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1,4,8,11-Tetrabenzyl-6,13-dimethylene-1,4,8,11-tetraazacyclotetradecane-2,3,-9,10-tetraone

Richard Gilardi,[a]* Robin N. Evans[a] and Paritosh R. Dave[b]

[a]Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375-5341, USA, and [b]Geo-Centers Inc. at Ardec, Building 3028, Picatinny Arsenal, NJ 07806-5000, USA

Correspondence e-mail: gilardi@nrl.navy.mil

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The title compound, $C_{40}H_{40}N_4O_4$, contains a 1,4,8,11-tetraazacyclotetradecane ring, with four benzyl and two methylene substituents and also four carbonyl groups. This molecule is only the second reported structure of the 1,4,8,11-tetraazacyclotetradecane ring with four carbonyl groups on C atoms 2, 3, 9 and 10. Large-ring nitrogen heterocycles are often useful for their ability to selectively coordinate with certain metal ions, and are also sometimes used as precursors to new energetic materials. In the crystal structure the molecule is centrosymmetric.

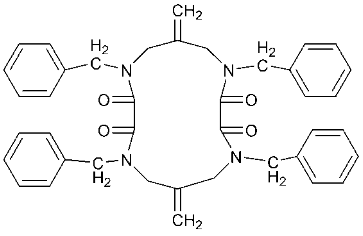
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.139
Data-to-parameter ratio = 13.5

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

Comment

The title compound, (I), contains a 1,4,8,11-tetraazacyclotetradecane ring, also referred to as a cyclam. This ring is quite a common fragment in the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002); a search for this ring structure yielded 1292 hits. Because this ring can act as a receptor ligand for a variety of metallic cations the majority of the structures containing this ring are bound to a metal ion (Bellouard *et al.*, 1999). Only 82 of the structures containing the tetraazacyclotetradecane ring do not contain a metal ion, and only one of these also contains four carbonyl groups on C atoms 2, 3, 9, and 10, but it differs considerably from (I) because its large ring is fused to two other rings (Bellouard *et al.*, 1999).


(I)

The C—C bond distance between C2 and C3 is 1.529 (3) Å, which is slightly longer than the average $Csp^2—Csp^2$ bond distance of 1.455 Å (Allen *et al.*, 1987). Atoms C2 and C3 are the two carbonyl C atoms in the diamide portion of the molecule. The average C—C bond distance for diamides in the CSD is 1.525 Å (334 fragment hits). The diamide linkages in this molecule are probably influenced by the strain of ring closure. The torsion angle O2—C2—C3—O3 is 86.9 (2)°. Only nine of the 334 diamide hits also exhibit an O═C—C═O torsion angle between 75 and 105°. The average C—C bond distance of these nine structures is 1.529 Å, which is exactly the bond distance found in (I).

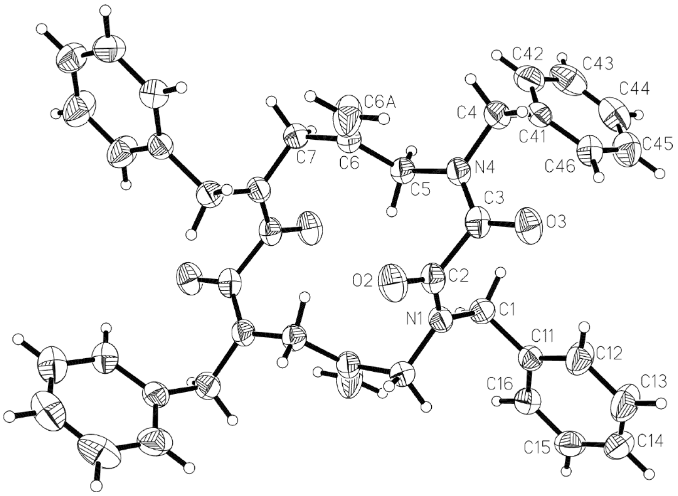


Figure 1
A drawing of the title compound with 25% atomic displacement ellipsoids. There is an inversion center (symmetry code: $1 - x$, $1 - y$, $1 - z$) in the center of the ring, making half of the molecule independent.

