixture turned from orange brown to dark green. The reaction was monitored by TLC (20/80, ethyl acetate/methylene chloride) and proton NMR. After 48 h at reflux, the reaction mixture was cooled to ambient temperature.

Cautiously and with stirring, 80 grams solid sodium bicarbonate were added until gas evolution ceased and pH 9 was achieved. The alkaline solution was then extracted with methylene chloride (2 × 200 ml), and the combined methylene chloride layers were washed successively with deionized water (100 ml) and brine (200 ml), then dried over sodium sulfate. Chromatography on silica gel, eluting with an eluent gradient (15/85, 20/80, 30/70 - ethyl acetate/ methylene chloride), afforded the spiro lactone which was crystallized from ethyl acetate/ methylene chloride to afford the title compound (1.37 g, 9.3%) as off-white plates (mp 546–548 K, 273–275 °C, lit (Cookson *et al.*, 1968): 560–562 K (287–289 °C).

Refinement

The structure exhibits large regions filled with heavily disordered solvent molecules. No obvious solvent model was discernible from the difference density Fourier maps and data collection at 100 K did not improve of the data quality (the crystal quality suffers upon cooling and the disorder of the solvent persists). Thus a correction for the diffuse solvent was applied using the Squeeze algorithm implemented in *PLATON* (Spek, 2007). The void volume was calculated by *PLATON* as 598.7 $Å^3$, the number of electrons it corrected for as 52.0.

Hydrogen atoms were added in calculated positions with C—H distances of 0.93 and 0.96 Å for aromatic and methyl H atoms, respectively, and were refined with $U_{iso}(H) = xU_{eq}(C)$ (x = 1.2 for C—H and 1.5 for CH_3). Methyl hydrogen atoms were allowed to rotate to best fit the experimental electron density.

The s.u. values of the cell parameters are taken from the software recognizing that the values are unreasonably small (Herbstein, 2000).

Figures

Fig. 1. Synthesis of the title compound.

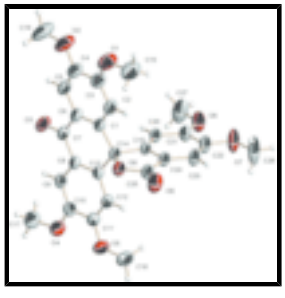


Fig. 2. Thermal elliposoid representation of the title compound with the atomic numbering scheme. Thermal displacement parameters are at the 50% probabilty level.

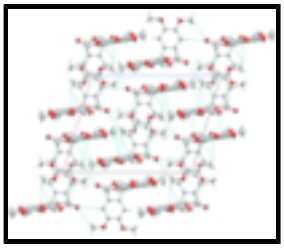


Fig. 3. Packing diagram of the title compound with 50% probability thermal ellipsoids. Blue dashed lines indicate close C—H···O and C—H···$C_{\pi\text{-arom}}$ interactions. View along the *b* axis.

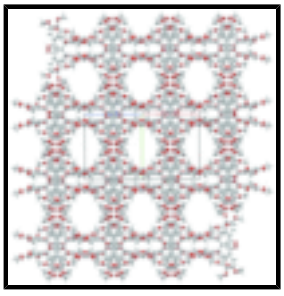


Fig. 4. Extended packing diagram (50% probability thermal ellipsoids) showing the large solvent filled channels stretching along the a-c diagonal. View is along [101].

2,3,5',6,6',7-Hexamethoxy-3'*H*,10*H*-spiro[anthracene-9,1'-isobenzofuran]- 3',10-dione

Crystal data

$C_{27}H_{24}O_9$	F_{000} = 1032
M_r = 492.46	D_x = 1.173 Mg m^{-3}
Monoclinic, *P*2/*n*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2yac	Cell parameters from 7450 reflections
a = 13.1371 (7) Å	θ = 2.8–30.5º
b = 13.3281 (7) Å	μ = 0.09 mm^{-1}
c = 16.6587 (9) Å	*T* = 298 (2) K
β = 107.043 (1)º	Block, colourless
V = 2788.7 (3) Å^3	0.48 × 0.42 × 0.27 mm
Z = 4	

