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Key indicators

Single-crystal X-ray study

$T = 143\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.043

wR factor = 0.119

Data-to-parameter ratio = 17.5

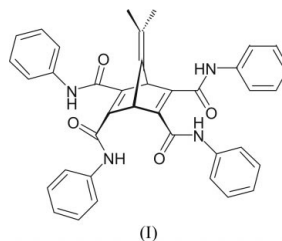
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A tetrakis(secondary amide) derivative of norbornadiene: 7-isopropylidene-*N,N',N'',N'''*-tetraphenylnorborna-2,5-diene-2,3,5,6-tetracarboxamide

The title compound, $\text{C}_{38}\text{H}_{32}\text{N}_4\text{O}_4$, displays crystallographic twofold symmetry. The four amide groups are arranged such that four intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are formed. The molecules are linked into chains by short $\text{C}-\text{H}\cdots\text{O}$ interactions involving the methine H atoms.

Comment

In pursuance of our research towards a photo-switchable ion carrier based on the norbornadiene-quadracyclane isomerization (Herges & Reif, 1994, 1996; Herges *et al.*, 1999; Starck *et al.*, 1998), we have synthesized several norbornadiene and quadracyclane tetra-amides. The tertiary derivatives are able to form stable complexes with alkali metal cations (Winkler *et al.*, 2003), but the secondary amides cannot. Here we present the structure of the title compound, (I), the first of a brief series of such structures.



The molecule of (I) (Fig. 1) possesses crystallographic twofold symmetry, with atoms C7 and C8 lying on the twofold axis. Molecular dimensions (Table 1) may be considered normal, e.g. the distorted bond angles of the norbornadiene system. The four amide groups are arranged such that four intramolecular hydrogen bonds (Table 2) of the type $\text{N}-\text{H}\cdots\text{O}$ are formed, each in a ring of graph set $R_1^1(7)$. This closed system is presumably responsible for the inability to form metal complexes. The hydrogen-bonding framework of all secondary amides presented in this series remains intact in solution in chloroform, whereas the hydrogen bonds are broken in dimethyl sulfoxide (Winkler, 2002).

The amide groups, which are each planar (r.m.s. deviation 0.043 \AA for C2/C11/N1/C12/O1 and 0.006 \AA for C3/C18/N2/C19/O2) subtend an angle of $43.32(3)^\circ$. The phenyl rings are very approximately parallel to the plane defined by atoms C2, C3, C2ⁱ and C3ⁱ, with interplanar angles of $27.09(3)$ and $26.50(3)^\circ$ [symmetry code: (i) $1 - x, y, \frac{3}{2} - z$].

The molecules are connected to form chains parallel to the c axis by intermolecular $\text{C1}-\text{H1}\cdots\text{O1}$ hydrogen bonds involving the methine H atoms (Fig. 2); ring systems of graph set $R_2^2(10)$ are thereby formed.

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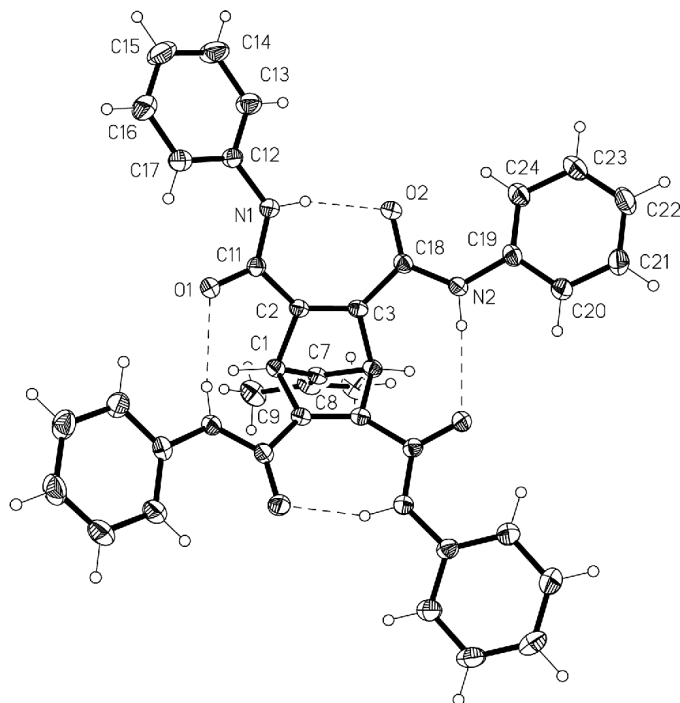


Figure 1
The molecule of the title compound in the crystal. Displacement ellipsoids are drawn at the 50% probability level. H-atom radii are arbitrary. Only the asymmetric unit is labelled. Hydrogen bonds are indicated by dashed lines.