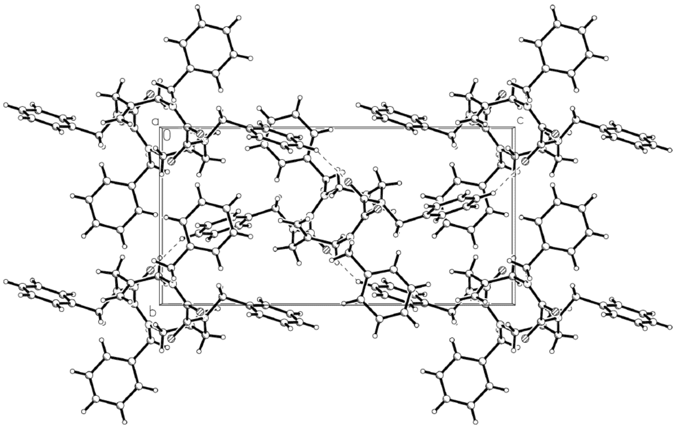


Figure 2
A packing diagram of the crystal looking down the *a* axis. The dashed bonds indicate weak hydrogen bonds occurring between atoms O2 and H14*A* in neighboring molecules.

The title compound also contains one possible weak hydrogen bond between phenyl atom H14*A* and the carbonyl atom O2^{i} of a neighboring molecule [symmetry code: (i) x, $\frac{3}{2} - y$, $z - \frac{1}{2}$]; it has an intermolecular distance of 2.42 Å, slightly less than the van der Waals contact 2.62 Å (Rowland & Taylor, 1996), and a C—H···O angle of 151.9°.

Experimental

Oxalyl chloride (2.4 g, 0.019 mol) was added to a solution of *N,N'*-dibenzyl-2-methylene-propane-1,3-diamine (5 g, 0.019 mol) and triethylamine (3.8 g, 0.038 mol) in methylene chloride (100 ml), and cooled in an ice bath under a nitrogen atmosphere. The resulting mixture was stirred over ice for an additional hour, then stirred at room temperature overnight. The reaction mixture was then successively washed with dilute aqueous HCl (5%, 100 ml), water (100 ml) and saturated sodium bicarbonate (100 ml). The organic layer was then dried over sodium sulfate, filtered and the filtrate was concentrated under reduced pressure. The residue was separated by silica-gel chromatography, eluting with 30–50% ethyl acetate/hexanes. The collected fractions upon evaporation formed crystals in several of the early fractions. These were filtered to obtain (I) as a colorless crystalline solid with a melting point of 283–285 K. Some later fractions also deposited a solid which was identified as 1,4-dibenzyl-6-methylene[1,4]diazepane.

Crystal data

$C_{40}H_{40}N_4O_4$
$M_r = 640.76$
Monoclinic, $P2_1/c$
$a = 9.9969$ (3) Å
$b = 9.3366$ (3) Å
$c = 18.6720$ (6) Å
$\beta = 90.758$ (2)°
$V = 1742.64$ (9) Å^3
$Z = 2$

$D_x = 1.221$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 3915 reflections
$\theta = 4.4$–60.6°
$\mu = 0.64$ mm^{-1}
$T = 295$ (2) K
Thin plate, colorless
0.18 × 0.16 × 0.03 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
$T_{\min} = 0.897$, $T_{\max} = 0.981$
10138 measured reflections

2938 independent reflections
1764 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.096$
$\theta_{\max} = 67.2°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 9$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.139$
$S = 0.91$
2938 reflections
218 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0048 (7)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14A···O2^{i}	0.93	2.42	3.274 (3)	152

Symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

H atoms were placed at ideal (Sheldrick, 1997) tetrahedral or trigonal positions and rode on their bonded neighbors during the refinement, with periodic re-idealization. The H-atom displacement parameters were set to be isotropic, with a value equal to $1.2U_{\rm eq}$ of the neighboring C atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001) and *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Allen, F. (2002). *Acta Cryst.* B**58**, 380–388.
Bellouard, F., Chuburu, F., Kervarec, N., Toupet, L., Triki, S., Le Mest, Y. & Handel, H. (1999). *J. Chem. Soc. Perkin Trans.* 1, pp. 3499–3505.
Bruker (2001). *SMART* (Version 5.624), *SAINT* (Version 6.04). Bruker AXS Inc., Madison, Wisconsin, USA.
Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Wuensch, B. & Prewitt, C. (1965). *Z. Kristallogr.* **122**, 24–59.