Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Diorthobenzenotetra(5′,2′-tetrazolo)[5′-(2)-2′-(6)]-cyclophane

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Received 8 January 2001
Accepted 17 January 2001
Online 30 January 2001

Key indicators

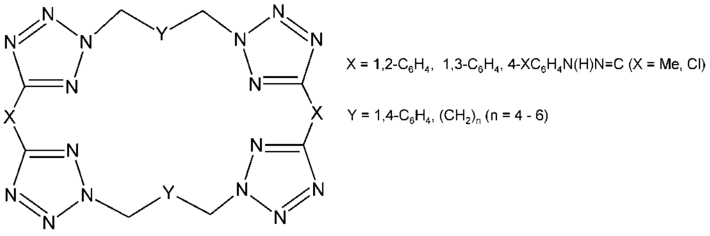
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.098
Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The first structure of the tetra-tetrazole macrocycle diorthobenzenotetra(5′,2′-tetrazolo)[5′-(2)-2′-(6)]cyclophane, $C_{28}H_{32}N_{16}$, has been determined. The interior of the rectangular cavity measures *ca* 11.2 × 5.7 Å.

Comment

We have been interested for some time in the synthesis of compounds with multiple tetrazole fragments (Bethel *et al.*, 1999; Bhandari *et al.*, 1999; Butler *et al.*, 1992; Butler & Fleming, 1997; Butler & NíBhrádaigh, 1994). One of us (RNB) has succeeded in generating tetratetrazole macrocyles of general formula (I) which include an apparent cavity of variable dimensions tailored by both the length and flexibility of the bridging groups *X* and *Y* (Butler & NíBhrádaigh, 1994; Butler *et al.*, 1992; Butler & Fleming, 1997). Such macrocycles represent an extension of other work which has led to the isolation of polyazole macrocycles containing pyrazole (Tarrago *et al.*, 1988) and triazole (Gal *et al.*, 1985; Cabezon *et al.*, 1995).



(I)

The structure of diorthobenzenotetra(5′,2′-tetrazolo)-[5′-(2)-2′-(6)]cyclophane [(I), *X* = 1,2–C_6H_4, *Y* = $(CH_2)_6$] is now reported (Fig. 1). The molecule is centrosymmetric about the inversion centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, which is intrinsic in the space-group symmetry. Of central importance is the rectangular nature of the macrocyle cavity, which measures *ca* 11.228 (3) (C14—N5′) by 5.678 (4) Å (C8—C8′), as this is the first structure of a macrocycle containing four sub-tetrazole rings surrounding such a feature. Cyclophanes with two tetrazole rings have been reported (Ried & Aboul-Fetouh, 1988; Ried *et al.*, 1989; Bethel *et al.*, 1999), but such systems do not constitute a cavity. The central void depicted in Fig. 1 is more apparent than real, as a space-filling representation (Fig. 2) illustrates. While there is clearly a void channel running parallel to, and between, the $(CH_2)_6$ chains, the orientations of the potentially coordinating tetrazole units are orthogonal to this channel. Much smaller voids are evident between pairs of tetrazoles attached to the same C_6H_4 unit (Fig. 2), though nitrogen lone pairs from each heterocycle are approximately

