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Anomeric effect for a 2,5,7-triazabicyclo[2.2.1]heptane derivative

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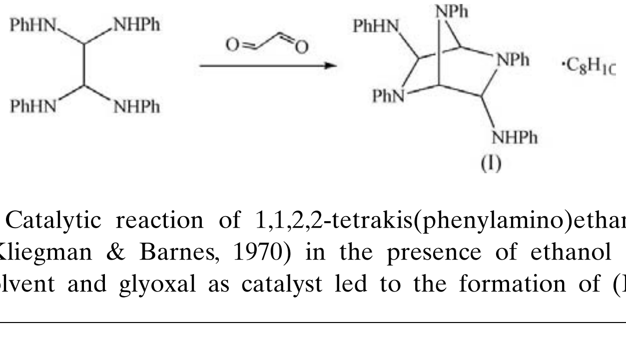
A new member of the polyazapolycyclic family of compounds, namely N^3,N^6,2,5,7-pentaphenyl-2,5,7-triazabicyclo[2.2.1]heptane-3,6-diamine xylene solvate, $C_{34}H_{31}N_5\cdot C_8H_{10}$, was synthesized for the first time and the crystal structure is reported. There are no hydrogen bonds joining the molecules. All four chiral C atoms have the same absolute configurations. With regard to the four N—C—N groups, anomeric effects are observed to cause a reduction of C—N bond length and N-atom pyramidality.

Comment

Polyazapolycyclics (Nielsen *et al.*, 1979), an important precursor for the syntheses of high-density and energetic compounds (Nielsen *et al.*, 1998), are constituted of saturated rings with multiple N atoms and are generally synthesized under catalytic reaction conditions. In norbornane skeletons, azanorbornane or azabicyclo[2.2.1]heptane (Archelas & Morin, 1984) and diazanorbornane derivatives (Alvaro *et al.*, 2007) have been synthesized and characterized so far, but triazanorbornane derivatives have seldom been reported (Nitravati & Sikhibhushan, 1939, 1941; Alphen, 1933). The syntheses and molecular structures of triazabicyclo[2.2.1]heptanes have been presented in a few papers without using X-ray crystal structure analysis (Potts & Husain, 1972; Potts *et al.*, 1974; Neunhoeffer & Fruhauf, 1969, 1970; Stanforth *et al.*, 2002). In order to reveal the structural features of this norbornane-like triazacyclo[2.2.1]heptane skeleton, the crystal structure of the title compound, (I), was carried out.



(I)

Catalytic reaction of 1,1,2,2-tetrakis(phenylamino)ethane (Kliegman & Barnes, 1970) in the presence of ethanol as solvent and glyoxal as catalyst led to the formation of (I), which is reported for the first time. Single crystals were formed by recrystallization from xylene solution.

There is one independent molecule and one xylene solvent molecule in the asymmetric unit. The crystal structure is racemic, so all *S*- and all *R*-configuration molecules are included. The molecular structure of (I) is shown in Fig. 1. The geometry is designated as a norbornane skeleton, which consists of a six-membered piperazine ring and an N atom bridging between the C1 and C4 positions. Despite the presence of two NH groups, *viz.* N3 and N6, and five N atoms carrying lone-pair electrons potentially available for hydrogen-bond formation, there are, in fact, no intra- or intermolecular N—H···N or C—H···N hydrogen bonds. As shown in the scheme, the skeleton has a good local twofold symmetry, namely through the N7 bridge and almost perpendicular to the least-squares plane of the piperazine ring. It is noteworthy that the symmetry involves not only the skeleton but also the peripheral phenyl groups, except for that attached to the bridging N7 atom.

The anomeric effect in N—C—N systems and its implications for structural stability, reactivity and conformational behavior have been studied extensively (Senderowitz *et al.*, 1992). The occurrence of anomeric effects in a system influences many structural and electronic properties. The general concept of the anomeric effect involves a stabilizing interaction between a lone pair on N and an antiperiplanar σ^* orbital of the adjacent C—N bond ($n_{\rm N} \rightarrow \sigma^*_{\rm C-N}$), which is best described as 'negative hyperconjugation' (Reed & Schleyer, 1988).

In (I), four unequal anomeric effects are observed in the N′—C—N″ fragments, and these effects are manifested by the bond distances and N-atom pyramidality. In the $n_{\rm N'} \rightarrow \sigma^*_{\rm C-N''}$ systems, the significance of the anomeric effect is indicated by the amount of geometrical deformation caused by the effect. Within the N′—C—N″ unit, the N′—C bond is shorter than

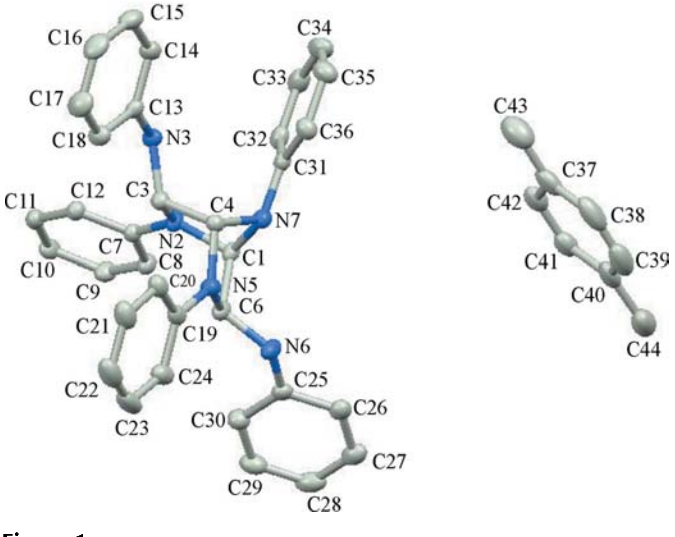


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. H atoms bound to C atoms have been omitted. Displacement ellipsoids are drawn at the 50% probability level.

