

Fig. 1. The conformation of 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-2-butanone.

61.8 (9)° to the C(31), C(4), O(1), C(5) grouping (Fig. 1). The resulting arrangement leads to the close approach of the *ortho*-H, H(72), to the triazolyl atoms N(1) and N(2), such that both N...H distances lie within the sum of the van der Waals radii of N and H (Fig. 1). There is an accompanying distortion of the exocyclic angles at C(71), with the O(2)–C(71)–C(72) bond angle of 124.2 (7)° being considerably larger than the value found for O(2)–C(71)–C(76) [114.7 (6)°].

The triazolyl ring is planar, with C(5) lying only 0.061 (7) Å from the mean plane (Table 4). Although the C(1)–N(1) and C(2)–N(3) distances are somewhat larger than those found for C(1)–N(3) and C(2)–N(2), in keeping with the uncharged canonical valence form, all four C–N distances are shorter than a normal single bond (1.47 Å). The N(1)–N(2) bond is also shorter than a normal single bond (1.45 Å) and

the three atoms bonded to N(1) are almost coplanar with it. Taken together these data indicate extensive delocalization within the heterocyclic ring. The most noteworthy feature of the heterocyclic ring is the asymmetry of the exocyclic angles at N(1) [119.5, 130.7 (6)°]. We have observed a similar pattern in related triazole systems (Anderson, Branch, Mann, Nowell & Walker, 1971, unpublished results) and it appears to be a function of the triazolyl ring itself rather than the influence of any inter- or intramolecular interactions.

The C(31), C(4), C(5), O(2), C(71) backbone is rather compressed resulting in the main from the orientation of the *tert*-butyl group, the C(31)–C(4)–C(5)–O(2) torsion angle being only 100.1 (7)°.

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Structure of the Benzylammonium Perchlorate Complex of 3,6,9,12,15,18,21,26-Octaoxabicyclo[21.2.1]hexacosal(25),23-diene-2,22-dione

BY N. K. DALLEY AND J. S. BRADSHAW

Department of Chemistry and Contribution 261 of the Thermochemical Institute, Brigham Young University, Provo, Utah 84602, USA

AND S. B. LARSON AND S. H. SIMONSEN

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, USA

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Abstract. C₁₈H₂₆O₁₀·C₇H₁₀N⁺·ClO₄⁻, *M_r* = 610.01, *F*(000) = 1288, monoclinic, *P*2₁/*c*, *a* = 11.710 (2), *b* = 15.087 (5), *c* = 17.574 (3) Å, β = 105.68 (2)° at *T* = 173 K, *Z* = 4, *V* = 2989.2 (13) Å³, *D_x* = 1.355, *D_m* (at

295 K) = 1.334 Mg m⁻³ (measured by flotation in CCl₄/*n*-hexane), colorless, m.p. 366.5–368 K. *R* = 0.040, *R_w* = 0.037 for 3645 reflections. The macrocyclic ligand is hydrogen-bonded to the organic cation

and is wrapped about it such that the benzene ring of the cation is sandwiched between the furan ring and the portion of the polyether which is opposite the furan ring. The cation interacts with the perchlorate ion *via* two hydrogen bonds.

Introduction. The title compound was synthesized by Bradshaw, Baxter, Lamb, Izatt & Christensen (1981) as part of a study to synthesize macrocyclic compounds which would complex metal and organic cations. Polyether ligands and their derivatives have the ability to complex cations and transport them across membranes. Striking differences between the 1H NMR spectra of the title compound and the uncomplexed macrocyclic ligand prompted this structural study.