DOI: 101107/S1600536801001398

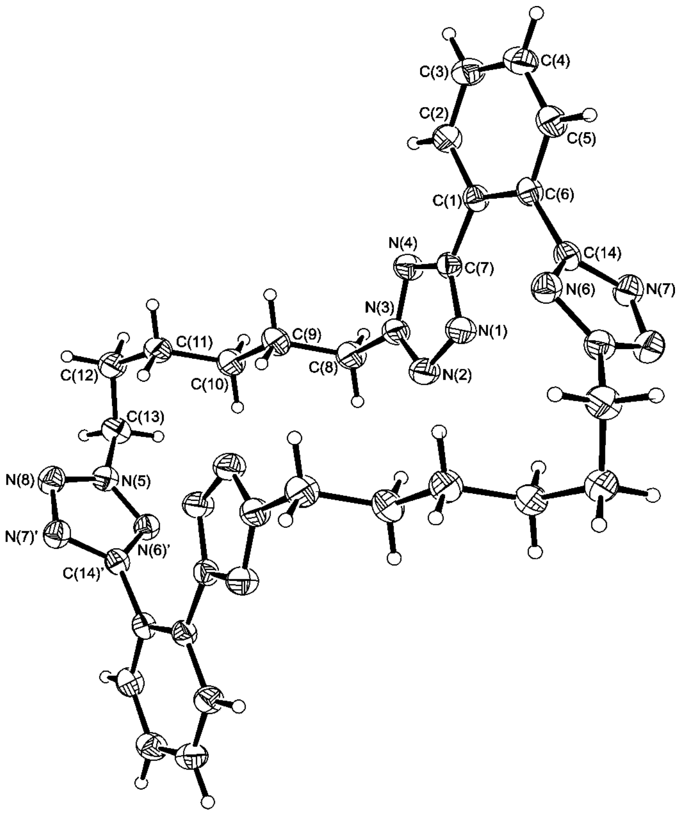


Figure 1
ORTEX (McArdle, 1995) plot of the asymmetric unit of diorthobenzenotetra(5′,2′-tetrazolo)[5′-(2)-2′-(6)]cyclophane showing the labelling scheme. Ellipsoids are represented at the 30% probability level. Primed labelled atoms are related to unprimed labelled atoms by the $1 - x$, $1 - y$, $1 - z$ symmetry operation.

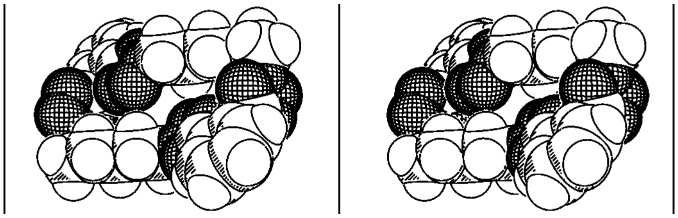


Figure 2
Space-filling stereoview of diorthobenzenotetra(5′,2′-tetrazolo)[5′-(2)-2′-(6)]cyclophane showing the restricted nature of the macrocycle cavity.

at right angles to each other (see below) and are not oriented for concerted metal-ion complexation.

Of the two unique tetrazoles, one is essentially coplanar with the phenyl group to which it is attached (torsion angle between ring planes 9.58°), while the other is approximately orthogonal (torsion angle 97.51°). This allows symmetry-related pairs of tetrazoles to adopt cofacial orientations with respect to each other across opposite sides of the rectangle. In other structures containing tetrazoles bonded at the *ortho* positions of a six-membered aromatic system, the two heterocycles are also found to be twisted with respect to the central ring (Bethel *et al.*, 1999). In one case, 2-(1,2)benzo-1(5,1),3(5,2)-bistetrazolocyclodecaphane, the twist angles (7.7 and 85.6°) are very similar to those found in the title compound (Ried & Aboul-Fetouh, 1988). Overall the macrocyle exists in a chair conformation with the -$(CH_2)_6$- linkages adopting a surprisingly rigid linear conformation (Fig. 1). Such a structure has been predicted by energy minimization calculations for the more rigid analogue of the title compound, (I) (X = 1,3–C_6H_4, Y = 1,4–C_6H_4), but was not anticipated for the title compound (Butler & Fleming, 1997).

Experimental

The title compound was synthesized according to the literature method of Butler & NíBhrádaigh (1994). Crystals suitable for X-ray diffraction were grown from dichloromethane/pentane (1:1).

Crystal data

$C_{28}H_{32}N_{16}$
M_r = 592.70
Triclinic, $P\overline{1}$
a = 7.170 (2) Å
b = 10.241 (3) Å
c = 10.729 (3) Å
α = 77.25 (3)°
β = 74.89 (3)°
γ = 73.47 (3)°
V = 719.9 (4) Å^3

Z = 1
D_x = 1.367 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13.9–17.7°
μ = 0.09 mm^{-1}
T = 293 (2) K
Block, colourless
0.35 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
2441 measured reflections
2238 independent reflections
1674 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.010
$\theta_{\rm max}$ = 24.0°

$h = 0 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 12$
1 standard reflection every 80 reflections frequency: 150 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.098
S = 1.19
2238 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 0.0022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.17 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.061 (7)

It was possible to refine all H-atom positions in this crystal structure. However, as 'free' refinement yielded a final position which was close (within the bounds of experimental error) to the calculated positions, we ultimately refined the H atoms riding on their relevant parent atoms.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CELDIM* in *CAD*-4-*PC Software;* data reduction: *XCAD* (McArdle & Higgins, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEX* (McArdle, 1995).

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