organic compounds

rac-12,14-Dicyclopropyl-5,8,13,18,21-pentaoxapentacyclo[13.8.0.0^{2,11}.0^{4,9}.-0^{17,22}]tricosa-1(15),2(11),3,9(10),-16,22(23)-hexaene

Viktor A. Tafeenko, Leonid A. Aslanov,* Nikolay A. Puretskiy, Aleksander N. Fedotov and Sergei S. Mochalov

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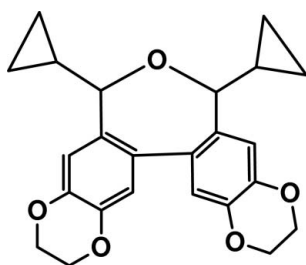Correspondence e-mail: Aslanov@struct.chem.msu.ru

The molecule of the title compound, $C_{24}H_{24}O_5$, has crystallographic twofold symmetry, with the central O atom lying on the rotation axis. The dihedral angle between the best planes of the benzene rings fused to the oxepine fragment is 38.5 (1)°. The dioxine ring adopts a twist form with the ethylene group C atoms deviating by 0.472 (5) and −0.248 (6) Å from the plane defined by the remaining ring atoms.

Related literature

For details on 2,2′-diacetyldiphenyl reduction, see: Hall *et al.* (1956).

Experimental

Crystal data

$C_{24}H_{24}O_5$	V = 1970.1 (7) Å^3
M_r = 392.43	Z = 4
Monoclinic, $C2/c$	Ag $K\alpha$ radiation
a = 14.325 (2) Å	λ = 0.56085 Å
b = 7.393 (2) Å	μ = 0.06 mm^{-1}
c = 19.7260 (12) Å	T = 295 K
β = 109.42 (2)°	0.10 × 0.05 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	966 reflections with $I > 2\sigma(I)$
1915 measured reflections	R_{int} = 0.024
1854 independent reflections	2 standard reflections every 120 min intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062	133 parameters
$wR(F^2)$ = 0.170	H-atom parameters constrained
S = 1.01	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
1855 reflections	$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2364).

References

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

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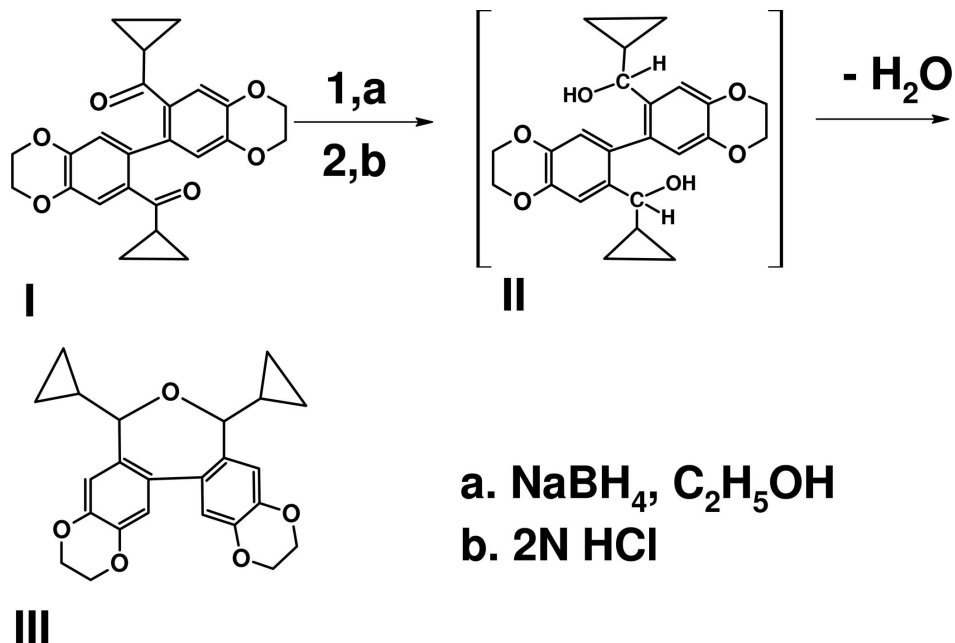
S1. Comment

