was used for the final interpretation of molecular geometry and crystal packing. All calculations were performed on a VAX 3100 workstation.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: VJ1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ligands for Application in Coordination Chemistry: Three Dicarboxylic Acids

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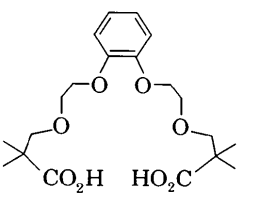
Abstract

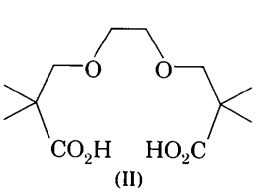
Three potential ligand molecules have been investigated. 6,6′-*o*-Phenylenedioxybis(2,2-dimethyl-4-oxahexanoic acid), $C_{20}H_{30}O_8$ (I), has twofold crystallographic symmetry and adopts a conformation in which the two pendant carboxylic arms minimize any potential molecular cavity between them; zigzag polymeric chains are formed as a result of C═O···H—O hydrogen bonding about inversion centers. 2,2,9,9-Tetramethyl-4,7-dioxadecanedioic acid, $C_{12}H_{22}O_6$ (II), also forms polymeric hydrogen-bonded chains involving the carboxylic acid moieties but differs from (I) in its molecular conformation. 2,2,6,6,10,10-Hexamethyl-4,8-dioxaundecanedioic acid, $C_{15}H_{28}O_6$ (III), forms discrete rectangular-shaped centrosymmetric dimers in which any potential molecular cavity is minimized as a result of the close proximity of two of the pendant etheral arms.

Comment

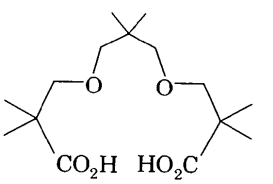
The structure determinations of the three polyether dicarboxylic acids (I), (II) and (III) were undertaken as part of a program directed towards the development of polyoxygenated ligands for use in the synthesis of transition metal complexes with O atoms in the coordination sphere. Such complexes, with several potentially labile metal–oxygen bonds which could facilitate the generation of free coordination sites for interaction with reactive molecules, might serve as soluble analogs of metal sites at transition-metal–oxide surfaces. The anticipated lability of metal–ether bonds in particular was expected to result in the formation of complexes with unusual structures and coordination geometries about metal atoms (Ferguson, McAlees, McCrindle, Restivo & Roberts, 1977; McAlees & McCrindle, 1981; McCrindle, Ferguson, McAlees & Roberts, 1981). We now report the structures of three dicarboxylic acids which may have potential application as chelating or bridging ligands in inorganic and organometallic coordination chemistry, and show that on their own in the solid state they associate by C═O···H—O hydrogen bonding about inversion centers forming both hydrogen-bonded polymers and dimers. In the structures of the Cu complexes $Cu_2(X)_2(L)_2$ [X = dicarboxylate of (II); L = H_2O, C_5H_5N and PPh_3], the O atoms of each carboxylate moiety bridge the two Cu atoms and both dicarboxylate ligands behave as macrocyclic chelates towards the Cu_2 unit (McCrindle, Ferguson, McAlees & Roberts, 1981).



(I)



(II)



(III)

6,6′-*o*-Phenylenedioxybis(2,2-dimethyl-4-oxahexanoic acid), (I) (Fig. 1), which resides on a twofold axis passing through the aromatic ring, adopts a

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conformation in which any potential molecular cavity between the pendant diether carboxylic acid chains is minimized. The pendant carboxylic acid groups are oriented away from each other and form C=O···H—O hydrogen bonds with the carboxylic acid groups of other inversion-symmetry-related molecules [O···O 2.668 (5) Å] resulting in the formation of zigzag hydrogen-bonded C=O···H—O polymeric chains which lie parallel to the *ac* plane. The principal bond lengths and angles are summarized in Table 4 and show no unusual features. The torsion angles in the dicarboxylic acid backbone of (I) are either close to *gauche* or fully *trans*, with the notable exception of C3—O4—C5—C6 which has the value 90.6 (5)°

