

C(7)	-0.0360 (7)	0.7383 (9)	0.4285 (1)	6.1 (2)
C(8)	0.0787 (7)	0.9407 (8)	0.4499 (1)	5.8 (2)
C(9)	0.2904 (6)	1.0298 (8)	0.4498 (1)	4.8 (1)
C(10)	0.3817 (7)	1.2307 (7)	0.4717 (1)	4.7 (1)
C(11)	-0.0988 (5)	-0.0536 (6)	0.3222 (1)	3.9 (1)
C(12)	0.0884 (6)	-0.0577 (7)	0.3027 (1)	4.8 (1)
C(13)	0.0932 (6)	-0.2424 (7)	0.2787 (1)	5.3 (1)
C(14)	-0.0871 (6)	-0.4182 (7)	0.2742 (1)	5.1 (1)
C(15)	-0.2739 (6)	-0.4109 (7)	0.2936 (1)	5.1 (1)
C(16)	-0.2826 (6)	-0.2283 (7)	0.3181 (1)	4.6 (1)

Table 2. Bond lengths (Å), valence angles (°) and geometrical parameters of selected intermolecular interactions (Å, °)

N(1)—N(2)	1.345 (5)	N(1)—C(5)	1.365 (5)	
N(1)—C(11)	1.416 (5)	N(2)—C(3)	1.336 (6)	
O(1)—C(10)	1.254 (5)	O(2)—C(10)	1.266 (5)	
C(3)—C(4)	1.391 (5)	C(4)—C(5)	1.357 (6)	
C(4)—C(6)	1.514 (5)	C(6)—C(7)	1.498 (6)	
C(7)—C(8)	1.502 (6)	C(8)—C(9)	1.284 (5)	
C(9)—C(10)	1.462 (6)	C(11)—C(12)	1.377 (5)	
C(11)—C(16)	1.385 (5)	C(12)—C(13)	1.392 (6)	
C(13)—C(14)	1.375 (5)	C(14)—C(15)	1.373 (5)	
C(15)—C(16)	1.401 (6)			
N(2)—N(1)—C(5)	111.1 (3)	C(8)—C(9)—C(10)	123.2 (4)	
N(2)—N(1)—C(11)	120.1 (3)	O(1)—C(10)—O(2)	121.1 (4)	
C(5)—N(1)—C(11)	128.8 (3)	O(1)—C(10)—C(9)	119.5 (4)	
N(1)—N(2)—C(3)	104.4 (3)	O(2)—C(10)—C(9)	119.3 (4)	
N(2)—C(3)—C(4)	112.4 (4)	N(1)—C(11)—C(12)	119.8 (3)	
C(3)—C(4)—C(5)	104.2 (3)	N(1)—C(11)—C(16)	119.1 (3)	
C(3)—C(4)—C(6)	128.3 (4)	C(12)—C(11)—C(16)	121.1 (3)	
C(5)—C(4)—C(6)	127.5 (3)	C(11)—C(12)—C(13)	119.2 (3)	
N(1)—C(5)—C(4)	107.9 (3)	C(12)—C(13)—C(14)	120.7 (3)	
C(4)—C(6)—C(7)	112.1 (3)	C(13)—C(14)—C(15)	119.5 (3)	
C(6)—C(7)—C(8)	115.6 (3)	C(14)—C(15)—C(16)	121.0 (3)	
C(7)—C(8)—C(9)	128.2 (4)	C(11)—C(16)—C(15)	118.4 (3)	
D—H...A	D...A	D—H	H...A	D—H...A
C(7)—H(C7)...O(1) ⁱ	3.569 (5)	1.13 (1)	2.469 (5)	164.3 (4)
C(9)—H(C9)...O(2) ⁱⁱ	3.547 (5)	1.07 (1)	2.484 (5)	170.3 (4)

Symmetry codes: (i) $x - 1, y - 1, z$; (ii) $x - 1, y, z$.

