

A NESTING CONFORMATION OF THE 5'-BROMO-1',3'-XYLYL-18-CROWN-5·*TERT*-BUTYLAMMONIUM
HEXAFLUOROPHOSPHATE COMPLEX; THE CORRELATION OF THE STRUCTURES OF CROWN ETHER
COMPLEXES IN THE SOLID STATE AND IN SOLUTION.

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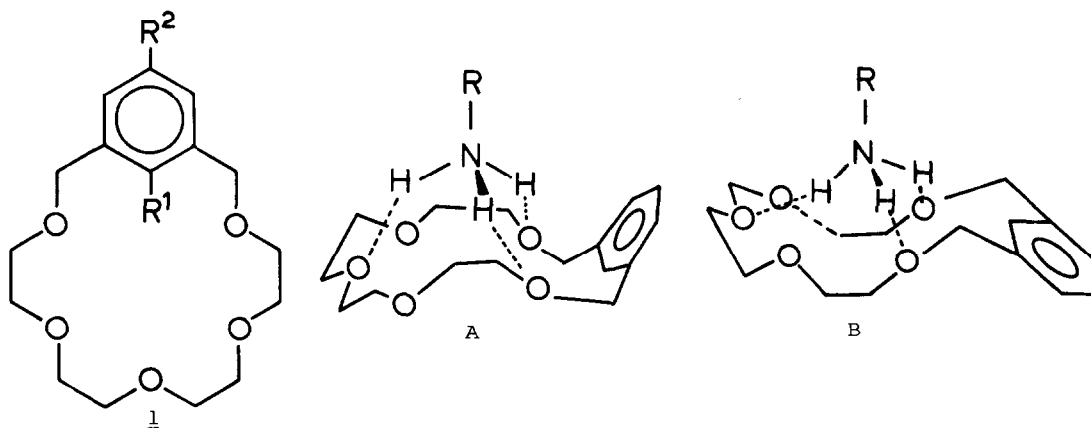
Abstract: Single-crystal X-ray analysis of the 5'-bromo-1',3'-xylyl-18-crown-5·*tert*-butylammonium hexafluorophosphate complex shows that the complex is of the "nesting" type in which the cation and the aryl group are on the same face of the macroring and that the macroring has a $(ag^+a)(ag^-a)(ag^+a)(ag^-a)(ag^+a)(ag^-a)$ conformation.

Among crown ethers with aryl-sub-units, 1',3'-xylyl crown ethers (1) have been studied in great detail. Our continuing interest in these crown ethers stems from structural factors¹: their preparation by the reaction of 1,3-bis(halomethyl)benzenes with polyethylene glycols² allows for 1',3' substitution in the aromatic ring and their ¹H NMR spectra are very useful for studying the thermodynamic and the kinetic stabilities of the crown ether complexes with ammonium salts⁴. Firstly the benzylic protons of the crown ethers 1 become non-equivalent when the exchange of salt and crown ether becomes slow on the ¹H NMR time scale and the rate of exchange can be determined from line-broadening studies⁴. Secondly the aryl group in 1 shields the alkyl protons in alkylammonium complexes of 1 and the up-field shift of these protons can be used for determining (relative) association constants under conditions of fast exchange^{4,5}.

By comparison of the thermodynamic stabilities of different complexes it was found that the replacement of a CH₂CH₂-O-CH₂CH₂-group in 18-crown-6 by a 1',3'-xylyl moiety decreases the thermodynamic stability by a factor of 10² in K_a-values^{4,5,7}. Cram *et al.*⁶ estimated this decrease in stability to be 3.19 kcal.mol⁻¹ at 24°C and attributed this difference to the loss of one favourable N⁺...O interaction in 1·(CH₃)₃CNH₃⁺X⁻ complexes compared with the corresponding 18-crown-6 complex. Because of the up-field chemical shift of the *tert*-butyl-protons in the ¹H NMR spectra of the complexes of 1 in chloroform solution Cram *et al.*⁷ proposed a structure in which

the aryl group and the cation are on the same face of the macroring (nesting conformation, A). However, they also found that in the solid state the complex of *tert*-butylamine and 2'-carboxy-1',3'-xylyl-18-crown-5 (1, $R^1 = \text{COOH}$ and $R^2 = \text{H}$) has the other possible conformation in which the *tert*-butylammonium cation and the aryl group are on opposite sides of the macroring (perching conformation, B)^{8,9}.

