Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A tetrakis(tertiary amide) derivative of quadricyclane: 3-isopropylidene-tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-1,5,6,7-tetracarboxylic acid tetrakis(diethylamide)

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Received 18 June 2003
Accepted 20 June 2003
Online 10 July 2003

The title compound, $C_{30}H_{48}N_4O_4$, displays approximate twofold symmetry in the central part of the molecule, but the ethyl groups depart from this symmetry. The carbonyl O atoms point alternately to different sides of the plane defined by the carbonyl C atoms. Four C—H···O interactions link the molecules to form layers parallel to the *bc* plane.

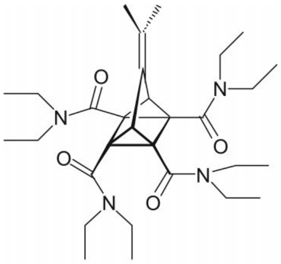
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.116
Data-to-parameter ratio = 19.7

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

Comment

For reasons presented in the first paper of this series (Winkler, Herges *et al.*, 2003*a*), we have synthesized several norbornadiene and quadricyclane tetra-amides. The tertiary amide derivatives were synthesized because they are able to form stable complexes with alkali metal cations (Winkler, Dix *et al.*, 2003), but the secondary amides cannot. Here we present the structure of the title compound, (I), the second tertiary amide of the series.



(I)

The molecule (Fig. 1) possesses no imposed symmetry; the ethyl groups depart from the approximate twofold symmetry of the rest of the molecule. Bond lengths and angles may be considered normal, *e.g.* the distorted bond angles of the quadricyclane system (Table 1). As in the analogous norbornadiene derivative (Winkle, Herges *et al.*, 2003*b*), but in contrast to the secondary amides in this series, the amide groups are not constrained to be approximately coplanar. Instead, the atoms O1 and O3 project into the molecular cavity (beneath the four-membered ring) and O2 and O4 away from it; referred to the least-squares plane of C11, C16, C21 and C26 (r.m.s. deviation 0.049 Å), the respective deviations for O1—O4 are −0.964 (1), 0.696 (2), −0.911 (1) and 0.731 (2) Å. Similar observations were made for the corresponding isopropyl derivatives of norbornadiene and quadricyclane; the former can complex sodium by rotating two amide groups such that all four O atoms are directed into the cavity (Winkler *et al.*, 2003*b*), but the latter has a much weaker association constant with sodium, indicating that its cavity may be too small.

DOI: 10.1107/S1600536803013898

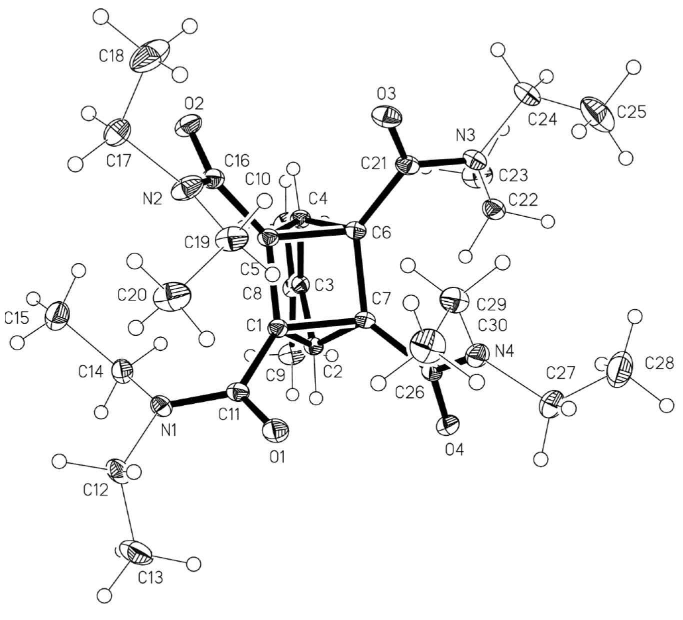


Figure 1
The molecule of the title compound in the crystal. Displacement ellipsoids are drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.

Four weak hydrogen bonds of the form C—H$\cdots$O connect the molecules to form a layer structure parallel to the *bc* plane (Table 2). By far the shortest H$\cdots$O contact involves the methine hydrogen H2.

Experimental

The title compound was prepared according to the method of Winkler (2002) and recrystallized by evaporation from pentane.