Data collection

Bruker SMART APEX CCD diffractometer	6913 independent reflections
Radiation source: fine-focus sealed tube	5390 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.033
T = 298(2) K	θ_{max} = 28.3º
ω scans	θ_{min} = 2.0º
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	*h* = −17→17
T_{min} = 0.950, T_{max} = 0.976	*k* = −17→17
28518 measured reflections	*l* = −22→22

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.179$	$w = 1/[\sigma^2(F_o^2) + (0.1077P)^2 + 0.2344P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
6913 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
333 parameters	$\Delta\rho_{min} = -0.19$ 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 $F^2 > 2$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	0.34942 (10)	0.82325 (10)	0.93258 (8)	0.0422 (3)
C2	0.35260 (12)	0.72354 (12)	0.95840 (10)	0.0528 (3)
H2	0.3407	0.7083	1.0094	0.063*
C3	0.37327 (14)	0.64693 (12)	0.90925 (11)	0.0599 (4)
C4	0.38934 (14)	0.67010 (13)	0.83124 (11)	0.0603 (4)
C5	0.38604 (13)	0.76802 (12)	0.80559 (10)	0.0541 (4)
H5	0.3964	0.7831	0.7540	0.065*
C6	0.36720 (11)	0.84590 (11)	0.85632 (9)	0.0449 (3)
C7	0.36996 (11)	0.95007 (11)	0.82749 (8)	0.0455 (3)
C8	0.35822 (10)	1.03066 (10)	0.88464 (8)	0.0412 (3)
C9	0.36988 (11)	1.12998 (11)	0.86106 (9)	0.0466 (3)
H9	0.3815	1.1431	0.8096	0.056*
C10	0.36419 (11)	1.20803 (11)	0.91344 (9)	0.0485 (3)
C11	0.34511 (11)	1.18716 (11)	0.99085 (9)	0.0477 (3)
C12	0.33219 (11)	1.08972 (11)	1.01351 (8)	0.0463 (3)
H12	0.3184	1.0768	1.0642	0.056*
C13	0.33963 (9)	1.00990 (10)	0.96077 (8)	0.0398 (3)
C14	0.32111 (10)	0.90436 (10)	0.98646 (7)	0.0388 (3)

C15	0.3615 (2)	0.52032 (15)	1.00657 (16)	0.0937 (8)
H15A	0.4143	0.5524	1.0516	0.140*
H15B	0.3680	0.4488	1.0131	0.140*
H15C	0.2918	0.5407	1.0077	0.140*
C16	0.4172 (3)	0.6076 (2)	0.70589 (15)	0.1035 (8)