In line with our investigations of the intra- and intermolecular transformations of diphenyl derivatives, the results of the transformation of 2,2′-dicyclopropylcarbonyl-bis-ethylenedioxydiphenyl under reduction by NaBH$_4$ are presented. Instead of diastereoisomers of 2,2′-bis-cyclopropylhydroxymethyldiphenyls (II) that we might expect based on the Hall's article (Hall *et al.*, 1956) it was shown that the reduction of 2,2′-dicyclopropylcarbonyl-bis-ethylenedioxydiphenyl (I) by NaBH$_4$ leads to the formation of 2,3,9,10-bis-ethylenedioxy-5,7-dicyclopropyl-5,7-dihydrodibenz[c,e]- oxepin (III), Fig.1. The ^{1}H NMR data of the compound III indicate one of two possible stereoisomeric forms (racemic or *meso*). To determine the structure of the compound III, we carried out an X-ray crystallographic study, which revealed that its structure corresponds to the *erythro* (racemic) form. The dihedral angle between the planes defined by the atoms (Fig.2) C9/C1/C2/C3/C4/C8/C5 (plane 1) and C9^i/C1^i/C2^i/C3^i/C4^i/C8^i/C5^i (plane 2) is 41.0 (1)°. Oxygen atom O1 is displaced from the plane 1 by -1.136 (1) and by 1.136 (1) Å from plane 2. The 6-membered dioxine ring adopts a twist conformation, with atoms C6, C7 of the ethylene group displaced from of plane of the remaining dioxine ring atoms by 0.472 (5) and -0.248 (6) Å, respectively. Exept for weak C—H···O interaction between the molecules, no other intermolecular contacts of interest are present.

S2. Experimental

The reaction scheme is presented in Fig. 1. A mixture of (I) (1.01 g, 2.5 mmol), NaBH$_4$ (0.19 g, 5.0 mmol) and 30 ml C$_2$H$_5$OH was heated (313–323 K) for 48 h and then decomposed with 2 N HCl. The mixture was poured into water (200 ml) and the solid separated, dried and purified by column chromatography. The resulting white precipitate was recrystallized from C$_2$H$_5$OH.

S3. Refinement

The positions of all H atoms were determined from Fourier difference maps however for the refinement they were placed in calculated positions and allowed to ride on their parent atoms [C—H = 0.93–0.97 Å] with U_{iso}(H) = 1.2 U_{eq}(C).

Figure 1

Reduction of (I) did not produce the expected compound (II) but the title compound (III).

Figure 2

The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Atoms C,O and C^i,O^i are related by a twofold axis. Symmetry code: (i) $1 - x$, y, $1.5 - z$;.

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Crystal data

$C_{24}H_{24}O_5$	$a = 14.325$ (2) Å
$M_r = 392.43$	$b = 7.393$ (2) Å
Monoclinic, $C2/c$	$c = 19.7260$ (12) Å
Hall symbol: -C 2yc	$\beta = 109.42$ (2)°

$V = 1970.1$ (7) Å^3

$Z = 4$

$F(000) = 832$

$D_x = 1.323$ Mg m^{-3}

Melting point < 505 K

Ag $K\alpha$ radiation, $\lambda = 0.56085$ Å

Cell parameters from 25 reflections

$\theta = 11$–13°

$\mu = 0.06$ mm^{-1}

$T = 295$ K

Prism, colorless

$0.10 \times 0.05 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4
   diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Non–profiled ω scans

1915 measured reflections

1854 independent reflections

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

$R_{int} = 0.024$

$\theta_{max} = 20.0°$, $\theta_{min} = 1.7°$

$h = -17 \rightarrow 16$

$k = 0 \rightarrow 8$

$l = 0 \rightarrow 24$

2 standard reflections every 120 min

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.170$

$S = 1.01$

1855 reflections

133 parameters

0 restraints

Primary atom site location: structure-invariant
   direct methods

Secondary atom site location: difference Fourier
   map

Hydrogen site location: inferred from
   neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.27$ e Å^{-3}