Crystal data

$C_{30}H_{48}N_4O_4$
$M_r = 528.72$
Triclinic, $P\overline{1}$
$a = 10.8375$ (8) Å
$b = 11.6922$ (8) Å
$c = 13.7337$ (10) Å
$\alpha = 109.065$ (3)°
$\beta = 101.073$ (3)°
$\gamma = 106.800$ (3)°
$V = 1493.59$ (19) Å^3
$Z = 2$
$D_x = 1.176$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6653 reflections
$\theta = 2.2$–28.5°
$\mu = 0.08$ mm^{-1}
$T = 133$ (2) K
Prism, colourless
0.39 × 0.23 × 0.19 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: none
17805 measured reflections
7353 independent reflections
5396 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 28.3°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.116$
$S = 1.06$
7353 reflections
373 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.0907P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C7	1.5259 (15)	C3—C8	1.3363 (16)
C1—C2	1.5274 (15)	C3—C4	1.4749 (16)
C1—C5	1.5683 (16)	C4—C5	1.5264 (15)
C2—C3	1.4782 (15)	C4—C6	1.5276 (15)
C2—C7	1.5264 (15)	C5—C6	1.5267 (15)
C11—C1—C7	125.11 (9)	C4—C5—C6	60.05 (7)
C11—C1—C2	121.06 (10)	C16—C5—C1	134.13 (9)
C7—C1—C2	59.99 (7)	C4—C5—C1	103.19 (9)
C11—C1—C5	131.89 (9)	C6—C5—C1	89.13 (8)
C7—C1—C5	90.50 (8)	C21—C6—C5	126.55 (10)
C2—C1—C5	103.96 (9)	C21—C6—C4	120.54 (9)
C3—C2—C7	110.12 (9)	C5—C6—C4	59.97 (7)
C3—C2—C1	110.08 (9)	C21—C6—C7	131.46 (9)
C7—C2—C1	59.96 (7)	C5—C6—C7	90.85 (8)
C8—C3—C4	129.07 (11)	C4—C6—C7	104.05 (9)
C8—C3—C2	129.53 (11)	C26—C7—C1	130.13 (9)
C4—C3—C2	101.39 (9)	C26—C7—C2	118.76 (10)
C3—C4—C5	110.66 (9)	C1—C7—C2	60.06 (7)
C3—C4—C6	109.84 (9)	C26—C7—C6	131.97 (10)
C5—C4—C6	59.99 (7)	C1—C7—C6	89.52 (8)
C16—C5—C4	118.08 (9)	C2—C7—C6	103.48 (8)
C16—C5—C6	127.69 (10)		
C7—C1—C11—O1	20.21 (17)	C5—C6—C21—O3	16.84 (17)
C2—C1—C11—O1	93.33 (13)	C4—C6—C21—O3	90.22 (13)
C5—C1—C11—O1	−109.96 (14)	C7—C6—C21—O3	−115.97 (14)
C7—C1—C11—N1	−160.21 (11)	C5—C6—C21—N3	−161.55 (11)
C2—C1—C11—N1	−87.08 (13)	C4—C6—C21—N3	−88.17 (13)
C5—C1—C11—N1	69.63 (16)	C7—C6—C21—N3	65.64 (16)
C4—C5—C16—O2	11.32 (16)	C1—C7—C26—O4	86.00 (15)
C6—C5—C16—O2	83.68 (15)	C2—C7—C26—O4	12.39 (15)
C1—C5—C16—O2	−140.05 (13)	C6—C7—C26—O4	−135.97 (12)
C4—C5—C16—N2	−171.29 (11)	C1—C7—C26—N4	−97.21 (14)
C6—C5—C16—N2	−98.92 (14)	C2—C7—C26—N4	−170.82 (10)
C1—C5—C16—N2	37.35 (19)	C6—C7—C26—N4	40.83 (17)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9—H9$A\cdots$O1$^{\rm i}$	0.98	2.66	3.2511 (16)	119
C2—H2$\cdots$O4$^{\rm i}$	1.00	2.41	3.2105 (14)	137
C15—H15$B\cdots$O2$^{\rm ii}$	0.98	2.62	3.3651 (18)	133
C24—H24$B\cdots$O2$^{\rm iii}$	0.99	2.55	3.3575 (16)	138

Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, 1-y, -z$.

The ethyl group C17/C18 is disordered over two positions with occupancy 0.756 (5):0.244 (5). Ordered methyl H atoms were located in a difference synthesis, idealized (C—H 0.98 Å, H—C—H 109.5°) and refined on the basis of rigid groups allowed to rotate but not tip. Other H atoms were included using a riding model, with fixed C—H bond lengths of 1.00 (methine) or 0.99 Å (methylene); U(H) values were fixed at 1.2 times $U_{\rm eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Mr A. Weinkauf for technical assistance.

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