ORGANIC COMPOUNDS

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Two Isomeric [2.1]Cryptahemispherand Diamides

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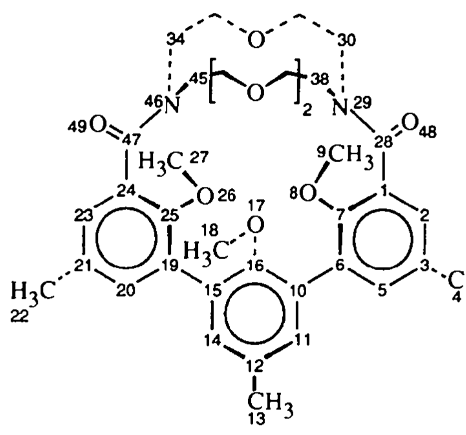
Abstract

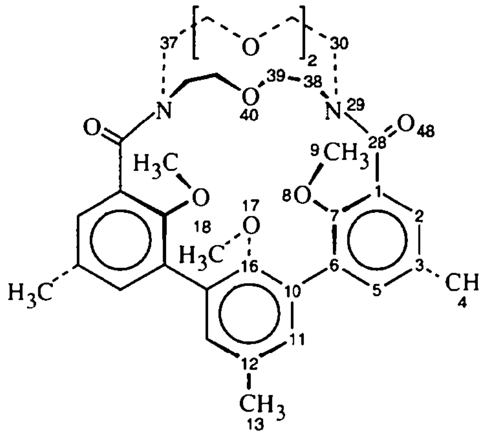
The geometrical isomers of 33,34,35-trimethoxy-5,10,15-trimethyl-22,25,30-trioxa-1,19-diazapentacyclo-[17.8.5.1^{3,7}.1^{8,12}.1^{13,17}]pentatriaconta-3,5,7(33),8,10,12(34),13,15,17(35)-nonaene-2,18-dione, $C_{36}H_{44}N_2O_8$, are intermediates in the synthesis of reduced cryptahemispherands. Their amide groups are characteristically coplanar with their attached atoms. Consequently, the N atoms in these structures are neither *exo* nor *endo*, unlike the N atoms in most other cryptands and cryptahemispherands. In the isomer formed in smaller amount, (II), the N atoms are about 1 Å closer to each other than in the other structure, (I), because the five-atom bridge between these N atoms is so constrained as to draw them together. Structure (I) is more dense than structure (II) by about 9%.

Comment

The title molecules were prepared as intermediates in the synthesis of certain of the cryptahemispherands (Cram, Ho, Knobler, Maverick & Trueblood, 1986). The molecules of (I) and (II) were found in a proportion that varied with the temperature of the reaction mixture; examination of models suggested that they might interconvert at higher temperatures. Isomer (I) was the more abundant, by a factor of about 2:1 when the ring closure was performed at room temperature and by a factor of about 12:1 at 323 K. Once the >C═O bond has been reduced, however, interconversion of the isomers becomes so facile that only the more stable one can be isolated. The structure of the K$^+$ complex of the [2.1]-cryptahemispherand reported in an accompanying paper (Knobler, Maverick, Trueblood & Ho, 1997*b*) has the two bridges in the relative positions found in present structure (I).



(I)



(II)

These molecules form at best only very weak complexes with alkali metal ions (Cram *et al.*, 1986), presumably because the N atoms have low basicity as a consequence of the amide functionality, in contrast to those in most other cryptahemispherands and cryptands. The trianisyl groups in (I) and (II) are similar to those found in other cryptahemispherands (see Maverick, Knobler, Trueblood & Ho, 1997). Some geometrical features are shown in Table 2. It is noteworthy that the N···N distance in (I) is about 1 Å greater than that in (II), and the attached amide C atoms are also appreciably farther apart. Each N atom is nearly in the plane of the three attached C atoms in each structure, as expected for an amide group; indeed, the amide O atom and the aromatic C atom attached to the >C═O group are also nearly coplanar with the other four atoms. This situation is in marked contrast to those in the structures described in the accompanying papers (Knobler *et al.*, 1997*a*,*b*; Maverick *et al.*, 1997), in which the N atoms are pyramidal, with either *endo-endo* or *exo-exo* conformations. Examination of Figs. 1 and 2 suggests why (II) is less stable and why it has the shorter N···N distance. In (I), the longer cryptand bridge (eight atoms) is in the front in this view, with the two flanking anisyl methoxy groups pointing towards the viewer. The shorter bridge is in the rear, out of the way of these two methoxy groups. In (II), on the other hand, the shorter

