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Preference for the Diels–Alder addition of dienes *syn* to the O atom in cross-conjugated spirocyclic cyclohexadienones

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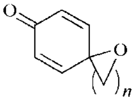
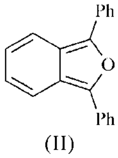
In the Diels–Alder reaction, the preferred addition of dienes *syn* to the O atom in cross-conjugated cyclohexadienones containing an oxa-spiro ring system is observed. The two structures reported here, namely *rel*-(1*R*,4a*R*,9*S*,9a*S*,10*R*)-4a,9,9a,10-tetrahydro-9,10-diphenylspiro[9,10-epoxyanthracene-1(4*H*),2′-oxiran]-4-one, $C_{27}H_{20}O_3$, and *rel*-(1*R*,4a*S*,9*R*,9a*S*,10*S*)-4a,9,9a,10-tetrahydro-9,10-diphenylspiro[9,10-epoxyanthracene-1(4*H*),2′-oxetane]-4-one, $C_{28}H_{22}O_3$, are the minor and sole products, respectively, of the reactions of diphenylisobenzofuran with two slightly different cyclohexadienones. These structures differ in the size of the oxa-spiro ring, by one C atom, and in the relative configuration at the spirocyclic ring C atom, leading to some minor conformational differences between the two compounds.

Comment

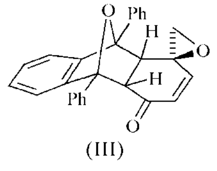
Cross-conjugated cyclohexadienones carrying an oxa-spiro ring, as in (I), hold interest as Diels–Alder dienophiles in that control of π-facial diastereoselectivity by the heteroatom is operative (Wipf & Kim, 1994; Tran-Hu-Dâu *et al.*, 2001; Silvero *et al.*, 1998; Takagi *et al.*, 2003; Paquette *et al.*, 2003).



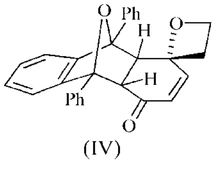
(I)



(II)



(III)



(IV)

Irrespective of the size of the spiro ring, and the resultant changes in basicity at the O center and overall steric contributions, diene approach from the direction *syn* to the O atom is heavily preferred (Ohkata *et al.*, 2004). 1,3-Diphenylisobenzofuran, (II) (Newman, 1961), one of the notably reactive dienes, is used in the present study because this compound often leads to crystalline products. We compare here the structural features of (III), the minor Diels–Alder adduct from the reaction of diphenylisobenzofuran with (I) ($n = 1$), with those of (IV), the sole [4+2] product formed upon reaction of diphenylisobenzofuran with (I) ($n = 2$).

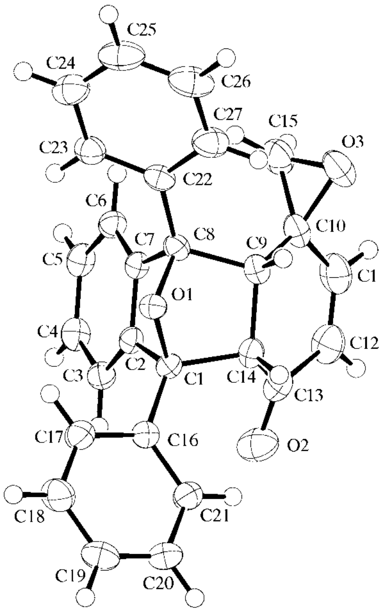


Figure 1
The structure of (III), drawn with 50% probability displacement ellipsoids.

Selected geometric parameters are given in Tables 1 and 2. The size of the oxa-spiro ring and the relative configuration of spirocyclic atom C10 are the main features that differentiate these two structures. For both structures, the six-membered ring containing the spiro C atom (C9–C14) is in a boat conformation. In (III), atoms C10 and C13 lie 0.112 (1) and 0.236 (1) Å, respectively, from the least-squares plane defined by atoms C9, C11, C12 and C14. In (IV), atoms C10 and C13 lie 0.382 (1) and 0.284 (1) Å, respectively, from the analogous plane. The two boat conformations are bent in opposite directions, as seen in Figs. 1 and 2.

Another conformational difference between the two structures is seen in the orientation of the benzene rings. This can be described by the dihedral angle between a benzene ring and the plane defined by atoms C1, O1 and C8. In (III), the dihedral angle between the C22–C27 benzene ring and the C1/O1/C8 plane is 84.0 (1)°. The analogous angle in (IV) is 83.9 (1)°, where the benzene ring consists of atoms C21–C26. Note that both benzene rings are located on the same end of the molecule as the spiro ring. For the other two benzene rings, the dihedral angles are significantly different; in (III) this dihedral angle is 44.5 (1)°, while in (IV) the angle is 11.9 (1)°.

