

Clathrates of Organic Onium Halides, V: Preparation of New Clathrates and Structure of the 1-Propanol Inclusion of a bis-Quinuclidinium Salt

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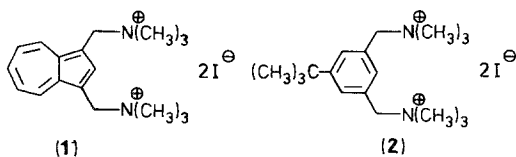
Abstract. Organic onium salts (**3–15**) are prepared and their inclusion capacity towards solvent molecules is investigated. The crystal structure of the 1 · propanol · H₂O clathrate of *N,N'*-[5-*tert*-butyl-1,3-phenylenebis(methylene)]bis(quinuclidinium)dibromide (**4**) is reported and compared with the X-ray structures of related clathrates described earlier.

Key words: Inclusion, clathrate, clathrand, host/guest, X-ray analysis, ammonium compounds, phosphonium compounds, quinuclidinium derivative.

Supplementary Data: Details of the crystal structure are available on request from the Fachinformationszentrum Energie-Physik-Mathematik, D-7517 Eggenstein, Leopoldshafen 2, by quoting the depository number CSD 50883, the names of the authors, and the journal citation.

1. Introduction

In previous communications, we have demonstrated that organic oligo-onium salts like (**1**) and (**2**) behave as versatile clathrate hosts [1–4].

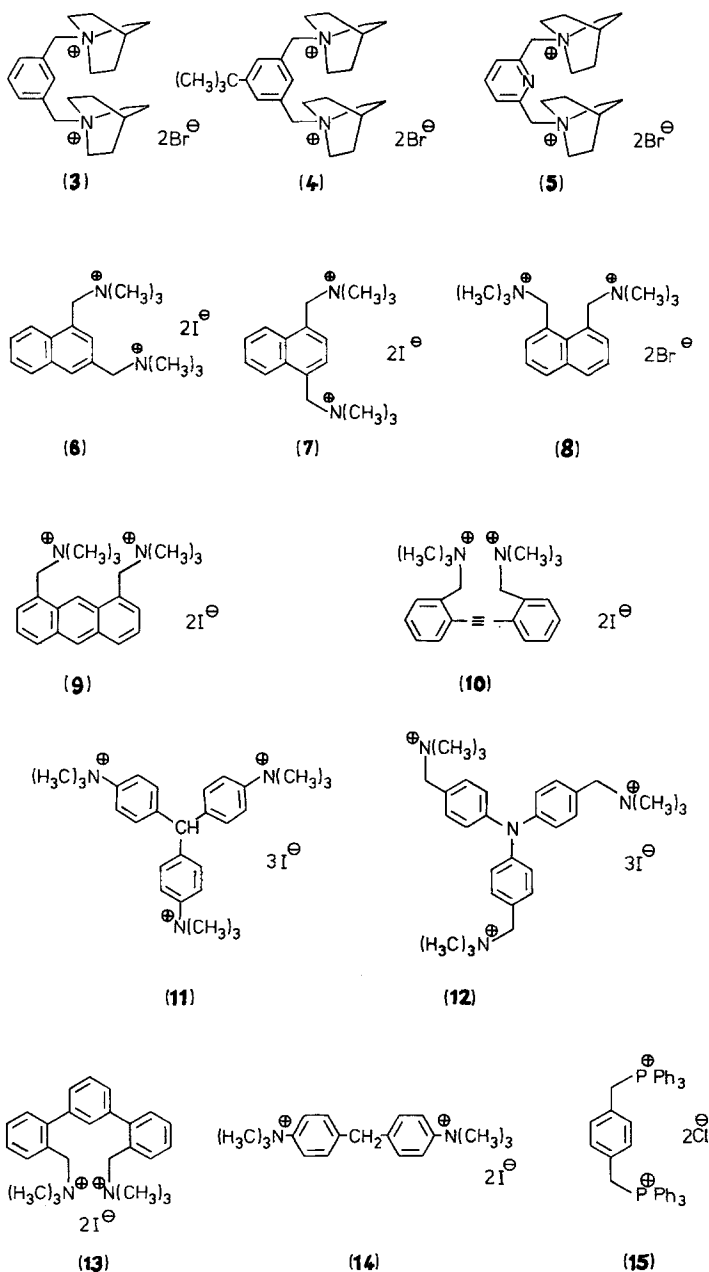


The host lattice and the conformation of the host molecule are governed by a special guest molecule and cage-type cavities with a cisoid arrangement of the charged side branches are formed in the azulene-bis(ammonium)diiodide (**1**) by including iodomethane [2] and 1,4-butanediol [4], whereas the ammonium substituents are orientated to the opposite sides

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of the azulene ring plane in the channel-type (1) · butanol inclusion compound [3]. Again, in the ethanol clathrate of the host (2) the onium arms are located above and below the benzene ring plane, the cavities, however, are of the cage-type [1].

