

Crystal Structure of 1:1 Complexes Between Urea and
Two Crown Ether Derivatives of Phthalic Acid,
2,3,5,6,8,9,11,12,14,15-Decahydrobenzo[1,4,7,10,13,16]hexaoxacyclo-
octadecin-18,19-dicarboxylic Acid (I) and 2,3,5,6,8,9,11,12-Octahydro-
benzo[1,4,7,10,13]pentaoxacyclopentadecin-15,16-dicarboxylic Acid (II)

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The crystal structures of the title compounds have been determined by X-ray diffraction. Urea, **I** crystallizes in the triclinic $P\bar{1}$ space group with cell dimensions $a = 8.336(2)$, $b = 11.009(2)$, $c = 13.313(2)$ Å, $\alpha = 105.55(3)$, $\beta = 103.62(3)$, $\gamma = 104.63(3)^\circ$ and $Z = 2$ final R value 0.072 for 2105 observations. Urea, **II** crystallizes in the orthorhombic $P2_12_12_1$ space group with cell dimensions $a = 8.750(2)$, $b = 10.844(3)$ and $c = 21.215(3)$ Å and $Z = 4$, final R value 0.083 for 599 observations. All the hydrogen atoms were located in the complex urea, **I**; urea molecules form hydrogen bonded dimers about centers of symmetry, these dimers are sandwiched between macrocyclic rings forming one simple and one bifurcated hydrogen bond from the "endo" hydrogen atoms to the ether oxygen atoms. These units are held by hydrogen bonding between the urea molecules and carboxylic acids in two other units; these hydrogen bonds are cyclic involving eight atoms (N-H(exo)...O(keto)-C-O-H...O(urea)-C). Only one carboxylic acid group per molecule takes part in these hydrogen bonds, the other forms a short, 2.490(7) Å, internal bond to the acceptor keto oxygen atom. N(H)...O bonds range from 2.930(7) to 3.206(7) Å, O(H)...O is 2.475(6) Å. In the complex urea, **II** each urea is hydrogen bonded to three different host molecules and vice versa; the urea "endo" hydrogen atoms bond to the ether oxygen atoms, while both "exo" hydrogen atoms take part in cyclic hydrogen bonds to carboxylic acids. There is not internal hydrogen bond. N(H)...O bonds range from 2.83 to 3.26(2) Å and the O...O bonds are 2.55 and 2.56(2) Å.

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Introduction.

Urea has a long history in host-guest chemistry, the clathrates in which it forms hydrogen bonded channels, selective for straight chain hydrocarbons, having been discovered nearly forty years ago [1]. More recently efforts have been made to obtain compounds which would encapsulate urea as a guest. Rheinhoudt and coworkers [2,3] have used crown macrocyclic polyethers as potential host molecules. Pedersen himself [4] investigated a range of substituted crown ethers as complexing agents for thiourea, reasoning that the tautomeric form $\text{SC}(\text{NH}_2)=\text{NH}_2^+$ should act as a substituted ammonium ion; he obtained adducts of a wide range of stoichiometry. It was with the unsubstituted 18-crown-6 that Harkema *et al.* [2] obtained the first urea adduct to be subjected to crystal structure analysis; it had stoichiometry 5 urea: 1 crown. Subsequently the structures of 18-crown-6 adducts with 4 thiourea [5] 2 thiourea [6] and 2 *N,N'*-dimethylthiourea [7] have been determined. In all, the 18-crown-6 molecule is (approximately or exactly) symmetrical with one urea, or thiourea, molecule donating hydrogen bonds from each side. The

remaining hydrogen atoms bond these coordinated amides to others. For stoichiometry greater than 2:1 the additional molecules take part only in hydrogen bonding to other urea or thiourea molecules.

To achieve encapsulation a ratio of 1:1 or less than urea per crown molecule is required. This suggests that the host should hydrogen bond with urea more strongly than it does with itself and that the host should not be too symmetrical so that there would be a preferred "side" for interaction. A 1:1 compound with 18-crown-6 was obtained [3] with uronium nitrate as the guest; the crown molecule adopted a conformation with the two sides different.

As intermediates in a synthesis, Parsons [8] isolated the two phthalic acid crown ether derivatives **I** and **II** (see Formula). Because substitution by a benzene ring in 18-crown-6 and in 15-crown-5 usually leads to conformations with differences between the two sides of the plane through the oxygen atoms, and because the carboxylic acid function might provide additional interaction, it seemed that these compounds might form complexes with urea. This proved to be the case, and, the stoichiometry

being 1:1, we determined their crystal structures. A preliminary account has appeared elsewhere [9]. Examination of closely related compounds has helped to distinguish adventitious from essential features.

EXPERIMENTAL

Colourless crystals of each adduct were supplied by Parsons, those of urea, **I** were chunks and those of urea, **II** prismatic needles. For urea, **I** observations were collected twice, once on a CAD-4 diffractometer with copper radiation, first set, and later

on a Philips PW1100 4-circle diffractometer with graphite monochromated molybdenum radiation. For urea, **II** the latter diffractometer was used. Table 1 shows the experimental details.