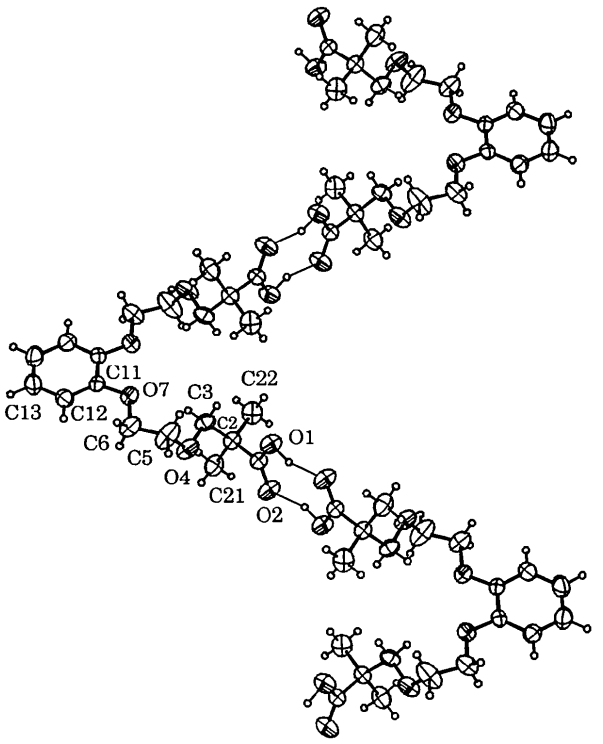

Fig. 1. A view of the polymeric zigzag chains in the lattice of molecule (I). The non-H atoms are depicted with their displacement ellipsoids drawn at the 30% probability level and H atoms drawn as spheres of arbitrary size.

2,2,9,9-Tetramethyl-4,7-dioxadecanedioic acid, (II), (Fig. 2) also forms polymeric hydrogen-bonded chains involving the carboxylic moieties, but differs from (I) in the relative orientations adopted by the carboxylic acid moieties and in its molecular packing. The two carboxylic —CO_2H moieties are involved in C=O···O—H hydrogen bonding with the carboxylic acid groups of inversion-symmetry-related molecules with O···O distances of 2.664 (4) and 2.660 (3) Å. As in (I), the torsion angles in the dicarboxylic acid backbone have

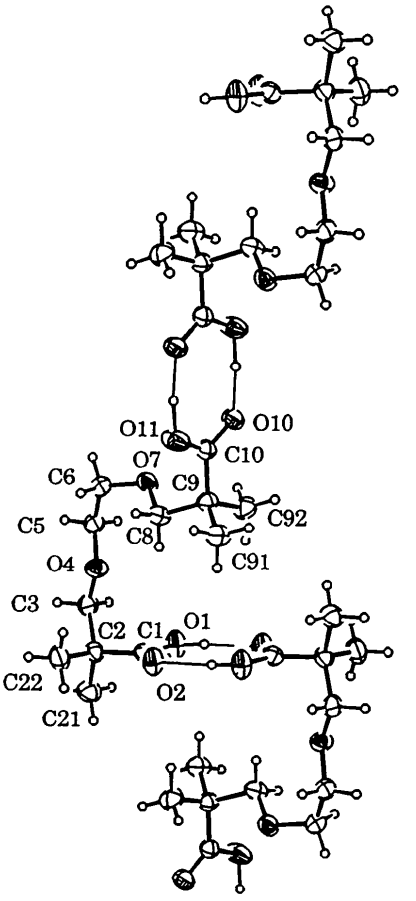

Fig. 2. A view of the polymeric zigzag chains in the lattice of molecule (II); ellipsoids as in Fig. 1.

either close to *gauche* or fully *trans* values with the exception of C5—C6—O7—C8 [−84.4 (2)°]. Presumably both here and in (I) this is a consequence of the demands of hydrogen-bond formation. Other dimensions (Table 4) are as anticipated.

