5-Dodecyl-2-(1-hydroxyethyl)benz-imidazolium Chloride

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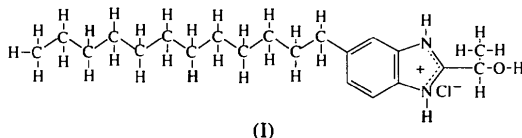*Laboratoire de Chimie-Physique Macromoléculaire, URA-CNRS 494, 1 Grandville BP 451, 54001 Nancy CEDEX, France*

(*Received* 13 *April* 1994; *accepted* 3 *October* 1994)

Abstract

The title compound, 5-dodecyl-2-(1-hydroxyethyl)benz-imidazolium chloride, $C_{21}H_{35}N_2O^+.Cl^-$, serves as a lipophilic model for hydrolytic metalloenzymes. The crystal structure determination shows that molecules are hydrogen bonded through the Cl atom and that the dodecyl chains have fully extended conformations.

Comment

Micellar catalysis has been studied extensively over the past two decades as the model of enzyme catalysis. Co-micelles of cationic surfactants and long-chain alkyl-benzimidazole ligands having a primary or a secondary hydroxyl group in their side chain have been examined for their esterolytic activity towards activated esters in the presence of a metal cation (*e.g.* Zn^{2+}) (Faivre, Brembilla, Roizard & Lochon, 1991). Indeed, the Zn^{2+} ion activates the benzimidazole ligand to form a complex, the geometry of which is an essential factor for the generation of full catalytic activities. Therefore, the establishment of a structure–activity relationship requires the determination of the X-ray crystal structure of this ligand. Experimental intramolecular distances of the hetero-cyclic ring of the title compound, (I), are in good agreement with those determined for benzimidazole (Escande & Galigné, 1974) and 2-hydroxymethylbenzimidazole (Aubry, Brembilla, Faivre & Lochon, 1995).

(I)

Examination of the intermolecular interatomic distances shows that each molecule is bonded to two identical neighbouring molecules by means of weak hy-

drogen bonds through the Cl atom: $N(1)$—$H \cdots Cl^i$ = 3.052 (3), $N(2)$—$H \cdots Cl$ = 3.082 (3) and $O(1)$—$H \cdots Cl^{ii}$ = 3.062 (4) Å [symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2} + y, z$]. Moreover, these four atoms are almost coplanar: $O(1) \cdots Cl \cdots N(2)$ = 109.39 (9), $N(1) \cdots Cl \cdots N(2)$ = 156.56 (8) and $O(1) \cdots Cl \cdots N(1)$ = 79.20 (9)°. The aliphatic chains of the molecules are fully extended with torsion angles equal to 180°.
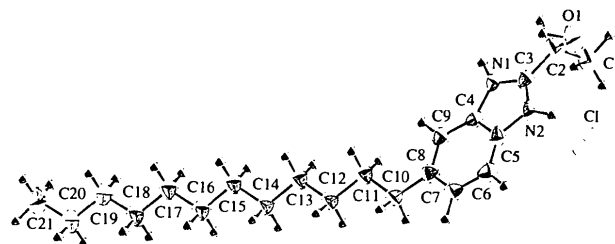
Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystal data

$C_{21}H_{35}N_2O^+.Cl^-$	Cu $K\alpha$ radiation
$M_r = 366.97$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 25
Cc	reflections
$a = 8.174\,(1)$ Å	$\theta = 20$–$30°$
$b = 7.228\,(1)$ Å	$\mu = 1.563$ mm^{-1}
$c = 36.114\,(3)$ Å	$T = 293$ K
$\beta = 86.96\,(1)°$	Parallelepiped
$V = 2131$ Å^3	$0.3 \times 0.2 \times 0.2$ mm
$Z = 4$	Colourless
$D_x = 1.144$ Mg m^{-3}	Crystal source: from ethanol/nitromethane (20/80 *v/v*)