To determine the influences of further structural modifications in the onium salts on the properties of clathrate formation, we have synthesized the onium halides (3)–(15) and investigated their inclusion ability.



2. Results and Discussion

The change from the most versatile host (**1**) with azulene as the anchor group to naphthalene derivatives (**6**)–(**8**) causes a decrease in the inclusion capacity. Only the 1,4-isomer (**7**) includes some guests, showing high affinity with BTX aromatics. The hosts (**3**)–(**5**) with quinuclidinium side branches and bromide as counterions prefer alcohol molecules as guests in their lattices (Table I, cf. Table I in [1]).

Table I. Clathrates of the host compounds (**3**)–(**5**), (**7**), (**11**) and (**15**)

Clathrand	Guest molecules	Molar ratio of host : guest ^a	Molar ratio of host : water ^b
(3)	methanol	1 : 1	–
	ethanol	2 : 1	2 : 1
(4)	ethanol	1 : 1	1 : 2
	1-propanol	1 : 1	1 : 1
	2-propanol	1 : 1	1 : 1
(5)	ethanol	ca.2 : 1	–
(7)	1-butanol	2 : 1	1 : 1
	benzene	2 : 1	1 : 1
	toluene	2 : 1	2 : 1
	1,2-xylene	2 : 1	1 : 1
	1,3-xylene	2 : 1	1 : 1
	1,4-xylene	2 : 1	1 : 1
(11)	dimethylformamide	1 : 1	–
	acetone	2 : 1	–
(15)	pyridine	1 : 1	–

^a The molar ratios of host : guest were determined by elemental analysis and/or by multiple integration of the ¹H-NMR spectra, employing [D₆]dimethylsulfoxide as solvent.

^b The molar ratios of host : water were determined by elemental analysis.

Although some of the salts do not include organic solvent molecules, they often retain water in stoichiometric amounts upon recrystallization (Table III). Also, many clathrates contain additional water.

The (**4**)·1-propanol·H₂O clathrate, obtained from 1-propanol by recrystallization, forms square-shaped, colourless, opaque crystals.

Crystal data: (**4**)·1-C₃H₇OH·H₂O[C₂₆H₄₂Br₂N₂·C₃H₈O·H₂O, M = 620.57, orthorhombic, space group *Pnma*, *a* = 1469.6(3), *b* = 1627.6(5), *c* = 1265.9(3) pm, *V* = 3.028 nm³, *Z* = 4, *d* = 1.33 g cm⁻³, *μ* = 26.23 cm⁻¹. Final *R* = 0.045 for 1702 unique reflexions [*θ* < 25°, *F* > 3σ(*F*)], using unit weights. The intensity data were measured at 188 K on a fourcircle diffractometer CAD4 (Enraf–Nonius) using MoK α -radiation and a graphite monochromator. No correction for absorption was made.

The position of the bromine atom was determined by direct methods (MULTAN 80) [5]. All carbon and nitrogen atoms, and even most of the hydrogen atoms, of the host molecule could be localized in a difference Fourier map. The oxygen atom of the water molecule and three atoms (C, O) of the 1-propanol guest are situated on the crystallographic mirror plane. The fourth C, resp. O, atom of the alcohol molecule was found beside the plane. Because of the space group symmetry, it appears twice and, thus, two orientations of the solvent are possible in the cavity.

The bond angles obtained differ considerably from expected values so that a disordering of the guest molecule may be assumed. It was not possible to distinguish between the C and O atoms of the alcohol. Hence, the position of the OH group could not be defined.

The refinement was carried out by full matrix least-squares methods (SHELX 76) [6]. Anisotropic temperature factors were applied for the Br, C, N and O atoms, while the H atoms of the host were included with constraints (C—H 108.0 pm) and a common isotropic temperature factor.