2,2,6,6,10,10-Hexamethyl-4,8-dioxaundecanedioic acid molecules, (III), (Fig. 3) form rectangular-shaped centrosymmetric dimers in which the central molecular cavity is minimized owing to the close proximity of one of the etheral arms and its symmetry-related equivalent across the inversion center. The two carboxylic —CO_2H groups involved in the C=O···H—O hydrogen bonding have O···O distances of 2.658 (2) and 2.666 (2) Å. The principal dimensions are summarized in Table 4 and are unexceptional. Diacid (III) has the most strain-free conformation of the three acids, the C—C—C—O torsion angles in the molecular backbone having close to *gauche* or fully *trans* values and the C—C—O—C angles having close to fully *trans* values.

There are no solvent molecules present in any of the compounds reported here and an examination of the crystal structures using *PLATON* (Spek, 1992) revealed no potential volume for any such molecules.

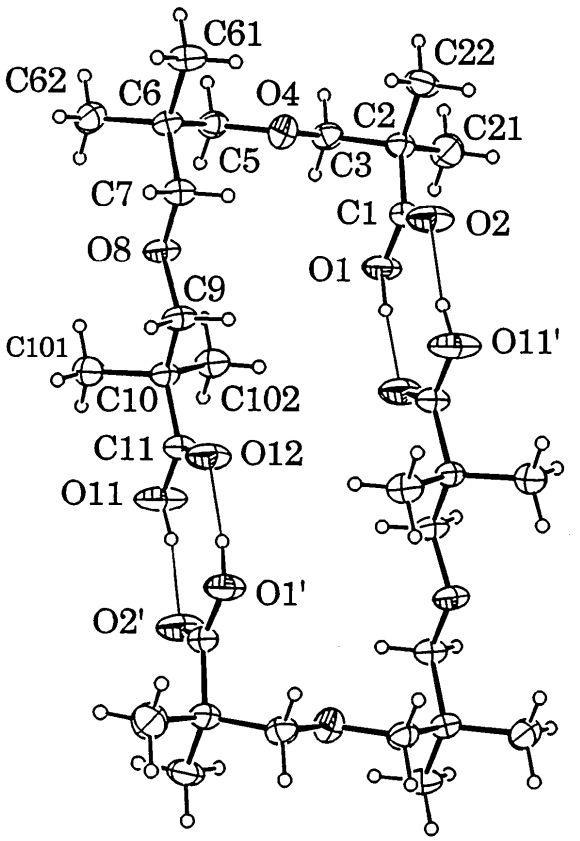

Fig. 3. A view of the dimeric hydrogen-bonded macrocycle of molecule (III); ellipsoids as in Fig. 1.

Experimental

Crystals of (I) (McAlees, 1994) suitable for X-ray studies were obtained by recrystallization from benzene. Compounds (II) and (III) were synthesized as described by McAlees & McCrindle (1981).

Compound (I)

Crystal data

$C_{20}H_{30}O_8$
M_r = 398.45
Orthorhombic
Pcan
a = 11.321 (3) Å
b = 10.782 (2) Å
c = 17.916 (4) Å
V = 2186.9 (8) Å^3
Z = 4
D_x = 1.210 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11.00–18.00°
μ = 0.09 mm^{-1}
T = 293 K
Block
0.40 × 0.35 × 0.25 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3344 measured reflections
1714 independent reflections
955 observed reflections [$I > 3.0\sigma(I)$]
R_{int} = 0.023
θ_{max} = 23.93°
h = 0 → 12
k = 0 → 12
l = −20 → 20
3 standard reflections
frequency: 60 min
intensity decay: 1.0%

