Crystal Structure of $N^1,N^{14}$-Dibenzy1-$N^5,N^{10},N^{18},N^{23}$-tetra(toluene-$p$-sulfonyl)-1,5,10,14,18,23-hexaazacyclohexacosane:
New 26-Membered Hexaaza-Coronand

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The title compound (Fig. 1) is a synthetic intermediate designed to be a cyclic dimer of a natural acyclic polyamine, spermine, for a better understanding of its function in a cell system. Details concerning the synthesis of the molecule will be reported elsewhere. In order to elucidate the ring conformation, the crystal structure was determined by an X-ray analysis.

Single crystals were grown in a chloroform-methanol solution. A colorless transparent needle having a size of 0.18×0.23×0.70 mm was used for the data collection with graphite-monochromatized Mo-Kα radiation ($\lambda=0.71073$). No decay or absorption corrections were applied ($\mu=0.196 \text{ mm}^{-1}$). Table 1 summarizes the crystal and experimental data. The hydrogen atoms were located by successive difference Fourier synthesis. The structure was refined with anisotropic temperature factors for all non-H atoms and isotropic ones for the H atoms. The atomic parameters are given in Table 2. The molecular structure and bond parameters are shown in Figs. 2 and 3, respectively.

The molecule has a center of symmetry. The ring conformation is a considerably deformed rectangular
shape. The bulkiness of rigid tosyl groups at N(5) and N(5)' is mainly responsible for the deformation. The two substituents cover both sides of the 26-membered ring plane. The N(1), N(5), and N(10) nitrogen atoms are 0.409(1), -0.799(2), and 0.377(1) Å apart, respectively, from the least-squares plane of six nitrogen atoms in the ring.

The torsion angles in the short side, consisting of N(10), C(11), C(12) and C(13), take two gauches (g) with the same signs and one trans (t). The bond sequence between the two edges, from C(9) to N(1)', is described as ...g,g,t,g... or ...-g,-g,t,-g,-g... . A similar situation was found for the rectangular form of a cyclic 34-membered alkane: cyclotetracontane \((\text{CH}_2)_{34}\). This macrocyclic ring consists of two parallel zigzag chains of 15 atoms, linked at each end by two closure atoms with a g,g,t conformation.

Dale has suggested, based on the conformation of macrocyclic hydrocarbons with the general formula \((\text{CH}_2)_{4n+2}\), the following: i) the most compact conformation could be favored over those with a large hole in the interior, ii) two parallel straight chains linked by two bridges of minimum length fill the space most effectively, and iii) if a CH\(_2\) group is replaced by NH or O without a bulky substituent the skeleton type may also remain the same. If the present compound had no N-substituent, the structure might have been similar to \((\text{CH}_2)_{26}\).

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References


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