The structure of urea, **I** was solved from the first set by direct methods, SHELX-76 [11a] on the Vax computer in Queen Mary College London. All the non-hydrogen atoms were located, and refined anisotropically to give $R = 0.12$, addition of hydrogen atoms in calculated positions 1.08 \AA from carbon atoms with an isotropic vibration parameter, $U = 0.05 \text{ \AA}^2$ reduced R to 0.094. In the subsequent difference map the strongest peak was spurious, the next four corresponded to the two carboxylic hydrogen

Table 1
Experimental Conditions

	Urea I		Urea II
	First set	Second set	
Formula	$C_{19}H_{28}N_2O_{11}$		$C_{17}H_{24}N_2O_{10}$
M	460.45		416.39
Crystal system	triclinic		orthorhombic
$a/\text{\AA}$	8.311(1)	8.336(2)	8.750(2)
$b/\text{\AA}$	13.926(3)	11.009(2)	10.844(3)
$c/\text{\AA}$	11.013(1)	13.313(2)	21.215(3)
$\alpha/^\circ$	66.07(7)	105.55(3)	
$\beta/^\circ$	104.48(7)	103.62(3)	
$\lambda/^\circ$	111.70(2)	104.63(3)	
$U/\text{\AA}^3$	1075.0(5)	1076.9(5)	2013.0(8)
Space group	$P\bar{1}$	$P\bar{1}$	$P2_12_1$
$Dm/g \text{ cm}^{-3}$	—	—	1.354
Z	2	2	4
$Dc/g \text{ cm}^{-3}$	1.422	1.420	1.374
F(000)	488	488	880
Radiation ($\lambda/\text{\AA}$)	1.5418	0.7107	0.7107
Reflections measured	4160	3162	1290
Scan method	[28]	$\theta/2\theta$	$\theta/2\theta$
Scan speed/ $^\circ\text{min}^{-1}$	—	1.8	1.2
Scan width/ $^\circ$	—	1.2	1.2
Background counts	—	20	20
$2\theta \text{ max}/^\circ$	138	46	46
$\sigma \text{ limit}[I > n\sigma(I)]$	3	$n = 3$	$n = 3$
Unique observed reflections	3219	2105	599
$[I > 3\sigma(I)]$			
No parameters	290	313	118
Weighting scheme w	unit	unit	unit
$R = (\Sigma F_o - F_c) / \Sigma F_o $	0.09	0.071	0.083
Final max shift e.s.d.	0.23	0.02	0.05
Size of crystal	$0.5 \times 0.32 \times 0.12$	$0.5 \times 0.32 \times 0.12$	$0.28 \times 0.1 \times 0.12 \text{ mm}$
$\mu \text{ cm}^{-1}$	9.04	1.10	1.06
Absorption correction	empirical [29]	—	—
No. of reflections to determine unit cell	25	25	25

atoms and to two hydrogen atoms of urea.

At this stage the second set of observations was collected, direct methods [11b] gave the locations of the atoms in the reduced cell. A difference map at $R = 0.0762$ from anisotropic refinement of the heavier atoms, including hydrogen atoms in calculated po-

Table 2a

Atomic Fractional Coordinates and U_{eq} ($\times 10^3$) with e.s.d.'s in Parentheses (Urea, I)

	x/a	y/b	z/c	U_{eq}/U_{iso} *
O(1)	.8656(4)	.2534(3)	.2767(3)	50(2)
C(2)	.9729(8)	.1910(5)	.3336(4)	56(3)
C(3)	1.0670(9)	.2848(6)	.4489(4)	66(3)
O(4)	1.1904(5)	.3982(4)	.4474(3)	66(2)
C(5)	1.2595(15)	.5052(7)	.5433(6)	153(6)
C(6)	1.3737(13)	.6211(7)	.5362(6)	129(5)
O(7)	1.3053(6)	.6581(5)	.4569(4)	107(4)
C(8)	1.4017(9)	.7719(6)	.4411(6)	84(4)
C(9)	1.2971(9)	.8581(6)	.4256(6)	83(4)
O(10)	1.1363(6)	.7847(4)	.3436(4)	73(2)
C(11)	1.0221(9)	.8546(6)	.3202(6)	73(4)
C(12)	.8505(9)	.7636(7)	.2425(6)	82(4)
O(13)	.7759(6)	.6622(4)	.2734(4)	87(2)
C(14)	.6138(8)	.5714(5)	.1996(5)	64(3)
C(15)	.6188(7)	.4527(5)	.1139(4)	57(3)
O(16)	.6995(5)	.3782(3)	.1714(3)	53(2)
C(17)	.7096(6)	.2624(4)	.1080(4)	40(2)
C(18)	.7966(6)	.1927(5)	.1650(4)	41(2)
C(19)	.8061(6)	.0742(4)	.1060(4)	42(2)
C(20)	.7377(6)	.0178(4)	-.0092(4)	39(2)
C(22)	.6409(6)	.2082(5)	-.0047(4)	46(1)
C(21)	.6526(6)	.0876(5)	-.0674(4)	43(2)
C(23)	.5632(6)	.0453(4)	-.1991(3)	26(0)
C(24)	.7623(7)	-.1119(5)	-.0588(4)	46(2)
O(11)	.7231(6)	-.1714(4)	-.1576(3)	75(2)
O(12)	.8327(6)	-.1596(4)	.0120(3)	62(2)
O(20)	.5745(7)	-.0488(5)	-.2587(3)	92(3)
O(21)	.4911(7)	.1153(5)	-.2233(3)	98(3)
C(25)	1.1360(7)	.4517(5)	.1373(4)	51(2)
O(30)	1.1204(5)	.3779(3)	.0422(3)	57(2)
N(1)	1.0935(8)	.5605(6)	.1496(5)	78(3)
N(2)	1.1974(7)	.4216(6)	.2258(4)	63(3)
H(5)	.8620(84)	-.2556(66)	-.0193(52)	114(23)*
H(66)	.6603(0)	-.0765(0)	-.2213(0)	43(29)*
H(76)	.5949(0)	-.1131(0)	-.2305(0)	50(31)*
H(1)	1.0496(89)	.5755(54)	.0958(54)	102(27)*
H(2)	1.1020(80)	.6154(63)	.2119(53)	95(23)*
H(3)	1.2199(73)	.3433(59)	.2198(45)	79(20)*
H(4)	1.1962(68)	.4714(52)	.2857(46)	64(18)*