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bridge is in front, where it must avoid, as much as possible, the methoxy groups and other atoms that might be in the way. This necessitates drawing closer the two N atoms to which it is attached. The longer bridge, which spans this same N···N distance with three more atoms than the short bridge, folds downward (in this view). The N···N distance in the K$^+$ complex of the [2.1]-cryptahemispherand (Knobler *et al.*, 1997*b*), with the two bridges in the same relative positions as in (I), is nearly the same as that in (II); in the K$^+$ complex, there are strong ion–dipole forces drawing the N atoms (as well as the O atoms) towards the cation. No such forces exist in the present structure. The internal strain in (II) is consistent with the fact that structures derived from (I) dominate in subsequent synthetic steps as well.

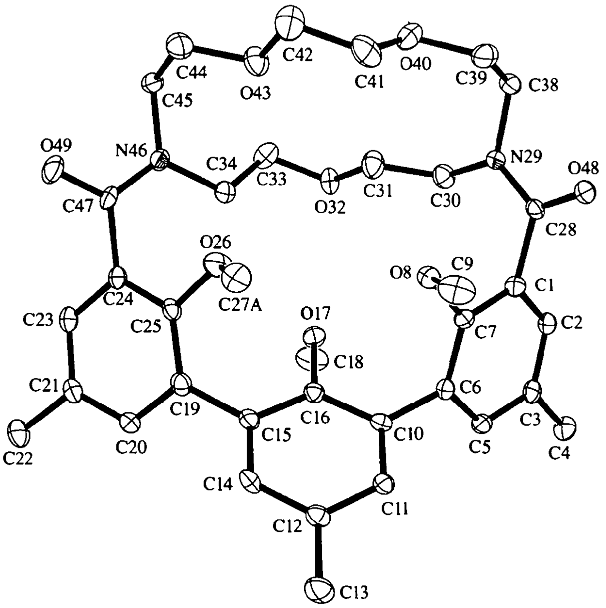

Fig. 1. *SHELXTL* (Sheldrick, 1995) view of (I). N atoms are shaded; H atoms and the disordered atom (C27*B*) have been omitted. Displacement ellipsoids are drawn to enclose 30% probability.

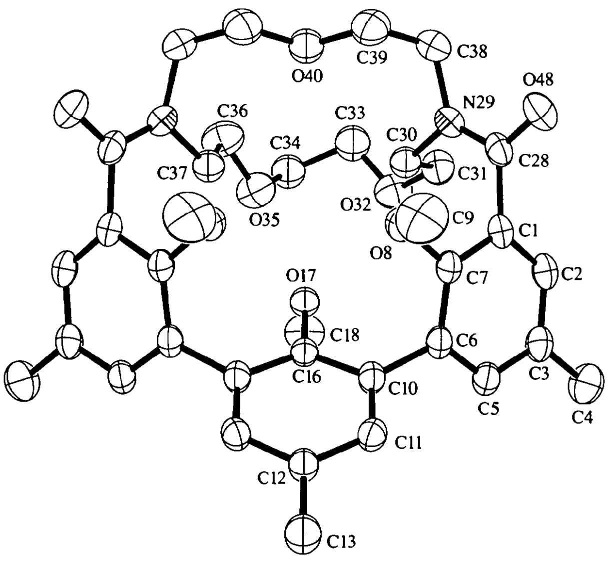

Fig. 2. *SHELXTL* (Sheldrick, 1995) view of (II). N atoms are shaded. For the longer (disordered) bridge, only atoms C30 to C37, not their mirror images, are shown (see text). Displacement ellipsoids are drawn to enclose 30% probability.