H16A	0.3542	0.6409	0.6724	0.155*
H16B	0.4254	0.5449	0.6801	0.155*
H16C	0.4781	0.6492	0.7100	0.155*
C17	0.40321 (18)	1.33035 (15)	0.82300 (13)	0.0754 (5)
H17A	0.4693	1.2982	0.8251	0.113*
H17B	0.4108	1.4017	0.8192	0.113*
H17C	0.3485	1.3069	0.7747	0.113*
C18	0.3161 (2)	1.25420 (16)	1.11426 (12)	0.0790 (6)
H18A	0.2482	1.2218	1.1040	0.119*
H18B	0.3145	1.3177	1.1410	0.119*
H18C	0.3704	1.2127	1.1501	0.119*
C19	0.20836 (10)	0.89023 (10)	0.99188 (7)	0.0378 (3)
C20	0.11237 (10)	0.89863 (10)	0.92945 (8)	0.0421 (3)
H20	0.1096	0.9158	0.8747	0.050*
C21	0.02056 (10)	0.88043 (12)	0.95190 (8)	0.0482 (3)
C22	0.02465 (11)	0.85366 (14)	1.03585 (9)	0.0543 (4)
C23	0.12101 (11)	0.84651 (13)	1.09667 (9)	0.0519 (4)
H23	0.1251	0.8296	1.1517	0.062*
C24	0.21265 (10)	0.86565 (11)	1.07280 (8)	0.0425 (3)
C25	0.32414 (11)	0.86351 (12)	1.12375 (8)	0.0464 (3)
O9	0.38586 (7)	0.88831 (8)	1.07356 (6)	0.0457 (2)
C27	−0.08961 (15)	0.9150 (2)	0.81444 (11)	0.0907 (8)
H27A	−0.0549	0.9783	0.8142	0.136*
H27B	−0.1637	0.9210	0.7839	0.136*
H27C	−0.0572	0.8650	0.7883	0.136*
C28	−0.07232 (16)	0.8096 (3)	1.13055 (13)	0.1115 (11)
H28A	−0.0353	0.7471	1.1458	0.167*
H28B	−0.1445	0.8023	1.1318	0.167*
H28C	−0.0376	0.8607	1.1696	0.167*
O1	0.37672 (14)	0.54860 (10)	0.92837 (10)	0.0835 (4)
O2	0.40807 (15)	0.58972 (11)	0.78676 (10)	0.0886 (5)
O3	0.38453 (11)	0.96868 (9)	0.75960 (7)	0.0650 (3)
O4	0.37502 (11)	1.30698 (9)	0.89689 (8)	0.0662 (3)
O5	0.33848 (11)	1.26936 (9)	1.03752 (7)	0.0656 (3)
O6	−0.07941 (8)	0.88615 (12)	0.89859 (7)	0.0694 (4)
O7	−0.07162 (8)	0.83723 (14)	1.04795 (7)	0.0807 (5)
O8	0.36383 (9)	0.84470 (11)	1.19671 (6)	0.0683 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0388 (6)	0.0497 (7)	0.0418 (6)	0.0019 (5)	0.0176 (5)	−0.0031 (5)
C2	0.0618 (9)	0.0523 (8)	0.0515 (8)	0.0030 (6)	0.0279 (7)	0.0017 (6)