sitions at 0.98 \AA from the carbon atoms and with $U = 0.08 \text{ \AA}^2$, showed all four hydrogen atoms of urea and one carboxylic acid hydrogen, H(5). After introduction and refinement of these atom positions, the subsequent difference map showed five peaks, three round C(23) and two about $\frac{1}{3} e \text{ \AA}^{-3}$, between the two carboxylic acid groups *i.e.* corresponding to a disordered internal hydrogen bond. These two atoms, H(66) and H(76) were assumed to have half occupation. This reduced R to 0.07 and the final difference map showed the largest peak to be $0.4 e \text{ \AA}^{-3}$. Unit weights were used, no significant trend in R with $|F_o|$ or $\sin \theta/\lambda$ could be discerned.

The atomic coordinates and isotropic or equivalent vibration parameters are in Table 2a. Anisotropic vibration parameters, calculated hydrogen atom coordinates and structure factors have been deposited. The designations of the atoms and most torsion angles are displayed in Figure 1a.

Table 2b

Atomic Fractional Coordinates and Isotropic Thermal Parameters ($\times 10^3 \text{ \AA}^2$) with e.s.d.'s in Parentheses (Urea, II)

	x/a	y/b	z/c	U_{iso}
O(1)	.1434(16)	.0259(12)	.4190(6)	44(4)
O(12)	.1597(20)	-.3753(16)	.5453(8)	79(6)
O(13)	.0235(15)	.1872(11)	.4918(6)	33(4)
O(21)	-.0054(17)	-.0352(13)	.7057(6)	56(4)
O(20)	-.1673(19)	-.1748(14)	.6713(7)	65(5)
O(4)	.0938(19)	.0863(16)	.2934(8)	80(6)
O(10)	-.1201(17)	.3834(13)	.4341(6)	49(4)
O(11)	.1009(20)	-.3166(15)	.6408(8)	73(6)
O(7)	.0326(20)	.3430(14)	.3169(8)	73(5)
O(30)	-.1246(18)	-.0354(14)	.8160(7)	58(5)
N(1)	-.2882(20)	-.1026(17)	.8947(8)	53(6)
N(2)	-.2525(22)	-.2158(17)	.8031(9)	59(6)
C(22)	-.2221(28)	-.1138(23)	.8383(11)	55(7)
C(2)	.1675(27)	-.0602(20)	.3701(10)	58(7)
C(3)	.2178(29)	.0158(24)	.3128(11)	66(8)
C(5)	.1340(37)	.1872(25)	.2540(13)	101(10)
C(6)	.1713(30)	.3004(24)	.2854(12)	78(9)
C(8)	.0556(25)	.4512(22)	.3516(10)	59(7)
C(9)	-.0800(28)	.4774(22)	.3897(11)	71(8)
C(11)	-.0380(27)	.3963(20)	.4916(9)	53(7)
C(12)	-.0508(26)	.2804(18)	.5287(9)	42(6)
C(14)	.0342(22)	.0684(17)	.5170(9)	30(6)
C(15)	.1050(25)	-.0188(19)	.4769(9)	40(6)
C(16)	.1196(27)	-.1384(20)	.4990(10)	46(6)
C(17)	.0726(26)	-.1705(19)	.5597(10)	48(7)
C(18)	.0044(23)	-.0831(19)	.5966(9)	36(6)
C(19)	-.0107(24)	.0393(19)	.5773(9)	42(6)
C(20)	-.0581(26)	-.1124(20)	.6624(9)	42(6)
C(21)	.1189(30)	-.2972(22)	.5804(11)	56(7)

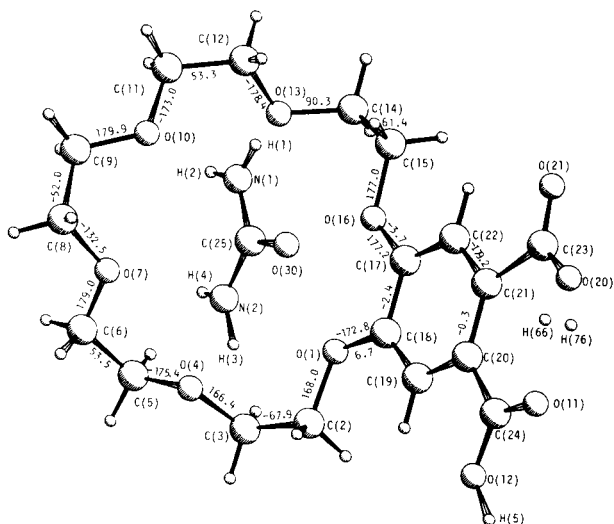


Figure 1a. The asymmetric unit of complex urea, **I** showing the designation of the atoms other than the hydrogen atoms attached to carbon atoms; these are depicted in calculated positions. For the macrocyclic ring and C(23)-C(21)-C(20)-C(24) the torsion angles are shown, estimated standard deviations are 0.9° at 0° and 0.5° at 180°.