$\Delta\rho_{min} = -0.18$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick,
   2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$

Extinction coefficient: 0.0097 (18)

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}
O1	0.5000	0.5604 (4)	0.7500	0.0542 (9)
O2	0.36252 (17)	−0.1674 (3)	0.56383 (12)	0.0562 (7)
O3	0.3779 (2)	0.1509 (4)	0.48729 (13)	0.0799 (9)
C1	0.4376 (2)	−0.0085 (4)	0.67251 (16)	0.0399 (8)
H1	0.4302	−0.1112	0.6975	0.048*
C2	0.4042 (2)	−0.0103 (4)	0.59872 (17)	0.0441 (8)
C3	0.4114 (2)	0.1436 (5)	0.56079 (17)	0.0508 (9)
C4	0.4576 (2)	0.2947 (5)	0.59835 (18)	0.0504 (9)
H4	0.4640	0.3970	0.5729	0.061*

C5	0.5540 (3)	0.4568 (4)	0.71343 (18)	0.0473 (9)
H5	0.6124	0.4067	0.7502	0.057*
C6	0.3625 (3)	−0.1719 (6)	0.4920 (2)	0.0745 (13)
H6A	0.3240	−0.2746	0.4671	0.089*
H6B	0.4297	−0.1860	0.4918	0.089*
C7	0.3195 (4)	−0.0022 (7)	0.4542 (2)	0.0971 (17)
H7A	0.3161	−0.0098	0.4044	0.116*
H7B	0.2527	0.0126	0.4552	0.116*
C8	0.4942 (2)	0.2987 (4)	0.67201 (17)	0.0415 (8)
C9	0.4821 (2)	0.1442 (4)	0.71016 (15)	0.0382 (7)
C10	0.5896 (3)	0.5892 (4)	0.67094 (19)	0.0540 (9)
H10	0.5379	0.6569	0.6346	0.065*
C11	0.6795 (3)	0.5512 (5)	0.6530 (2)	0.0632 (11)
H11A	0.6813	0.5922	0.6068	0.076*
H11B	0.7137	0.4381	0.6698	0.076*
C12	0.6811 (3)	0.6909 (6)	0.7077 (2)	0.0762 (13)
H12A	0.7163	0.6627	0.7577	0.091*
H12B	0.6839	0.8168	0.6947	0.091*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.079 (2)	0.0269 (17)	0.073 (2)	0.000	0.0467 (19)	0.000
O2	0.0672 (15)	0.0504 (15)	0.0497 (14)	−0.0187 (13)	0.0176 (12)	−0.0134 (12)
O3	0.102 (2)	0.083 (2)	0.0439 (16)	−0.0305 (18)	0.0109 (14)	0.0079 (14)
C1	0.0506 (18)	0.0265 (17)	0.0463 (18)	−0.0009 (14)	0.0210 (15)	0.0034 (14)
C2	0.0438 (18)	0.041 (2)	0.0496 (19)	−0.0039 (16)	0.0190 (15)	−0.0035 (16)
C3	0.056 (2)	0.056 (2)	0.040 (2)	−0.0070 (18)	0.0159 (16)	0.0017 (18)
C4	0.062 (2)	0.038 (2)	0.055 (2)	−0.0074 (17)	0.0250 (18)	0.0071 (17)
C5	0.067 (2)	0.0287 (17)	0.054 (2)	−0.0012 (17)	0.0308 (17)	−0.0006 (16)
C6	0.084 (3)	0.088 (3)	0.054 (2)	−0.036 (3)	0.027 (2)	−0.026 (2)
C7	0.112 (4)	0.116 (5)	0.046 (2)	−0.045 (3)	0.003 (2)	0.002 (3)
C8	0.0517 (19)	0.0297 (18)	0.050 (2)	−0.0026 (15)	0.0261 (16)	−0.0006 (15)
C9	0.0441 (17)	0.0272 (16)	0.0469 (17)	−0.0004 (15)	0.0199 (15)	−0.0025 (14)
C10	0.070 (2)	0.0336 (19)	0.064 (2)	0.0011 (18)	0.0299 (19)	0.0089 (17)
C11	0.067 (2)	0.058 (2)	0.075 (3)	0.001 (2)	0.038 (2)	0.014 (2)
C12	0.094 (3)	0.060 (3)	0.073 (3)	−0.035 (2)	0.027 (2)	−0.003 (2)