There are several unusually short intermolecular distances in (I), but none in (II). In (I), all the shortest distances are possible C—H···O interactions, both intra- and intermolecular, with C···O distances varying from 2.98 (2) to 3.251 (6) Å, and C—H···O angles from 89 to 161°. Some of these intermolecular contacts involve C27, the disordered methoxy methyl group, in each of the positions found for it; they may help promote the disorder. There are two very short distances between the (calculated) positions of H atoms in (I): intramolecular, H33*B*···H45*B* 2.02 Å, and intermolecular, H33*B*···H38*B*$(1-x,\ 1-y,\ z-\frac{1}{2})$ 2.14 Å. In (II), there is one intramolecular inter-bridge C—H···O interaction, with a C···O distance of 3.144 (8) Å and a C—H···O angle of 130°, and another with a C···O distance of 3.128 (9) Å but a C—H···O angle of only 110°. The shortest intermolecular distance between non-H atoms is from a methyl group, C13, to carbonyl oxygen O48 in the molecule at $\frac{3}{2}-x,\ 1-y,\ z-\frac{1}{2}$. This may be a weak C—H···O interaction; the C—H···O angle is 165°, but the C···O distance is long at 3.608 (3) Å.

Structure (I) is more dense than structure (II) by about 9%. The C—H···O interactions in (I) may help explain this difference, which may also be influenced by the fact that the molecule in (II) is more spherical (contrast Figs. 1 and 2). Packing drawings show that the molecules of (I) interleave significantly, while the (more spherical) molecules of (II) tend to pack in layers.

The displacement parameters are too imprecise to warrant any detailed discussion of overall or internal librational motion (Dunitz, Maverick & Trueblood, 1988). However, the general pattern is the same as in the other spherand and hemispherand structures: overall librational movement is small and the methoxy methyl groups are moving significantly (presumably wagging) with respect to most of the rest of the host molecule.

Experimental

The title compounds were prepared according to Cram *et al.* (1986). Compound (I) was crystallized from methanol–CH_2Cl_2–ethyl acetate and (II) from methanol–CH_2Cl_2.

Compound (I)

Crystal data

$C_{36}H_{44}N_2O_8$	Mo $K\alpha$ radiation
$M_r = 632.73$	$\lambda = 0.71073$ Å

Orthorhombic
$Pna2_1$
$a = 7.8350\,(14)$ Å
$b = 37.230\,(8)$ Å
$c = 11.318\,(3)$ Å
$V = 3301.4\,(13)$ Å^3
$Z = 4$
$D_x = 1.273$ Mg m^{-3}
D_m not measured
Cell parameters from 15 reflections
$\theta = 10$–14°
$\mu = 0.090$ mm^{-1}
$T = 117\,(2)$ K
Nearly rectangular parallelepiped
0.46 × 0.29 × 0.28 mm
Colorless

Data collection

Syntex $P\bar{1}$ diffractometer
Profiles from $\theta/2\theta$ scans
Absorption correction: none
3733 measured reflections
3733 independent reflections
2933 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 27.56°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 48$
$l = 0 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.162$
$S = 1.050$
3733 reflections
422 parameters
H atoms riding; fixed C—H distances, $\langle u^2\rangle(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$, except for CH_3 groups, for which factor was 1.5; CH_3 groups rotating about C—C or O—C bond
$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 2.8088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.673$
$\Delta\rho_{\max} = 0.535$ e Å^{-3}
$\Delta\rho_{\min} = -0.286$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0005 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.3 (19)

Compound (II)

Crystal data

$C_{36}H_{44}N_2O_8$
$M_r = 632.73$
Orthorhombic
Pnma
$a = 16.055\,(4)$ Å
$b = 15.370\,(4)$ Å
$c = 14.640\,(3)$ Å
$V = 3612.6\,(15)$ Å^3
$Z = 4$
$D_x = 1.163$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 15 reflections
$\theta = 25.5$–30.0°
$\mu = 0.669$ mm^{-1}
$T = 293\,(2)$ K
Cut fragment
0.5 × 0.5 × 0.3 mm
Colorless