Experimental

The title compound was prepared according to Winkler (2002) and recrystallized from a solution in dichloromethane/methanol by evaporation.

Crystal data

$C_{38}H_{32}N_4O_4$	$D_x = 1.343 \text{ Mg m}^{-3}$
$M_r = 608.68$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 5762 reflections
$a = 26.8424 (16) \text{ \AA}$	$\theta = 2.7\text{--}28.6^\circ$
$b = 7.8024 (6) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 14.8652 (10) \text{ \AA}$	$T = 143 (2) \text{ K}$
$\beta = 104.708 (3)^\circ$	Tablet, yellow
$V = 3011.3 (4) \text{ \AA}^3$	$0.46 \times 0.38 \times 0.19 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART 1000 CCD diffractometer	3255 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.043$
Absorption correction: none	$\theta_{\text{max}} = 28.5^\circ$
22552 measured reflections	$h = -36 \rightarrow 36$
3818 independent reflections	$k = -10 \rightarrow 10$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 1.8321P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.119$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
3818 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
218 parameters	
H atoms treated by a mixture of independent and constrained refinement	

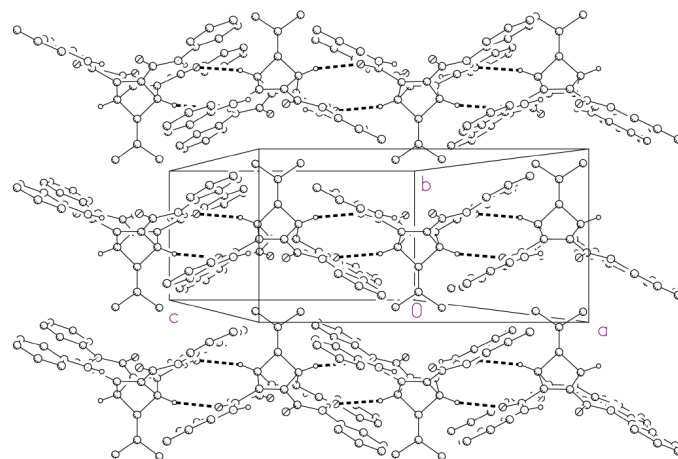


Figure 2
Packing diagram of the title compound, viewed perpendicular to the bc plane. H atoms not involved in hydrogen bonds have been omitted. Intermolecular hydrogen bonds are shown as thick dashed lines and intramolecular hydrogen bonds have been omitted.

Table 1

Selected geometric parameters (\AA , $^\circ$).

$C3-C2-C11$	134.68 (10)	$C2-C3-C18$	129.80 (10)
$C3-C2-C1$	107.08 (9)	$C2-C3-C1^1$	106.70 (9)
$C11-C2-C1$	117.87 (9)	$C18-C3-C1^1$	123.41 (9)
$C3-C2-C11-O1$	-148.12 (12)	$C2-C3-C18-O2$	-28.73 (18)
$C1-C2-C11-O1$	23.86 (14)	$C1^1-C3-C18-O2$	155.10 (11)
$C3-C2-C11-N1$	34.02 (17)	$C2-C3-C18-N2$	151.17 (11)
$C1-C2-C11-N1$	-154.00 (9)	$C1^1-C3-C18-N2$	-25.00 (14)

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

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H01 \cdots O2$	0.891 (17)	1.955 (17)	2.7729 (13)	152.0 (15)
$N2-H02 \cdots O1^1$	0.887 (16)	2.205 (16)	3.0726 (12)	166.0 (14)
$C1-H1 \cdots O1^{ii}$	1.00	2.40	3.3725 (13)	164

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

H atoms bonded to N atoms were refined freely. Methyl H atoms were located in difference syntheses, idealized ($C-H$ 0.98 \AA and $H-C-H$ 109.5 $^\circ$) 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 0.95 \AA (aromatic); $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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References

- Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.
- Herges, R. & Reif, W. (1994). *Chem. Ber.* **127**, 1143–1145.
- Herges, R. & Reif, W. (1996). *Liebigs Ann. Chem.* pp. 761–768.
- Herges, R., Starck, F., Winkler, T. & Schmittel, M. (1999). *Chem. Eur. J.* **5**, 2965–2969.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Starck, F., Jones, P. G. & Herges, R. (1998). *Eur. J. Org. Chem.* pp. 2533–2539.
- Winkler, T. (2002). PhD thesis, Technical University of Braunschweig, Germany.
- Winkler, T., Dix, I., Jones, P. G. & Herges, R. (2003). *Angew. Chem.* In the press.