C3	0.0726 (10)	0.0490 (8)	0.0658 (10)	0.0076 (7)	0.0324 (8)	0.0004 (7)
C4	0.0730 (10)	0.0542 (9)	0.0618 (9)	0.0076 (7)	0.0322 (8)	−0.0077 (7)
C5	0.0631 (9)	0.0573 (8)	0.0501 (8)	0.0044 (7)	0.0294 (7)	−0.0046 (6)
C6	0.0442 (7)	0.0522 (7)	0.0437 (7)	0.0016 (5)	0.0211 (5)	−0.0027 (6)
C7	0.0479 (7)	0.0534 (8)	0.0412 (6)	−0.0012 (6)	0.0225 (6)	−0.0031 (5)
C8	0.0372 (6)	0.0504 (7)	0.0395 (6)	−0.0017 (5)	0.0166 (5)	−0.0022 (5)
C9	0.0474 (7)	0.0543 (8)	0.0427 (7)	−0.0017 (6)	0.0203 (6)	0.0023 (6)
C10	0.0486 (7)	0.0477 (7)	0.0529 (8)	−0.0026 (6)	0.0206 (6)	0.0003 (6)
C11	0.0486 (7)	0.0503 (7)	0.0470 (7)	−0.0038 (6)	0.0184 (6)	−0.0071 (6)
C12	0.0494 (7)	0.0540 (8)	0.0390 (6)	−0.0036 (6)	0.0186 (5)	−0.0043 (5)
C13	0.0347 (6)	0.0490 (7)	0.0377 (6)	−0.0030 (5)	0.0136 (5)	−0.0017 (5)
C14	0.0364 (6)	0.0487 (7)	0.0333 (6)	0.0009 (5)	0.0131 (5)	−0.0005 (5)
C15	0.155 (2)	0.0540 (11)	0.0931 (15)	0.0093 (12)	0.0686 (16)	0.0100 (10)
C16	0.154 (2)	0.0929 (16)	0.0772 (14)	0.0276 (16)	0.0558 (16)	−0.0206 (12)
C17	0.1085 (16)	0.0566 (10)	0.0755 (12)	−0.0067 (9)	0.0496 (12)	0.0078 (8)
C18	0.1155 (16)	0.0720 (11)	0.0632 (11)	−0.0147 (11)	0.0475 (11)	−0.0201 (9)
C19	0.0378 (6)	0.0449 (6)	0.0344 (6)	−0.0002 (5)	0.0163 (5)	−0.0009 (5)
C20	0.0420 (6)	0.0539 (7)	0.0325 (6)	0.0007 (5)	0.0144 (5)	0.0016 (5)
C21	0.0371 (6)	0.0706 (9)	0.0367 (6)	−0.0013 (6)	0.0104 (5)	0.0034 (6)
C22	0.0404 (7)	0.0850 (11)	0.0418 (7)	−0.0022 (7)	0.0189 (6)	0.0072 (7)
C23	0.0443 (7)	0.0804 (10)	0.0347 (6)	0.0013 (7)	0.0176 (5)	0.0077 (6)
C24	0.0389 (6)	0.0567 (7)	0.0335 (6)	0.0024 (5)	0.0128 (5)	0.0012 (5)
C25	0.0430 (7)	0.0618 (8)	0.0359 (6)	0.0016 (6)	0.0138 (5)	−0.0004 (6)
O9	0.0370 (5)	0.0627 (6)	0.0371 (5)	0.0021 (4)	0.0104 (4)	0.0018 (4)
C27	0.0496 (9)	0.177 (2)	0.0399 (8)	0.0076 (12)	0.0042 (7)	0.0125 (11)
C28	0.0528 (10)	0.232 (3)	0.0572 (11)	−0.0124 (14)	0.0275 (8)	0.0384 (16)
O1	0.1349 (13)	0.0486 (7)	0.0837 (9)	0.0129 (7)	0.0581 (9)	0.0029 (6)
O2	0.1426 (14)	0.0599 (8)	0.0828 (9)	0.0164 (8)	0.0632 (9)	−0.0102 (7)
O3	0.0956 (9)	0.0632 (7)	0.0502 (6)	−0.0026 (6)	0.0431 (6)	−0.0024 (5)
O4	0.0938 (9)	0.0494 (6)	0.0679 (7)	−0.0064 (6)	0.0430 (7)	−0.0004 (5)
O5	0.0939 (9)	0.0524 (6)	0.0597 (7)	−0.0077 (6)	0.0368 (6)	−0.0113 (5)
O6	0.0382 (5)	0.1238 (11)	0.0437 (6)	−0.0032 (6)	0.0083 (4)	0.0122 (6)
O7	0.0392 (6)	0.1572 (14)	0.0492 (6)	−0.0051 (7)	0.0185 (5)	0.0239 (7)
O8	0.0516 (6)	0.1142 (10)	0.0359 (5)	0.0038 (6)	0.0080 (4)	0.0105 (6)