Crystals of urea, **II** diffracted poorly. Preliminary photographs established the approximate unit cell, with *a* as the needle axis, and the space group. Observations were collected on the Philips diffractometer, see Table 1. The structure was solved by direct methods [11b] and all non-hydrogen atoms located. Because there were so few observations only isotropic vibration parameters

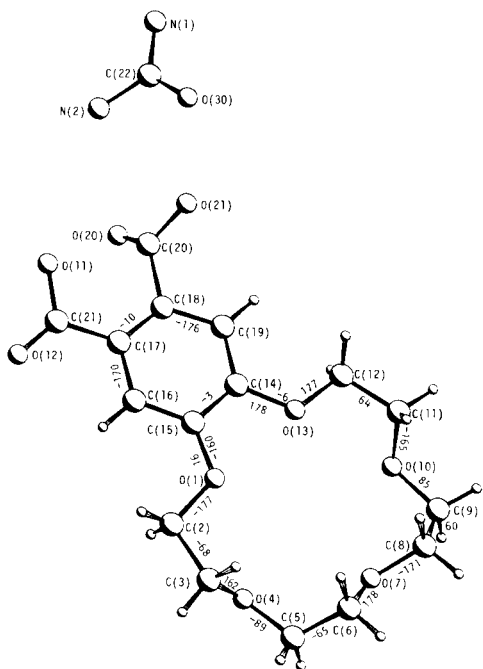


Figure 1b. The asymmetric unit of urea, **II** showing the designations of the atoms located and hydrogen atoms which are attached to carbon atoms in calculated positions. For the macrocyclic ring and C(21)-C(17)-C(18)-C(20) the torsion angles are shown, e.s.d.s. are 3° at 0° and 2° at 180°.

were allowed in refinement. Hydrogen atoms on carbon atoms were included at calculated positions with C-H 0.98 Å and $U_{iso} = 0.06 \text{ \AA}^2$. The final R value was 0.08 with unit weights. The atomic coordinates and isotropic vibration parameters are in Table 2b, hydrogen atom coordinates, and observed and calculated structure amplitudes have been deposited. The designation of the atoms are in Figure 1b. For each compound the geometry was calculated with the program PARST [12] on the VAX 11/750 computer in Padua and the Cray computer in the University of London Computer Centre; this gave bond lengths and angles, corrected for vibration [13] where appropriate, torsion angles, mean planes and interatomic distances including hydrogen bonding interactions. Thermal parameters, hydrogen atom coordinates and observed and calculated structure factors are available on request from one of the authors (F. B.)

Results and Discussion.

Unequivocal location of the N-H and O-H hydrogen atoms in urea, **I** shows that the entities present consist of urea molecules and dicarboxylic acid molecules. For urea, **II** deductions can be made from the C-O bond lengths in the carboxylic acids and the N...O and O...O distances, again indicating that the adduct is not a uronium salt.

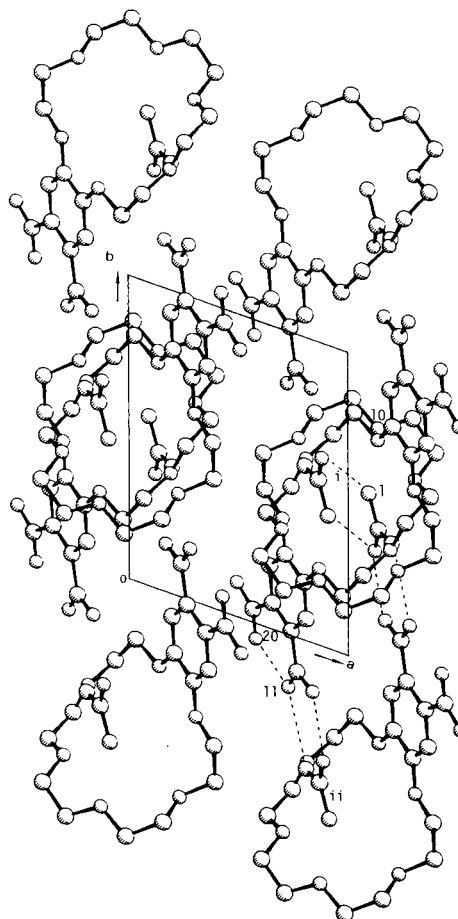


Figure 2a. A projection of the structure of urea, **I** onto (001). Oxygen atoms shown as the smaller circles, O(10), O(11) and O(20) and N(1) of the asymmetric unit are labelled. Broken lines indicate hydrogen bonds, the equivalent positions are defined in Table 3a.

Tables 3a and 3b show the distances of possible hydrogen bonding contacts which are indicated in the packing diagrams Figures 2a and 2b.