Data collection

Syntex $P\bar{1}$ diffractometer
Profiles from $\theta/2\theta$ scans
Absorption correction: none
2732 measured reflections
2732 independent reflections
2245 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 75.18°$ (see text below)
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: see text below

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.172$
$S = 1.056$
2732 reflections
238 parameters
H atoms riding; fixed C—H distances, $\langle u^2\rangle(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$, except for CH_3 groups, for which factor was 1.5; CH_3 groups rotating about C—C or O—C bond
$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 1.3388P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -2.035$
$\Delta\rho_{\max} = 0.523$ e Å^{-3}
$\Delta\rho_{\min} = -0.166$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0074 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	U_{eq}
C1	0.7609 (2)	0.4868 (2)	0.8245 (2)	0.0574 (7)
C2	0.6970 (2)	0.5470 (2)	0.8310 (2)	0.0645 (7)
C3	0.6269 (2)	0.5416 (2)	0.7754 (2)	0.0653 (7)
C4	0.5574 (2)	0.6080 (2)	0.7826 (3)	0.0953 (11)
C5	0.6208 (2)	0.4719 (2)	0.7161 (2)	0.0591 (7)
C6	0.6836 (2)	0.4101 (2)	0.7075 (2)	0.0525 (6)
C7	0.7551 (2)	0.4206 (2)	0.7606 (2)	0.0546 (6)
O8	0.81955 (11)	0.36158 (12)	0.75557 (13)	0.0688 (6)
C9	0.8776 (2)	0.3793 (3)	0.6853 (3)	0.1173 (14)
C10	0.67551 (14)	0.3288 (2)	0.65270 (15)	0.0507 (6)
C11	0.67231 (15)	0.3275 (2)	0.5578 (2)	0.0538 (6)
C12	0.6699 (2)	1/4	0.5091 (2)	0.0537 (9)
C13	0.6646 (3)	1/4	0.4062 (2)	0.0719 (11)
C16	0.6747 (2)	1/4	0.6989 (2)	0.0483 (8)
O17	0.67605 (14)	1/4	0.79385 (15)	0.0547 (6)
C18	0.5956 (3)	1/4	0.8343 (3)	0.0836 (13)
C28	0.8353 (2)	0.4837 (2)	0.8878 (2)	0.0609 (7)
N29	0.82862 (12)	0.42823 (15)	0.95872 (15)	0.0645 (6)
C30†	0.7541 (4)	0.3771 (6)	0.9823 (6)	0.064 (4)
C31†	0.7009 (4)	0.4252 (4)	1.0514 (4)	0.078 (2)
O32†	0.6385 (3)	0.3696 (4)	1.0871 (4)	0.090 (2)
C33†	0.6689 (4)	0.3144 (4)	1.1576 (4)	0.095 (2)
C34†	0.6285 (4)	0.2257 (3)	1.1485 (3)	0.089 (2)
O35†	0.6529 (4)	0.1829 (4)	1.0670 (3)	0.096 (2)
C36†	0.7309 (4)	0.1397 (6)	1.0701 (4)	0.102 (2)
C37†	0.7547 (5)	0.1261 (7)	0.9710 (5)	0.068 (4)
C38	0.9037 (2)	0.4067 (2)	1.0107 (2)	0.0808 (9)
C39	0.9477 (2)	0.3274 (2)	0.9765 (3)	0.0879 (10)
O40	0.9063 (2)	1/4	1.0044 (2)	0.0755 (8)
O48	0.89806 (13)	0.52683 (14)	0.87257 (15)	0.0817 (7)

† Site occupancy = 0.50.

Table 2. *Some features of the geometry of compounds (I) and (II) (Å, °)*

Atoms designated with a prime in (II) (*e.g.* N29′) are at $x, \frac{1}{2} - y, z$.

