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Peter C. Junk[a]; Jerry L. Atwood[a]
[a] Department of Chemistry, University of Alabama, Tuscaloosa, AL

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On the crystal structure of hexathia-18-crown-6

PETER C. JUNK and JERRY L. ATWOOD*

Department of Chemistry, University of Alabama, Tuscaloosa, AL35487

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Hexathia-18-crown-6 (18-S-6) exhibits a cyclic structure with all the heteroatoms being directed out of the macrocyclic ring (exodentate conformation). In a previous report on a different crystalline modification of this compound, the crown contains two C-S linkages which are *anti*, rather than all such linkages being *gauche*. The title compound crystallizes in the monoclinic space group $P2_1/c$ with a = 5.833(1), b = 11.148(1), c = 13.191(1) Å, $\beta = 93.29(1)°$, and $D_c = 1.404\,g\,cm^{-3}$ for Z = 2. Refinement based on 983 observed reflections led to R = 0.058.

INTRODUCTION

Crown ether-like molecules of the type $-(-CH_2-CH_2-E-)_n-$ have varied use in coordination chemistry.[1] The importance of conformational effects is particularly important in the coordinating and chelating power of crown ethers. Upon metal ion complexation, those containing O- or N-atoms normally have the heteroatoms pointing into the crown (endodentate conformation).[2] Prior structural work has shown that thio crown ethers typically contain inside-out conformations where the heteroatoms are directed out of the macrocyclic ring (exodentate conformation).[3-5] In this contribution we show that a new crystal form of hexathia-18-crown-6 (18-S-6) does not violate this rule, but exists in a different conformation from that previously found which contained two endodentate S-atoms.[6] The new structure displays two *anti*-placements around the C-S linkage in contrast to the established preference for gauche arrangements. C-O linkages usually adopt the *anti* conformation.[6]

As part of our study of liquid clathrates based on crown ether/oxonium ion chemistry,[7-9] we have investigated the reaction of 18-S-6 with HCl(g) in moist toluene. Liquid clathrate formation does not occur, but large, colorless crystals of the title compound were obtained. In Table 1 the crystal data for the literature structure of 18-S-6 is compared to that of the new structure. Bond lengths are typical for both structures, wth C-S distances of 1.800(6)–1.822(6) Å and C-C distances of 1.501(8)–1.507(9) Å, but differences may be seen in a comparison of the torsion angles around the C-S linkages (see Table 2).

Previous work has highlighted the preference, almost without exception,[6] for a gauche arrangement around the C-S linkages of a variety of thio crown ethers. This study shows that 18-S-6 contains two C-C-S-C linkages that are *anti* and two S-C-C-S ones that are *gauche*. This violates the previously established guidelines, which are based on arguments that the repulsive *gauche* effect along S-C-C-S linkages inhibits this arrangement, and therefore forces the C-C-S-C linkages to adopt this conformation, since for the

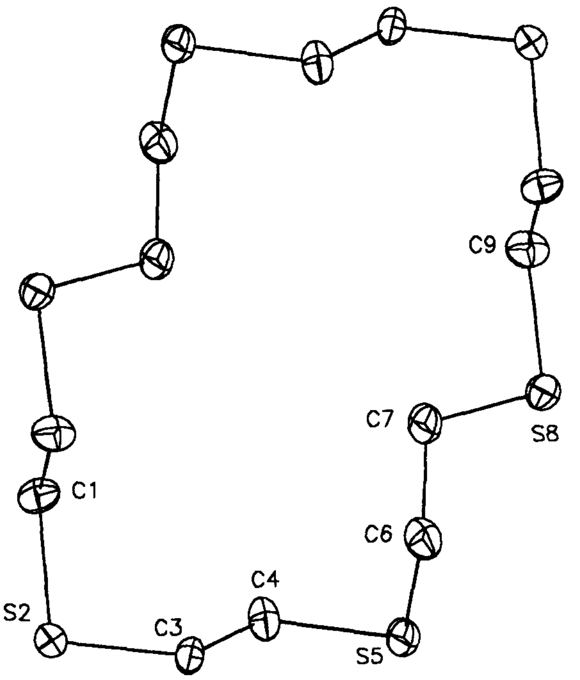

Figure 1 Structure of hexathia-18-crown-6 in the exodentate conformation.

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* To whom correspondence should be addressed.

Table 1 Comparison of crystal data and summary of data collection for hexathia-18-crown-6

Compound	*This work*	*Cooper et al.*[6]
Space group	$P2_1/c$	Fdd2
a, Å	5.833(1)	20.466(1)
b, Å	11.148(1)	33.222(3)
c, Å	13.191(1)	5.213(4)
α, deg	90	90
β, deg	93.29(1)	90
γ, deg	90	90
V, $Å^3$	856.4	3544.6
molecules/unit cell	2	8
D_c, g cm^{-3} (calc)	1.404	1.35
radiation	MoKα	MoKα
no. reflcns collcd	1228	1616
no. of obsd reflcns	983	834
no. of params varied	82	81
R	0.058	0.067
R_w	0.060	0.069

Table 2 Torsion angles along C-C and C-S linkages

Angle	*This work*	*Cooper et al.*[6]
C1-S2-C3-C4	−63.8°	−116.5°
S2-C3-C4-S5	−178.3	179.2
C3-C4-S5-C6	−69.3	73.3
C4-S5-C6-C7	−72.5	84.2
S5-C6-C7-S8	−71.7	−174.6
C6-C7-S8-C9	−173.5	−78.3

compound to be cyclic there must be some *gauche* conformers. There is little or no repulsion between protons on the 1,4-positions in the C-C-S-C linkage which has been used to explain why this linkage is able to adopt the *gauche* conformation.

The question of the reason for two different crystallographic forms of 18-S-6 remains. It is attractive to ascribe this result to the crystallization in the present study from a highly ionic medium. However, any verification must await further study. It is also likely that energetic differences between conformers of 18-S-6 would be small. The related 16-S-4 is known to crystallize in three different morphologies, highlighting the small energetic differences in these compounds.[10] This work does indicate, however, the danger in reaching conclusions about the prediction of conformation in compounds with low energetic barriers between conformers.

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