

2,9,10-Trioxa-6-aza-1-silatricyclo[4,3,3,0^{1,6}]dodecane. A Novel Heterocyclic System: Synthesis, X-ray Crystal and Molecular Structure of the 1-Chloromethyl Derivative

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Summary A representative of the novel heterocyclic system, 1-chloromethyl-2,9,10-trioxa-6-aza-silatricyclo[4,3,3,0^{1,6}]dodecane, has been synthesized and the geometry and molecular packing in the crystal have been determined by X-ray analysis; the presence of apparently shortened interatomic distances in a rather rigid 6-membered heterocycle has been established, as well as the disorder of the 5-membered heterocycles.

THE first derivative of the novel heterocyclic system, 1-chloromethyl-2,9,10-trioxa-6-aza-1-silatricyclo[4,3,3,0^{1,6}]dodecane (I) was synthesized in 60% yield by heating 3-hydroxypropylbis(2-hydroxyethyl)amine with chloro-

methyltriethoxysilane in the presence of sodium ethoxide, m.p. 120 °C (from n-heptane). Previous attempts to synthesize this ring system, which is a silatrane analogue in which one of the characteristic 5-membered heterocycles has been extended to a 6-membered one, had failed.¹

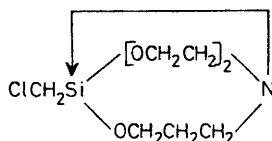
Continuing our X-ray investigation of silatranes² we have determined the molecular and crystal structure of compound (I).

Crystal data: C₈H₁₆ClNO₃Si, *M* = 237.8, monoclinic, *a* = 7.120(1), *b* = 12.033(3), *c* = 13.054(4) Å, β = 99.13°, *Z* = 4, space group *P*2₁/*c*, *D*_m = 1.43, *D*_c = 1.43 g cm⁻³.

Intensities of 1189 independent non-zero reflections were obtained by the θ-2θ scanning method on a Syntex automatic P2₁ diffractometer using monochromatic Cu radiation, θ_{max} = 50°.

The structure was solved by direct methods using the program MULTAN³ and refined by least-squares taking into account the hydrogen atom co-ordinates and using 1022 reflections with *I* > 1.96 σ(*I*) to an *R* value of 0.068 (anisotropic approximation).

The molecular geometry is shown in the Figure. The 6-membered heterocycle, with apparently considerably



(I)

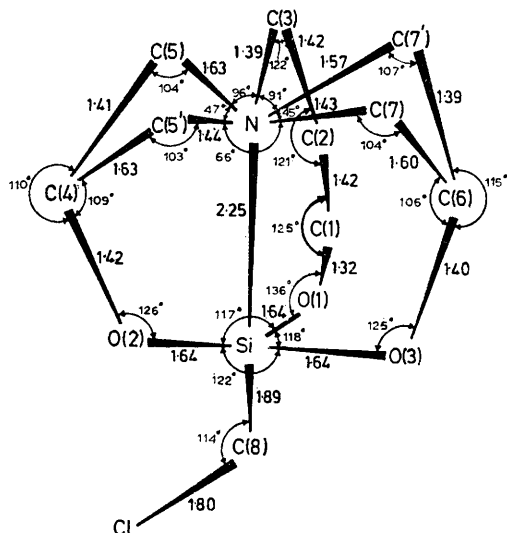


FIGURE. Bond distances (in Å) and angles for compound (I).

shorter interatomic distances than normally found, is in an approximately semi-chair conformation, the line joining O(1), C(1), and C(2) being bent by 22° away from the ring.

The sum of the inner bond angles within this ring is 714° , which is only 6° less than the sum of a planar hexagon.

The 5-membered rings are disordered as in the structure of the α -form of 1-phenylsilatrane⁴ owing to disorder of the two carbon atoms directly connected to the nitrogen atom, which is confirmed by the bifurcation (at a distance of *ca.* 1.2 Å) of the electron density distribution peaks. In contrast, the C(3) atom of the 6-membered heterocycle shows only one maximum on the electron density map which indicates the rigidity of this heterocycle.

The co-ordination polyhedron around silicon is a distorted trigonal bipyramid, the silicon atom being displaced by 0.167 Å towards C(8) out of the plane of the equatorial O(1), O(2), and O(3) atoms. The length of the donor-acceptor bond, N-Si, is 2.25 Å, the three Si-O bonds showing approximately three-fold symmetry about the axis defined by this bond, with O-Si-O angles of 117, 118, and 120° . The dihedral angle between the mean plane of the 6-membered heterocycle and that defined by Cl, C(8), and Si, is 1.11° . The mean value of the bond angle N-Si-O in the 5-membered heterocycles is 81.5° and in the 6-membered one is 90° .

The intermolecular distances in the crystal are not less than the sum of the van der Waals' radii of the atoms.

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