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.0256$
diffractometer	$\theta_{max} = 70°$
ω–2θ scans	$h = -13 \rightarrow 13$
Absorption correction:	$k = 0 \rightarrow 9$
none	$l = 0 \rightarrow 16$
3925 measured reflections	2 standard reflections
2042 independent reflections	frequency: 120 min
1981 observed reflections	intensity decay: none
[$I > \sigma(I)$]	

Refinement

Refinement on F	$w = 1.645/[\sigma^2(F)$
$R = 0.0463$	$+ 0.0014F^2]$
$wR = 0.0541$	$(\Delta/\sigma)_{max} = 0.05$
$S = 1.725$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
1981 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
228 parameters	Atomic scattering factors
Only coordinates of H atoms	from *International Tables*
refined	*for X-ray Crystallography* (1974, Vol. IV)

$C_{21}H_{35}N_2O^+.Cl^-$

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_i.a_j.$$

	x	y	z	B_{eq}
Cl	0.3794	0.291	0.3211	6.09 (3)
O(1)	−0.0046 (4)	0.4789 (5)	0.2688 (1)	5.75 (7)
C(2)	−0.1342 (4)	0.3599 (5)	0.2777 (1)	4.11 (7)
C(1)	−0.1220 (7)	0.1946 (7)	0.2524 (1)	5.7 (1)
C(3)	−0.1297 (4)	0.2992 (4)	0.3177 (1)	3.35 (6)
N(1)	−0.2615 (4)	0.2610 (4)	0.33960 (8)	3.44 (5)
C(4)	−0.2095 (4)	0.1951 (4)	0.37343 (9)	3.15 (6)
C(5)	−0.0389 (4)	0.1995 (4)	0.37054 (9)	3.28 (6)
N(2)	0.0050 (4)	0.2663 (4)	0.33539 (8)	3.48 (5)
C(6)	0.0511 (4)	0.1377 (5)	0.3995 (1)	3.77 (6)
C(7)	−0.0358 (4)	0.0697 (5)	0.43021 (9)	3.75 (6)
C(8)	−0.2093 (4)	0.0651 (4)	0.43320 (9)	3.34 (6)
C(9)	−0.2970 (4)	0.1300 (4)	0.40424 (9)	3.27 (6)
C(10)	−0.2929 (4)	−0.0182 (5)	0.4679 (1)	4.02 (7)
C(11)	−0.4716 (4)	0.0220 (5)	0.4752 (1)	3.90 (7)
C(12)	−0.5418 (4)	−0.0697 (5)	0.5105 (1)	3.94 (7)
C(13)	−0.7222 (5)	−0.0309 (6)	0.5191 (1)	4.19 (7)
C(14)	−0.7927 (4)	−0.1267 (6)	0.5538 (1)	4.01 (7)
C(15)	−0.9724 (4)	−0.0827 (5)	0.5629 (1)	4.21 (7)
C(16)	−1.0433 (5)	−0.1813 (6)	0.5971 (1)	4.11 (7)
C(17)	−1.2224 (5)	−0.1370 (6)	0.6067 (1)	4.34 (7)
C(18)	−1.2919 (5)	−0.2365 (6)	0.6410 (1)	4.36 (7)
C(19)	−1.4695 (5)	−0.1901 (6)	0.6513 (1)	4.64 (8)
C(20)	−1.5382 (6)	−0.2896 (7)	0.6855 (1)	5.3 (1)
C(21)	−1.7161 (7)	−0.2448 (8)	0.6955 (2)	6.3 (1)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(2)	1.389 (5)	C(8)—C(10)	1.518 (5)
C(2)—C(1)	1.506 (6)	C(10)—C(11)	1.499 (5)
C(2)—C(3)	1.511 (5)	C(11)—C(12)	1.523 (5)
C(3)—N(1)	1.331 (4)	C(12)—C(13)	1.517 (5)
C(3)—N(2)	1.324 (5)	C(13)—C(14)	1.518 (5)
N(1)—C(4)	1.398 (4)	C(14)—C(15)	1.522 (5)
C(4)—C(5)	1.394 (4)	C(15)—C(16)	1.516 (5)
C(4)—C(9)	1.374 (4)	C(16)—C(17)	1.520 (5)
C(5)—N(2)	1.387 (4)	C(17)—C(18)	1.516 (6)
C(5)—C(6)	1.383 (5)	C(18)—C(19)	1.517 (6)
C(6)—C(7)	1.377 (5)	C(19)—C(20)	1.511 (6)
C(7)—C(8)	1.417 (5)	C(20)—C(21)	1.515 (7)
C(8)—C(9)	1.381 (5)		
O(1)—C(2)—C(1)	109.0 (3)	C(7)—C(8)—C(9)	119.5 (3)
O(1)—C(2)—C(3)	110.1 (3)	C(7)—C(8)—C(10)	118.5 (3)
C(1)—C(2)—C(3)	110.3 (3)	C(9)—C(8)—C(10)	122.0 (3)
C(2)—C(3)—N(1)	124.6 (3)	C(4)—C(9)—C(8)	117.4 (3)
C(2)—C(3)—N(2)	125.2 (3)	C(8)—C(10)—C(11)	117.4 (3)
N(1)—C(3)—N(2)	110.1 (3)	C(10)—C(11)—C(12)	112.6 (3)
C(3)—N(1)—C(4)	108.4 (3)	C(11)—C(12)—C(13)	114.2 (3)
N(1)—C(4)—C(5)	106.0 (3)	C(12)—C(13)—C(14)	113.9 (3)
N(1)—C(4)—C(9)	130.9 (3)	C(13)—C(14)—C(15)	113.7 (3)
C(5)—C(4)—C(9)	123.0 (3)	C(14)—C(15)—C(16)	113.6 (3)
C(4)—C(5)—N(2)	106.6 (3)	C(15)—C(16)—C(17)	114.1 (3)
C(4)—C(5)—C(6)	120.4 (3)	C(16)—C(17)—C(18)	113.6 (3)
N(2)—C(5)—C(6)	132.9 (3)	C(17)—C(18)—C(19)	114.1 (3)
C(3)—N(2)—C(5)	108.8 (3)	C(18)—C(19)—C(20)	113.9 (4)
C(5)—C(6)—C(7)	116.9 (3)	C(19)—C(20)—C(21)	113.9 (4)
C(6)—C(7)—C(8)	122.8 (3)		