This discrepancy between the structure in solution and the crystalline state, together with our own interest in the complexes of 1',3'-xylyl crown ethers, led us to investigate the structure of a *tert*-butylammonium salt with a 1',3'-xylyl-18-crown-5 that has no substituent at the intra-annular 2'-position.



- a; $R^1 = \text{H}$, $R^2 = \text{H}$
 b; $R^1 = \text{H}$, $R^2 = \text{Br}$
 c; $R^1 = \text{H}$, $R^2 = \text{COOCH}_3$
 d; $R^1 = \text{H}$, $R^2 = \text{CN}$

Complexes of 1a - 1d and *tert*-butylammonium hexafluorophosphate were prepared by equilibration of solutions of crown ether in chloroform with aqueous solutions of *tert*-butylammonium hexafluorophosphate. The association constants of the complexes were determined in dry deuteriochloroform by the previously reported "titration technique" with the 15-crown-5-*tert*-butylammonium hexafluorophosphate complex as the reference compound^{5,10}.

The thermodynamic stabilities show the same trend ($K_{1a} = 1.4 \times 10^5 > K_{1c} = 0.48 \times 10^5 > K_{1b} = 0.34 \times 10^5 > K_{1d} = 0.23 \times 10^5 \text{ l.mol}^{-1}$) in the hexafluorophosphate series as that reported by Cram *et al.*³ for the perchlorate, picrate and isothiocyanate salt complexes.

Addition of diethyl ether to a solution of the 5'-bromo-1',3'-xylyl-18-crown-5 (1b)-*tert*-butylammonium hexafluorophosphate complex yielded a crystalline complex. Whereas recrystallization from a mixture of pet. ether 60-80 and chloroform yielded the analytically pure complex m.p. 162-165°C¹¹, recrystallization from a mixture of chloroform and diethyl ether gave a crystalline complex solvated with CHCl_3 (1:1). The latter crystals were used for a single-crystal X-ray analysis.

Crystal data: $C_{21}H_{36}NO_5F_6P_1Cl_3Br$; triclinic; space group $P\bar{1}$, $a = 12.416(6)$, $b = 13.571(4)$, $c = 9.731(4)$ Å, $\alpha = 104.64(3)$, $\beta = 91.03(4)$, $\gamma = 89.21(4)^\circ$, $Z = 2$; $d_{\text{calc.}} 1.494 \text{ g.cm}^{-3}$. The crystal structure determination was based upon 1501 reflections with an intensity greater than three times the estimated standard deviation. Intensities were measured on an Enraf Nonius CAD4 diffractometer ($\text{MoK}\alpha$ radiation (0.7017 Å), graphite monochromator, $\theta - 2\theta$ scan mode, $0^\circ < 2\theta < 45^\circ$).

The structure was solved by direct methods and refined with anisotropic temperature factors for Br, Cl and P atoms and isotropic thermal parameters for the other atoms (hydrogen atoms were not located) to a final R factor of 11.2%¹². The structure is shown in fig. 1.

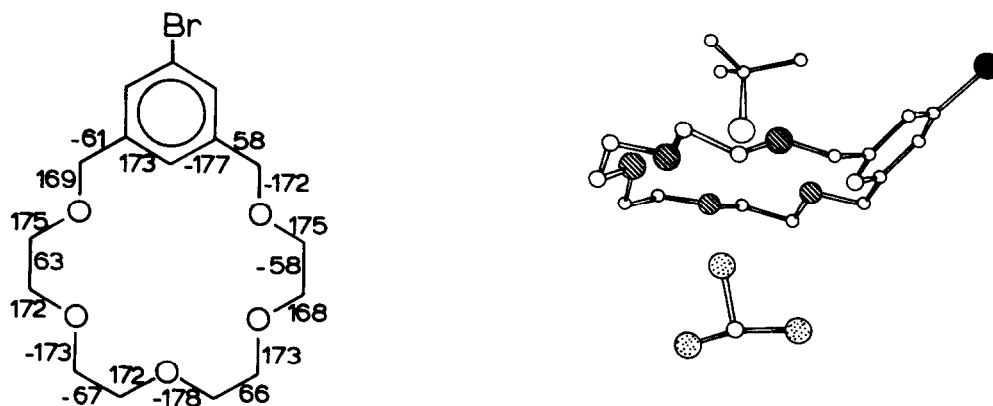


Fig. 1

The structure of the complex of **1b** in the crystalline state is clearly of the nesting type (A) with three oxygen atoms O(1), O(3) and O(5) in the ideal position to form hydrogen bonds with the *tert*-butylammonium ion. Surprisingly, there are no F-O distances of less than 4 Å in the crystal. Chloroform replaces the anion (PF_6^-) on the opposite face of the 1',3'-xylyl-18-crown-5 ring.