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The H atoms were found in a difference synthesis and included as fixed contributors with an overall isotropic thermal parameter [$U = 0.109(4) \text{ \AA}^2$]. The programs used were *SHELXS86* (Sheldrick, 1985), *SHELX76* and *ORTEP* (Johnson, 1965). The refinement was by full-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55420 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1023]

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Structures of Three Alicyclic α -Dioximes with a Ring Size of Six to Eight

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Abstract

The structures of (I) 1,2-cyclohexanedione dioxime, (II) 1,2-cycloheptanedione dioxime and (III) 1,2-cyclooctanedione dioxime have been studied by X-ray diffraction. In (I) the cyclohexane fragment has a twist conformation. The cycloheptane ring in (II) exhibits a distorted chair conformation. The cyclooctane moiety in (III) has a boat–chair conformation. In structures (I)–(III), molecules form layered structures through a hydrogen-bonding system. There are two types of hydrogen bond (OH...O and OH...N) in (I) and (III) but only one type (OH...N) in (II). The bond lengths in the dioxime fragments correspond to the statistical averages obtained from an analysis of data held on the Cambridge Structural Database [Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987). *J. Chem. Soc. Perkin Trans.* **2**, pp. S1–S19]. In the α -dioxime (II), which has the most strained seven-membered ring, the N–N intramolecular distance and the torsion angle between dioxime groups [2.731 (4) Å and 47.2°] are substantially larger than those in (I) and (III) [2.683 (3) and 2.667 (3) Å, and 26.2 and 26.6°, respectively]. These structural features are also retained in solution,

accounting for substantial differences in coordination-chemical properties in the alicyclic α -dioxime series.

Comment

Despite the considerable number of papers which have dealt with the determination of the crystal and molecular structures of α -dioximes and their complexes (Peshkova, Savostina & Ivanova, 1977) the literature lacks data on the structure of alicyclic dioximes. The stability of metal complexes with the latter are much higher than with acyclic ones.

Unlike cyclic α -dioximes, for which the existence of the *cis* form alone is possible, acyclic ones are in the *trans* form in both the solid (Jeffrey, Ruble & Pople, 1982; Raston, Skelton & White, 1980) and in solution (Voloshin, Kostromina & Nazarenko, 1990*a,b*). To pass from a *trans* to a *cis* conformation during complex formation for cyclic dioximes there is a decrease in complex stability. Besides, the established fact of great differences between the kinetic and thermodynamic parameters of complexation reaction in the alicyclic dioximes series 1,2-cyclohexanedione dioxime (nioxime, H_2N_x), 1,2-cycloheptanedione dioxime (heptoxime, H_2G_x) and 1,2-cyclooctanedione dioxime (octoxime, H_2O_x), call for an explanation. For instance, a substantial decrease (by a factor of about 500) has been found for the protonated $Fe(H_2G_x)_2^+$ tris(heptoximate) stability constant and for the synthesis rate constant of the $FeG_x_3(BOH)_2$ clathrochelate complex compared with the corresponding constants for nioxime and octoxime complexes (Voloshin, Kostromina & Nazarenko, 1990*a,b*). We have investigated the crystal and molecular structures of nioxime (I), heptoxime (II) and octoxime (III).

A general view of the compound investigated with the hydrogen-bond system is shown in Fig. 1(*a*, *b* and *c*). Bond lengths and angles in (I), (II) and (III) are given in Table 2. The hydrogen-bond parameters are listed in Table 3.

In (I) the cyclohexane fragment has a twist conformation. The cycloheptane ring in (II) exhibits a distorted chair conformation. The deviations of the apices from the base midplane (± 0.06 Å) are $+0.71$ Å [C(4)], -0.86 and -1.15 Å [C(1) and C(7), respectively]. The cyclooctane moiety in (III) has approximate C_s symmetry (boat-chair conformation). The bond angle between the planes C(1)C(2)C(6)C(7) (± 0.08 Å max.) and C(2)C(3)C(5)C(6) (± 0.02 Å max.) is 59° . The deviations of the C(8) and C(4) atoms from these planes coincide in the absolute value and are ± 0.68 Å.