Geometric parameters (Å, °)

C1—C6	1.3905 (18)	C16—H16A	0.9600
C1—C2	1.394 (2)	C16—H16B	0.9600
C1—C14	1.5193 (18)	C16—H16C	0.9600
C2—C3	1.385 (2)	C17—O4	1.420 (2)
C2—H2	0.9300	C17—H17A	0.9600
C3—O1	1.346 (2)	C17—H17B	0.9600
C3—C4	1.411 (2)	C17—H17C	0.9600
C4—O2	1.365 (2)	C18—O5	1.408 (2)
C4—C5	1.370 (2)	C18—H18A	0.9600
C5—C6	1.4055 (19)	C18—H18B	0.9600
C5—H5	0.9300	C18—H18C	0.9600
C6—C7	1.473 (2)	C19—C24	1.3723 (17)

C7—O3	1.2265 (16)	C19—C20	1.3840 (18)
C7—C8	1.4731 (18)	C20—C21	1.3848 (18)
C8—C13	1.3878 (17)	C20—H20	0.9300
C8—C9	1.402 (2)	C21—O6	1.3549 (17)
C9—C10	1.374 (2)	C21—C22	1.4291 (19)
C9—H9	0.9300	C22—O7	1.3554 (17)
C10—O4	1.3633 (19)	C22—C23	1.373 (2)
C10—C11	1.412 (2)	C23—C24	1.3976 (18)
C11—O5	1.3608 (17)	C23—H23	0.9300
C11—C12	1.377 (2)	C24—C25	1.4620 (19)
C12—C13	1.4012 (19)	C25—O8	1.2002 (17)
C12—H12	0.9300	C25—O9	1.3649 (16)
C13—C14	1.5107 (19)	C27—O6	1.421 (2)
C14—O9	1.4667 (15)	C27—H27A	0.9600
C14—C19	1.5218 (16)	C27—H27B	0.9600
C15—O1	1.426 (3)	C27—H27C	0.9600
C15—H15A	0.9600	C28—O7	1.427 (2)
C15—H15B	0.9600	C28—H28A	0.9600
C15—H15C	0.9600	C28—H28B	0.9600
C16—O2	1.407 (3)	C28—H28C	0.9600
C6—C1—C2	119.41 (12)	H16A—C16—H16C	109.5
C6—C1—C14	121.41 (12)	H16B—C16—H16C	109.5
C2—C1—C14	119.11 (12)	O4—C17—H17A	109.5
C3—C2—C1	120.93 (14)	O4—C17—H17B	109.5
C3—C2—H2	119.5	H17A—C17—H17B	109.5
C1—C2—H2	119.5	O4—C17—H17C	109.5
O1—C3—C2	125.22 (15)	H17A—C17—H17C	109.5
O1—C3—C4	115.30 (14)	H17B—C17—H17C	109.5
C2—C3—C4	119.45 (15)	O5—C18—H18A	109.5
O2—C4—C5	124.92 (15)	O5—C18—H18B	109.5
O2—C4—C3	115.32 (16)	H18A—C18—H18B	109.5
C5—C4—C3	119.76 (14)	O5—C18—H18C	109.5
C4—C5—C6	120.73 (14)	H18A—C18—H18C	109.5
C4—C5—H5	119.6	H18B—C18—H18C	109.5
C6—C5—H5	119.6	C24—C19—C20	121.57 (11)
C1—C6—C5	119.70 (14)	C24—C19—C14	109.11 (11)
C1—C6—C7	121.95 (12)	C20—C19—C14	129.32 (11)
C5—C6—C7	118.33 (12)	C19—C20—C21	117.18 (11)
O3—C7—C6	121.11 (13)	C19—C20—H20	121.4
O3—C7—C8	121.51 (13)	C21—C20—H20	121.4
C6—C7—C8	117.35 (11)	O6—C21—C20	124.53 (12)
C13—C8—C9	120.48 (12)	O6—C21—C22	113.99 (12)
C13—C8—C7	121.67 (12)	C20—C21—C22	121.48 (12)
C9—C8—C7	117.82 (12)	O7—C22—C23	125.28 (13)
C10—C9—C8	120.42 (12)	O7—C22—C21	114.63 (12)
C10—C9—H9	119.8	C23—C22—C21	120.09 (12)
C8—C9—H9	119.8	C22—C23—C24	117.53 (12)
O4—C10—C9	125.15 (13)	C22—C23—H23	121.2
O4—C10—C11	115.61 (13)	C24—C23—H23	121.2