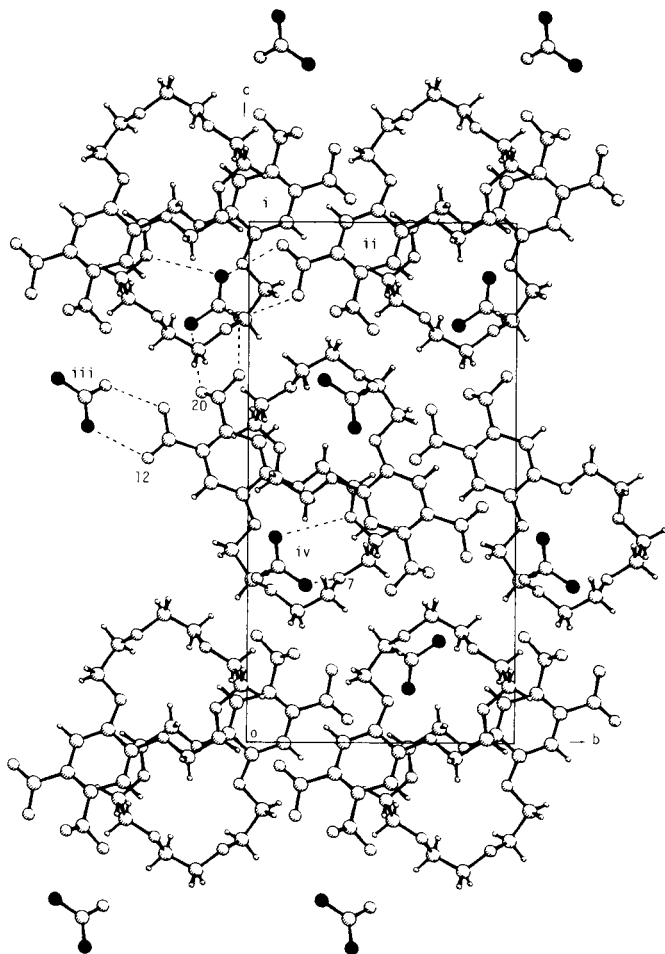


Figure 2b. Projection of the structure of urea, II down the a axis of the crystal. Nitrogen atoms are filled circles, carbon atoms are shown with hydrogen atoms attached open circles are oxygen atoms. Broken lines indicate hydrogen bonds, and equivalent positions are defined in Table 3b.

In each structure the asymmetric unit we chose consists of a crown ether phthalic acid molecule and a urea molecule, which are linked by hydrogen bonds. Figures 1a and 1b illustrated two of the three kinds of contact found. In Figure 1a the interaction between the "endo" hydrogen atoms of urea and some of the ether oxygen atoms is shown. While H(2)...O(10) is a single hydrogen bond, H(4) takes part in a bifurcated system. As indicated in Table 3a, although N(2)...O(4) distance is smaller than the N(2)...O(7) distance, H(4) is nearer O(7) and the angles subtended at H(4) and at N(2) indicate the O(7) is the principal acceptor. Incidentally the C(6)-O(7)-C(8) bond angle is larger than the usual value in crown ethers, 115-116°. There is a cyclic hydrogen bond system about a center of symmetry at 1, 1/2, 0 linking two urea molecules N(1)-H(1)...O(30'), Table 3a, so

that a dimer of urea is sandwiched between two crown ether rings, Figure 2a. The third type of hydrogen bond is also cyclic and involves N(2)-H(3)...O(11^{iv}) *i.e.* the keto oxygen of a carboxylic acid, and O(30)_{urea}...H(5)-O(12^{iv}) the acidic hydrogen of the carboxylic acid. This type is shown in Figure 1b for the urea, II asymmetric unit, and can be seen in Figure 2a to hold the encapsulated dimers in chains along the crystallographic b axis. Hydrogen bonding holds the crystal in the bc plane, the carboxylic acid groups C(23)-O(21)-O(22) are more than 6 Å apart across the centers of symmetry at 1/200 and 1/201/2 *etc.*, Figure 2a.

In the phthalic acid entity of I, the carboxylic acid C(23)-O(21)-O(22) acts as a donor in the short internal hydrogen bond, O(20)...O(11) = 2.490(7) Å. It is complicated by disorder manifest in the residual electron density peaks round C(23), in the improbable bond lengths involving this atom in Table 3a, and in the two sites for the hydrogen atom H(66) and H(76). Disorder involving twisting about the C(21)-C(23) bond would be consistent with the anisotropic vibration parameters which appear to correspond to a maximum mean square displacement of 0.145 Å² normal to the plane of the carboxylic acid. This phenomenon was found with each set of observations from the same crystal.

Because of the triclinic symmetry all planes of the same entity are parallel. For the hydrogen bonded dimer of urea molecules the "step" across the center of symmetry is 0.6 Å. The normal to the plane of the urea molecule is at 58.4(2)° to the normal to the, poor, plane through the six ether oxygen atoms, Figure 1a, at 10.2(2)° to the normal to the benzene ring and 5.2(2)° to the normal through the carboxylic acid C(20)-C(24)-O(11)-O(12) to which it is hydrogen bonded, Figure 2a. The normals to the carboxylic acids are + and - 5.2(2)° from the normal to the plane through the benzene ring and 8.3(2)° from each other.

