

CRYSTAL STRUCTURES OF 1:1 COMPLEXES BETWEEN UREA AND TWO CROWN ETHER DERIVATIVES OF PHTHALIC ACID

Franco Benetollo,^a Gabriella Bombieri,^b and Mary R. Truter.^c

^aIstituto di Chimica e Tecnologia dei C.N.R., 35100 Padua, Italy

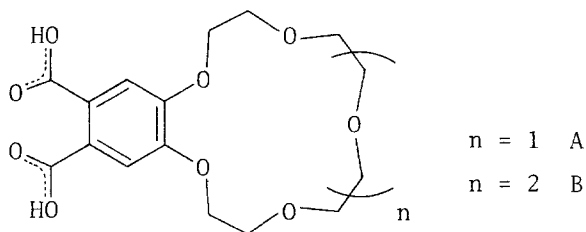
^bIstituto di Chimica Farmaceutica e Tossicologica, Università di Milano, 20131 Milan, Italy

^cDepartment of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

INTRODUCTION

Interest in urea inclusion compounds has changed in three decades from its properties as a host to its potential as a guest, more or less directly in the hope that improvement in artificial kidneys can be achieved. There is a fine balance between the tendency of urea molecules to hydrogen bond to each other and to form external bonds, as required for encapsulation. Further, it may form uronium salts with strong acids.

We have determined the crystal structures of 1:1 adducts of urea with the host molecules A and B based on phthalic acid as a functionalised crown ether.



CRYSTAL DATA

Urea-A, C₁₇H₂₄N₂O₁₀, M=416.4. Orthorhombic, Space group P2₁2₁2₁, a=8.750(2), b=10.844(3), c=21.215(3) Å. U=2013(1) Å³. λ=0.71069 Å. Z=4, D_c=1.37 g cm⁻³, R=0.083 for 599 observations (I≥3σ[I]).

Urea-B, $C_{19}H_{28}N_2O_{11}$, $M=460.4$. Triclinic, Space group $P\bar{1}$, $a=8.336(2)$, $b=11.009(2)$, $c=13.313(2)$ Å, $\alpha=105.55(3)$, $\beta=103.62(3)$, $\gamma=104.63(3)$ °. $U=1076.9(5)$ Å³. $Z=2$, $D_c=1.420$ g cm⁻³. $\lambda=0.71069$ Å. $R=0.072$ for 2105 observations ($I \geq 3\sigma[I]$).

RESULTS AND DISCUSSION

The location of all the hydrogen atoms in urea-B shows unequivocally that it is not a uronium salt. A similar conclusion can be drawn from the hydrogen-bonding pattern of urea-A. In both structures N-H...O bonds lie in the range 2.9 to 3.2 Å and O-H...O bonds in the range 2.4 to 2.6 Å.

The environment of the urea molecules.

In each structure the urea molecules have three double hydrogen-bonding interactions, donor bonds by the two 'endo' hydrogen atoms to ether oxygen atoms and two sets of N-H... donor and ...O receptor giving eight-membered rings.

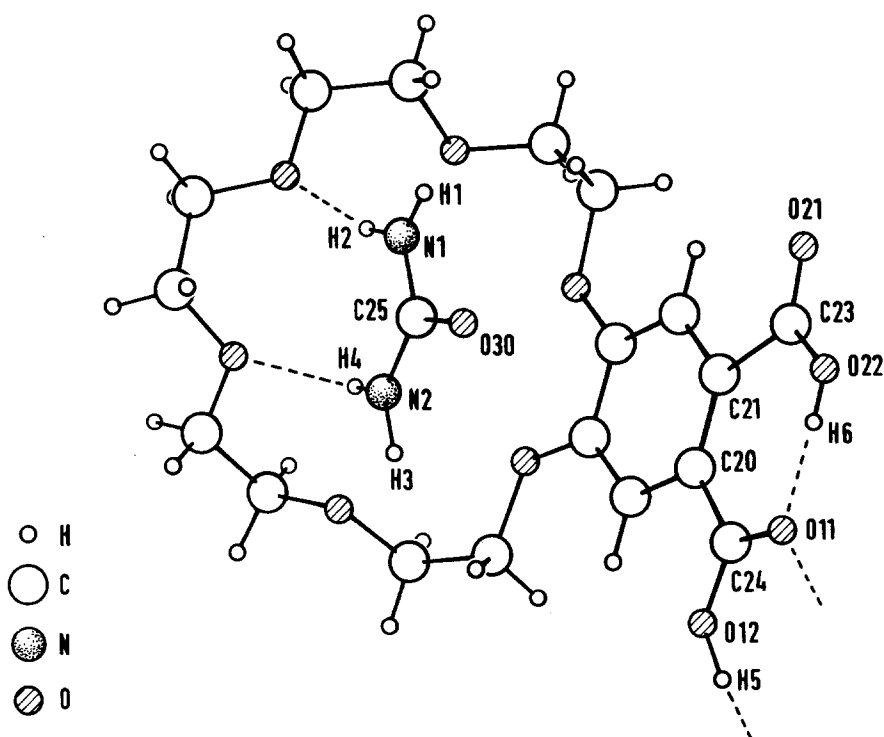


Fig. 1. One molecule of B and of urea with numbering of some atoms. Broken lines indicate hydrogen bonds.