The close proximity of the *tert*-butyl hydrogen atoms to the aryl moiety observed in the crystal is reflected in the up-field shift of the absorption of the hydrogen atoms in the ^1H NMR spectrum of the complex, $\delta(\text{CH}_3)_3\text{C} : 0.93$ ppm, compared with the value of 1.36 ppm of the corresponding protons in the complex of 18-crown-6¹².

Stoddart *et al.*¹⁵ have emphasized that not only constitutional factors but also conformational factors in the macroring determine the thermodynamic stability of crown ether complexes. An analysis of the conformation of **1b**. $(\text{CH}_3)_3\text{CNH}_3^+\text{PF}_6^-$ indicates that the conformation hardly differs from the conformation of the macroring in the 18-crown-6.benzylammonium thiocyanate complex¹⁶ and monopyrido-18-crown-5. $(\text{CH}_3)_3\text{NH}_3^+\text{ClO}_4^-$ complex¹⁴ ($\text{ag}^+\text{a ag}^-\text{a ag}^+\text{a ag}^-\text{a ag}^+\text{a ag}^-\text{a}$, see fig.1). These complexes have a much higher thermodynamic stability ($K_a^{\text{CHCl}_3} \sim 10^7 \text{ l.mol}^{-1}$)^{1,4}.

Therefore our results support Cram's postulation that the decrease of complex stability, when one $\text{CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2$ unit in 18-crown-6 is replaced by a 1',3'-xylyl moiety, is due to the loss of one favourable $\text{N}^+\dots\text{O}$ interaction. The decrease is

not due to an unfavourable conformation of the macroring in the 1',3'-xylyl crown ether complexes compared with 18-crown-6 complexes.

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References and notes:

1. D.N. Reinhoudt and F. de Jong in "Progress in macrocyclic Chemistry", vol. 1 [Ed. R.M. Izatt and J.J. Christensen] Wiley, N.Y., 1979, p. 157.
2. R.T. Gray, D.N. Reinhoudt, C.J. Smit and I. Veenstra, Recl. Trav. Chim. Pays Bas 95, 258 (1976).
3. S.S. Moore, T.L. Tarnowski, M. Newcomb and D.J. Cram, J.Amer.Chem.Soc. 99,6398 (1977).
4. F. de Jong and D.N. Reinhoudt, Adv. in Phys. Org. Chem. 17, 279 (1980).
5. F. de Jong, D.N. Reinhoudt and C.J. Smit, Tetrahedron Lett. 1976, 137.
6. J.M. Timko, S.S. Moore, D.M. Walba, P.C. Hilberty and D.J. Cram, J. Amer. Chem Soc. 99, 4207 (1977).
7. D.J. Cram and J.M. Cram, Acc. Chem. Res. 11, 8 (1978).
8. M. Newcomb, S.S. Moore and D.J. Cram, J. Amer. Chem. Soc. 99, 6405 (1977).
9. I. Goldberg, Acta Cryst. B 31, 2592 (1975).
10. F. de Jong, D.N. Reinhoudt, C.J. Smit and R. Huis, Tetrahedron Lett. 1976, 4783.
11. Found: % C 40.45, % H 5.89, % N 2.22; Calc. for $C_{20}H_{35}NO_5BrPF_6$: % C 40.41, % H 5.94, % N 2.36.
12. All relevant crystallographic data are deposited at the Cambridge Crystallographic Data Centre (C.C.D.C.).
13. The chemical shift of the $(CH_3)_3C$ -protons in the monopyrido-18-crown-5 complex is 1.35 ppm. Trueblood et al.¹⁴ have shown that this complex has a perching conformation due to the participation of the pyridine nitrogen atom in the bonding.
14. E. Maverick, L. Grossenbacher and K.N. Trueblood, Acta Cryst. B 35, 2233 (1979).
15. A.C. Coxon, D.A. Laidler, R.B. Pettman and J.F. Stoddart, J. Amer. Chem. Soc. 100, 8260 (1978).
16. M.J. Bovill, D.J. Chadwick, I.O. Sutherland and D. Watkin, J.C.S. Perkin II, 1980, 1529.

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