The oxetane ring in (IV) can be compared with the structure of oxetane (C_3H_6O), which was determined at two

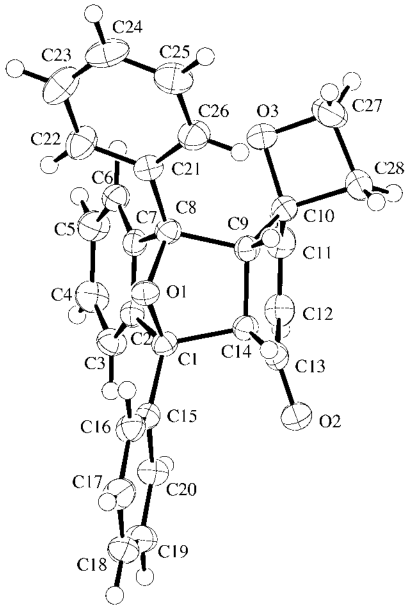


Figure 2
The structure of (IV), drawn with 50% probability displacement ellipsoids.

temperatures, *viz*. 90 and 140 K (Luger & Buschmann, 1984). Oxetane was found to have several interesting features, including ring puckering, as described by the dihedral angle between the C/O/C and C/C/C planes, of 10.7 (1)° at 90 K and 8.7 (2)° at 140 K, long C—O bond lengths of 1.460 (1) Å at 90 K and 1.443 (2) Å at 140 K, and an acute C—C—C angle of 84.79 (9)° at 90 K and 85.0 (1)° at 140 K. These same features are observed in (IV), with a ring-puckering angle of 5.8 (1)°, long O3—C27 and O3—C10 bond lengths of 1.4514 (17) and 1.4656 (15) Å, and an acute C27—C28—C10 angle of 85.8 (1)°. There is only one other structure in the Cambridge Structural Database (Allen, 2002; Version 5.25 of November 2003) that contains an analogous spiro-oxetane ring, where the spiro C atom is located adjacent to the O atom, namely 6,8,9-tris(ethyleneoxy)-2,4,10-trioxatricyclo[3.3.1.1]decane (Paquette *et al.*, 2001). This compound contains three spiro-oxetane rings and exhibits the above-mentioned features of (IV) and oxetane.

Experimental

To a solution (1.0 *M*) of (I) in benzene was added one equivalent of (II). The reaction mixture was shielded from laboratory light and heated at reflux temperature. When the reaction was complete (8.5 h for *n* = 1 and 6 h for *n* = 2), the volatile constituents were removed under reduced pressure, and the residue was purified by column chromatography on silica gel. The reaction with *n* = 1 resulted in the isolation of two adducts in a 78:22 ratio, with (III) as the minor component. When the co-reactant was (I) with *n* = 2, compound (IV) was formed exclusively. Compounds (III) and (IV) were crystallized by dissolving each in the minimum amount of ethyl acetate and then adding hexane until the solution turned slightly cloudy. The melting points of (III) and (IV) are 406–408 and 411–413 K, respectively.

Compound (III)

Crystal data

$C_{27}H_{20}O_3$
M_r = 392.43
Monoclinic, $P2_1/n$
a = 10.322 (1) Å
b = 14.239 (1) Å
c = 14.138 (1) Å
β = 110.254 (4)°
V = 1949.3 (3) Å^3
Z = 4
D_x = 1.337 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4662 reflections
θ = 2.0–27.5°
μ = 0.09 mm^{-1}
T = 200 (2) K
Chunk, pale yellow
0.35 × 0.31 × 0.19 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
41 110 measured reflections
4474 independent reflections
3424 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.036
$\theta_{\rm max}$ = 27.5°
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.118$
S = 1.05
4474 reflections
271 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 0.4364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (III).

O3—C15	1.427 (2)	C10—C15	1.472 (2)
O3—C10	1.4572 (17)	C11—C12	1.324 (2)
C9—C10	1.5221 (19)	C12—C13	1.461 (2)
C9—C14	1.5657 (19)	C13—C14	1.5180 (19)
C10—C11	1.465 (2)		
C1—O1—C8	98.75 (9)	O3—C10—C9	114.77 (12)
C15—O3—C10	61.35 (10)	C11—C10—C9	118.41 (13)
O3—C10—C11	111.66 (12)	C15—C10—C9	121.91 (13)
O3—C10—C15	58.33 (9)	O3—C15—C10	60.32 (10)
C11—C10—C15	116.09 (14)		

Compound (IV)

Crystal data

$C_{28}H_{22}O_3$
M_r = 406.46
Monoclinic, $P2_1/c$
a = 8.434 (1) Å
b = 13.586 (1) Å
c = 17.597 (2) Å
β = 90.646 (4)°
V = 2016.3 (4) Å^3
Z = 4
D_x = 1.339 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4806 reflections
θ = 2.0–27.5°
μ = 0.09 mm^{-1}
T = 200 (2) K
Rectangular chunk, pale yellow
0.35 × 0.27 × 0.23 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
38 808 measured reflections
4609 independent reflections
3513 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.035
$\theta_{\rm max}$ = 27.5°
$h = -10 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.112$
S = 1.04
4609 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.2487P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.24 e Å^{-3}

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Table 2
Selected geometric parameters (Å, °) for (IV).

O3—C27	1.4514 (17)	C10—C28	1.5531 (17)
O3—C10	1.4656 (15)	C11—C12	1.3291 (19)
C9—C10	1.5328 (17)	C12—C13	1.4638 (18)
C9—C14	1.5494 (16)	C13—C14	1.5046 (17)
C10—C11	1.4896 (19)	C27—C28	1.517 (2)
C1—O1—C8	98.66 (8)	O3—C10—C28	90.19 (9)
C27—O3—C10	91.53 (9)	C11—C10—C28	112.11 (11)
O3—C10—C11	111.83 (11)	C9—C10—C28	115.18 (11)
O3—C10—C9	111.08 (10)	O3—C27—C28	92.18 (10)
C11—C10—C9	114.12 (10)	C27—C28—C10	85.80 (10)

The H atoms for both structures were placed at calculated positions and treated using a riding model, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). The C—H distances ranged from 0.95 to 1.00 Å, depending on the type of C atom. *PLATON* (Spek, 2003) was used to calculate some geometric parameters.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1490). Services for accessing these data are described at the back of the journal.

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