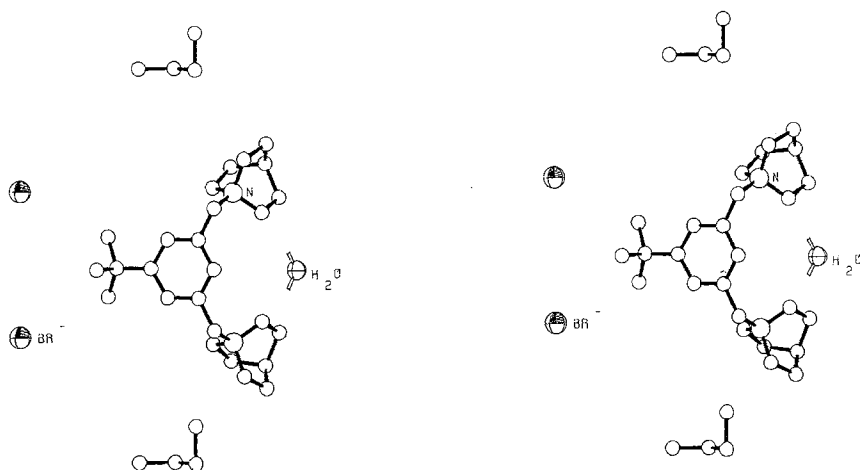


Fig. 1. Conformation of the host and guest molecules in the (4)·1-propanol·H₂O clathrate (stereoscopic illustration).

Figure 1 shows the conformation of the host and guest molecules in detail. In addition to the stoichiometric amount of propanol, a molecule of water is also enclosed. The small distance of 3.48 Å between bromide and H₂O suggests the existence of hydrogen bonds. The shortest distance between water and propanol amounts to more than 4.1 Å, excluding any hydrogen bonding in this case.

In contrast to the ethanol inclusion compound of (2), the two ammonium side branches of the quinuclidinium salt are arranged cisoid (*C_s* symmetry of the host), but again, four host molecules limit a cage-type cavity containing the propanol guest (Figures 2 and 3).

As shown in previous studies, systematic modifications of structural moieties lead to further clathrate-formers of the onium type, provided that certain features are preserved [1]. The findings that rigid, planar aromatic rings serve as proper anchor groups, and that methylene bridges are suitable as spacers, are verified by this work.

Trimethylammonium groups have been proved to be suitable as charged side branches in onium clathrands, whereas triethylammonium groups are less suited. This investigation demonstrates that the more rigid and bulky quinuclidinium group represents a better substitute, offering new possibilities for further structural variability.

Further investigations should allow predictions of how a specific onium compound has to be designed to enable the selective lattice inclusion of a specific guest molecule.

Table II. Atomic coordinates and anisotropic temperature factors (10^2 pm^2)^a

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br	0.26015(4)	0.06542(4)	0.03243(5)	5.17(3)	5.09(4)	3.88(3)	0.95(3)	0.01(3)	0.19(3)
C(1)	0.29306(53)	0.17464(41)	0.34831(48)	9.68(56)	5.05(42)	3.25(32)	-0.46(33)	-0.91(36)	-0.13(42)
C(2)	0.25618(59)	0.25000	0.40505(62)	4.74(49)	3.55(44)	3.19(41)	0.0	-1.13(42)	0.0
C(3)	0.15153(68)	0.25000	0.39860(81)	5.00(58)	10.53(94)	4.85(60)	0.0	-2.04(50)	0.0
C(4)	0.28093(46)	0.25000	0.52141(62)	2.37(37)	2.66(40)	3.41(42)	0.0	-0.56(35)	0.0
C(5)	0.28977(32)	0.17654(35)	0.57928(40)	2.42(26)	3.54(32)	3.12(28)	-0.24(27)	-0.89(23)	0.02(24)
C(6)	0.30721(32)	0.17587(34)	0.68626(40)	1.74(25)	3.51(31)	3.19(28)	0.45(26)	0.07(22)	0.27(23)
C(7)	0.31490(49)	0.25000	0.74016(60)	2.61(38)	3.24(42)	2.94(41)	0.0	0.11(34)	0.0
C(8)	0.31276(33)	0.09465(31)	0.74335(43)	2.45(26)	3.23(29)	3.39(29)	0.51(27)	0.35(24)	-0.53(24)
C(9)	0.40883(26)	0.05978(27)	0.75159(32)	2.95(22)	3.02(24)	2.78(22)	0.26(23)	-0.07(19)	-0.33(21)
C(10)	0.45285(35)	0.05182(38)	0.64429(42)	3.40(30)	4.78(38)	3.05(29)	0.56(29)	0.63(24)	0.05(28)
C(11)	0.54173(39)	0.00445(41)	0.65377(50)	4.04(33)	4.97(40)	4.79(36)	0.24(33)	0.45(29)	1.03(31)
C(12)	0.56657(39)	-0.00643(37)	0.76930(47)	3.37(30)	4.73(37)	4.65(38)	0.38(32)	-0.27(28)	0.89(30)
C(13)	0.56537(39)	0.07842(39)	0.82239(53)	3.81(32)	4.96(41)	5.73(41)	-0.14(34)	-1.47(30)	0.41(32)
C(14)	0.46792(36)	0.11141(35)	0.82240(48)	3.63(32)	3.34(34)	4.81(37)	-0.33(30)	-1.27(28)	-0.23(26)
C(15)	0.40047(38)	-0.02524(34)	0.80017(45)	4.61(33)	2.95(31)	3.75(31)	0.81(28)	0.16(28)	-0.06(28)
C(16)	0.49499(38)	-0.05950(39)	0.82284(50)	4.77(34)	3.91(36)	5.12(37)	0.80(33)	-0.06(29)	0.86(32)
O(1)	0.37818(54)	0.25000	1.01512(66)	8.34(55)	8.24(57)	9.39(61)	0.0	2.20(49)	0.0
C(1P)	0.11118(75)	0.25000	0.90342(81)	7.02(70)	8.92(85)	4.76(60)	0.0	0.99(57)	0.0
C(2P)	0.08401(82)	0.25000	1.10253(92)	8.23(82)	8.49(89)	5.98(72)	0.0	-0.32(63)	0.0
C(3P)	0.07787(93)	0.34410(80)	1.0987(13)	6.23(88)	3.73(77)	10.7(12)	-4.73(85)	4.74(87)	-2.21(69)
C(4P)	0.04741(96)	0.25000	0.9980(10)	6.89(88)	36.9(30)	5.30(82)	0.0	-1.31(67)	0.0