Refinement

Refinement on F
R = 0.071
wR = 0.082
S = 2.04
955 reflections
131 parameters
Hydroxyl H atoms refined isotropically, others riding (C—H 0.95 Å)
$w = 1/[\sigma^2(F) + 0.0010F^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.4159 (3)	0.4709 (3)	0.0832 (2)	0.086 (2)
O2	0.4078 (3)	0.6179 (3)	0.0000 (2)	0.089 (2)
C1	0.3739 (4)	0.5758 (4)	0.0590 (3)	0.056 (2)
C2	0.2865 (4)	0.6385 (3)	0.1094 (2)	0.060 (2)
C21	0.2224 (5)	0.7430 (5)	0.0670 (3)	0.088 (3)
C22	0.3533 (5)	0.6921 (5)	0.1751 (3)	0.095 (4)
C3	0.1979 (4)	0.5455 (4)	0.1387 (3)	0.075 (3)
O4	0.1414 (4)	0.4907 (3)	0.07598 (19)	0.092 (2)
C5	0.0805 (6)	0.3775 (5)	0.0928 (4)	0.122 (5)
C6	−0.0431 (5)	0.3941 (4)	0.1140 (3)	0.088 (3)
O7	−0.0477 (3)	0.4482 (3)	0.18594 (16)	0.0691 (18)
C11	−0.1559 (4)	0.4720 (3)	0.2155 (2)	0.054 (2)
C12	−0.2612 (4)	0.4437 (4)	0.1814 (3)	0.076 (3)
C13	−0.3666 (5)	0.4719 (6)	0.2155 (3)	0.103 (4)

Compound (II)

Crystal data

$C_{12}H_{22}O_6$
M_r = 262.30
Monoclinic
$P2_1/a$
a = 12.457 (3) Å
b = 9.828 (2) Å
c = 12.588 (2) Å
β = 106.79 (2)°
V = 1475.4 (4) Å^3
Z = 4
D_x = 1.181 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9.00–18.00°
μ = 0.09 mm^{-1}
T = 293 K
Block
0.35 × 0.25 × 0.20 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3347 measured reflections
3209 independent reflections
1511 observed reflections [$I > 3.0\sigma(I)$]
R_{int} = 0.026
θ_{max} = 26.91°
h = −15 → 15
k = 0 → 12
l = 0 → 16
3 standard reflections
frequency: 120 min
intensity decay: 2.0%

Refinement

Refinement on F
R = 0.038
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}

$wR = 0.052$
$S = 1.35$
1511 reflections
172 parameters
Hydroxyl H atoms refined isotropically, others riding (C—H 0.95 Å)
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{max} = 0.006$
Extinction correction: Larson (1970)
Extinction coefficient: 4.4 (15) × 10^3
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O1	0.00869 (16)	−0.15882 (19)	0.07014 (17)	0.0744 (13)
O2	0.13893 (14)	−0.01560 (18)	0.05392 (16)	0.0734 (12)
C1	0.1121 (2)	−0.1220 (2)	0.0900 (2)	0.0514 (14)
C2	0.1974 (2)	−0.2201 (2)	0.1606 (2)	0.0541 (14)
C21	0.1905 (3)	−0.3551 (3)	0.0974 (2)	0.078 (2)
C22	0.3143 (2)	−0.1604 (3)	0.1865 (2)	0.0770 (19)
C3	0.1655 (2)	−0.2470 (2)	0.2669 (2)	0.0606 (16)
O4	0.16385 (14)	−0.12087 (15)	0.31971 (13)	0.0622 (11)
C5	0.1285 (2)	−0.1305 (3)	0.4173 (2)	0.0620 (16)
C6	0.1362 (2)	0.0060 (3)	0.4708 (2)	0.0636 (17)
O7	0.05352 (14)	0.09987 (17)	0.41246 (14)	0.0655 (11)
C8	0.0817 (2)	0.1699 (2)	0.3257 (2)	0.0623 (16)
C9	−0.0049 (2)	0.2824 (2)	0.2840 (2)	0.0548 (14)
C91	−0.1209 (2)	0.2233 (3)	0.2328 (2)	0.0724 (17)
C92	0.0337 (3)	0.3649 (3)	0.1976 (2)	0.0737 (19)
C10	−0.0043 (2)	0.3750 (2)	0.3802 (2)	0.0530 (14)
O10	−0.08870 (14)	0.39596 (18)	0.40930 (14)	0.0663 (11)
O11	0.08976 (15)	0.4315 (2)	0.42822 (18)	0.0938 (15)

Compound (III)

