

3.036 (5) Å and the angles are 169.9 (3) and 152.4 (2)°, respectively [symmetry codes: (i) $x - 1, y, z$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, 2 - z$]. On the whole, the crystal packing is stabilized by hydrogen bonding between polar groups and van der Waals interactions between non-polar groups.

Experimental

The synthesis of the compound will be published elsewhere. The compound was recrystallized from acetone at room temperature.

Crystal data

$C_{16}H_{15}NO_4S$
 $M_r = 317.35$
 Orthorhombic
 $P2_12_12_1$
 $a = 6.698 (1) \text{ \AA}$
 $b = 7.171 (1) \text{ \AA}$
 $c = 30.604 (5) \text{ \AA}$
 $V = 1470.0 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.434 \text{ Mg m}^{-3}$
 $D_m = 1.423 (3) \text{ Mg m}^{-3}$
 D_m measured by flotation in xylene- CCl_4

Data collection

Siemens $R3m/V$ diffractometer
 ω scans
 Absorption correction: none
 1591 measured reflections
 1527 independent reflections
 1171 reflections with $I > 2\sigma(I)$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 8-19^\circ$
 $\mu = 0.238 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Equidimensional
 $0.14 \times 0.14 \times 0.14 \text{ mm}$
 Colourless

$R_{int} = 0.08$
 $\theta_{max} = 25.03^\circ$
 $h = 0 \rightarrow 7$
 $k = 0 \rightarrow 8$
 $l = 0 \rightarrow 33$
 2 standard reflections every 98 reflections
 intensity decay: $< 1\%$

Refinement

Refinement on F^2
 $R(F) = 0.044$
 $wR(F^2) = 0.09$
 $S = 1.120$
 1527 reflections
 199 parameters
 H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.0522P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.219 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.217 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *SHELXL93* (Sheldrick, 1993)

All non-H atoms were found by direct methods and their parameters were refined with a full-matrix least-squares procedure. The H atoms were positioned geometrically and refined using the riding model.

Data collection: *R3m/V* software (Siemens, 1983). Cell refinement: *R3m/V* software. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990a). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990b). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX* (Gabe *et al.*,

1987). Software used to prepare material for publication: *SHELXL93*.

We thank Bangalore University for providing the facilities for working on this structure.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1392). Services for accessing these data are described at the back of the journal.

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3-Methyl-1-(1,2,3,4-tetrahydroisoquinolin-2-ylcarbonyl)imidazolium iodide

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Abstract

The title compound, $C_{14}H_{16}N_3O^+ \cdot I^-$, crystallizes as discrete ion pairs with close C—H...I contacts of 3.04 and 3.06 Å. The two C—N bonds of the urea functional group have significantly different bond lengths of 1.327 (6) and 1.466 (6) Å. This is the first crystal structure determination of a carbamoyl imidazolium salt.

Comment

Carbamoyl chlorides are widely used as carbamoyl cation equivalents in organic synthesis. However, they are often difficult to obtain pure, and must be synthesized from an amine and the toxic gas phosgene. Recently, we demonstrated the synthetic utility of carbamoyl imidazolium iodides, (1), as stable carbamoyl cation equivalents. They are usually crystalline solids prepared from a secondary amine and *N,N'*-carbonyldiimidazole, followed by methylation with methyl iodide. For example, the addition of a secondary amine to the salt (1) proceeds with ease at room temperature to yield unsymmetrical tetrasubstituted ureas, (2), in excellent yields (Batey *et al.*, 1998). One example of (1) is the title compound, (4). Refluxing 1,2,3,4-tetrahydroisoquinoline and *N,N'*-carbonyldiimidazole in tetrahydrofuran affords carbamoyl imidazole, (3), in 88% yield. Compound (3) is then methylated with iodomethane to give (4) (see scheme). Imidazolium salts have also attracted interest in the scientific community for use as ionic liquids (Freemantle, 1998).

The crystal structure of (4) exists as discrete ion pairs of iodide anions and 3,4-dihydro-1*H*-isoquinoline-2-carbamoyl-3-methylimidazolium (ICMI⁺) cations. The closest distances of an iodide to a non-H atom of the ICMI⁺ cation are 3.829 (4), 3.858 (5) and 3.951 (4) Å, for I1 to N1, C2 and O8, respectively, where an iodide lies approximately above the plane of these three atoms. There may also be weak C—H···I hydrogen bonds in the lattice, as the close contacts of 3.04 Å for H5···I1ⁱ and 3.06 Å for H6B···I1ⁱⁱ, with angles of 158° for C5—H5···I1ⁱ and 162° for C6—H6B···I1ⁱⁱ, are what might

be expected for hydrogen-bond geometry [symmetry codes: (i) $\frac{1}{2} - x, -\frac{1}{2} + y, z$; (ii) $-\frac{1}{2} + x, y, \frac{1}{2} - z$].

