interactions significantly shorter than van der Waals distances. The result is essentially an independent ion-pair group with the conformation determined mainly by intramolecular forces and packing.

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S-tert-Butylthiouronium Perchlorate–1,4,7,10,13,16-Hexaoxacyclooctadecane (2:1)

BY J. W. H. M. UITERWIJK, S. HARKEMA AND G. J. VAN HUMMEL

Chemical Physics Laboratory, Twente University of Technology, PO Box 217, 7500 AE Enschede, The Netherlands

AND J. GEEVERS AND D. N. REINHOUDT

Organic Chemistry Laboratory, Twente University of Technology, PO Box 217, 7500 AE Enschede, The Netherlands

Abstract. $C_{12}H_{24}O_6.2C_5H_{13}N_2S^+.2ClO_4^-$, $M_r = 729.70$, triclinic, $P\bar{1}$, $a = 10.905$ (3), $b = 10.722$ (4), $c = 9.329$ (5) Å, $\alpha = 111.41$ (3), $\beta = 98.47$ (2), $\gamma = 110.40$ (2)°, $V = 903.48$ Å³, $Z = 1$, $D_c = 1.34$ g cm⁻³, $\mu = 0.36$ cm⁻¹. The crystal structure was solved by direct methods. All H atoms have been located. $R_w = 4.6\%$ for 2524 observed reflexions. The macrocyclic ring has approximate D_{3d} symmetry. One of the NH_2 groups is hydrogen-bonded to the ring, the other NH_2 group forms hydrogen bonds to two perchlorate ions.

Introduction. As shown already by Pedersen (1971) macrocyclic polyethers are capable of forming stable crystalline complexes with organic and inorganic molecules and ions. As part of a project aimed at the synthesis of macrocyclic receptors for small urea-like molecules, we report here the crystal structure of a (2:1) complex of S-tert-butylthiouronium perchlorate

with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) (BTPC).

BTPC (2:1) was prepared by extraction of an aqueous solution of S-tert-butylthiouronium chloride (4 mmol) and lithium perchlorate (4 mmol) with a solution of 18-crown-6 (1 mmol) in chloroform. The compound was precipitated by addition of diethyl ether and recrystallized from ethanol/petroleum ether.

A BTPC (1:1) complex can be obtained in a similar way by changing the ratio of the above mentioned compounds to 4:1:4. Attempts to solve the crystal structure of the (1:1) complex were hampered by disorder in one of the two macrocyclic rings in the crystal structure at 150 K.

Intensities for BTPC (2:1) were measured at room temperature with a Philips PW 1100 diffractometer (Mo $K\alpha$ radiation, graphite monochromator). Reflexions up to $\theta = 25°$ were measured in the $\theta/2\theta$ scan

mode. The number of reflexions measured was 3383, of which 2524 independent reflexions had $I > \sigma(I)$ and these were used in the solution and refinement of the structure. The structure was solved by MULTAN (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares with ORFLS (Busing, Martin & Levy, 1962). The weight for each reflexion was taken to be $w = [\sigma(F_o) + 0 \cdot 01|F_o|]^{-2}$ where $\sigma(F_o)$ is the e.s.d. of the structure factor derived from counting statistics. Scattering factors were taken from International Tables for X-ray Crystallography (1974). For H the scattering factors of Stewart, Davidson & Simpson (1965) were used. All H atoms were found in a difference Fourier synthesis. The final values of R and R_w were 4·8% and 4·6% respectively (total number of parameters refined: 300; scale factor, isotropic extinction parameter, position parameters, anisotropic thermal parameters for non-H atoms, isotropic thermal parameters for H).* The asymmetric part of the unit cell contains one S-tert-butylthiouronium perchlorate molecule and one half of the 18-crown-6 ring. The other half is generated by a centre of symmetry.

Discussion. Final atomic positional parameters are given in Table 1. The numbering of the atoms is

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* Lists of structure factors, anisotropic thermal parameters for the non-H atoms, positional and isotropic thermal parameters for the H atoms and complete lists of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36725 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
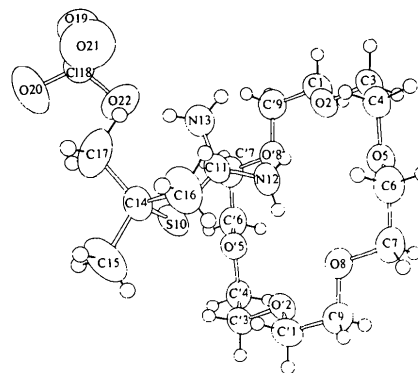

