Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.007$
$R = 0.044$	$\Delta\rho_{max} = 0.19$ e Å^{-3}
$wR = 0.048$	$\Delta\rho_{min} = -0.14$ e Å^{-3}
$S = 1.126$	Extinction correction:
1978 reflections	Larson (1969)
195 parameters	Extinction coefficient:
H atom attached to O22	143 (9)
refined freely; H atoms	Scattering factors from *Inter-*
attached to C iteratively	*national Tables for X-ray*
re-idealized	*Crystallography* (Vol. IV)
Chebychev polynomial	
(Carruthers & Watkin,	
1979)	

Table 2. *Selected geometric parameters (Å, °) for (3)*

C1—C2	1.409 (2)	C3—C4	1.374 (2)
C1—C6	1.402 (2)	C4—C5	1.384 (2)
C1—C11	1.475 (2)	C5—C6	1.375 (2)
O2—C2	1.350 (2)	C11—N12	1.285 (2)
O2—H2	0.96 (2)	C11—C111	1.495 (2)
C2—C3	1.394 (2)	N12—C121	1.429 (2)
C2—C1—C6	118.0 (1)	C3—C4—C5	120.8 (1)
C2—C1—C11	121.0 (1)	C4—C5—C6	119.6 (1)
C6—C1—C11	120.9 (1)	C1—C6—C5	121.4 (1)
C1—C2—O2	121.9 (1)	C1—C11—N12	118.3 (1)
C1—C2—C3	120.0 (1)	C1—C11—C111	118.3 (1)
O2—C2—C3	118.1 (1)	N12—C11—C111	123.4 (1)
C2—C3—C4	120.2 (1)	C11—N12—C121	123.0 (1)

Crystals of (2) formed as large plates developed in (001) which fragmented into very small shards when cut. The crystal used for data collection was thus rather large by normal standards. A 1.2 mm collimator was used for data collection. Values of R_{int} for data with $I < 2\sigma(I)$ were very high (1.04 and 4.49) for both crystal structures. Given this very poor internal agreement, these data were omitted from the refinement. The range of transmission coefficients determined experimentally for compound (2) is at some variance with that anticipated on the basis of the dimensions of the crystal. This is attributed to the difficulty in measuring the thickness of a very thin plate.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1990*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990*b*); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structures: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996); software used to prepare material for publication: *CRYSTALS*.

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2,3-Benzoquino[15]crown-5

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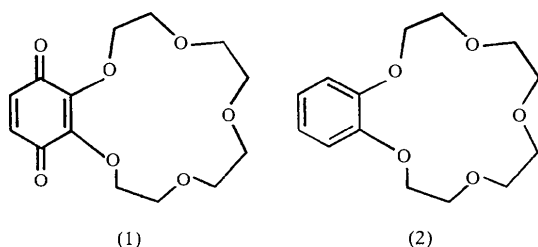
Abstract

The X-ray structure analysis of the title compound, 2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-15(1),17-diene-16,19-dione, $C_{14}H_{18}O_7$, reveals that the fused quinone causes a significant deformation of the crown ring from the expected rectangular form, because of the serious steric repulsion between the two carbonyl groups and the two adjacent OCH_2CH_2 units. One of these units deviates significantly from the mean plane of the quinone, while the other bends inward, remaining coplanar with the quinone. Such a constrained and folded structure is reflected in the abnormal sp^2 bond angles (110 and 130°) of one of the bridgehead quinonoid C atoms.

Comment

The crystal structures of crown ethers have received constant attention in view of the cation-binding abilities

of such macrocyclic polyethers (Izatt & Christensen, 1978). It is well recognized that ring substitution affects both cation selectivity and binding stability (Izatt *et al.*, 1985; Inoue & Gokel, 1990). The benzene ring is a strong torsional constraint, which leads to a significant reduction in conformational freedom in the fused ring system. Benzo[15]crown-5, (2), has been shown to adopt a quasi-rectangular conformation with an approximate plane of symmetry in its uncomplexed form (Hanson, 1978). The X-ray structure of (2) is very similar to that calculated by the *MOPAC* program (version 6) using the *PM*3 method (Stewart, 1989; the calculation was performed with a Cache Work-System). For comparison, we have carried out the crystal structure analysis of benzoquino[15]crown-5, (1), to establish the structural effects on the crown ring.
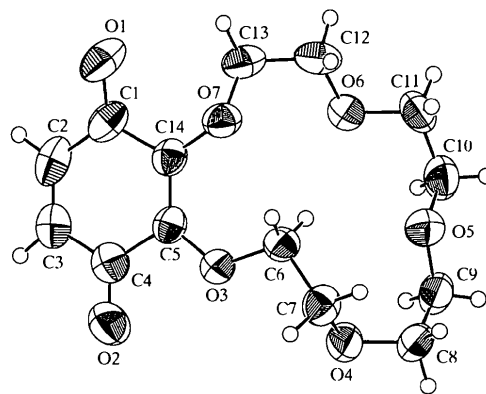