C9—C10—C11	119.23 (13)	C19—C24—C23	122.15 (12)
O5—C11—C12	124.68 (13)	C19—C24—C25	108.70 (11)
O5—C11—C10	114.93 (13)	C23—C24—C25	129.15 (12)
C12—C11—C10	120.36 (13)	O8—C25—O9	120.74 (13)
C11—C12—C13	120.49 (13)	O8—C25—C24	130.98 (13)
C11—C12—H12	119.8	O9—C25—C24	108.28 (11)
C13—C12—H12	119.8	C25—O9—C14	111.40 (10)
C8—C13—C12	119.01 (12)	O6—C27—H27A	109.5
C8—C13—C14	122.05 (11)	O6—C27—H27B	109.5
C12—C13—C14	118.86 (11)	H27A—C27—H27B	109.5
O9—C14—C13	108.73 (10)	O6—C27—H27C	109.5
O9—C14—C1	108.02 (10)	H27A—C27—H27C	109.5
C13—C14—C1	114.04 (10)	H27B—C27—H27C	109.5
O9—C14—C19	102.45 (9)	O7—C28—H28A	109.5
C13—C14—C19	111.87 (10)	O7—C28—H28B	109.5
C1—C14—C19	110.98 (10)	H28A—C28—H28B	109.5
O1—C15—H15A	109.5	O7—C28—H28C	109.5
O1—C15—H15B	109.5	H28A—C28—H28C	109.5
H15A—C15—H15B	109.5	H28B—C28—H28C	109.5
O1—C15—H15C	109.5	C3—O1—C15	118.01 (14)
H15A—C15—H15C	109.5	C4—O2—C16	117.77 (16)
H15B—C15—H15C	109.5	C10—O4—C17	117.17 (13)
O2—C16—H16A	109.5	C11—O5—C18	117.95 (13)
O2—C16—H16B	109.5	C21—O6—C27	117.04 (12)
H16A—C16—H16B	109.5	C22—O7—C28	117.07 (13)
O2—C16—H16C	109.5		
C6—C1—C2—C3	0.0 (2)	C6—C1—C14—C13	−13.64 (17)
C14—C1—C2—C3	177.03 (14)	C2—C1—C14—C13	169.44 (12)
C1—C2—C3—O1	−179.18 (17)	C6—C1—C14—C19	113.80 (13)
C1—C2—C3—C4	−1.2 (3)	C2—C1—C14—C19	−63.12 (16)
O1—C3—C4—O2	−1.1 (3)	O9—C14—C19—C24	−1.95 (14)
C2—C3—C4—O2	−179.32 (17)	C13—C14—C19—C24	−118.25 (12)
O1—C3—C4—C5	179.22 (17)	C1—C14—C19—C24	113.14 (12)
C2—C3—C4—C5	1.0 (3)	O9—C14—C19—C20	178.28 (13)
O2—C4—C5—C6	−179.35 (17)	C13—C14—C19—C20	61.98 (17)
C3—C4—C5—C6	0.2 (3)	C1—C14—C19—C20	−66.64 (18)
C2—C1—C6—C5	1.2 (2)	C24—C19—C20—C21	−0.5 (2)
C14—C1—C6—C5	−175.67 (13)	C14—C19—C20—C21	179.28 (14)
C2—C1—C6—C7	−177.02 (13)	C19—C20—C21—O6	179.53 (15)
C14—C1—C6—C7	6.1 (2)	C19—C20—C21—C22	−0.3 (2)
C4—C5—C6—C1	−1.4 (2)	O6—C21—C22—O7	0.8 (2)
C4—C5—C6—C7	176.93 (15)	C20—C21—C22—O7	−179.36 (16)
C1—C6—C7—O3	−179.16 (14)	O6—C21—C22—C23	−179.11 (16)
C5—C6—C7—O3	2.6 (2)	C20—C21—C22—C23	0.7 (3)
C1—C6—C7—C8	2.9 (2)	O7—C22—C23—C24	179.71 (17)
C5—C6—C7—C8	−175.40 (13)	C21—C22—C23—C24	−0.4 (3)
O3—C7—C8—C13	178.71 (13)	C20—C19—C24—C23	0.8 (2)
C6—C7—C8—C13	−3.34 (19)	C14—C19—C24—C23	−178.98 (13)
O3—C7—C8—C9	−3.3 (2)	C20—C19—C24—C25	−179.50 (13)