Fig. 1. Atomic numbering in BTPC. Primed atoms are related to the corresponding unprimed atoms by a centre of symmetry (the centrosymmetrically related S-tert-butylthiouronium perchlorate is not shown).
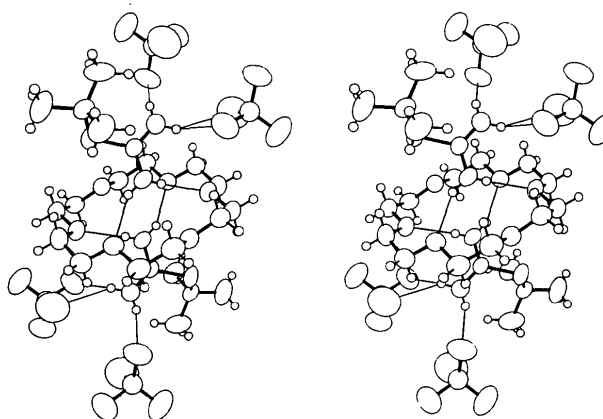

Fig. 2. Stereoscopic view of BTPC, showing the arrangement of hydrogen bonds (thin lines).

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for non-H atoms*

	x	y	z	U_{eq}* (Å²)
C(1)	195 (4)	2350 (5)	4038 (4)	71 (2)
O(2)	269 (2)	2531 (2)	2613 (2)	61 (1)
C(3)	−511 (4)	3282 (4)	2301 (4)	66 (2)
C(4)	−405 (4)	3415 (3)	796 (4)	65 (2)
O(5)	−1008 (2)	1965 (2)	−530 (2)	58 (1)
C(6)	−936 (4)	1997 (4)	−2019 (4)	68 (2)
C(7)	−1523 (4)	450 (4)	−3333 (4)	68 (2)
O(8)	−626 (2)	−211 (2)	−3123 (2)	61 (1)
C(9)	−1105 (4)	−1678 (4)	−4382 (4)	68 (2)
S(10)	3451 (1)	659 (1)	−501 (1)	73 (1)
C(11)	2731 (3)	1679 (3)	724 (3)	55 (1)
N(12)	1433 (3)	1315 (4)	156 (4)	66 (2)
N(13)	3476 (4)	2759 (4)	2153 (4)	83 (2)
C(14)	4658 (3)	2018 (3)	−1019 (4)	62 (2)
C(15)	5027 (7)	1015 (6)	−2344 (7)	111 (3)
C(16)	3923 (6)	2747 (7)	−1666 (7)	93 (3)
C(17)	5916 (4)	3160 (6)	415 (7)	105 (3)
Cl(18)	6630 (1)	3624 (1)	5348 (1)	70 (1)
O(19)	6921 (3)	4360 (3)	7047 (3)	116 (2)
O(20)	7616 (3)	3111 (4)	5078 (5)	164 (3)
O(21)	6666 (4)	4687 (4)	4783 (4)	153 (2)
O(22)	5288 (3)	2445 (3)	4664 (3)	117 (2)

* Defined according to Willis & Pryor (1975).

according to Fig. 1. Bond lengths and angles are shown in Table 2. Torsion angles in the macrocyclic ring are in Table 3. A stereoscopic view (Johnson, 1965) of the molecular complex is given in Fig. 2. From this figure it can be seen that one of the two NH_2 groups is engaged in hydrogen bonding to two O atoms of the ring. The $N \cdots O$ distances and $N-H \cdots O$ angles for these bonds are: $N(12) \cdots O(2)$ 2·898 (5), $N(12) \cdots O(8)$ 2·972 (5) Å; $N(12)-H(12B) \cdots O(2)$ 171 (6), $N(12)-H(12A) \cdots O(8)$ 150 (6)°. Contrary to the results for the related compound urea–18-crown-6 (5 : 1) (Harkema, van Hummel, Daasvatn & Reinhoudt, 1981), the hydrogen bonding is not to neighbouring O atoms in the macrocyclic ring, but to next nearest neighbours. The hydrogen-bonding scheme also differs from the one found in the complex of 18-crown-6 with benzenesulphonamide (1:2) (Knöchel, Kopf, Oehler & Rudolph, 1978). In that complex the NH_2 group is hydrogen-bonded to two opposite O atoms of the centrosymmetric ring. The second NH_2 group is hydrogen-bonded to two perchlorate ions by

