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Tetrakis[(4-phenylpiperazin-1-yl)methyl]methane

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.061
wR factor = 0.156
Data-to-parameter ratio = 14.8

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

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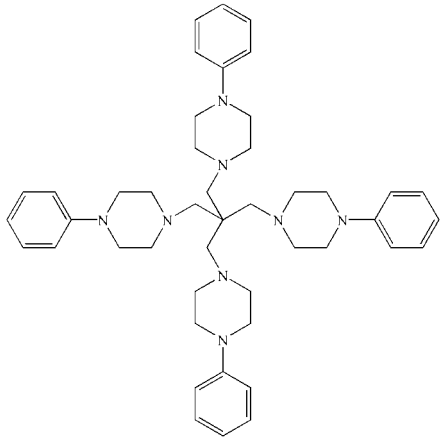
The title compound, $C_{45}H_{60}N_8$, is a symmetric molecule with four chemically identical substituents bonded to a central C atom. In the crystal structure, the 4-phenylpiperazin-1-yl groups exhibit four different conformations, with no obvious pseudosymmetry.

Comment

It has been reported that many molecules can crystallize with $Z' > 1$, the crystal structures containing several molecules in the asymmetric unit (Brock & Duncan, 1994; Lehmler *et al.*, 2002; Kuleshova *et al.*, 2003; Bats *et al.*, 2003; Lu *et al.*, 2003). Previous reports indicate that the same molecules can exist in different conformations without obvious pseudosymmetry. Logically the following question may arise: can identical substituents of a molecule exhibit different conformations in the solid state? To answer such a question, we are focusing our work on the structures of molecules containing chemically identical substituents.



(I)

The title compound, (I), is a dendrimer with a central C atom bearing four (4-phenylpiperazin-1-yl)methyl groups. The molecular structure of (I), with the atom-labeling scheme, is shown in Fig. 1. Selected bond and torsion angles are given in Table 1. In the crystal structure, there are some short intermolecular C—H···C interactions (see Table 2) and a C—H···π interaction involving C8—H8 and the C40^{i}–C45^{i} ring; the H8···centroid distance is 2.77 Å and the C8—H8···centroid angle is 127° [symmetry code: (i) $1-x, -y, 1-z$].

The bond angles C1—C2—N1, C1—C13—N3 and C1—C24—N5 are slightly different [115.1 (2), 116.5 (2) and 114.1 (2)°, respectively], whereas bond angles C1—C35—N7 and C1—C2—N1 are the same [115.2 (2) and 115.1 (2)°,

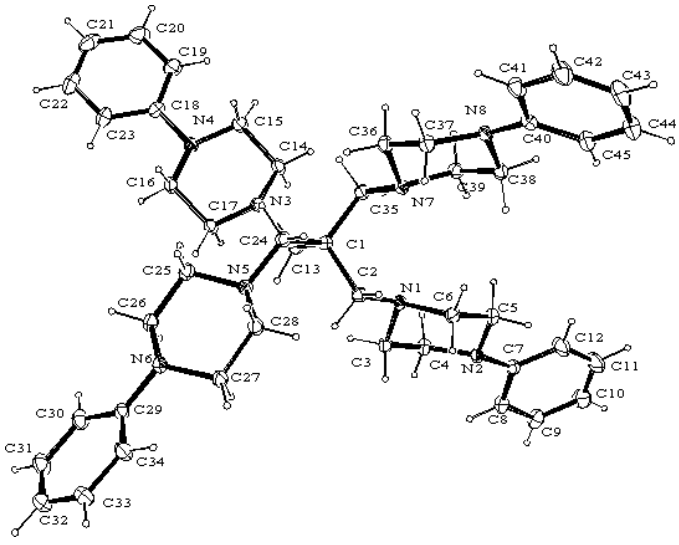


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 10% probability level and H atoms are shown as small spheres of arbitrary radii.

respectively]. However, bond angle C37—N8—C38 [112.2 (2)°] is larger than C4—N2—C5 [110.8 (2)°]. This implies that the structural parameters of the four substituents are not strictly equal.