Table 1. Fractional atomic coordinates ($\times 10^5$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for the non-hydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	x	y	z	U_{eq}
Cl	42023 (4)	28191 (3)	26149 (3)	350 (2)
O(1Cl)	35042 (13)	20792 (9)	26948 (10)	539 (6)
O(2Cl)	54253 (12)	25499 (13)	27980 (8)	590 (6)
O(3Cl)	40998 (18)	34629 (13)	31834 (14)	970 (10)
O(4Cl)	38396 (17)	31296 (15)	18320 (12)	868 (9)
C(1)	102031 (17)	15398 (14)	36091 (13)	434 (8)
C(2)	96465 (19)	7319 (15)	38091 (12)	430 (8)
O(3)	84654 (12)	8012 (9)	36302 (8)	419 (5)
C(4)	78431 (21)	158 (15)	37946 (17)	474 (9)
C(5)	66120 (21)	3035 (16)	37782 (15)	476 (9)
O(6)	66423 (12)	7391 (10)	45003 (9)	461 (6)
C(7)	55262 (20)	10763 (16)	45251 (15)	481 (9)
C(8)	55747 (23)	13946 (15)	53303 (15)	560 (10)
O(9)	63328 (13)	21401 (9)	55267 (8)	449 (5)
C(10)	64371 (27)	24511 (19)	63144 (14)	603 (11)
C(11)	72395 (24)	32221 (19)	64890 (13)	553 (10)
O(12)	67236 (12)	39279 (10)	59782 (7)	412 (5)
C(13)	74218 (22)	47106 (19)	61191 (15)	571 (10)
C(14)	68312 (25)	53956 (17)	55511 (15)	550 (10)
O(15)	67593 (11)	51061 (8)	47667 (8)	382 (5)
C(16)	62799 (20)	57664 (14)	41881 (14)	445 (9)
C(17)	60547 (19)	53714 (15)	33911 (14)	446 (8)
O(18)	71480 (12)	50755 (9)	32687 (8)	408 (5)
C(19)	70406 (24)	48586 (16)	24711 (13)	509 (9)
C(20)	82320 (28)	47095 (16)	23558 (16)	589 (11)
O(21)	86999 (13)	38643 (9)	27067 (8)	462 (6)
C(22)	98612 (22)	37432 (16)	28116 (13)	511 (9)
C(23)	102954 (19)	28802 (15)	31519 (13)	481 (9)
C(24)	114264 (21)	25794 (19)	34104 (16)	617 (11)
C(25)	113599 (21)	17249 (19)	36994 (17)	604 (11)
O(26)	95206 (11)	22457 (9)	32676 (8)	394 (5)
O(27)	102141 (14)	976 (11)	40999 (10)	579 (6)
O(28)	105208 (16)	42851 (12)	26548 (10)	704 (7)
N(29)	67060 (15)	32943 (12)	43546 (11)	282 (6)
C(30)	77322 (17)	28758 (15)	41451 (11)	318 (7)
C(31)	88328 (15)	29106 (12)	48285 (10)	275 (6)
C(32)	95096 (18)	36771 (14)	49753 (13)	392 (7)
C(33)	105119 (19)	37189 (16)	56065 (15)	500 (9)
C(34)	108558 (20)	30007 (15)	60893 (14)	459 (8)
C(35)	102036 (18)	22291 (15)	59443 (12)	397 (8)
C(36)	91886 (17)	21842 (13)	53159 (11)	322 (7)

A suitable single crystal ($0.45 \times 0.45 \times 0.50$ mm) was mounted on a Syntex $P2_1$ diffractometer. Lattice parameters (listed in the *Abstract*) were determined by a least-squares refinement of the 2θ values of 45 reflections ($25^\circ < 2\theta < 30^\circ$) measured at 173 K. Intensity data were collected at 173 K by an ω -scan procedure ($\Delta\omega = 1.5^\circ$, scan rate = $2-6^\circ \text{ min}^{-1}$) using $Mo K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) to a 2θ maximum of 50° . Systematically extinct reflections ($0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$) identified the space group as $P2_1/c$. Intensities for 5483 unique reflections were measured, of which 1600 were considered unobserved ($I < 3\sigma_I$) and 231 were systematically extinct. Backgrounds were measured 1° on either side of the peak with the total background time equal to the scan time. Four standard reflections (002, 040, 200, 111) were measured every 96 reflections to monitor instrument and crystal stability. The data were corrected for Lorentz and polarization effects, absorption and crystal decomposition. The correction coefficients for the latter two ranged from 1.075 to 1.102 and from 0.994 to 1.000 respectively.

Use of *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed positions for all of the non-hydrogen atoms except two O atoms of the ClO_4^- . Fourier methods revealed the other atoms. Positional parameters for all atoms, anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for H atoms were refined by a full-matrix least-squares procedure. Also, the extinction parameter ($E = 4.7861 \times 10^{-7}$) was refined. The final R was 0.040 and $R_w = 0.037$. The weights were set equal to $(\sigma_F + |\Delta F|/3.4)^{-2}$. Seven reflections which had unsymmetrical backgrounds were not included in the final refinement. The goodness-of-fit term was equal to 1.008 with $m = 3645$ and $n = 515$. Final positional and equivalent isotropic thermal parameters are listed in Table 1.* Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965). Those for all other atoms and for the anomalous-dispersion terms for Cl were obtained from *International Tables for X-ray Crystallography* (1974). The final difference map had no significant spurious peaks, the largest peak being 0.49 e \AA^{-3} .

Discussion. The conformation of the complex and the anion, and the atom labels are shown in Figs. 1 and 2. It can be seen in these figures that the organic cation is sandwiched by the ligand and interacts with the ligand

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances, bond angles, torsion angles, H-bond details and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36669 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

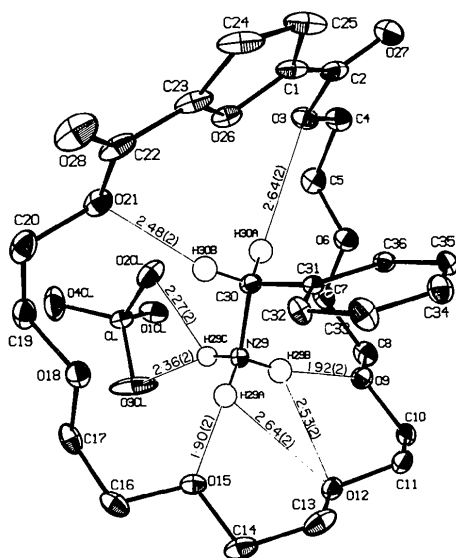


Fig. 1. A view of the title compound giving atomic labels and illustrating the role of the hydrogen bonds of the organic cation to the ligand and anion (Johnson, 1965).