In crystals of (I)–(III) molecules form layered structures. The molecules in the layers are connected by a hydrogen-bonding system (Table 3). A

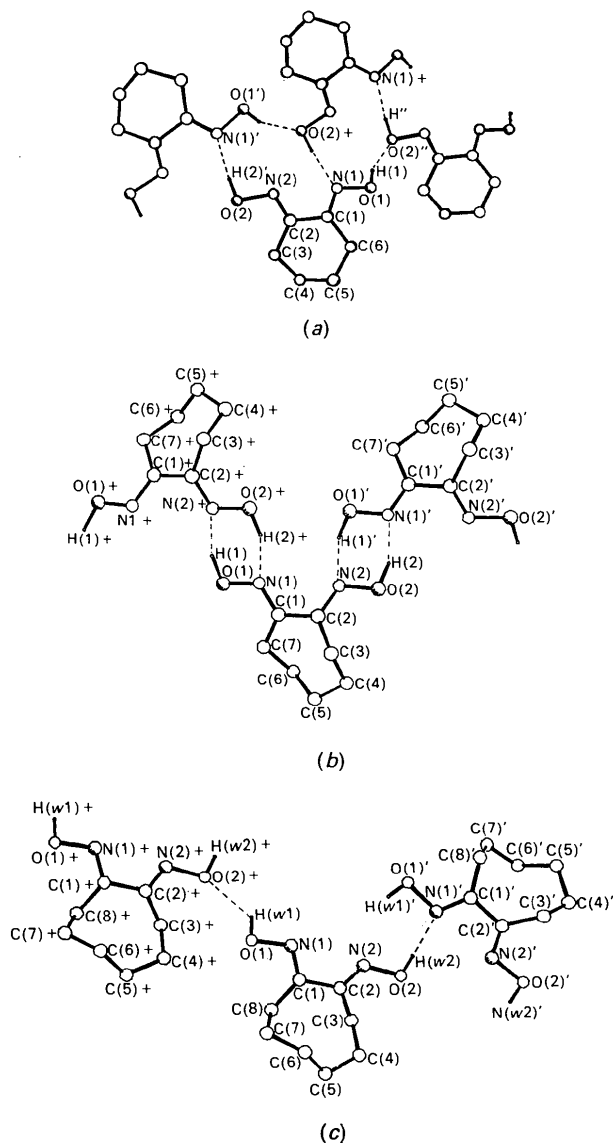


Fig. 1. Labelled diagrams of (*a*) nioxime (I), (*b*) heptoxime (II) and (*c*) octoxime (III).

difference has been found in the nature of these bonds between seven-membered dioxime and six- or eight-membered dioximes. For instance, in (I) and (III) there are hydrogen bonds of the $OH\cdots N$ and $OH\cdots O$ types, which form infinite chains in the [001] direction. The spacing between the layers is larger than the sum of the van der Waals radii (Fig. 2*a*). In (II) there is a hydrogen bond of only one type ($OH\cdots N$), the oxime groups of neighbouring molecules being assembled into a seven-membered ring, which results in the absence of net structure in the layer (Fig. 1*b*). No contacts less than the sum of the van der Waals radii were found between the layers (Fig. 2*b*).

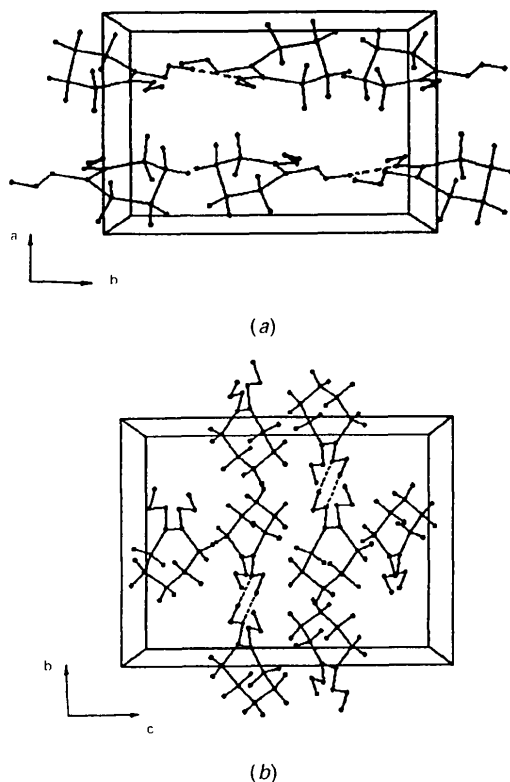


Fig. 2. Packing diagrams for (a) nioxime projected along the *c* axis and (b) heptoxime projected along the *c* axis.