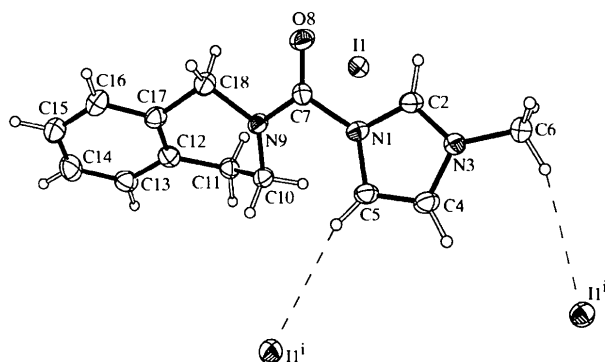
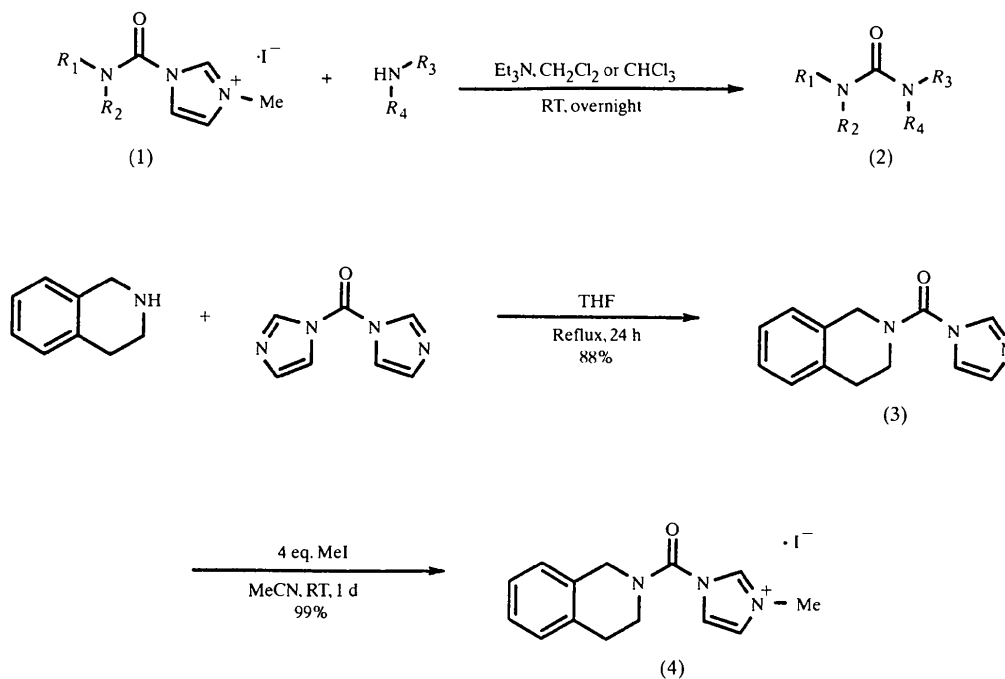


Fig. 1. View of the title molecule showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii [symmetry codes: (i) $\frac{1}{2} - x, -\frac{1}{2} + y, z$; (ii) $-\frac{1}{2} + x, y, \frac{1}{2} - z$].

The C7—N9 and N1—C7 bond lengths are 1.327 (6) and 1.466 (6) Å, respectively. C7—N9 has more double-bond character, which is presumably due to donation of electrons from the lone pair on atom N9. In turn, the N1—C7 bond is more polarized, by virtue of the positive charge on the imidazolium group, and hence it is longer. A search of the Cambridge Structural Database (Allen *et al.*, 1979) revealed that there were no other structures of carbamoyl imidazolium salts with which to compare these bond lengths. The distances in the imida-



