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Two conformers of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene spiro-linked with homobenzoquinone epoxide

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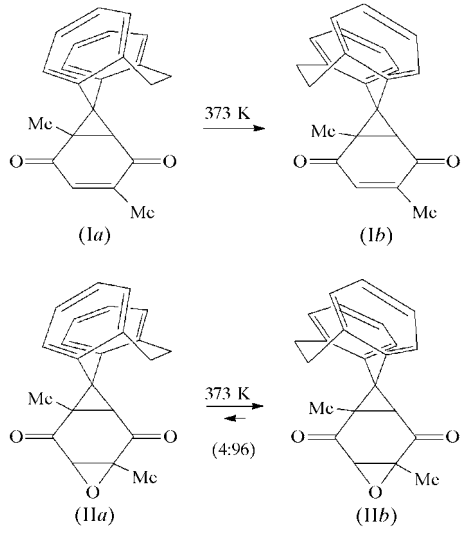
The crystal structures of the two thermally equilibrated conformational isomers of the epoxide 1′,5′-dimethylspiro-[10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,8′-4′-oxatricyclo-[5.1.0.0^{3,5}]octane]-2′,6′-dione, $C_{23}H_{20}O_3$, have been determined by X-ray diffraction. In the tricyclic dione skeleton, the oxirane and cyclopropane rings adopt an *anti* structure with respect to the conjunct quinone frame. The spiro-linked 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene ring of the major isomer has a fairly twisted boat form, folding opposite to the adjoining cyclopropane methyl substituent, whereas the seven-membered ring of the minor isomer has an almost ideal twist–boat form, inversely folding to the side of the relevant methyl group. The conformational structures of these isomers have been compared with those of the corresponding isomers of the unepoxidized homobenzoquinone.

Comment

10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene and its derivatives have received considerable pharmacological attention because of their potential as suitable subunits for drug-receptor concave–convex interactions (Burger, 1983). In a previous paper, we reported that the reaction of 5-diazo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene and 2,5-dimethyl-1,4-benzoquinone gave the corresponding spirohomobenzoquinone (I*a*) *via* the conformationally locked nitrogen release of the primary adduct pyrazoline (Oshima & Nagai, 1994). Compound (I*a*) was found to transform to the more stable conformer (I*b*) at 373 K by way of a complete one-way conformational inversion of the spiro-linked 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene moiety (Oshima *et al.* 1999). We also found that the epoxidation of conformers (I*a*) and (I*b*) proceeded without any conformational inversion to give the corresponding epoxides (II*a*) and (II*b*), respectively, but that thermal equilibration was attained at 373 K in $CDCl_3$ with a preference for (II*b*) (96%, by ^{1}H NMR) (Asahara *et al.*, 2006).

In this paper, we describe the conformational details of isomers (II*a*) and (II*b*), as determined by X-ray crystallography, and compare them with the parent unepoxidized conformers (I*a*) and (I*b*). Selected geometric parameters for (II*a*) and (II*b*) are given in Tables 1 and 2.



As shown in Fig. 1, the dibenzo-fused cycloheptene ring in (II*a*) adopts a fairly twisted boat conformation, folding opposite to the cyclopropane methyl substituent in analogy with (I*a*), but the dihedral angle [θ = 33.1 (4)°] of the –CH_2—CH_2– bridge and the intramolecular bond angle [ω = 108.9 (2)°] centered at the spiro C atom are larger than the corresponding values for (I*a*) [27.3 (3) and 107.8 (2)°, respectively]. On the other hand, as shown in Fig. 2, conformationally inverted (II*b*) adopts a more highly twisted boat conformation, with θ = 63.6 (3)° and ω = 113 (2)°; the corresponding angles for (I*b*) are 55.5 (9) and 111.3 (7)°. It was also found that ω is well correlated with θ, probably because of the constrained dibenzo fusion (*i.e.* $\omega = 0.133\theta + 104$, n = 4 and R = 0.99, where n and R are the number of data points and the correlation coefficient, respectively).