In the urea, II complex there is no interaction between urea molecules. Each is hydrogen bonded to three different host molecules and these bonds hold the structure in three dimensions, Figure 2b. The phthalic acid does not have an internal hydrogen bond, O(11) and O(20) are 2.88(2) Å apart; this separation results from the twisting of the carboxylic acid groups out of the plane of the benzene ring, that of C(18)-C(20)-O(20)-O(21) by 59.6(6)° and of C(17)-C(21)-O(11)-O(12) by 13.5(8)°, the angle between them being 63.7(8)°. Both carboxylic acid groups form cyclic hydrogen bonds with urea molecules, that of O(20) and O(21) constitutes the chosen asymmetric unit in Figure 1b, the normal to the carboxylic acid plane is at 19.6(6)° to that of the urea molecule. The carboxylic acid of O(11) and O(12) forms a similar bonding system involving N(1) of urea at iii Figures 2b and Table 3b, the angle between the normals to the planes of the carboxylic acid and the urea to which it is bonded is 22.6(6)°. The third hydrogen bond-

ing contact for urea is between the nitrogen atoms and the oxygen atoms of the macrocyclic ether. Although the "endo" hydrogen atoms have not been located the dimensions indicate an N(2)...O(7) bond and a bifurcated one at N(1) with O(10') rather than O(13') as the principal acceptor. It is these hydrogen bonds which hold the crystal along the needle axis.

It is not obvious why crystals of urea, **II** diffract poorly despite the three-dimensional hydrogen bonding. The packing is relatively looser than in urea, **I**, the volume per asymmetric unit is only 35 Å³ less whereas the usual difference is about 60 Å³ per CH₂CH₂O unit in crown ethers and their complexes. For the urea molecules the average isotropic vibration parameters are 0.057(5) Å² and

Table 3a
Interatomic Distances, Å, and Angles, °, in Urea, **I** Bond Lengths in the Macrocyclic Ether

Type	mean	range	corrected* mean	range
(H ₂)C-O	1.390(48)	1.292(11)-1.454(8)	1.414(37)	1.308-1.459
(H ₂)C-C(H ₂)	1.467(30)	1.427(12)-1.503(8)	1.477(29)	1.452-1.511
arom. C-C	1.399(27)	1.364(7)-1.426(8)	1.401(26)	1.366-1.429
	Individual	uncorrected	corrected [a]	
	O(1)-C(18)	1.363(5)	1.371	
	O(16)-C(17)	1.361(6)	1.373	
	C(20)-C(24)	1.491(8)	1.497	
	C(24)-O(11)	1.222(6)	1.260	
	C(24)-O(12)	1.292(8)	1.314	
	C(21)-C(23)	1.618(6)	1.628	
	C(23)-O(20)	1.165(7)	1.220	
	C(23)-O(21)	1.156(8)	1.209	
	O(12)-H(5)	1.14(8)		
	O(20)-H(66)	0.94(6)		
	O(20)-H(67)	0.92(6)		

Selected Bond Angles in the Macrocyclic Ether

C(23)-C(21)-C(20)	128.2(5)
C(21)-C(23)-O(21)	113.5(4)
C(21)-C(23)-O(20)	119.7(5)
C(24)-C(20)-C(21)	126.4(4)
C(20)-C(24)-O(11)	125.0(5)
C(20)-C(24)-O(12)	114.6(5)
O(20)-C(23)-O(21)	126.8(5)
O(11)-C(24)-O(12)	120.4(5)
C(24)-O(12)-H(5)	119(4)
C(6)-O(7)-C(8)	120.5(7)

Bond Lengths in Urea

	uncorrected	corrected [a]		
O(30)-C(25)	1.264(6)	1.278	N(1)-H(1)	0.80(8)
C(25)-N(1)	1.313(9)	1.344	N(1)-H(2)	0.86(6)
C(25)-N(2)	1.331(8)	1.346	N(2)-H(3)	0.91(7)
			N(2)-H(4)	0.84(6)

[a] Correction for riding motion, reference [13].

Table 3a (continued)

Bond Angles in Urea. I.

N(1)-C(25)-N(2)	119.3(6)
O(30)-C(25)-N(1)	119.9(5)
O(30)-C(25)-N(2)	120.8(5)
C(25)-N(1)-H(1)	119(5)
C(25)-N(1)-H(2)	125(5)
H(1)-N(1)-H(2)	116(7)
C(25)-N(2)-H(3)	122(4)
C(25)-N(2)-H(4)	116(4)
H(3)-N(2)-H(4)	122(5)

Hydrogen Bonding Contacts

O(20)...O(11)	2.490(7)	H(66)...O(11)	1.62(5)
		H(67)...O(11)	1.64(5)
O(12)...O(30 ⁱⁱ)	2.475(6)	H(5)...O(30 ⁱⁱ)	1.35(8)
		O(12)-H(5)...O(30 ⁱ)	167(7)
N(1)...O(30 ⁱ)	3.091(8)	H(1)...O(30 ⁱ)	2.30(8)
		N(1)-H(1)...O(30 ⁱ)	164(7)
N(1)...O(10)	2.930(7)	H(2)...O(10)	2.09(6)
		N(1)-H(2)...O(10)	165(6)
N(2)...O(11 ⁱⁱ)	2.952(8)	H(3)...O(11 ⁱⁱ)	2.07(7)
		N(2)-H(3)...O(11 ⁱⁱ)	162(5)
N(2)...O(4)	3.043(7)	H(4)...O(4)	2.50(7)
		N(2)-H(4)...O(4)	123(5)
N(2)...O(7)	3.206(7)	H(4)...O(7)	2.41(5)
		N(2)-H(4)...O(7)	157(5)
C(25)-N(2)...O(4)	171.1(5)	C(25)-N(2)...O(7)	119.4(5)
C(25)-N(1)...O(10)	133.0(5)		

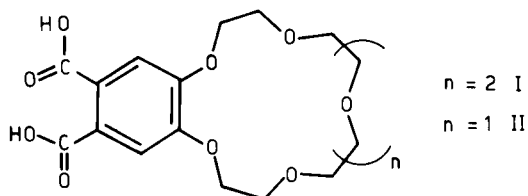
Roman numeral superscripts refer to equivalent positions

- i 1-x, 1-y, -z
ii 1-x, -y, -z

For mean values the numbers in parentheses are the standard deviations in individual values calculated from the spread about the mean,

$$\frac{\sum \left(\frac{(1-u)u}{z(x-x)} \right)^2}{\sum} = s$$

0.063(3) Å² in urea, **II** and urea, **I** respectively, and the vibration parameters of the host molecules are also similar so vibration (or disorder) does not account for the poor diffraction.