Program used to solve structure: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Molecular graphics: *ORTEP* (Johnson, 1965). Full-matrix least-squares refinement: *SHELXS*86 (Sheldrick, 1990). Following recommendations by Taylor & Kennard (1983), the H atoms of the N—H groups were placed at 1.03 Å from their N atoms in the direction obtained by refinement.

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Octaanisyl Cavitands and a Related Caviplex

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Abstract

The macrocyclic host 41,42,43,44,45,46,47,48-octa-methoxy-4,9,14,19,24,29,34,39-octamethylnonacyclo-$[35.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}.1^{22,26}.1^{27,31}.1^{32,36}]$octa-tetraconta-1(41),2,4,6(42),7,9,11(43),12,14,16(44),17,-19,21(45),22,24,26(46),27,29,31(47),32,34,36(48),37,-39-tetracosaene [(I), $C_{64}H_{64}O_8$] contains a cavity lined with eight O atoms. This 'cavitand' complexes a caesium ion more strongly than any other alkali-metal ion, as expected from molecular models. The structure of a CH_2Cl_2 solvate of (I) [which we term (I*a*)] was determined at 113 K. The conformation of the macrocycle appears to be stabilized by the intrusion of a 4-methyl group from a neighboring molecule. This conclusion was reinforced by the determination, at 115 K, of the structure of the ethanol solvate (I*b*)