We also compared angles θ and ω with the corresponding crystalline values [57.9 (2) and 114.6 (2)°] for the least strained pure 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene,

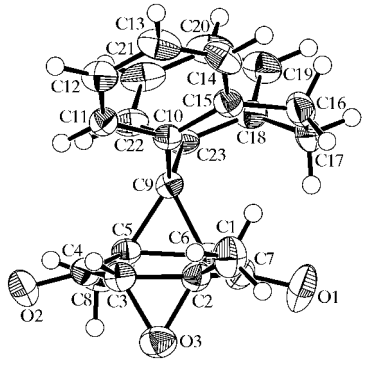


Figure 1
The molecular structure of isomer (II*a*), with the atomic numbering scheme. Displacement ellipsoids are plotted at the 35% probability level. H atoms are drawn as spheres of arbitrary radii.

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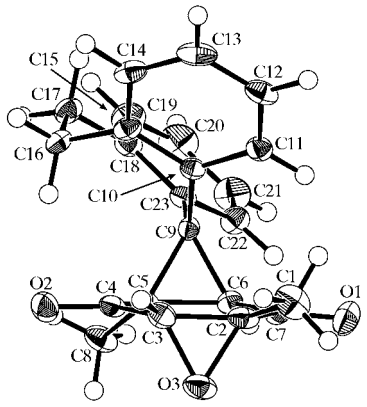

Figure 2
The molecular structure of isomer (II*b*), with the atomic numbering scheme. Displacement ellipsoids are plotted at the 35% probability level. H atoms are drawn as spheres of arbitrary radii.

(III) (Reboul & Cristau, 1981). The less stable conformers (I*a*) and (II*a*) possess considerably smaller θ values than the ideal *gauche* angle, while the stable isomers (I*b*) and (II*b*), as well as (III), adopt substantially the *gauche* conformations for the $-CH_2-CH_2-$ bridge.

A perusal of the X-ray structure of (II*a*) indicates that several atoms of the dibenzo-fused seven-membered ring occupy crowded positions almost touching the underlying quinone component, as represented by the very short spatial distances between atoms C8 and H20 (2.72 Å), O1 and H16 (2.75 Å), and O1 and H14 (2.87 Å). These unfavorable non-bonding interactions may be taken as a driving force for the conformational isomerization. However, such a van der Waals contact was also observed for stable (II*b*), in particular, between the ethano-bridge H14 atom and the facing carbonyl O2 atom (2.44 Å), appreciably raising the strain energy of (II*b*).

With respect to the structure of the quinone frame, (II*b*) is especially characterized by being almost planar, as shown by the torsion angles of 177.8 (2) and −176.1 (2)° for the bond linkages O2—C4—C3—C2 and O1—C7—C2—C3, respectively, whereas conformers (I*a*), (I*b*) and (II*a*) adopt slightly folded (12–22°) boat conformations, as indicated by the corresponding angles of 157.7 (3) and −163.5 (3)° for (I*a*), 164.0 (14) and −168.2 (13)° for (I*b*), and 163.8 (3) and −164.4 (3)° for (II*a*). Of further interest is the fact that the C atoms of the oxirane rings of (II*a*) and (II*b*) are almost planar, as indicated by the angle sums of at least 355° for the three angles made by the substituents of the oxirane ring and another carbon center. Such a geometrical planarity of oxirane C atoms is commonly known for most of the oxirane derivatives in the Cambridge Structural Database (Version 5.22 of January 2002; Allen, 2002) (Oki *et al.*, 2003).

Experimental

Samples of (II*a*) and (II*b*) were synthesized by epoxidation of the parent compounds (I*a*) and (I*b*), respectively, and were recrystallized from a mixture of pentane and *tert*-butyl methyl ether (10:1). Isomer (II*a*): m.p. 456.3–457.9 K; ^{1}H NMR ($CDCl_3$): δ 0.77 (3H, *s*), 1.60 (3H, *s*), 2.44 (1H, *s*), 2.73–2.97 (2H, *m*), 3.00 (1H, *s*), 3.30–3.40 (1H, *m*), 4.08–4.17 (1H, *m*), 6.95–6.99 (2H, *m*), 7.00–7.26 (6H, *m*); ^{13}C NMR ($CDCl_3$): δ 13.4, 18.5, 29.8, 31.6, 38.0, 44.9, 48.1, 59.7, 60.6, 125.8, 126.3, 126.5, 126.9, 128.1, 128.1, 130.2, 132.2, 134.9, 138.6, 139.2, 140.4, 197.4, 201.0. Isomer (II*b*): m.p. 425.4–426.3 K; ^{1}H NMR ($CDCl_3$): δ 1.21 (3H, *s*), 1.34 (3H, *s*), 2.71–2.95 (2H, *m*), 2.73 (1H, *s*), 2.97 (1H, *s*), 3.41–3.67 (2H, *m*), 7.0–7.37 (8H, *m*); ^{13}C NMR ($CDCl_3$): δ 14.6, 16.3, 30.3, 32.2, 37.9, 39.5, 48.8, 60.1, 61.0, 126.1, 126.2, 126.8, 127.2, 128.2, 128.7, 130.2, 131.7, 135.5, 136.9, 138.4, 141.0, 199.0, 199.4.

