

Diaza[3.3]benzenopyridino[2]phane

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.047

wR factor = 0.130

Data-to-parameter ratio = 14.1

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

The structure of 14,16-bis(ethoxycarbonyl)-2,11-bis(4-tolylsulfonyl)-2,11-diaza[3.3](1,3)benzeno(2,6)pyridino[2]phane, $\text{C}_{35}\text{H}_{37}\text{N}_3\text{O}_8\text{S}_2$, has been established by X-ray crystallographic analysis. The compound was used, after further derivatization, for the preparation of nanometre-sized molecular ribbons.

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Comment

Building blocks composed of diaza[3.3]metacyclophane units have been used to construct molecules of nanometre size with a ribbon or tube shape (Vögtle *et al.*, 1996). The breadth of these ribbons was further extended using biphenyl units as the building blocks (Boomgaarden *et al.*, 1999). The skeleton of molecular ribbons and tubes can lead, after derivatization with catalytically active groups, to synthetic catalysts with an outer sphere which sterically protects the reaction centre from the movement of the solvent molecules, as in enzymes.

The title compound, (I), crystallizes in the *syn* conformation (Fig. 1), which is the preferred conformation of diaza[3.3]-metacyclophanes. The $\text{CH}_2-\text{N}-\text{CH}_2$ bridges result in a boat-boat conformation. Both aromatic units show little distortion and the aromatic planes are oriented at an angle of about 35° to each other.

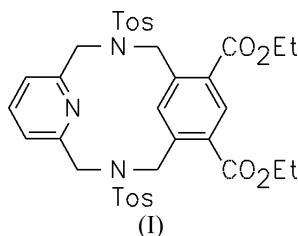


Fig. 2 shows a packing diagram for (I). A weak intermolecular $\text{C}27-\text{H}27\text{A}\cdots\text{O}112^i$ hydrogen bond is observed,

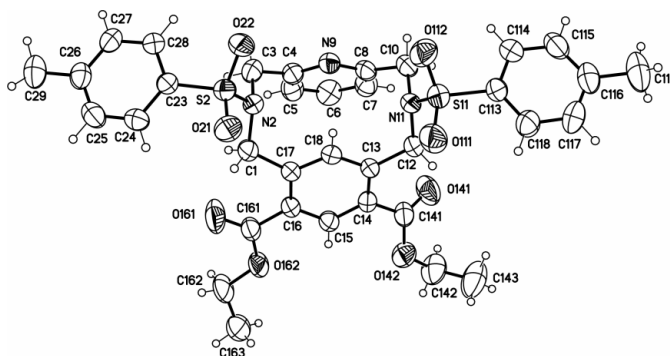


Figure 1

A perspective view of the molecule of (I), showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level.

and the details of this bond are given in Table 1 [symmetry code: (i) $2 - x, 2 - y, 1 - z$].

Experimental

The title compound, (I), was synthesized by cyclization of 2,4-bis[(4-tolylsulfonyl)aminomethyl]benzene-1,5-dicarboxylate with 2,6-bis-(bromomethyl)pyridine (Boomgaarden, 1998). The crystal used for the present data collection was obtained by slow vapour diffusion of methanol into a solution of (I) in chloroform [$R_F = 0.18$ (chloroform-acetone, 50:1); m.p. 496–498 K]. Spectroscopic analysis, ^1H NMR (400 MHz, CDCl_3 , δ , p.p.m.): 1.30 (*t*, $J = 7$ Hz, 6H, CH_3), 2.40 (*s*, 6H, Tos- CH_3), 4.28 (*q*, $J = 7$ Hz, 4H, OCH_2), 4.44 (*s*, 4H, NCH_2), 4.69 (*s*, 4H, NCH_2), 6.78 (*d*, $J = 7$ Hz, 2H, Ar-H), 7.18 (*t*, $J = 7$ Hz, 1H, Ar-H), 7.35 (*d*, $J = 8$ Hz, 4H, Tos-H), 7.81 (*d*, $J = 8$ Hz, 4H, Tos-H), 7.90 (*s*, 1H, Ar-H), 7.95 (*s*, 1H, Ar-H); ^{13}C NMR (100 MHz, CDCl_3 , δ , p.p.m.): 14.28 (CH_3), 21.63 (Tos- CH_3), 51.93 (NCH_2), 56.50 (NCH_2), 61.49 (OCH_2), 122.71, 127.59, 128.41, 130.11, 131.42, 135.31, 135.62, 137.52, 139.47, 143.85, 155.24 (6 Ar-CH + 5 Ar-Cq, where Cq is a quaternary C atom), 166.42 (CO); EI-MS, 70 eV, m/z (%): 691.1 (29) M^+ , 646.1 (34) $M - \text{C}_2\text{H}_5\text{O}^+$, 536.2 (100) $M - \text{Tos}^+$; found: $M - \text{Tos}^+$ 536.1856; $M - \text{Tos}^+$ requires 536.1855; MALDI-TOF (matrix: 9-nitroanthracene) m/z (%): 730.4 (55) $[M + \text{K}]^+$, 714.4 (100) $[M + \text{Na}]^+$, 692 (48) $[M + \text{H}]^+$.