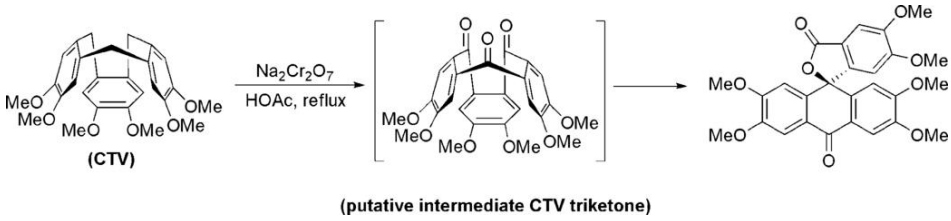
C6—C7—C8—C9	174.62 (12)	C14—C19—C24—C25	0.70 (15)
C13—C8—C9—C10	0.7 (2)	C22—C23—C24—C19	−0.4 (2)
C7—C8—C9—C10	−177.28 (13)	C22—C23—C24—C25	−179.97 (16)
C8—C9—C10—O4	179.59 (14)	C19—C24—C25—O8	−179.15 (17)
C8—C9—C10—C11	−0.8 (2)	C23—C24—C25—O8	0.5 (3)
O4—C10—C11—O5	1.0 (2)	C19—C24—C25—O9	0.96 (16)
C9—C10—C11—O5	−178.61 (13)	C23—C24—C25—O9	−179.39 (15)
O4—C10—C11—C12	179.55 (13)	O8—C25—O9—C14	177.79 (14)
C9—C10—C11—C12	−0.1 (2)	C24—C25—O9—C14	−2.30 (16)
O5—C11—C12—C13	179.46 (13)	C13—C14—O9—C25	121.13 (12)
C10—C11—C12—C13	1.1 (2)	C1—C14—O9—C25	−114.62 (12)
C9—C8—C13—C12	0.30 (19)	C19—C14—O9—C25	2.59 (14)
C7—C8—C13—C12	178.21 (12)	C2—C3—O1—C15	−2.2 (3)
C9—C8—C13—C14	176.85 (12)	C4—C3—O1—C15	179.8 (2)
C7—C8—C13—C14	−5.25 (19)	C5—C4—O2—C16	−4.8 (3)
C11—C12—C13—C8	−1.2 (2)	C3—C4—O2—C16	175.6 (2)
C11—C12—C13—C14	−177.86 (12)	C9—C10—O4—C17	−5.6 (2)
C8—C13—C14—O9	133.87 (12)	C11—C10—O4—C17	174.81 (16)
C12—C13—C14—O9	−49.58 (15)	C12—C11—O5—C18	−0.4 (2)
C8—C13—C14—C1	13.27 (17)	C10—C11—O5—C18	177.99 (16)
C12—C13—C14—C1	−170.18 (11)	C20—C21—O6—C27	−1.4 (3)
C8—C13—C14—C19	−113.70 (13)	C22—C21—O6—C27	178.44 (19)
C12—C13—C14—C19	62.85 (15)	C23—C22—O7—C28	−0.5 (3)
C6—C1—C14—O9	−134.63 (12)	C21—C22—O7—C28	179.6 (2)
C2—C1—C14—O9	48.45 (16)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C23—H23···O8^{i}	0.93	2.50	3.3892 (17)	161
C20—H20···O3^{ii}	0.93	2.37	3.2965 (16)	175
C17—H17B···O2^{iii}	0.96	2.56	3.513 (2)	171
C15—H15B···O5^{iv}	0.96	2.48	3.411 (2)	165
C2—H2···Cg1	0.93	2.56	2.8621 (17)	100
C12—H12···Cg1	0.93	2.62	2.9142 (16)	99
C28—H28B···Cg2^{v}	0.96	2.88	3.671 (2)	141

Symmetry codes: (i) −*x*+1/2, *y*, −*z*+5/2; (ii) −*x*+1/2, *y*, −*z*+3/2; (iii) *x*, *y*+1, *z*; (iv) *x*, *y*−1, *z*; (v) −*x*, −*y*+2, −*z*+2.

Fig. 1



(putative intermediate CTV triketone)