Crystal data

$C_{15}H_{28}O_6$
$M_r = 304.38$
Triclinic
$P\bar{1}$
$a = 5.765$ (2) Å
$b = 11.951$ (2) Å
$c = 13.325$ (2) Å
$\alpha = 98.17$ (2)°
$\beta = 91.71$ (2)°
$\gamma = 101.48$ (2)°
$V = 889.0$ (3) Å^3
$Z = 2$
$D_x = 1.137$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9.00$–20.00°
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Block
0.40 × 0.20 × 0.20 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3866 measured reflections
3866 independent reflections
2008 observed reflections [$I > 3.0\sigma(I)$]
$\theta_{max} = 26.90°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 1.0%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.057$
$S = 1.55$
2008 reflections
199 parameters
Hydroxyl H atoms refined isotropically, others riding (C—H 0.95 Å)
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 1.5 (9) × 10^3
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (III)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O1	0.9480 (3)	0.30937 (15)	0.08673 (12)	0.0751 (10)
O2	1.3350 (3)	0.37190 (15)	0.10601 (13)	0.0837 (11)
C1	1.1359 (4)	0.38058 (17)	0.12883 (15)	0.0508 (11)
C2	1.0872 (4)	0.47917 (16)	0.20541 (14)	0.0515 (11)
C21	0.9584 (5)	0.5544 (2)	0.1488 (2)	0.0767 (18)
C22	1.3203 (5)	0.5501 (2)	0.2576 (2)	0.0704 (14)
C3	0.9265 (4)	0.42770 (18)	0.28290 (15)	0.0538 (11)
O4	1.0474 (2)	0.35808 (12)	0.33298 (11)	0.0577 (9)
C5	0.9153 (4)	0.30244 (17)	0.40600 (15)	0.0513 (11)
C6	1.0597 (4)	0.22684 (16)	0.45158 (14)	0.0479 (11)
C61	1.2895 (4)	0.3004 (2)	0.50456 (18)	0.0667 (14)
C62	0.9120 (5)	0.1637 (2)	0.52775 (17)	0.0671 (15)
C7	1.1238 (3)	0.14002 (17)	0.36721 (15)	0.0498 (11)
O8	0.9138 (2)	0.07096 (12)	0.31744 (10)	0.0567 (8)
C9	0.9547 (4)	−0.00265 (18)	0.22991 (15)	0.0531 (11)
C10	0.7156 (3)	−0.06416 (16)	0.17768 (14)	0.0459 (10)
C101	0.5622 (5)	−0.1298 (2)	0.25027 (18)	0.0679 (14)
C102	0.5886 (4)	0.0238 (2)	0.13940 (17)	0.0639 (14)
C11	0.7579 (4)	−0.14781 (17)	0.08726 (15)	0.0533 (12)
O11	0.5711 (3)	−0.21681 (18)	0.04338 (15)	0.0968 (13)
O12	0.9569 (3)	−0.15011 (14)	0.05777 (13)	0.0820 (11)

Table 4. *Summary of some principal dimensions* (Å, °) *for* (I), (II) *and* (III)

	(I)	(II)	(III)
Csp^2—O	1.301 (5)	1.280 (3), 1.291 (3)	1.286 (3), 1.294 (3)
Csp^2=O	1.212 (6)	1.224 (3), 1.227 (3)	1.217 (3), 1.228 (3)
Csp^2—Csp^3	1.500 (6)	1.513 (3), 1.518 (3)	1.511 (3), 1.522 (3)
Csp^3—O(mean)	1.423 (8)	1.418 (5)	1.411 (2)
O(H)···O	2.668 (5)	2.660 (3), 2.664 (4)	2.658 (2), 2.666 (2)
O—H	1.03 (6)	0.92 (4), 1.10 (5)	0.90 (4), 0.95 (4)
O—H···O	161 (5)	167 (4), 172 (4)	171 (4), 173 (4)

The systematic absences for (I) (0*kl* absent if $l = 2n + 1$, *h*0*l* absent if $h = 2n + 1$ and *hk*0 absent if $h + k = 2n + 1$) uniquely determine the space group to be *Pcan* [a non-standard setting of *Pbcn* (No. 60) with equivalent positions x, y, z; $-x, -y, -z$; $-x, y, \frac{1}{2} + z$; $x, -y, \frac{1}{2} - z$; $\frac{1}{2} + x, \frac{1}{2} - y, z$; $\frac{1}{2} - x, \frac{1}{2} + y, -z$; $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$]. The systematic absences for molecule (II) (0*k*0 absent if $k = 2n + 1$, *h*0*l* absent if $h = 2n + 1$) uniquely determine the space group to be $P2_1/a$. Molecule (III) crystallized in the triclinic system, space group $P1$ or $P\bar{1}$; $P\bar{1}$ was assumed and confirmed by the analysis. In all three cases, all H atoms were clearly resolved in difference maps. The hydroxyl H atoms were refined isotropically and the H atoms attached to the C atoms were positioned on geometric grounds and included as riding atoms (C—H 0.95 Å) in the structure-factor calculations.