Table 2. *Bond distances (Å) and angles (°)*

C(1)—O(2)	1·422 (5)		S(10)—C(14)	1·858 (3)
O(2)—C(3)	1·425 (5)		C(11)—N(12)	1·296 (4)
C(3)—C(4)	1·479 (5)		C(11)—N(13)	1·295 (5)
C(4)—O(5)	1·422 (4)		C(14)—C(15)	1·525 (7)
O(5)—C(6)	1·415 (4)		C(14)—C(16)	1·502 (8)
C(6)—C(7)	1·486 (6)		C(14)—C(17)	1·504 (6)
C(7)—O(8)	1·423 (5)		Cl(18)—O(19)	1·415 (3)
O(8)—C(9)	1·423 (5)		Cl(18)—O(20)	1·383 (4)
C(9)—C'(1)	1·477 (7)		Cl(18)—O(21)	1·411 (4)
S(10)—C(11)	1·752 (3)		Cl(18)—O(22)	1·412 (3)
C'(9)—C(1)—O(2)	110·0 (3)		S(10)—C(14)—C(15)	101·9 (3)
C(1)—O(2)—C(3)	112·0 (3)		S(10)—C(14)—C(16)	109·8 (4)
O(2)—C(3)—C(4)	109·2 (3)		S(10)—C(14)—C(17)	111·6 (3)
C(3)—C(4)—O(5)	109·0 (3)		C(15)—C(14)—C(16)	111·0 (5)
C(4)—O(5)—C(6)	112·5 (3)		C(15)—C(14)—C(17)	111·1 (5)
O(5)—C(6)—C(7)	109·6 (3)		C(16)—C(14)—C(17)	111·1 (5)
C(6)—C(7)—O(8)	109·7 (3)		O(19)—Cl(18)—O(20)	107·1 (3)
C(7)—O(8)—C(9)	112·4 (3)		O(19)—Cl(18)—O(21)	106·1 (2)
O(8)—C(9)—C'(1)	110·1 (4)		O(19)—Cl(18)—O(22)	108·8 (2)
C(11)—S(10)—C(14)	104·0 (2)		O(20)—Cl(18)—O(21)	113·9 (3)
S(10)—C(11)—N(12)	117·9 (3)		O(20)—Cl(18)—O(22)	111·7 (3)
S(10)—C(11)—N(13)	120·8 (3)		O(21)—Cl(18)—O(22)	109·1 (2)
N(12)—C(11)—N(13)	121·3 (4)			

Table 3. *Torsion angles in the macrocyclic ring (°)*

C'(9)—C(1)—O(2)—C(3)	−175·5 (3)		C(1)—O(2)—C(3)—C(4)	179·3 (3)
O(2)—C(3)—C(4)—O(5)	63·4 (4)		C(3)—C(4)—O(5)—C(6)	−179·5 (3)
C(4)—O(5)—C(6)—C(7)	177·3 (3)		O(5)—C(6)—C(7)—O(8)	70·2 (4)
C(6)—C(7)—O(8)—C(9)	−177·7 (3)		C(7)—O(8)—C(9)—C'(1)	175·7 (3)
O(8)—C(9)—C'(1)—O'(2)	64·7 (4)			

two hydrogen bonds, one of which is bifurcated. The dimensions of the hydrogen bonds are: N(13)···O''(19) 3·104 (5), N(13)···O''(21) 3·225 (5), N(13)···O(22) 3·031 (5) Å; N(13)—H(13B)···O''(19) 139 (6), N(13)—H(13B)···O''(21) 147 (6), N(13)—H(13A)···O(22) 139 (6)° (the doubly primed atoms are related to the original ones by the transformation $1 - x$, $1 - y$, $1 - z$). From Table 3 it can be seen that the sequence of torsion angles (O—C, C—C, C—O) in the independent part of the ring is $ag^+aag^-aag^+a$, giving rise to an almost ideal 'crown' conformation with approximate D_{3d} symmetry. In this conformation the O atoms lie alternately above and

below the mean plane of the ring, making hydrogen bonding to O atoms, which are next nearest neighbours, possible. The same conformation of the ring has been found in most crystal structures of complexes of 18-crown-6 (Goldberg, 1980). The mean values of the C—C bond length [1·481 (3) Å], the C—O bond length [1·422 (2) Å], the O—C—C bond angle [109·6 (2)°] and C—O—C bond angle [112·3 (2)°] compare well with the average values for a number of different 18-crown-6 structures given by Goldberg (1980) (1·495, 1·42 Å, 109·5 and 112·6° respectively).

The shortening of the C—C bond [single paraffinic C—C bond: 1·541 (3) Å (Kennard, 1962)] is largely, but not completely, due to the neglect of the effect of thermal motion on bond lengths (Maverick, Seiler, Schweizer & Dunitz, 1980).

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