Geometric parameters (Å, º)

O1—C5	1.441 (3)	C6—C7	1.484 (6)
O2—C2	1.380 (4)	C6—H6A	0.9700
O2—C6	1.417 (4)	C6—H6B	0.9700
O3—C3	1.368 (4)	C7—H7A	0.9700
O3—C7	1.430 (5)	C7—H7B	0.9700
C1—C2	1.373 (4)	C8—C9	1.410 (4)
C1—C9	1.385 (4)	C9—C9^i	1.482 (6)
C1—H1	0.9300	C10—C11	1.470 (5)

C2—C3	1.385 (4)	C10—C12	1.475 (5)
C3—C4	1.381 (5)	C10—H10	0.9800
C4—C8	1.371 (4)	C11—C12	1.487 (5)
C4—H4	0.9300	C11—H11A	0.9700
C5—C10	1.486 (4)	C11—H11B	0.9700
C5—C8	1.517 (4)	C12—H12A	0.9700
C5—H5	0.9800	C12—H12B	0.9700
C5^i—O1—C5	115.7 (3)	C6—C7—H7A	109.4
C2—O2—C6	112.0 (3)	O3—C7—H7B	109.4
C3—O3—C7	113.4 (3)	C6—C7—H7B	109.4
C2—C1—C9	120.8 (3)	H7A—C7—H7B	108.0
C2—C1—H1	119.6	C4—C8—C9	118.5 (3)
C9—C1—H1	119.6	C4—C8—C5	122.4 (3)
C1—C2—O2	118.5 (3)	C9—C8—C5	119.0 (3)
C1—C2—C3	120.2 (3)	C1—C9—C8	119.4 (3)
O2—C2—C3	121.3 (3)	C1—C9—C9^i	120.3 (2)
O3—C3—C4	118.2 (3)	C8—C9—C9^i	120.3 (2)
O3—C3—C2	122.8 (3)	C11—C10—C12	60.7 (2)
C4—C3—C2	118.9 (3)	C11—C10—C5	120.2 (3)
C8—C4—C3	122.2 (3)	C12—C10—C5	118.3 (3)
C8—C4—H4	118.9	C11—C10—H10	115.5
C3—C4—H4	118.9	C12—C10—H10	115.5
O1—C5—C10	105.9 (2)	C5—C10—H10	115.5
O1—C5—C8	112.2 (2)	C10—C11—C12	59.8 (2)
C10—C5—C8	116.2 (3)	C10—C11—H11A	117.8
O1—C5—H5	107.3	C12—C11—H11A	117.8
C10—C5—H5	107.3	C10—C11—H11B	117.8
C8—C5—H5	107.3	C12—C11—H11B	117.8
O2—C6—C7	110.1 (4)	H11A—C11—H11B	114.9
O2—C6—H6A	109.6	C10—C12—C11	59.5 (2)
C7—C6—H6A	109.6	C10—C12—H12A	117.8
O2—C6—H6B	109.6	C11—C12—H12A	117.8
C7—C6—H6B	109.6	C10—C12—H12B	117.8
H6A—C6—H6B	108.1	C11—C12—H12B	117.8
O3—C7—C6	111.0 (3)	H12A—C12—H12B	115.0
O3—C7—H7A	109.4		

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.