

X-Ray Crystal Structure of a 1,4-Dihydropyridine-Crown Ether-Sodium Perchlorate Complex Crystallized with a Molecule of Acetone

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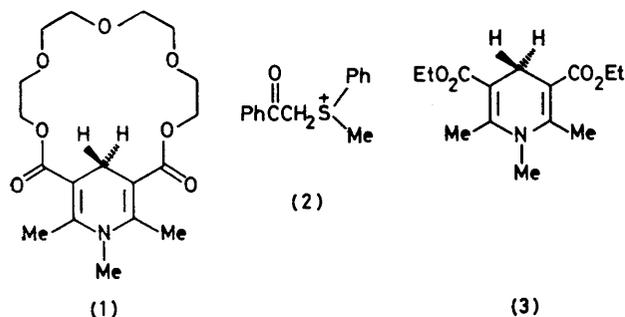
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Summary The crown ether-1,4-dihydropyridine (1) complexes with NaClO₄ and forms crystals containing a molecule of acetone co-ordinated to Na⁺; an X-ray structural determination reveals the dihydropyridine ring to be in a pronounced boat conformation and tilted relative to the polyethyleneglycol chain.

CROWN ETHERS containing¹ or attached to² 1,4-dihydropyridine rings have been synthesized. Such compounds exhibit enhanced rates of hydride donation to appropriate (positively charged) substrates that can complex with the crown ether portion of the molecule. Further synthetic development of the structures of such compounds opens the way to other types of reactions, an example being the asymmetric reduction of carbonyl compounds by chiral crown ether-1,4-dihydropyridines.³

We showed that (1) reduces the methylphenacylphenylsulphonium salt (2) to acetophenone and phenyl methyl sulphide 2.7×10^3 times (at 70 °C) faster than the non-crown compound (3).¹ This effect was attributed to complexation of the salt (2) by (1) leading to an enhanced



rate of hydride transfer within the resulting complex. A strong argument for this contention was that Na⁺ ions, which should fit very well in the cavity of (1), strongly inhibit the rate of hydride transfer to (2). We have now purified the complex of (1) with NaClO₄, which crystallizes with a molecule of acetone. The X-ray structural determination of the resulting complex, (1)-NaClO₄·Me₂CO (4), reveals several notable points concerning the shape of the molecule and the reasons for its lack of reactivity.

Suitable crystals of (4) were mounted on capillaries in a Tixco-cap in order to avoid decomposition. The

† X-RAY system (1978), Dutch version (1978) of the X-RAY 76 system, Tech. Report TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

‡ In the refinement 3133 reflections with $|F_0| > 3\sigma_c(F_0)$ were used, where $\sigma(F_0)$ is the standard deviation in $|F_0|$ due to counting statistics.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

crystals are monoclinic, space group $P2_1/c$, $a = 7.769(2)$, $b = 14.957(3)$, $c = 22.660(3)$ Å, $\beta = 97.56(4)$, $Z = 4$, $U = 2610.2$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å. Using a Nonius CAD3 diffractometer with Zr-filtered Mo radiation and the θ - 2θ scanning method, 3133 independent reflections were measured with $I > 0$. The structure was solved by direct methods with the program MULTAN of the X-RAY† system. 549 reflections with $E > 1.6$ were used in refinement. Anisotropic refinement of the non-hydrogen atoms was carried out by the full-matrix least-squares technique; function Q minimized $Q = \sum |F_0| - k^{-1} |F_c|$.² Scattering factors for non-hydrogen atoms were taken from Cromer and Mann.⁴ The index R dropped to 0.103 for the 3133 reflections. Further refinement with 3036 reflections led to a final R of 0.089. An ORTEP projection of the molecule is shown in the Figure which also gives some bond lengths and angles.§

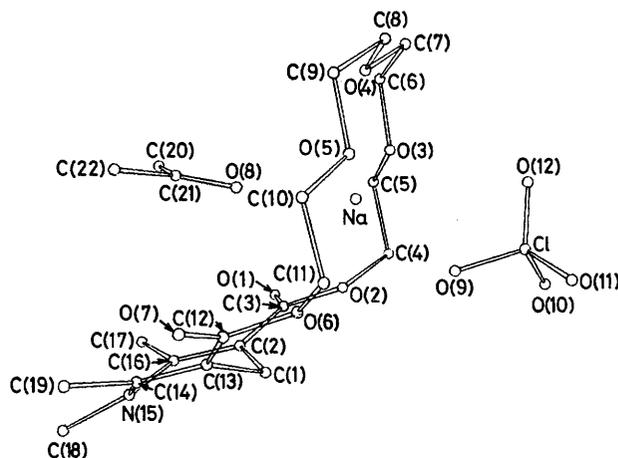


FIGURE. An ORTEP projection of the complex (1)-NaClO₄·Me₂CO (4). Torsion angles (°): C(3)-O(2)-C(4)-C(5), 83.5; C(9)-O(5)-C(10)-C(11), 2.7; C(1), C(2), C(16) with C(3), O(1), O(2), 8.4; C(4)-C(5)-O(3)-C(6), 1.3; C(10)-C(11)-O(6)-C(12), 83.4; C(1), C(13), C(14) with C(12), O(6), O(7), 11.9; C(5)-O(3)-C(6)-C(7), 1.6; O(2)-C(4)-C(5)-O(3), 71.2; C(6)-C(7)-O(4)-C(8), 0.5; O(3)-C(6)-C(7)-O(4), 62.6; C(7)-O(4)-C(8)-C(9), 0.1; O(4)-C(8)-C(9)-O(5), 60.5; C(8)-C(9)-O(5)-C(10), 4.0; O(5)-C(10)-C(11)-O(6), 68.9. Bond distances (Å): C(1)-C(2), 1.48(1); C(2)-C(16), 1.36(1); C(16)-N(15), 1.38(1); N(15)-C(18), 1.50(1); C(16)-C(17), 1.50(1); C(2)-C(3), 1.46(1); C(3)-O(1), 1.19(1); C(3)-O(2), 1.35(1). Boat angles of dihydropyridine ring (°): C(1), C(2), C(13) with C(2), C(13), C(14), C(16), 36.0(8); N(15), C(14), C(16) with C(2), C(13), C(14), C(16), 27.7(8).

This is, to the best of our knowledge, the first structural determination of a crown ether containing a dihydropyridine ring. Particularly striking features are the pronounced boat form of the dihydropyridine ring, which is in contrast to the reported planarity of the dihydropyridine rings of nicotinamide derivatives.⁵ The dihydropyridine ring is also tilted relative to the plane of the tetraethyleneglycol chain, making an angle of 55°. The polyethyleneglycol cavity, which has normal bond angles and lengths,⁶ has a radius of 2.5 Å and the sodium ion fits in the centre.

The sodium ion, the perchlorate ion with one oxygen pointed toward Na⁺, and the oxygen atom of acetone which

lies *ca.* 3.6 Å above the dihydropyridine ring, are nearly co-linear. The acetone oxygen is 2.25(1) Å from Na⁺ and the closest perchlorate oxygen is 2.31(1) Å removed and on the other side of the cavity.

As the figure clearly shows, the potential hydride donating site of the dihydropyridine (C-1) is too far removed [4.04(1) Å] and incorrectly oriented, at least in the crystal, to interact with C-21 of acetone.

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