zolium group of (4) are similar to those in the structures of 1-methyl-3-ethylimidazolium iodide, (5) (Abdul-Sada *et al.*, 1986), and 3-methyl-1-vinylimidazolium iodide, (6) (Moers *et al.*, 1995); specifically, the N1—C7 distance in (4) is in agreement with the equivalent C—N distances of 1.476 (7) Å for (5), and 1.445 and 1.423 Å for (6) (which contains two molecules in the asymmetric unit). As (4) is an *N,N',N'',N'''*-tetrasubstituted urea, it is possible to compare the C7—N9 distance with the C—N distances in compounds such as 1,1,3,3-tetramethylurea, (7) (Frampton & Parkes, 1996), where the C—N distance equivalent to C7—N9 is 1.3706 (13) Å, and also with *N,N',N'',N'''*-tetramethyl-1,5-bis(1-naphthylureido)naphthalene, (8) (Yamaguchi *et al.*, 1991), and *p*-phenylene-bis[*N*-(*N,N'*-dimethylphenylureido-*p*-phenylene)-*N,N'*-dimethylurea], (9) (Yamaguchi *et al.*, 1991), where the C—N distances range from 1.372–1.379 Å for six unique values from both compounds.

In (4), the C7—N9 distance of 1.326 (7) Å is closer to those in acyclic amides (Allen *et al.*, 1987), which range from 1.325 (6) Å for primary amides to 1.346 (11) Å for tertiary amides. For amides, the N atom is expected to be fully *sp*² hybridized and the amide group to be planar, but in (4), atom N9 is slightly pyramidal. To calculate the extent of *sp*²/*sp*³ hybridization at atom N9 we have defined the angle ε , which is the angle the C7—N9 bond makes with the plane of atoms N9, C18, C10. For an ideally tetrahedral *sp*³ N atom, the value of ε is 35.3°, while for an *sp*² hybridized N atom ε is 0°. The value of ε is 16.2° in (4) and 23° in (5), and for (6) and (7) the values range between 6.8 and 29.8°. Also worthy of note is a large deviation of the bond angle (from that expected from hybridization principles) of 131.3 (4)° for C5—N1—C7.

We intend to carry out further syntheses and structure analyses of this class of compounds to investigate their geometric features and to compare them with the ones outlined here for (4).

Experimental

To a suspension of *N,N'*-carbonyldiimidazole (3.25 g, 20.0 mmol) in tetrahydrofuran (30 ml) was added 1,2,3,4-tetrahydroisoquinoline (2.27 ml, 18.2 mmol). The mixture was refluxed for 24 h before cooling to room temperature. Removal of solvent under vacuum gave a viscous yellow oil, which was dissolved in CH₂Cl₂ (30 ml) and washed twice with 30 ml portions of water. The organic layer was dried over anhydrous MgSO₄, filtered and concentrated under vacuum to yield compound (3) as a straw-coloured solid (3.65 g, 88%). To a solution of (3) (1.14 g, 5.0 mmol) in acetonitrile (10 ml) was added methyl iodide (1.25 ml, 20.0 mmol). The mixture was stirred at room temperature for 1 d. The solvent was removed under vacuum to yield (4) as an off-white solid (1.85 g, 99%). Fine needles grew from dry methanol.

Crystal data

C₁₄H₁₆N₃O⁺·I⁻
M_r = 369.20

Mo K α radiation
 λ = 0.71073 Å

Orthorhombic
Pbca
a = 13.2974 (6) Å
b = 7.9474 (4) Å
c = 27.3988 (14) Å
V = 2895.5 (2) Å³
Z = 8
D_x = 1.694 Mg m⁻³
D_m not measured

Data collection

Nonius Kappa CCD diffractometer
 φ scans
Absorption correction: multi-scan (*Denzo-SMN*; Otwinowski & Minor, 1997)
*T*_{min} = 0.557, *T*_{max} = 0.957
15 794 measured reflections
2918 independent reflections

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.041
wR(*F*²) = 0.091
S = 0.981
2918 reflections
174 parameters
H atoms constrained
w = 1/[$\sigma^2(F_o^2) + (0.0174P)^2 + 3.1213P$]
where *P* = (*F*_o² + 2*F*_c²)/3

Cell parameters from 2918 reflections
 θ = 4.00–26.36°
 μ = 2.208 mm⁻¹
T = 293 (2) K
Needle
0.30 × 0.05 × 0.02 mm
Pale yellow

1829 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.105
 θ _{max} = 26.36°
h = 0 → 16
k = 0 → 9
l = -34 → 0