The bond-length values (Table 2) for oxime moieties in (I)–(III) are similar and do not differ much from those in the acyclic analogue glyoxime (Jeffrey, Ruble & Pople, 1982) and dimethylglyoxime (Raston, Skelton & White, 1980) which have a *trans* configuration. These bond-length values [C=N 1.288, 1.288, N—O 1.388, 1.410, C—C 1.455, 1.474 Å, respectively] agree with our data for (I), (II) and (III) and also with mean values for such bond types obtained by a statistical analysis of the CSD (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The C—C bond length in the oxime moiety increases in the series: glyoxime (1.455), dimethylglyoxime (1.474), alicyclic dioximes (1.486 Å).

Comparison of geometric characteristics showed that in the alicyclic dioxime series there is a substantial difference in the structure of the fragment involved in complex formation.

The N—N intramolecular distance and the torsion angle between dioxime groups [2.731 (4) Å and 47.2°] for heptoxime is much larger than for nioxime and octoxime [2.683 (3), 2.667 (3) Å and 26.2, 26.6°, respectively]. These differences appear to be retained also in solution: an increase in torsion angle between dioxime groups causes a decrease in the conjugation

of their systems and hence must lead to a shift of intramolecular π – π^* transition bands towards the UV region. Indeed, the electronic absorption spectrum of aqueous heptoxime solution is strongly shifted towards higher frequencies compared with the spectra of nioxime and octoxime (Fig. 3).

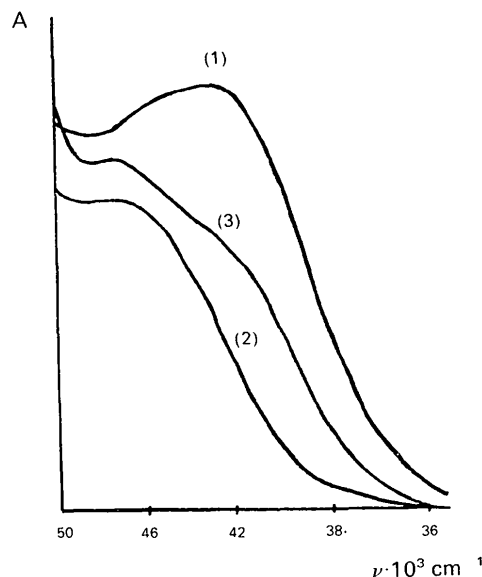


Fig. 3. Fragment of electronic absorption spectra of nioxime (1), heptoxime (2) and octoxime (3).

The structural features revealed account for the great differences in coordination–chemical properties in the cyclic dioxime series, which give rise to considerable changes in kinetic and thermodynamic complexation parameters.

Experimental

Compound (I)

Crystal data

$C_6H_{10}N_2O_2$
 $M_r = 142.16$
 Orthorhombic
*Pbc*2₁
 $a = 7.902$ (2) Å
 $b = 12.009$ (3) Å
 $c = 7.474$ (2) Å
 $V = 709.2$ (3) Å³
 $Z = 4$
 $D_x = 1.331$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 16 reflections
 $\theta = 23$ – 28°
 $\mu = 0.0948$ mm⁻¹
 $T = 298$ K
 Prismatic
 $0.15 \times 0.15 \times 0.15$ mm
 Colorless

Data collection

Syntex $P\bar{1}$ diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 none

$\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 10$

726 measured reflections
726 independent reflections
603 observed reflections
[$I \geq 3\sigma(I)$]

Refinement

Refinement on F^2
Final $R = 0.024$
 $wR = 0.027$
 $S = 1.13$
603 reflections
131 parameters
All H-atom parameters re-
fined
 $w = 1/[\sigma^2(F) + 0.00066F^2]$