The torsion angles about bonds C2—N1, C13—N3, C24—N5 and C35—N7 are given in Table 1 and show them to be different. It should be noted that the differences between any two corresponding torsion angles are far larger than their uncertainties. Table 1 also presents some selected torsion angles involving non-bonding atoms. The corresponding torsion angles C1—C2—N1···N2, C1—C13—N3···N4, C1—C24—N5···N6 and C1—C35—N7···N8 are different from each other. Furthermore, the different twists between the phenyl group and the piperazine ring are distinguishable, indicating that the four 4-phenylpiperazin-1-yl groups exist in four different conformations.

This comprehensive analysis suggests that the four chemically identical substituents are different in the solid state. Similar features have also been seen in the $Z' = 4$ crystal structure of bis(4-phenylpiperazin-1-yl)methane (Lu *et al.*, 2003), where 4-phenylpiperazin-1-yl groups actually exhibit eight different conformations.

Experimental

Compound (I) was synthesized by reacting pentaerythrityl bromide, Na_2CO_3 and 1-phenylpiperazine [which was prepared *in situ* by a modification of the literature method of Garrard & Partridge (1993)], in dry DMF at 333 K for 12 h. Work-up gave the desired product (yield 86.5%), which was purified by recrystallization from DMF to obtain white crystals of (I) (m.p. 447–449 K). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.56 (*s*, 8H), 2.72 (*s*, 16H), 3.17 (*s*, 16H), 6.83–7.28 (*m*, 20H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 49.5, 50.7, 56.1, 62.8, 115.7, 119.4, 129.0, 151.3; IR (KBr) ν: 2954, 2794, 1600, 1502, 1457, 1382, 1236, 1010, 925, 754, 687 cm^{-1}.

Crystal data

$C_{45}H_{60}N_8$	$Z = 2$
$M_r = 713.01$	$D_x = 1.165$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 11.712$ (4) Å	Cell parameters from 976 reflections
$b = 12.708$ (4) Å	$\theta = 2.8$–$22.3°$
$c = 15.354$ (5) Å	$\mu = 0.07$ mm^{-1}
$\alpha = 80.869$ (4)°	$T = 293$ (2) K
$\beta = 68.461$ (4)°	Prism, colourless
$\gamma = 73.281$ (4)°	0.15 × 0.10 × 0.05 mm
$V = 2032.2$ (12) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	4019 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$
φ and ω scans	$\theta_{max} = 25.0°$
Absorption correction: none	$h = -11 \rightarrow 13$
8572 measured reflections	$k = -15 \rightarrow 13$
7066 independent reflections	$l = -15 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.3853P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.061$	
$wR(F^2) = 0.156$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
7066 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
478 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (°).

C1—C2—N1	115.1 (2)	C4—N2—C5	110.8 (2)
C1—C13—N3	116.5 (2)	C15—N4—C16	111.0 (2)
C1—C24—N5	114.1 (2)	C26—N6—C27	110.7 (2)
C1—C35—N7	115.2 (2)	C37—N8—C38	112.2 (2)
C1—C35—N7—C39	136.2 (2)	C1—C24—N5···N6	169.8 (4)
C1—C35—N7—C36	−104.0 (3)	C1—C35—N7···N8	−167.1 (3)
C1—C24—N5—C28	107.7 (3)	C4···C5···C8···C12	150.4 (2)
C1—C24—N5—C25	−128.7 (2)	C4···C5···C12···C8	−22.92 (17)
C1—C13—N3—C17	−137.9 (2)	C15···C16···C19···C23	−167.0 (2)
C1—C13—N3—C14	102.1 (3)	C15···C16···C23···C19	10.03 (16)
C1—C2—N1—C6	130.1 (2)	C26···C27···C30···C34	−142.28 (18)
C1—C2—N1—C3	−109.0 (2)	C26···C27···C34···C30	29.15 (14)
C1—C2—N1···N2	−172.5 (3)	C37···C38···C41···C45	160.69 (19)
C1—C13—N3···N4	165.7 (3)	C37···C38···C45···C41	−14.84 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
C34—H34···C21^{ii}	0.93	2.63	3.471 (6)	151
C39—H39A···C40^{iii}	0.97	2.69	3.622 (4)	162

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

H atoms were included using a riding model, with C—H = 0.95 Å and $U_{iso} = 1.2U_{eq}$ of the parent C atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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