Interplanar angles between adjacent aromatic rings†

	(I)	(II)
1 to 2	67.0 (2)	62.8 (2)
2 to 3	52.9 (2)	[62.8 (2)]

Some intramolecular non-bonded distances

	(I)		(II)
N29· · ·N46	6.472 (7)	N29· · ·N29′	5.479 (5)
C28· · ·C47	8.065 (8)	C28· · ·C28′	7.185 (6)
C1· · ·C24	7.564 (8)	C1· · ·C1′	7.280 (5)

† Ring 1 starts with C1, ring 2 with C10, and ring 3 with C19.

The low-temperature device used was that described by Strouse (1976). For (II), intensity data were collected to θ = 50° in bisecting mode; the three standard reflections fluctuated by about 1%, with no significant decay. The remaining data were collected in parallel mode. The one standard reflection (15,0,1) fluctuated by about 5%, with only a very gradual decay (about 4% in 100 h), until the very end, when it began to drop significantly, falling about 10% in the last 20 h (out of some 270 h total). No effort was made to correct for the decay of this standard. The refinement of (I) went smoothly; there is twofold disorder in the position of one of the flanking methoxy methyl groups (C27), the occupancies being 0.64 and 0.36. Atoms C27*A* and C27*B* were refined with a common isotropic displacement parameter. The two largest shift/error values in the final least-squares cycle, 0.67 and 0.36, were for methyl torsions (on C22 and C27). No others were above 0.10. Except for the longer cryptand bridge, the structure of (II) conforms well to the space group *Pnma*, with the molecule lying on a mirror plane. The longer bridge, C30—C31—O32—C33—C34—O35—C36—C37, would have a mirror plane between C33 and C34 if the space-group symmetry was strictly obeyed. In the final model, the distances of atoms C34 to C37 from the mirror images of atoms (C33 to C30) that would be their equivalents vary from 0.17 (for C37 to C30′) to 1.14 Å (for C36 to C31′). The atoms in this disordered bridge were refined isotropically, with the *PART* and *DFIX* options of *SHELXL*93 (Sheldrick, 1993); each atom in a disordered pair was assigned an occupancy factor of 0.5. The largest shift/error value in the final least-squares cycle (2.04) was for the torsion angle about the C3—C4 bond, which depends upon the (imprecise) positions of the H atoms on C4. The next largest shift/error value (0.28) was for a displacement parameter. The largest shifts in atomic positions in the final cycle were of the order of 0.001 Å. Because this structure is disordered, no further refinement seemed warranted.

For both compounds, data collection: Syntex *P*$\bar{1}$ diffractometer software; cell refinement: Syntex *P*$\bar{1}$ diffractometer software; data reduction: *CARESS* (*UCLA Crystallographic Package*, 1984); program(s) used to solve structures: *MULTAN*80 (Declercq, Germain & Woolfson, 1979); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1281). Services for accessing these data are described at the back of the journal.

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(±)-2,3-Dihydro-3-oxo-1*H*-indenecarboxylic Acid: Hydrogen-Bonding Patterns in a γ-Keto Acid and its Monohydrate

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Abstract

Crystal structures have been determined for the title compound in both its anhydrous, (I), $C_{10}H_8O_3$, and monohydrate, (II), $C_{10}H_8O_3.H_2O$, forms. In (I), helical monoenantiomeric hydrogen-bonding (carboxyl-to-ketone) catemers, counteraligned with chains of the opposite chirality, pass through the cell in the **b** direction; a close contact of 2.57 Å is found between the sp^2 carboxyl O atom and aromatic H6 atom on a neighboring molecule of the same chirality. The hydrate (II) displays a complex hydrogen-bonding pattern in which each water molecule participates in three hydrogen bonds to three different keto acid molecules. A 2.54 Å close contact is found between the ketone and aromatic H4 atom on a neighboring centrosymmetrically-related molecule, as well as a 2.54 Å close contact between H1 and the ketone of a molecule of identical chirality translated one cell in the **a** direction.

Comment

Keto-carboxylic acids offer opportunities for variation on the standard pattern of dimeric hydrogen bonding observed in functionally unelaborated acids. In most cases, however, the ketone does not participate and mutually hydrogen-bonded dimers result. Less frequently, inter-