(Δ/σ)_{max} = 0.002
 $\Delta\rho$ _{max} = 0.457 e Å⁻³
 $\Delta\rho$ _{min} = -0.488 e Å⁻³
Extinction correction: *SHELXTL* (Bruker, 1998)
Extinction coefficient: 0.00095 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N1—C2	1.334 (6)	N3—C6	1.463 (7)
N1—C5	1.390 (6)	C4—C5	1.330 (7)
N1—C7	1.466 (6)	C7—O8	1.211 (6)
C2—N3	1.318 (6)	C7—N9	1.327 (6)
N3—C4	1.386 (6)		
C2—N1—C5	107.7 (4)	C5—C4—N3	107.3 (4)
C2—N1—C7	120.2 (4)	C4—C5—N1	107.5 (5)
C5—N1—C7	131.3 (4)	O8—C7—N9	126.7 (5)
N3—C2—N1	109.0 (4)	O8—C7—N1	116.5 (5)
C2—N3—C4	108.4 (5)	N9—C7—N1	116.7 (4)

Data collection: *Kappa CCD Server Software* (Nonius, 1997). Cell refinement: *Denzo-SMN* (Otwinowski & Minor, 1997). Data reduction: *Denzo-SMN*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *SHELXTL* (Bruker, 1998). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1529). Services for accessing these data are described at the back of the journal.

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1,2-Bis[2-(pyridin-2-yloxy)ethoxy]benzene

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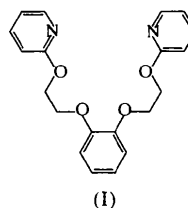
Abstract

The structure of the title compound, C₂₀H₂₀N₂O₄, exhibits several intermolecular arene interactions. For example, π -stacking is observed between two arene rings, with an interplanar distance of roughly 3.6 Å.

Comment

Recent work in our group has focused on the substitution of relatively flexible ethylene linkages in crown ether molecules with more rigid groups such as benzo, cyclohexano and furano (Bryan *et al.*, 1998; Burns *et al.*, 1996). Making crown ether molecules more rigid limits conformational flexibility and can affect their extraction properties (Sachleben *et al.*, 1996; Vögtle & Weber, 1992). Replacement of crown ethylene groups

with pyridine can provide added rigidity and modify the nature of the crown donor groups. In the course of this work, we have prepared and structurally characterized the title compound, (I), as a potential precursor to a pyridino-substituted crown ether extractant.



The title compound is illustrated in Fig. 1. All bond lengths and angles are in good agreement with standard values (Allen *et al.*, 1987). For example, the aromatic C=C bonds vary from 1.356 (3) to 1.405 (2) Å. The interplanar angles between the arene rings (N1, C1–C5 = A1; N2, C16–C20 = A2; C8–C13 = A3) are A1–A2 = 50.5 (1), A1–A3 = 73.9 (1), and A2–A3 = 83.0 (1)°. All three aromatic rings are planar, with the largest deviations from planarity being 0.007 (2) Å (C1 on A1, or C8 on A3).

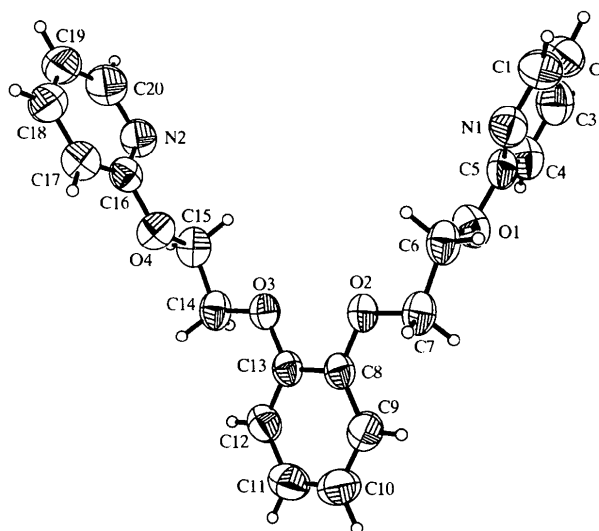


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of an arbitrary radius.

Examination of the packing of this molecule reveals several edge-to-face interactions and one face-to-face interaction between arene rings, some of which are depicted in Fig. 2. The face-to-face ring interaction is between A1 and A3ⁱⁱⁱ, which stack in the lattice roughly along **b**, with an interplanar distance of roughly 3.6 Å and a centroid–centroid distance of 3.93 Å. Close edge-to-face arene contacts are observed between A2 and A3ⁱ, and the equivalent pair A3 and A2ⁱ, with an in-