Compound (II)*Crystal data*

$C_7H_{12}N_2O_2$
 $M_r = 156.19$
Orthorhombic
 $Pcab$
 $a = 8.690$ (1) Å
 $b = 12.134$ (3) Å
 $c = 16.267$ (3) Å
 $V = 1716.3$ (6) Å³
 $Z = 8$
 $D_x = 1.212$ Mg m⁻³

Data collection

Nicolet P3 diffractometer
 $\theta/2\theta$ scans
Absorption correction:
none
719 measured reflections
719 independent reflections
621 observed reflections
[$I \geq 3\sigma(I)$]

Refinement

Refinement on F^2
Final $R = 0.032$
 $wR = 0.037$
 $S = 2.43$
606 reflections
148 parameters
All H-atom parameters re-
fined
 $w = 1/[\sigma^2(F) + 0.00016F^2]$

Compound (III)*Crystal data*

$C_8H_{14}N_2O_2$
 $M_r = 170.22$
Orthorhombic
 $P2_12_12_1$
 $a = 8.734$ (1) Å
 $b = 12.821$ (2) Å
 $c = 7.775$ (1) Å

3 standard reflections
monitored every 100
reflections
intensity variation: $\pm 2\%$

$(\Delta/\sigma)_{\max} = 0.382$
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.36$ e Å⁻³
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
Cell parameters from 16
reflections
 $\theta = 23-28^\circ$
 $\mu = 0.0846$ mm⁻¹
 $T = 298$ K
Prismatic
 $0.20 \times 0.15 \times 0.10$ mm
Colorless

$\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 19$
3 standard reflections
monitored every 100
reflections
intensity variation: $\pm 2\%$

$(\Delta/\sigma)_{\max} = 0.376$
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.36$ e Å⁻³
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
Cell parameters from 16
reflections
 $\theta = 23-28^\circ$
 $\mu = 0.0883$ mm⁻¹
 $T = 298$ K

$V = 870.6$ (4) Å³
 $Z = 4$
 $D_x = 1.302$ Mg m⁻³

Data collection

Nicolet P3 diffractometer
 $\theta/2\theta$ scans
Absorption correction:
none
649 measured reflections
649 independent reflections
606 observed reflections
[$I \geq 3\sigma(I)$]

Refinement

Refinement on F^2
Final $R = 0.029$
 $wR = 0.038$
 $S = 0.89$
606 reflections
164 parameters
All H-atom parameters re-
fined
 $w = 1/[\sigma^2(F) + 0.00194F^2]$

Prismatic
 $0.20 \times 0.20 \times 0.15$ mm
Colorless

$\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 11$
3 standard reflections
monitored every 100
reflections
intensity variation: $\pm 2\%$

$(\Delta/\sigma)_{\max} = 0.356$
 $\Delta\rho_{\max} = 0.28$ e Å⁻³
 $\Delta\rho_{\min} = -0.36$ e Å⁻³
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)*