Fig. 2

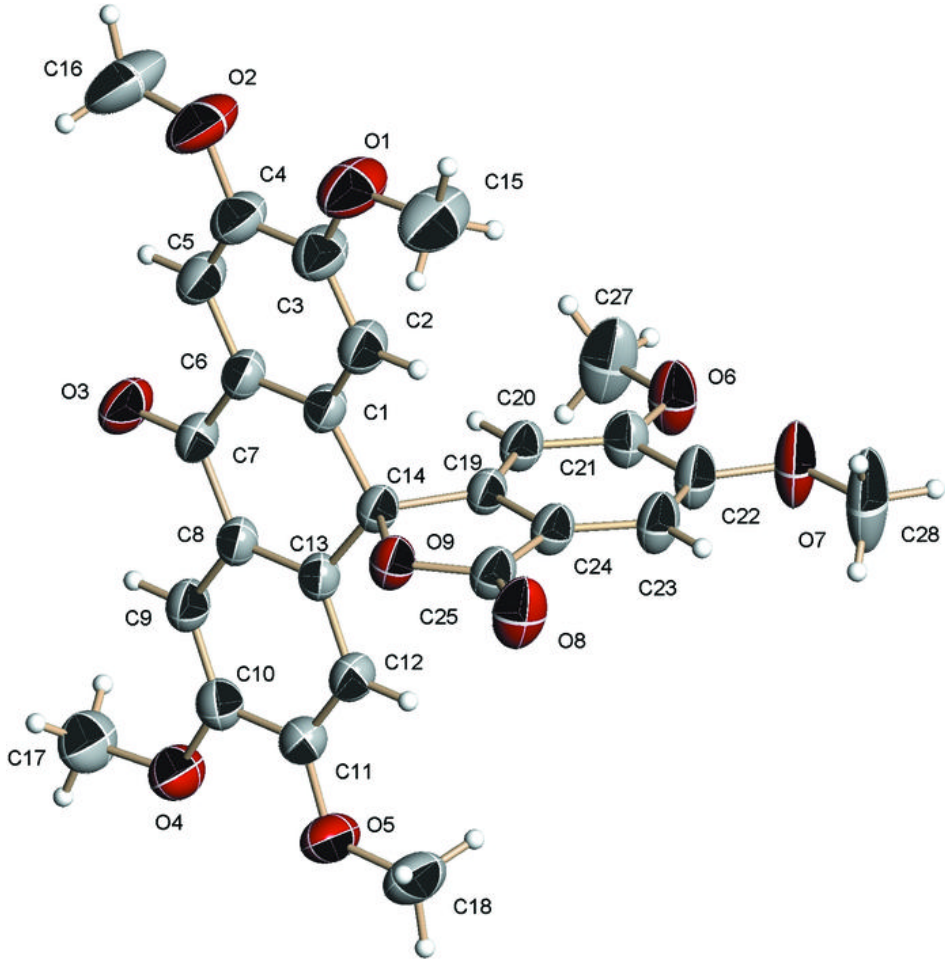

C16
O2
O1
C4
C15
C5
C3
C2
C27
C6
O6
O3
C1
C20
C7
C14
C19
C21
C22
C8
C13
O9
C24
O7
C28
C23
C9
C25
O8
C12
C10
C17
C11
O4
O5
C18

Fig. 3

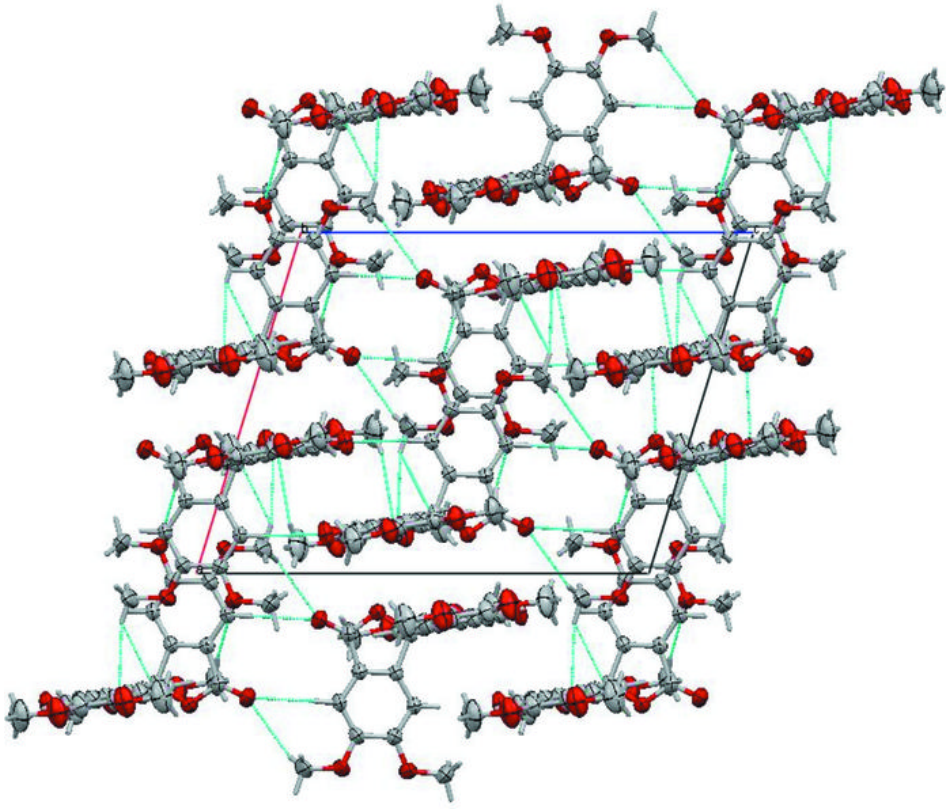


Fig. 4