Crystal data

$\text{C}_{35}\text{H}_{37}\text{N}_3\text{O}_8\text{S}_2$	$Z = 2$
$M_r = 691.80$	$D_x = 1.344 \text{ Mg m}^{-3}$
Triclinic, $\overline{P}1$	Cu $K\alpha$ radiation
$a = 9.504$ (1) \AA	Cell parameters from 25 reflections
$b = 11.359$ (1) \AA	$\theta = 30\text{--}44^\circ$
$c = 17.548$ (1) \AA	$\mu = 1.88 \text{ mm}^{-1}$
$\alpha = 104.69$ (1) $^\circ$	$T = 293$ (2) K
$\beta = 97.85$ (1) $^\circ$	Plate, colourless
$\gamma = 106.77$ (1) $^\circ$	$0.45 \times 0.23 \times 0.10 \text{ mm}$
$V = 1709.0$ (3) \AA^3	

Data collection

Nonius MACH3 diffractometer	$R_{\text{int}} = 0.056$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 67.9^\circ$
Absorption correction: ψ scan (<i>SHELXTL-NT</i> ; Sheldrick, 2001)	$h = -11 \rightarrow 10$
$T_{\text{min}} = 0.685$, $T_{\text{max}} = 0.829$	$k = -3 \rightarrow 12$
8256 measured reflections	$l = -21 \rightarrow 21$
6149 independent reflections	2 standard reflections
5009 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity variation: $\pm 4\%$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.6802P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
6149 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
435 parameters	
H-atom parameters constrained	

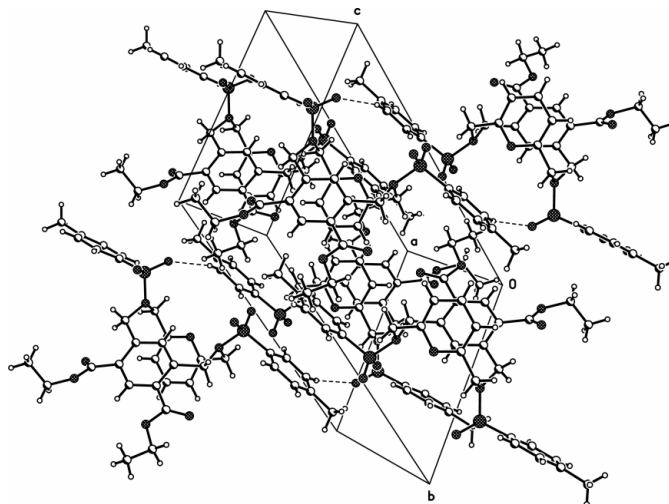


Figure 2

The molecular packing of (I) in the crystal structure. Hydrogen bonds are shown as dashed lines.

Table 1

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C}27-H27 \cdots \text{O}112^i$	0.93	2.41	3.276 (3)	155

Symmetry code: (i) $2 - x, 2 - y, 1 - z$.

Data collection: *CAD-4-PC* (Nonius, 1989); cell refinement: *CAD-4-PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 2001); software used to prepare material for publication: *SHELXL97*.

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