In Fig. 1 the view is down the N-H...O hydrogen bonds from the 'endo' hydrogen atoms in urea to the ether oxygen atoms of one host molecule. Urea molecules are hydrogen bonded about centres of symmetry, N1-H1...O30' and O30...H1'-N1' to give dimers: each dimer is sandwiched between two host molecules. The third hydrogen bonding interaction holds the (urea-B)₂ dimers in a chain and is from N2-H3 to the carbonyl oxygen O11'' with an acceptor at O30 from O12''-H5''. Broken lines in Fig. 1 indicate the direction of the urea molecule in the next dimer in the chain.

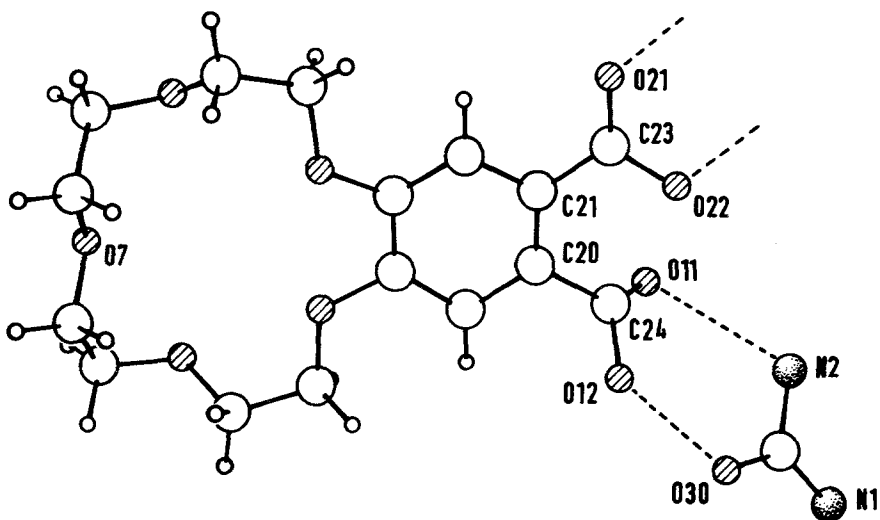


Fig. 2. One molecule of host A and of urea with the numbering of some atoms. Broken lines indicate hydrogen bonds.

In Fig. 2 one set of carboxylic acid-urea hydrogen bonding is shown. In this structure there is no urea-urea interaction, each molecule of urea is surrounded by three host molecules, one as shown, a second hydrogen bonded to the other O21,O22 carboxylic acid and the third by two 'endo' N-H bonds to ether oxygen atoms. These hydrogen bonding interactions hold the crystal in three dimensions but the crystal diffracts poorly.

Dimensions of the molecules.

In neither complex do the bond lengths and angles of the urea molecule differ significantly from those in urea itself.¹ The benzo-15-crown-5 entity of A is essentially the same as in the uncomplexed molecule or one of the very weakly bound ligands² in Na(benzo-15-crown-5)₂BPh₄⁻ while the benzo-18-crown-6 entity of B has the same bond lengths and angles but a subtly different conformation from those in comparable complexes.³

It is in the ortho-dicarboxylic acid entities that A and B differ most significantly. B shows a strong internal hydrogen bond, O22-H6...O11 2.462(8) Å such as is usually found in hydrogen phthalates, leading to near coplanarity of the carboxylic acids and the benzene ring. In A there is no internal hydrogen bond, the distance O22...O30' 2.55 Å corresponds to a hydrogen bond while O11 to O22 is 2.88(2) Å. The separation results from a twisting of the carboxylic acids from the plane of the benzene ring, the angle between them being 64°. This twisting allows the planes of the carboxylic acid groups to be at about 20° to those of the urea molecules to which they are hydrogen bonded.

Chirality?

Although the formulae of both urea and A suggest the possibility of planes of symmetry (for A through O7 and the centre of the C20-C21 bond) the inclusion compound crystallises in an enantiomeric space group. It is the twist of the carboxylic acids which gives 'handedness' to the molecules, all those in our crystal have the dihedral angle C23-C21-C20-C24 -10(3)° (or all may be +10°). In urea-B the corresponding angle is -0.3(0.9)° in half the molecules and +0.3° in the other half.

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REFERENCES

1. S. Swaminathan, B.M. Craven, and R.K. McMullan, *Acta Cryst.*, B40, 1984, 300.
2. J.D. Owen, *J. Chem. Soc. (Dalton)*, 1980, 1066.
3. J.A. Bandy and M.R. Truter, *Acta Cryst.*, B38, 1982, 2639.