Phthalic Acid Crown Ether Derivatives **I** and **II**

An intriguing feature is that urea, **II** crystallizes in an enantiomorphic space group although both urea and **II** have potentially at least one plane of symmetry. The "handedness" arises from the twisting of the carboxylic acids so that the dihedral angle C(20)-C(18)-C(17)-C(21) is -10(3)°, Figure 1b, compared with approximately zero in Figure 1a, and this angle is -10° in all the molecules in the crystal. (This is not an absolute configuration, all the molecules might have the angle +10° with the signs of all the other torsion angles reversed).

Table 3a shows that correction for riding motion [13] increases the apparent mean bond lengths, as expected, and also reduces the spread about the mean suggesting that

Table 3b

Interatomic Distances, Å, and Angles, °, in Urea, **II**.

Type	mean*	range
(H ₂)C-O	1.42(2)	1.39(3)-1.46(3)
(H ₂)C-C(H ₂)	1.48(4)	1.43(4)-1.53(3)
arom. C-C	1.39(2)	1.37(3)-1.42(3)

Individual

O(1)-C(15)	1.36(2)	O(13)-C(14)	1.40(3)
O(12)-C(21)	1.18(3)	O(20)-C(20)	1.19(3)
O(11)-C(21)	1.31(3)	O(21)-C(20)	1.33(3)
C(17)-C(21)	1.50(3)	C(18)-C(20)	1.53(3)

Selected Bond Angles (°) in the Macrocyclic Ether

C(21)-C(17)-C(18)	126(2)	C(20)-C(18)-C(17)	122(2)
C(17)-C(21)-O(12)	124(2)	C(18)-C(20)-O(20)	123(2)
C(17)-C(21)-O(11)	114(2)	C(18)-C(20)-O(21)	112(2)
O(11)-C(21)-O(12)	123(2)	O(20)-C(20)-O(21)	122(2)

Bond Lengths in Urea

O(30)-C(22)	1.29(3)
N(1)-C(22)	1.33(3)
N(2)-C(22)	1.36(3)

Bond Angles in Urea

N(1)-C(22)-N(2)	119(2)
O(30)-C(22)-N(1)	124(2)
O(30)-C(22)-N(2)	118(2)

Hydrogen Bonding Contacts

donor	acceptor	donor	acceptor
O(21)...O(30)	2.56(2)		
N(2)...O(20)	2.93(2)		
N(2)...O(7 ⁱ)	2.83(3)	O(7)...N(2 ^{iv})	C(22)-N(2)...O(7 ⁱ)
N(1)...O(10 ⁱ)	3.26(2)	O(10)...N(1 ^{iv})	C(22)-N(1)...O(10 ⁱ)
N(1)...O(13 ⁱ)	3.05(2)	O(13)...N(1 ^{iv})	C(22)-N(1)...O(13 ⁱ)
N(1)...O(12 ⁱⁱ)	2.99(3)	O(12)...N(1 ^{iv})	
O(11)...O(30 ⁱⁱⁱ)	2.55(2)	O(30)...O(11 ^{iv})	O(21)...O(30)...O(11 ^{iv})

(i) $-1/2-x, -y, 1/2+z$ (ii) $-x, 1/2+y, 3/2-z$ (iii) $-x, -1/2+y, 3/2-z$ (iv) $-1/2-x, -y, -1/2+z$

the corrections are valid. As usual [10], the estimated standard deviations from least squares appear too optimistic. For urea, **II** isotropic refinement and the small number of observations has given larger standard deviations from the full matrix least squares refinement and these seem, Table 3b, to be realistic. There is no trouble with disorder in the carboxylic acids which show the usual distinction between the C-O(H) bonds, about 1.3 Å, and C=O bonds, about 1.2 Å, and confirms that neither hydrogen atom has been transferred to form a carboxylate anion and uronium cation.

Dimensions in the urea molecules do not differ significantly from those in urea itself [14]. The average dimensions in the crown ethers are the same as those usually found, including the short CH₂-CH₂ bonds. The torsion angles of the 15-crown-5 ring, Figure 1b, do not differ significantly from those of benzo-15-crown-5 [15] or of the weakly bound molecule in the (benzo-15-crown-5)₂ sodium tetraphenylborate [16]. The normal to the benzene ring is at 18.4(6)° to the, poor, plane through the five oxygen atoms. The torsion angles of the benzo-18-crown-6 entity in **I**, differ in detail from those found in complexes with

metals [17]; the enforced angle of 0° at the benzene ring precludes attainment of the ideal 180° or $\pm 60^\circ$ in all 17 angles, in this case the angles at O(13)-C(14) and O(7)-C(8) are more than 30° from the ideal.