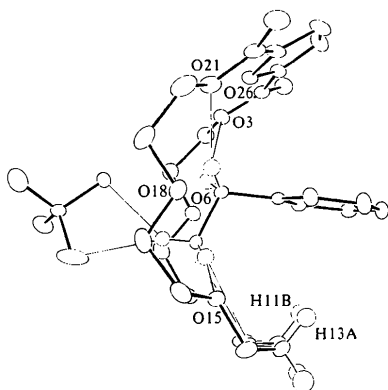


Fig. 2. A view of the title compound rotated about 90° from that of Fig. 1. The figure illustrates how the cation is sandwiched by the macrocyclic ligand (Johnson, 1965).

and the anion through a system of hydrogen bonds. The benzene ring of the cation is nearly parallel to the polyether fragment C(10) to C(14) and makes a dihedral angle of about 37° with the furan ring.

The upfield shift of part of the methylene signal in the ¹H NMR spectra for the complex but not for the uncomplexed molecule suggests that the phenyl ring of the cation lies directly over the H atoms of the C atoms [C(11) and C(13)] farthest from the furan ring (Bradshaw, Baxter, Lamb, Izatt & Christensen, 1981). The NMR spectra also suggest that the furan oxygen [O(26)] does not participate in hydrogen bonding with the organic cation. The results of the single-crystal X-ray study verify both of these proposed structural features. As shown in Fig. 2, H(11B) and H(13A) are

directly beneath the phenyl ring of the cation at distances of 2.92 (2) and 3.01 (2) Å, respectively, from its plane. Also, the furan O is not involved in hydrogen bonding as there are no O(26)–cation H distances of less than 2.94 Å.

Using the criterion that a hydrogen bond exists when the H...O distance is less than 2.4 Å [0.2 Å less than the sum of the van der Waals radii of H and O (Hamilton & Ibers, 1968)] it can be seen that the three H atoms of the ammonium group are involved in hydrogen bonds. H(29A) and H(29B) form rather strong hydrogen bonds with O(15) and O(9), respectively. Both H atoms also interact very weakly with O(12). H(29C) forms two rather weak hydrogen bonds with O(2Cl) and O(3Cl) of the ClO₄⁻. In addition to these interactions, H(30A) and H(30B) approach O(3) and O(21) of the ligand. The H...O interatomic distances are about equal to the sum of their van der Waals radii (2.6 Å). These interactions appear to have some role in folding the furan portion of the ligand over towards the cation. Similar C–H...O interactions are reported in the structure of bis(dimethyl sulfone)–18-crown-6 (Bandy, Truter & Vögtle, 1981). The result of these interactions is a guest cation with H bonds directed through the opening of the ligand to the ClO₄⁻.

The structural features of the macrocyclic ligand are similar to those reported for other polycyclic ether diester molecules (Dalley & Larson, 1979*a,b*). The average ether C–C and C–O bond lengths, 1.481 (9) and 1.422 (7) Å respectively, and C–O–C and C–C–O bond angles, 112.6 (4) and 109.5 (6)° respectively, are normal for such molecules. The geometry of the ester groups and the furan ring is as expected. The torsion angles about C–C bonds are close to 60°, *gauche*, and those about C–O bonds are near 180°, *anti*. Similar torsion-angle values are found in the rather planar symmetrically shaped 18-crown-6 cation complexes (Dunitz, Dobler, Seiler & Phizackerley, 1974). While the ligand is far from planar, the large ring has sufficient flexibility so that these values are obtained. Least-squares-planes data for four fragments of the ligand and for the phenyl ring of the cation have been deposited.

The average Cl–O bond distance in the ClO₄⁻ is 1.420 (14) Å. This agrees with the expected distance of 1.42–1.43 Å found for uncorrected bond lengths in ClO₄⁻ groups (Maverick, Grossenbacher & Trueblood, 1979). The involvement of O(2Cl) and O(3Cl) in hydrogen bonding is suggested by the deviation of the O(2Cl)–Cl–O(3Cl) angle [113.5 (1)°] from a normal tetrahedral value. The average of the other O–Cl–O angles is 108.6 (8)°. No attempt was made to correct ClO₄⁻ parameters for the large thermal motion observed because the main interest of the study was the conformation of the complex.

While there are several H...H intramolecular contacts of about 2.5 Å there are no intermolecular

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-Butylthiuronium 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

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Abstract. $C_{12}H_{24}O_6 \cdot 2C_5H_{13}N_2S^+ \cdot 2ClO_4^-$, $M_r = 729.70$, triclinic, $P1$, $a = 10.905$ (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-butylthiuronium 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-butylthiuronium 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 $\theta = 25^\circ$ were measured in the $\theta/2\theta$ scan