

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

VI: *cis*-2-Et-(C₄H₇S=N-Ts), (struct. anal. is in progress)

VII: *trans*-2-Et-(C₄H₇S=N-Ts), VIII: *cis*-2-*t*-Bu(C₄H₇S=N-Ts)

In IV the tosylimino group assumes *axial* position and the conformation of the five-membered ring is near to a half-chair form with a C₂ symmetry axis bisecting the C(2) atom. [The puckering parameters (Cremer & Pople, J. Amer. Chem. Soc., 97, 1354 (1975) are listed below.]

As it has been shown by g.e.d., the thiolane ring with bivalent sulfur atom exhibits much greater puckering amplitude and a twofold axis bisecting the S(1) atom [Náhlavská, Náhlavský & Seip, Acta Chem. Scand. (1969) 23, 3534.] In the *cis* compound VIII the NTs substituent retains its *axial* position, while the 2-*t*-Bu group is *equatorial*, the twofold axis of the distorted half-chair form shifted toward the C(4) atom. In the *trans* isomers V and VII the NTs group can be found in *pseudo-axial* position, while the 2-Me and 2-Et groups with similar torsion angles assume *pseudo-equatorial* orientations. In both cases the thiolane rings appear in similar envelope conformations with a mirror (C_s) plane approximately bisecting the C(4) atom, and only their puckering amplitudes differ considerably.

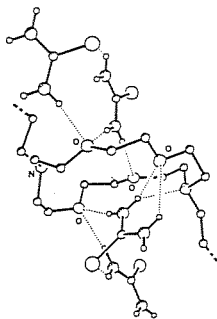
	q(Å)	φ(°)	C _s	C ₂
IV	0.41	40.7	-	C(2)
V	0.45	100.3	C(4)	-
VII	0.37	104.6	C(4)	-
VIII	0.46	199.0	-	C(4)
thiolane (g.e.d.)	0.47	270.0	-	S(1)

The bonding of "cyclic N-tosyl sulfilimines" investigated agree well with the corresponding parameters of other sulfilimines as summarized recently by Kálmán, Párkányi & Kucsman (Acta Cryst. (1980) B38, 1440. Apart from III, the amount of rotations about S(VI)-N and S(VI)-C_{ar} bonds fall in the range expected on the basis of a conformational study of N-substituted arylsulfonamides [Kálmán, Czugler & Argay, Acta Cryst. (1981) B37, 886].

09.2-25 A 14:1 ADDUCT BETWEEN THIOUREA AND AN N,N'-DISUBSTITUTED MACROCYCLIC AMINO-POLYETHER. By G. Weber and G.M. Sheldrick, Institut für Anorganische Chemie der Universität, D-3400 Göttingen, Fed. Rep. of Germany

In all complexes between (thio)urea and annular oligoethers so far studied by X-ray methods (Harkema, van Hummel, Daasvatn & Reinhoudt, Chem. Commun. (1981), 368; Weber, Acta Cryst. (1982) B38, 2712, and J. Incl. Phen., in press), one (thio)urea molecule is attached at either side of the ligand, thus giving rise to 2:1 core adducts.

The present compound N,N'-didecyl-1,7,10,16-tetraoxa-4,13-diaza-cyclo-octadecane.14 thiourea (Pc, a = 28.425(9), b = 16.326(6), c = 9.802(4) Å, β = 94.20(4)°, R = 0.069) is the first example of a (thio)urea/crown ether complex containing a 4:1 core adduct (see Fig.). Its irregular pattern of hydrogen bonds is associated with an irregular conformation of the macrocycle. The remaining ten thiourea molecules are involved in an intricate system of bridging N-H...S linkages.

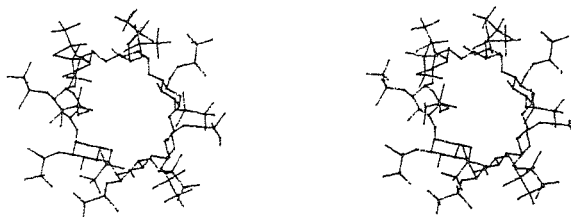


The 4:1 core adduct

09.2-26 THE CRYSTAL STRUCTURE OF per-2,6-O-*t*-BUTYL-DIMETHYL-SILYL-β-CYCLODEXTRIN. Heinz Pöhlmann, Emil Eckle, Gottfried Geiger and John J. Stezowski, Institut für Organische Chemie, Biochemie und Isotopenforschung der Universität Stuttgart, Pfaffenwaldring 55, 7000 Stuttgart 80, FRG.

Because of the potential that selectively modified cyclodextrins would be suitable as medium molecular weight enzyme models, there has been great interest in their chemical substitution. The redundancy in their chemical structure introduces considerable complication into the preparation of pure derivatives. Wife et al.² have characterized the chemistry of a series of cyclodextrin silyl adducts (*t*-butyl-dimethyl substituents) that provide the potential for the preparation of monosubstituted β-cyclodextrins with the substituent on a secondary hydroxyl group. The selectivity of their procedure is very likely the result of steric interactions between the silyl-substituents. We report the crystal structure of one of what we expect to be a small series of derivatives that we plan to study in an effort to elucidate the steric principals involved.

The title compound crystallizes with space group symmetry P2₁ with a = 15.206(4), b = 34.236(6), c = 18.622(5) and β = 98.27(2) for a crystal at ~120 K; Z = 2 for C₁₂₆H₂₆₆O₃₅Si₁₄ (no clearly defineable solvent has yet been found). The present R value is 0.137 for 10530 contributing data.



A stereoscopic projection of per-2,6-O-*t*-butyl-dimethyl-silyl-β-cyclodextrin.

¹R. L. Wife, D. E. Reed and H. C. Volger in "Proceedings of the First International Symposium on Cyclodextrins, J. Szejtli (Ed) Akademiai Kiado, Budapest, 1982 pp 289-300.

²R. L. Wife, D. E. Reed, D. P. Leworthy, D. M. Barnett, P. D. Regan and H. C. Volger, *ibid.* pp 301-325.