	$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	x	y	z	U_{eq}
(I)				
O(1)	0.3218 (2)	0.0525 (1)	-0.0239 (3)	0.048 (1)
O(2)	0.2260 (2)	0.1790 (1)	0.6694 (3)	0.044 (1)
N(1)	0.2827 (2)	0.0949 (1)	0.1459 (3)	0.037 (1)
N(2)	0.2723 (2)	0.1553 (1)	0.4912 (3)	0.035 (1)
C(1)	0.2846 (2)	0.0189 (2)	0.2651 (3)	0.031 (1)
C(2)	0.2426 (2)	0.0535 (2)	0.4512 (3)	0.032 (1)
C(3)	0.1683 (4)	-0.0314 (2)	0.5762 (4)	0.047 (1)
C(4)	0.1330 (3)	-0.1422 (2)	0.4861 (4)	0.045 (1)
C(5)	0.2874 (3)	-0.1791 (2)	0.3834 (4)	0.046 (1)
C(6)	0.3158 (3)	-0.1020 (2)	0.2238 (4)	0.044 (1)
(II)				
N(1)	0.1662 (2)	0.1475 (2)	0.6224 (1)	0.045 (1)
N(2)	0.4773 (2)	0.1483 (2)	0.6463 (1)	0.047 (1)
O(1)	0.0226 (2)	0.1398 (2)	0.5822 (1)	0.062 (1)
O(2)	0.6191 (2)	0.1461 (2)	0.6894 (1)	0.063 (1)
C(1)	0.2454 (3)	0.0593 (2)	0.6171 (2)	0.042 (1)
C(2)	0.3956 (3)	0.0627 (2)	0.6596 (2)	0.041 (1)
C(3)	0.4410 (5)	-0.0336 (3)	0.7124 (3)	0.060 (2)
C(4)	0.5139 (6)	-0.1258 (4)	0.6617 (4)	0.083 (2)
C(5)	0.3994 (10)	-0.1876 (6)	0.6097 (6)	0.087 (3)
C(6)	0.3180 (4)	-0.1200 (3)	0.5440 (2)	0.072 (1)
C(7)	0.1924 (4)	-0.0437 (3)	0.5759 (3)	0.079 (2)
(III)				
C(1)	0.5859 (7)	0.1846 (5)	0.0580 (8)	0.029 (2)
C(2)	0.5929 (3)	0.1538 (2)	0.2429 (3)	0.027 (1)
C(3)	0.4869 (4)	0.2042 (3)	0.3690 (5)	0.038 (1)
C(4)	0.5555 (4)	0.2989 (3)	0.4634 (5)	0.045 (1)
C(5)	0.5864 (4)	0.3958 (2)	0.3565 (4)	0.049 (1)
C(6)	0.7095 (4)	0.3848 (2)	0.2191 (4)	0.050 (1)
C(7)	0.6482 (7)	0.3755 (4)	0.0351 (7)	0.049 (2)
C(8)	0.5303 (3)	0.2899 (2)	0.0088 (4)	0.039 (1)
N(1)	0.6314 (3)	0.1142 (2)	-0.0495 (3)	0.036 (1)
O(1)	0.6294 (5)	0.1522 (3)	-0.2201 (4)	0.051 (1)
N(2)	0.6935 (2)	0.0841 (2)	0.2827 (2)	0.032 (1)
O(2)	0.6891 (2)	0.0594 (1)	0.4592 (2)	0.042 (1)
H(w1)	0.6656 (34)	0.0982 (26)	-0.2689 (42)	0.079 (10)
H(w2)	0.7508 (50)	0.0053 (33)	0.4576 (48)	0.079 (11)

Table 2. Geometric parameters (Å, °)

