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A tetrakis(tertiary amide) derivative of norbornadiene: 7-isopropylidenenorborna-2,5-diene-2,3,5,6-tetracarboxylic acid tetrakis(diethylamide)

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The molecule of 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. A three-dimensional hydrogen-bonding network is built up from five C—H⋯O interactions.

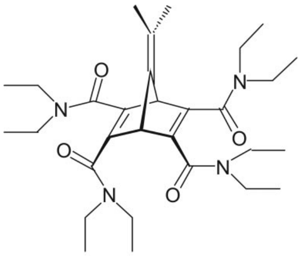
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.114
Data-to-parameter ratio = 17.8

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



(I)

The molecule of (I) (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 norbornadiene system (Table 1). Because the N atoms, in contrast to the secondary amide derivatives, no longer bear an H atom, there is no intramolecular hydrogen bonding and the amide groups are no longer constrained to be approximately coplanar. Instead, atoms O2 and O4 project into the molecular cavity (in the 'angle' of the norbornadiene system) and atoms O1 and O3 away from it; referred to the least-squares plane of C11, C16, C21 and C26 (r.m.s. deviation = 0.079 Å), the respective deviations for atoms O1—O4 are 0.889 (2), −1.052 (2), 0.875 (2) and −1.015 (2) Å. Similar observations were made for the isopropyl derivative, which, however can complex sodium by rotating two amide groups such that all four O atoms are directed into the cavity (Winkler *et al.*, 2003*b*).

Five weak hydrogen bonds of the type C—H⋯O connect the molecules to form a three-dimensional network (Table 2).

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Experimental

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

Crystal data

$C_{30}H_{48}N_4O_4$
$M_r = 528.72$
Monoclinic, $P2_1/n$
$a = 10.7945\ (12)$ Å
$b = 25.449\ (3)$ Å
$c = 11.6710\ (12)$ Å
$\beta = 106.353\ (3)^\circ$
$V = 3076.4\ (6)$ Å^3
$Z = 4$

$D_x = 1.142$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4910 reflections
$\theta = 2.2$–28°
$\mu = 0.08$ mm^{-1}
$T = 133\ (2)$ K
Prism, colourless
0.44 × 0.27 × 0.22 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: none
19202 measured reflections
6300 independent reflections

4102 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\rm max} = 26.4^\circ$
$h = -13 \rightarrow 13$
$k = -31 \rightarrow 25$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.114$
$S = 0.94$
6300 reflections
353 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C3—C2—C11	131.97 (14)	C2—C3—C16	132.06 (13)
C3—C2—C1	106.81 (12)	C2—C3—C4	107.02 (13)
C11—C2—C1	120.83 (13)	C16—C3—C4	120.62 (12)
C3—C2—C11—O1	−120.22 (18)	C6—C5—C21—O3	−122.55 (18)
C1—C2—C11—O1	51.52 (19)	C4—C5—C21—O3	45.8 (2)
C3—C2—C11—N1	59.1 (2)	C6—C5—C21—N3	55.3 (2)
C1—C2—C11—N1	−129.20 (15)	C4—C5—C21—N3	−136.28 (15)
C2—C3—C16—O2	−104.94 (19)	C5—C6—C26—O4	−105.61 (19)
C4—C3—C16—O2	67.78 (18)	C1—C6—C26—O4	66.01 (19)
C2—C3—C16—N2	77.0 (2)	C5—C6—C26—N4	76.4 (2)
C4—C3—C16—N2	−110.30 (15)	C1—C6—C26—N4	−111.95 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
C27—H27B···O1$^{\rm i}$	0.99	2.52	3.423 (2)	151
C22—H22B···O2$^{\rm ii}$	0.99	2.40	3.299 (2)	151
C15—H15B···O3$^{\rm iii}$	0.98	2.58	3.286 (2)	129
C9—H9A···O4$^{\rm iv}$	0.98	2.61	3.425 (2)	141
C10—H10C···O4$^{\rm iv}$	0.98	2.55	3.383 (2)	143

Symmetry codes: (i) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y, z-1$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$.

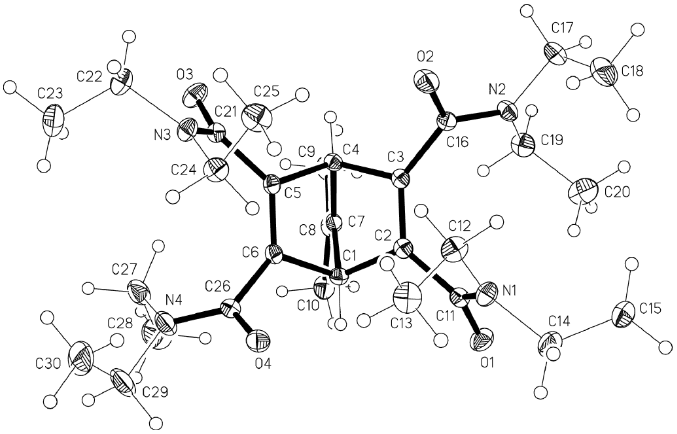

Figure 1
The molecule of the title compound in the crystal. Displacement ellipsoids are drawn at the 30% probability level. H-atom radii are arbitrary.

Methyl H atoms were located in difference syntheses, idealized (C—H 0.98 Å and H—C—H 109.5°) and refined on the basis of rigid groups allowed to rotate but not to 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); $U_{\rm iso}$(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.

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