Fig. 1. A view of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

Although (2) has an approximate plane of symmetry, the analogous benzoquino[15]crown-5, (1), loses this symmetric conformation (Fig. 1). This deformation is due to the two carbonyl groups at the *para* positions. The most appreciable difference between (1) and (2) is that (1) has a *syn*-C6—O3—C5—C14 linkage, but the corresponding unit of (2) has an *anti* linkage. This unusual *syn* arrangement for (1) may be rationalized by the relief of the possible steric repulsion of the quinone carbonyl O atom, which would be expected in the *anti* conformation. However, this is not the case for the comparable C13—O7—C14—C5 linkage, where the steric repulsion is avoided by the deviation of C13 from the mean plane of the, quinone, as indicated by the C13—O7—C14—C1 torsion angle of −48.6 (2)°. In consequence of this twisted form, the O1 atom of the carbonyl function is appreciably bent from the plane of the six-membered quinone ring, as noted by the O1—C1—C14—C5 torsion angle of 166.9 (3)°, while the strain-free O2 atom remains in the same plane as the quinone. Subsequently, it was found that the conformational features mentioned above also bring about a substantial deformation of bond and torsion angles in other parts of (1). In particular, one of the fused quinonoid C atoms, C5, is subject to abnormal sp^2 bond angles (110 and 130°), and the C8—O4—C7—C6 linkage has an unfavourable torsion angle of 111.3 (2)°, far from the normal *gauche* or *anti* value.

Contrary to the case of benzo[15]crown-5, there is some difference between the crystal structure of (1) and its structure as calculated by *MOPAC*, in that the calculated form adopts a bent ellipsoidal ring conformation, while retaining an approximate plane of symmetry similar to (2).

As a result of the steric congestion due to the two quinone carbonyl groups, the overall crystal structure of (1) can be seen as a folded one, in which the approximate plane composed of the O7, C14, C5, O3, C6 and C7 atoms intersects with the mean plane involving the crown O atoms, O4, O5, O6 and O7, at the line through O7 and C7. The dihedral angle formed by the two planes is 46 (3)°. In contrast, whilst the crown in (2) is also folded, the dihedral angle formed by the two planes is 31° and the intersection line passes through atoms O3 and O7, perpendicular to the approximate plane of symmetry.

Experimental

Crystal data

$C_{14}H_{18}O_7$	Mo $K\alpha$ radiation
$M_r = 298.29$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 19
$P2_1/a$	reflections
$a = 10.892\,(6)$ Å	$\theta = 15.9–17.6°$
$b = 15.82\,(1)$ Å	$\mu = 0.107$ mm^{-1}
$c = 8.223\,(3)$ Å	$T = 293$ K
$\beta = 98.55\,(4)°$	Polyhedron
$V = 1401\,(1)$ Å^3	$1.2 \times 1.0 \times 0.2$ mm
$Z = 4$	Red
$D_x = 1.41$ Mg m^{-3}	
D_m not measured	

Data collection

MacScience MXC3 diffractometer	$\theta_{max} = 26.43°$
$\theta/2\theta$ scans	$h = 0 \rightarrow 14$
Absorption correction: none	$k = -20 \rightarrow 0$
3595 measured reflections	$l = -10 \rightarrow 10$
2855 independent reflections	3 standard reflections
2217 reflections with	every 100 reflections
$I > 2\sigma(I)$	intensity decay: not
$R_{int} = 0.028$	significant

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.009$
$R = 0.061$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$wR = 0.063$	$\Delta\rho_{min} = -0.29$ e Å^{-3}
$S = 1.316$	Extinction correction: none
2217 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
262 parameters	
All H atoms refined	
$w = 1/[\sigma^2(F_o) + 0.001F_o^2]$	