(I)				
O(1)—N(1)	1.401 (3)	O(2)—N(2)	1.410 (3)	
N(1)—C(1)	1.275 (3)	N(2)—C(2)	1.281 (2)	
C(1)—C(2)	1.489 (3)	C(1)—C(6)	1.505 (3)	
C(2)—C(3)	1.503 (3)	C(3)—C(4)	1.517 (3)	
C(4)—C(5)	1.508 (4)	C(5)—C(6)	1.526 (4)	
(II)				
N(1)—O(1)	1.412 (3)	N(1)—C(1)	1.274 (4)	
N(2)—O(2)	1.417 (3)	N(2)—C(2)	1.276 (4)	
C(1)—C(2)	1.478 (4)	C(1)—C(7)	1.492 (5)	
C(2)—C(3)	1.503 (5)	C(3)—C(4)	1.527 (6)	
C(4)—C(5)	1.506 (10)	C(5)—C(6)	1.522 (9)	
C(6)—C(7)	1.522 (5)			
(III)				
C(1)—C(2)	1.492 (7)	C(1)—C(8)	1.485 (7)	
C(1)—N(1)	1.293 (7)	C(2)—C(3)	1.495 (4)	
C(2)—N(2)	1.291 (3)	C(3)—C(4)	1.540 (5)	
C(4)—C(5)	1.520 (4)	C(5)—C(6)	1.522 (4)	
C(6)—C(7)	1.532 (7)	C(7)—C(8)	1.519 (6)	
N(1)—O(1)	1.413 (4)	O(1)—H(w1)	0.850 (33)	
N(2)—O(2)	1.409 (2)	O(2)—H(w2)	0.878 (43)	
(I)				
O(1)—N(1)—C(1)	111.8 (2)	O(2)—N(2)—C(2)	111.4 (2)	
N(1)—C(1)—C(2)	116.8 (2)	N(1)—C(1)—C(6)	123.2 (2)	
C(2)—C(1)—C(6)	119.8 (2)	N(2)—C(2)—C(1)	116.3 (2)	
N(2)—C(2)—C(3)	125.1 (2)	C(1)—C(2)—C(3)	118.6 (2)	
C(2)—C(3)—C(4)	113.0 (2)	C(3)—C(4)—C(5)	109.6 (2)	
C(4)—C(5)—C(6)	109.8 (2)	C(1)—C(6)—C(5)	113.6 (2)	
(II)				
O(1)—N(1)—C(1)	113.0 (2)	O(2)—N(2)—C(2)	112.6 (2)	
N(1)—C(1)—C(2)	115.0 (2)	N(1)—C(1)—C(7)	124.6 (3)	
C(2)—C(1)—C(7)	120.4 (3)	N(2)—C(2)—C(1)	124.6 (3)	
N(2)—C(2)—C(3)	125.7 (3)	C(1)—C(2)—C(3)	118.5 (3)	
C(2)—C(3)—C(4)	111.8 (3)	C(3)—C(4)—C(5)	113.2 (5)	
C(4)—C(5)—C(6)	115.7 (5)	C(5)—C(6)—C(7)	115.0 (4)	
C(1)—C(7)—C(6)	116.2 (3)			
(III)				
C(2)—C(1)—C(8)	120.2 (4)	C(2)—C(1)—N(1)	115.2 (4)	
C(8)—C(1)—N(1)	124.7 (5)	C(1)—C(2)—C(3)	119.5 (3)	
C(1)—C(2)—N(2)	116.3 (3)	C(3)—C(2)—N(2)	124.3 (2)	
C(2)—C(3)—C(4)	114.4 (3)	C(3)—C(4)—C(5)	116.9 (3)	
C(4)—C(5)—C(6)	115.7 (3)	C(5)—C(6)—C(7)	114.5 (3)	
C(6)—C(7)—C(8)	114.7 (4)	C(1)—C(8)—C(7)	113.6 (4)	
C(1)—N(1)—O(1)	111.2 (4)	N(1)—O(1)—H(w1)	97.7 (22)	
C(2)—N(2)—O(2)	111.8 (2)	N(2)—O(2)—H(w2)	98.5 (25)	

Table 3. Hydrogen-bond parameters (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
(I)				
O(1)—H(10)...O(2) ⁱ	0.82	2.10	2.85	153
O(2)—H(20)...N(1) ⁱⁱ	0.91	1.85	2.76	174
(II)				
O(1)—H(1)...N(2) ⁱⁱⁱ	1.08	1.77	2.80	158
O(2)—H(2)...N(1) ^{iv}	1.00	1.81	2.76	159
(III)				
O(1)—H(w1)...O(2) ^j	0.85	2.18	2.81	131
O(2)—H(w2)...N(1) ^y	0.88	1.85	2.72	176
Symmetry codes: (i) $x, y, -1+z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (v) $\frac{3}{2}-x, -y, \frac{1}{2}+z$.				

The starting alicyclic α -dioximes were synthesized by the method reported (Peshkova, Savostina & Ivanova, 1977). The single crystals suitable for X-ray analysis were obtained by recrystallization of water-methanol-ethyl acetate (I, III) and benzene-2-propanol (II) mixtures.

The program package *SHELXTL* (Sheldrick, 1984) was used throughout.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55658 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS0102]

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Structure of *p*-Isopropylcalix[4]arene-Toluene (1/1) Complex†

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Abstract

In the 5,11,17,23-tetraisopropyl-25,26,27,28-tetrahydroxycalix[4]arene-toluene (1/1) complex, a fourfold axis runs through the center of the calixarene (host) molecule and the toluene (guest) molecule adopts

† 5,11,17,23-Tetraisopropylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosane-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecacene-25,26,27,28-tetraol-toluene (1/1).