Data collection and cell refinement: *CAD-4/PC Software* (Enraf–Nonius, 1992). Data reduction, structure solution and refinement, preparation of material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *ORTEP*II (Johnson, 1976).

GF thanks NSERC Canada for Grants in Aid of Research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1215). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hindered Cavity-Shaped *N*-Oxides

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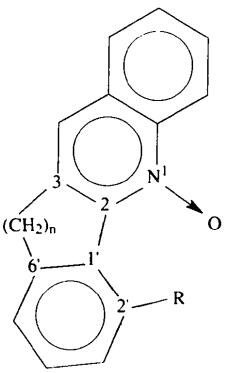
Abstract

The crystal structures of 1-hydroxy-5,6-dihydro-12-azabenz[*a*]anthracene *N*-oxide (1), $C_{17}H_{13}NO_2$, and 1-methoxy-5,6-dihydro-12-azabenz[*a*]anthracene *N*-oxide (2), $C_{18}H_{15}NO_2$, have been determined. In both (1) and (2), the 2-phenylquinoline *N*-oxide skeleton has been strengthened by a —CH_2—CH_2— linkage through the 3- and 6′-positions. Moreover, in compound (1) a strong intramolecular O—H···O hydrogen bond is formed which accounts for the fact that a more planar conformation of molecule (1) is observed compared with molecule (2). Modes of steric strain compensation in both (1) and (2) are discussed.

Comment

Annelation of 2-phenylquinoline *N*-oxide at the 3- and 6′-positions gives a series of cavity-shaped molecules whose shapes depend on the number and hybridization of C atoms in the 3,6′-bridge. The introduction of a substituent at position 2′ causes steric strain in the bay region of the molecule which can affect its reactivity. In particular, these compounds have been synthesized as model compounds in order to study the mechanism of the observed facile deoxidation of orellanine (3,3′,4,4′-tetrahydroxy-2,2′-bipyridine 1,1′-dioxide) (Antkowiak & Gessner, 1979, 1984; Antkowiak, Antkowiak & Czerwiński, 1990). We present here the crystal structures of 1-hydroxy-5,6-dihydro-12-azabenz[*a*]anthracene *N*-oxide and 1-methoxy-5,6-dihydro-12-azabenz[*a*]anthracene *N*-oxide [hereinafter referred to as (1) and (2), respectively].



(1) $n = 2$, R = OH
(2) $n = 2$, R = OMe

The asymmetric unit of compound (2) contains two molecules, denoted as *A* and *B*, which do not differ significantly. The differences in bond lengths and angles are less than $2\sigma_+$ [$\sigma_+ = (\sigma_1^2 + \sigma_2^2)^{1/2}$]. The geometries of molecules (1) and (2) are affected by two elements, namely, steric hindrance and/or intramolecular hydrogen bonding. We have selected some structural parameters of (1) and (2) in order to analyse steric hindrance (Table 5); these include: the sum of the deviations, $\Sigma|d|$, of the atoms from the least-squares planes of the aromatic systems, the dihedral angle between the aromatic ring planes (denoted α), the distance between atoms N12 and C1 (denoted $d_{12,1}$) and the O12—N12—C11a and O1—C1—C12b bond angles. All the special features of the molecular structure result from the tendency towards steric hindrance minimization. Examination of Table 5 shows that the modes of steric strain compensation in compounds (1) and (2) differ. In (1), a short intramolecular O1—H1···O12 hydrogen bond [O1···O12 2.450 (3), H1···O12 1.47 (4) Å, O1—H1···O12 159 (3)°] is formed, which restrains the con-

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