As in the benzocrown complexes with metal cations, the urea molecule is bonded to the side of the plane through the polyether oxygen atoms which is the same as that of the benzene ring substituent, in agreement with our expectations. The N...O(ether) hydrogen bond distances are in the same range as those found for the 18-crown-6 complexes including the two examples where hydrogen atoms are involved, viz both "endo" and one "exo". These examples are the 2:1 thiourea [6] and the 1:1 uronium nitrate [3] complexes; in the former, the 18-crown-6 has the centrosymmetrical "D_{3h}" conformation while in the latter it has an unusual conformation with an approximate two-fold axis. Protonation of the uronium ion, in line with the zwitterion tautomer of the neutral molecule, is on the oxygen atom and there is a strong hydrogen bond from it to an oxygen atom of a nitrate ion, 2.48 Å, so it does not directly affect the conformation of the crown ether.

Our ligands can also be compared with carboxylic acids which form complexes with urea. Salicylic acid gives 1:1 stoichiometry [18] and resembles urea, **I** in having a centrosymmetric hydrogen bonded urea dimer with N-H...O 2.932(5) Å and an 8-membered cyclic system of the carboxylic acid O-H...O(urea) 2.540(4) Å and O(keto)...(H)N 2.903(4) Å. One of the two "endo" hydrogen atoms does not take part in hydrogen bonding and the other bonds to a hydroxy group. In the 1:1 oxalic acid:urea complex, which has been studied by neutron [19] and by X-ray diffraction [19], the urea molecules lie on 2-fold axes. There is a resemblance to urea, **II** because the carbonyl oxygen is an acceptor of two carboxylic acid hydrogen atoms, O(H)...O(urea) 2.553(1) Å and the two "exo" hydrogen atoms donate to the keto oxygen atoms of the carboxylic acids, N(H)...O 3.030(1) Å to form cyclic systems like that of Figure 1b; the "endo" hydrogen atoms donate, N(H)...O 3.085(1) Å, to acidic oxygen atoms of two further oxalic acids molecule. In all examples N(H)...O is of the order of 3 Å while O(H)...O(urea) is less than 2.6 Å; the latter is significantly shorter than the O(H)...O(keto) of the carboxylic acid dimers in salicylic acid [20], 2.65 Å, β -oxalic acid [21], 2.702 Å and phthalic acid [22], 2.68 Å. The carbonyl oxygen atom of urea appears to be a stronger acceptor of O-H...O but not of N-H...O hydrogen bonds than the keto oxygen atoms of carboxylic acids.

A variety of arrangements have been found in phthalic acid and its derivatives, paralleling the difference between molecules **I** and **II**. In the crystal the acid itself is on a 2-fold axis which relates the two keto oxygen atoms of the carboxylic acids, a twist of 43° out of the plane of the benzene ring gives a distance of 2.85 Å between them (*cf.* O(11) and O(20) in **II**) while the acidic hydrogen atoms are

on the outer oxygen atoms and take part in formation of dimers about centers of symmetry. In lithium hydrogen phthalate [23] two independent anions each show strong internal hydrogen bonds, O...O 2.388(4) and 2.393(4) Å with the carboxylic acid groups twisted $\pm 20^\circ$ and $\pm 25^\circ$, respectively, from the planes of their benzene rings so that the O-H...O atoms are all on the same side of the ring. In contrast the hydrogen phthalate anion in the strontium salt [24] has no internal hydrogen bond, the carboxy anion group is 71° and the carboxylic acid group is 28° from the plane of the benzene. Finally the dianion in the potassium salt [25] has the carboxylate groups 34.8° and 62.3° to the plane of the benzene ring.

Comparison of our two structures suggests that urea does not show a strong preference between hydrogen bonding to another urea molecule or to a carboxylic acid. It also suggests that, as shown in Table 4, the hydrogen bonding contacts tend to be nearly coplanar with the urea molecule. This confirms the prediction behind the successful complex formation of the uronium ion [3] in the larger macrocyclic ether, benzo-27-crown-9, where all five hydrogen atoms form donor bonds to the ether and recently (26) of urea with (2-carboxyl-1,3-xylyl-30-crown-9) [26] and the lithium perchlorate complex of (2,6-pyrido-27-crown-9). Our apparently successful prediction of the "onesidedness" of the benzo substituted crown rings has recently been disproved. Watson and Jain [27] have determined the crystal structures of the benzo-15-crown-5 complexes having stoichiometry 1:1 with dithiooxamide and 2:1 with thioacetamide; in each compound there are NH₂ groups on each side of the plane through the five oxygen atoms and each such group forms one single and one bifurcated hydrogen bond.

Table 4

Deviations Å, of Atoms from Plane Through the Urea Molecules.
Atoms Used in Calculating the Equation of the Plane are in Italics

urea, **I**

O(30) 0.000(4), N(1) -0.001(7), N(2) -0.001(6), C(25) 0.003(6)

H(1) 0.03(8), H(2) -0.06(7), H(3) 0.04(7), H(4) 0.05(6), O(10) 0.310(5), O(4) 0.944(6), O(7) 0.408(6), O(30), 0.593(4), N(1) 0.594(7), O(11^u) 1.106(5), O(12^u) 0.177(5)

urea, **II**

O(30), N(1), N(2) all 0.00(2), C(22) 0.02(2)

O(20) 0.86(2), O(21) 0.22(2), O(13) -0.21(2), O(10) -1.26(2), O(7) 0.94(2), O(11^u) 0.61(2), O(12^u) -0.19(2).

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