Isomer (II*a*)

Crystal data

$C_{23}H_{20}O_3$
M_r = 344.41
Monoclinic, $P2_1/a$
a = 12.517 (1) Å
b = 10.206 (1) Å
c = 14.704 (2) Å
β = 111.747 (7)°
V = 1744.7 (4) Å^3
Z = 4
D_x = 1.311 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13852 reflections
θ = 2.7–27.5°
μ = 0.09 mm^{-1}
T = 223.2 K
Platelet, colorless
0.30 × 0.20 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.974, T_{max} = 0.991
15836 measured reflections
3922 independent reflections
2584 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.081
θ_{max} = 27.5°
$h = -16 \rightarrow 16$
$k = -13 \rightarrow 13$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.086
$wR(F^2)$ = 0.188
S = 1.96
3922 reflections
235 parameters
H-atom parameters constrained
$w = 1/(\sigma^2(F_o^2) + \{0.05[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2)$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (II*a*).

O1—C7	1.218 (4)	C9—C10	1.512 (4)
O2—C4	1.227 (4)	C9—C23	1.516 (4)
O3—C2	1.451 (4)	C10—C15	1.408 (5)
O3—C3	1.454 (3)	C15—C16	1.524 (4)
C2—C3	1.465 (4)	C16—C17	1.548 (5)
C5—C6	1.541 (4)	C17—C18	1.507 (4)
C5—C9	1.531 (4)	C18—C23	1.408 (5)
C6—C9	1.539 (3)		
C10—C9—C23	108.9 (2)		
O1—C7—C2—O3	−99.5 (4)	C15—C16—C17—C18	33.1 (4)
O2—C4—C3—C2	163.8 (3)		

Isomer (II*b*)

Crystal data

$C_{23}H_{20}O_3$
M_r = 344.41
Orthorhombic, *Pbca*
a = 9.4653 (3) Å
b = 14.6974 (4) Å
c = 25.3890 (9) Å
V = 3532.0 (2) Å^3
Z = 8
D_x = 1.295 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26252 reflections
θ = 1.6–27.5°
μ = 0.09 mm^{-1}
T = 213.2 K
Platelet, colorless
0.30 × 0.30 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.974, T_{max} = 0.992
38732 measured reflections
3955 independent reflections
2670 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.085
θ_{max} = 27.4°
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 16$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.176
S = 1.90
3955 reflections
235 parameters
H-atom parameters constrained
$w = 1/(\sigma^2(F_o^2) + \{0.05[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2)$
$(\Delta/\sigma)_{max}$ = 0.008
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II*b*).

O1—C7	1.218 (4)	C9—C10	1.517 (3)
O2—C4	1.220 (3)	C9—C23	1.515 (4)
O3—C2	1.460 (3)	C10—C15	1.400 (4)
O3—C3	1.452 (3)	C15—C16	1.502 (4)
C2—C3	1.466 (4)	C16—C17	1.518 (4)
C5—C6	1.503 (4)	C17—C18	1.524 (4)
C5—C9	1.557 (3)	C18—C23	1.413 (4)
C6—C9	1.530 (3)		
C10—C9—C23	113.0 (2)		
O1—C7—C2—C3	−176.1 (2)	C15—C16—C17—C18	63.6 (3)
O2—C4—C3—C2	177.8 (2)		

H atoms were placed in geometrically idealized positions (C—H = 0.95–0.98 Å) and refined as riding atoms [U_{iso}(H) = 1.2U_{eq}(C)].

For both compounds, data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1087). Services for accessing these data are described at the back of the journal.

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