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.217(3)	O7—C14	1.359(2)
O2—C4	1.211(3)	C1—C2	1.482(3)
O3—C5	1.332(2)	C1—C14	1.477(3)
O3—C6	1.448(2)	C2—C3	1.309(4)
O4—C7	1.400(3)	C3—C4	1.461(3)
O4—C8	1.416(3)	C4—C5	1.504(3)
O5—C9	1.406(3)	C5—C14	1.345(3)
O5—C10	1.420(3)	C6—C7	1.491(3)
O6—C11	1.412(3)	C8—C9	1.484(3)
O6—C12	1.401(3)	C10—C11	1.468(4)
O7—C13	1.457(3)	C12—C13	1.486(3)
C5—O3—C6	122.2(2)	O3—C5—C14	130.1(2)
C7—O4—C8	116.4(2)	C4—C5—C14	120.0(2)
C9—O5—C10	113.8(2)	O3—C6—C7	106.3(2)
C11—O6—C12	113.0(2)	O4—C7—C6	113.5(2)
C13—O7—C14	118.2(2)	O4—C8—C9	112.6(2)
O1—C1—C2	120.7(2)	O5—C9—C8	109.2(2)
O1—C1—C14	120.9(2)	O5—C10—C11	108.2(2)
C2—C1—C14	118.3(2)	O6—C11—C10	108.5(2)
C1—C2—C3	121.2(2)	O6—C12—C13	108.7(2)
C2—C3—C4	121.2(2)	O7—C13—C12	107.7(2)
O2—C4—C3	121.2(2)	O7—C14—C1	117.6(2)
O2—C4—C5	120.4(2)	O7—C14—C5	122.2(2)
C3—C4—C5	118.4(2)	C1—C14—C5	119.8(2)
O3—C5—C4	109.9(2)		
C6—O3—C5—C4	178.2(2)	C2—C1—C14—C5	-12.2(2)
C5—O3—C6—C7	-178.5(2)	C1—C2—C3—C4	-1.7(2)
C6—O3—C5—C14	-1.3(2)	C2—C3—C4—O2	177.1(3)
C8—O4—C7—C6	111.3(2)	C2—C3—C4—C5	-4.7(2)
C7—O4—C8—C9	-99.6(2)	O2—C4—C5—O3	1.2(2)
C10—O5—C9—C8	-179.0(3)	O2—C4—C5—C14	-179.3(3)
C9—O5—C10—C11	171.3(3)	C3—C4—C5—O3	-177.0(2)
C12—O6—C11—C10	168.1(3)	C3—C4—C5—C14	2.5(2)
C11—O6—C12—C13	178.6(2)	O3—C5—C14—O7	-2.6(2)
C13—O7—C14—C1	-48.6(2)	O3—C5—C14—C1	-174.6(3)
C13—O7—C14—C5	139.2(2)	C4—C5—C14—O7	178.0(3)
C14—O7—C13—C12	-142.3(2)	C4—C5—C14—C1	6.0(2)
O1—C1—C2—C3	-169.0(3)	O3—C6—C7—O4	72.3(2)
O1—C1—C14—O7	-5.5(2)	O4—C8—C9—O5	67.4(2)
O1—C1—C14—C5	166.9(3)	O5—C10—C11—O6	-67.5(2)
C2—C1—C14—O7	175.4(3)	O6—C12—C13—O7	69.8(2)
C14—C1—C2—C3	10.1(2)		

Data collection: *CRYSTAN* (Edwards *et al.*, 1995). Cell refinement: *CRYSTAN*. Data reduction: *CRYSTAN*. Program(s) used to solve structure: *CRYSTAN*. Program(s) used to refine structure: *CRYSTAN*. Molecular graphics: *CRYSTAN*. Software used to prepare material for publication: *CRYSTAN*.

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New Examples of Donor–Acceptor Conjugated Systems Involving the 1,3-Dithiole Moiety

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Abstract

The crystal structures of 6-(4,5-dimethyl-2*H*-1,3-dithiol-2-ylidene)-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene-5,7-dione, $C_{20}H_{14}O_2S_2$, and 6-(4,5,6,7-tetrahydro-2*H*-1,3-benzodithiol-2-ylidene)-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene-5,7-dione, $C_{22}H_{16}O_2S_2$, have been determined. Strong intramolecular interactions are observed between the carbonyl groups of the seven-membered ring and the S atoms of the 1,3-dithiole ring.

Comment

In the course of our investigations on donor–acceptor conjugated systems involving the 1,3-dithiole moiety, we have determined the crystal structure of 2-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3-indandione, (I) (Bulgarovskaya *et al.*, 1988). Strong intramolecular interactions between the carbonyl groups of the planar 1,3-indandione moiety and S atoms of the planar 1,3-dithiole moiety are considered to be responsible for the coplanarity of both moieties [see also Watson *et al.*