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the C—N″ bond. On the other hand, the pyramidality of N′ (the sum of the three bond angles around N′) is larger than that of N″. These geometric parameters related to the anomeric effect are shown in Table 1. Among them, the $n_{N5} \rightarrow \sigma^*_{C4-N7}$ system shows a prominent anomeric interaction and the largest bond-length difference [0.022 (2) Å], which is comparable to that reported for an analogous molecule (*ca* 0.01 Å; Senderowitz *et al.*, 1992).

However, the pyramidality differences in the N′—C—N″ units are not so indicative. The differences within the N5—C4—N7 and N7—C1—N2 systems are 23.4 (2) and 24.0 (2)°, respectively, and these are much larger than those for the N6—C6—N5 and N3—C3—N2 groups (2.7 and 4.4°, respectively). Moreover, the calculated pyramidalities for atoms N3 and N6 are not accurate because they include H atoms, whose positions were determined from a difference Fourier synthesis. Thus, the anomeric effect on the pyramidality is not clear in this molecule. It could be that the anomeric effect on the angle is buried among the steric effects caused by the crowding of the substituent groups, which would strongly affect the molecular structure.

Reflecting the local twofold symmetry, the corresponding N atoms in this symmetric skeleton (N2 and N5, and N3 and N6) have nearly the same pyramidality. The pyramidality angle of N7 [330.08 (17)°] is rather small, and the attached phenyl group is inclined from the local twofold axis in the direction of atoms N2, C3 and N3. Corresponding to this inclination, the C32—C31—N7 angle [122.94 (12)°] is distorted from the ideal value of 120°, which is attributable to the short contact between the voluminous phenyl ring and the skeleton. For example, the H32···H1 separation (atom C1 is the bridgehead) is only 2.281 Å. The same distortion is seen in another norbornane derivative [122.5 (4)°; Watson *et al.*, 1990] for the phenyl ring on the bridging N7 atom.

The angle at the bridging N atom, C1—N7—C4, is 93.97 (10)°. Although this bridge angle is comparable to those reported for norbornane and diazanorbornane (Davies *et al.*, 1992), it still indicates the presence of ring strain.

Experimental

Aqueous glyoxal (40% *w*/*w*, 1.15 ml, 0.01 mol) was added dropwise to a stirred solution of 1,1,2,2-tetrakis(phenylamino)ethane (3.94 g, 0.01 mol) in ethanol (50 ml). The solution temperature was kept at 273 K during the reaction. The mixture was put aside for 24 h at a temperature of 278–283 K. The resulting white precipitate was filtered off and washed with cold ethanol to give 2.53 g (55% yield) of (I) (m.p. 428 K). ^{1}H NMR (CDCl$_3$): δ_H 6.59–7.30 (*m*, 25H, CH$_{Ar}$), 5.69 (*s*, 2H, CH), 4.93 (*d*, 2H, *J* = 10 Hz, CH), 3.69 (*d*, 2H, *J* = 10 Hz, NH). Addition of D$_2$O to the NMR sample caused the NH signals to disappeared and the CH doublet quickly converted to a singlet. ^{13}C NMR (CDCl$_3$): δ_C 144.8, 144.2, 143.6, 129.3, 129.7, 122.1, 119.4, 118.7, 117.4, 113.7, 113.2 (CH$_{Ar}$), 76.0 (CH), 72.4 (CH).

Table 1
Geometric parameters relating anomeric interactions in the N′—C—N″ unit of (I) (Å, °).

Pyr denotes the pyramidality of the N atoms (the sum of the three angles around the N atom; s.u. values are estimated from the sum of s.u. values when they are available).

Parameters	$n_{N3} \rightarrow \sigma^*_{C3-N2}$	$n_{N7} \rightarrow \sigma^*_{C1-N2}$	$n_{N5} \rightarrow \sigma^*_{C4-N7}$	$n_{N6} \rightarrow \sigma^*_{C6-N5}$
N′—C	1.4474 (16)	1.4562 (16)	1.4581 (16)	1.4431 (17)
C—N″	1.4590 (16)	1.4722 (16)	1.4798 (16)	1.4612 (17)
N′—C—N″	110.26 (10)	103.06 (10)	99.61 (10)	109.73 (11)
Pyr N′	349.7	330.08 (17)	353.50 (18)	350.8
Pyr N″	354.12 (17)	354.12 (17)	330.08 (17)	353.50 (18)

Crystal data

$C_{34}H_{31}N_5 \cdot C_8H_{10}$
M_r = 615.80
Monoclinic, $P2_1/n$
a = 12.9790 (8) Å
b = 18.0643 (11) Å
c = 14.1838 (8) Å
β = 90.682 (2)°
V = 3325.2 (3) Å^3
Z = 4
Mo *K*α radiation
μ = 0.07 mm^{-1}
T = 100 K
0.21 × 0.18 × 0.05 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
37513 measured reflections
9690 independent reflections
6265 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.125
S = 1.01
9690 reflections
426 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

The H atoms of the NH groups were located in a difference Fourier map and were refined using a rigid model with U_{iso}(H) values fixed at $1.2U_{eq}$(N). The C-bound H atoms were placed in calculated positions and refined using a riding model with fixed displacement parameters [U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(C) for CH and CH$_3$ H atoms, respectively].

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3005). Services for accessing these data are described at the back of the journal.

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