^a The anisotropic temperature factors are defined as $T = \exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hab^* U_{12} + \dots)]$.

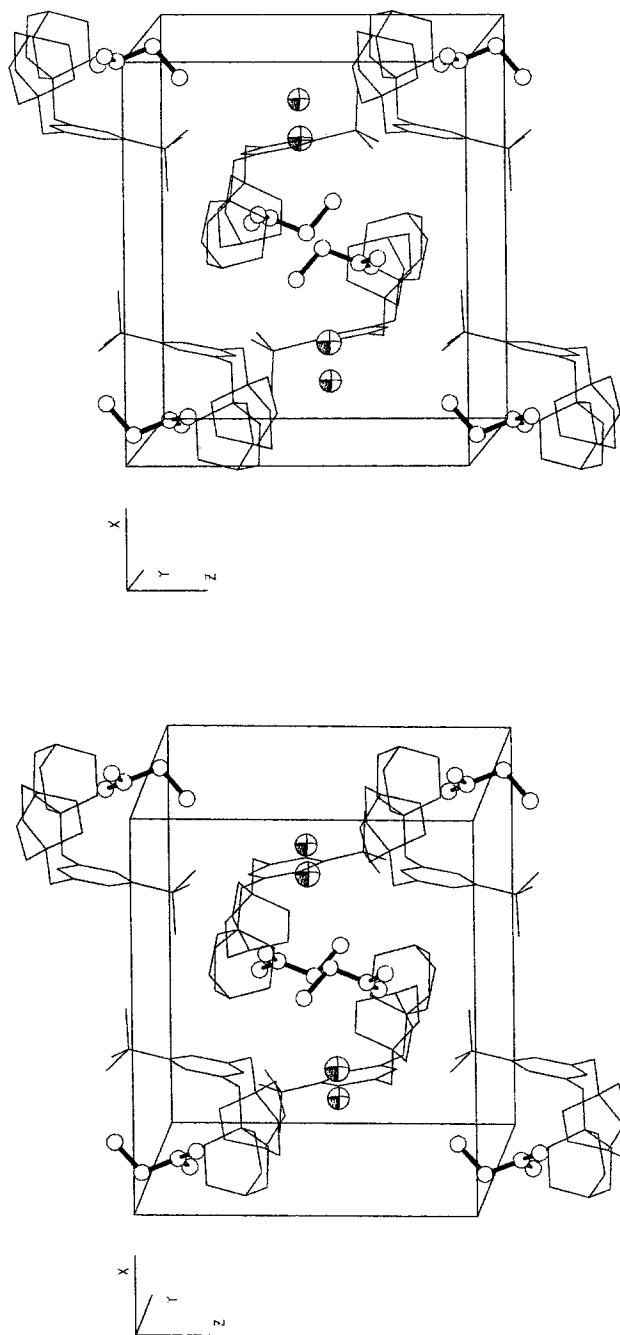


Fig. 2. Unit cell of the $(4) \cdot C_3H_7OH \cdot H_2O$ clathrate (stereoscopic illustration).

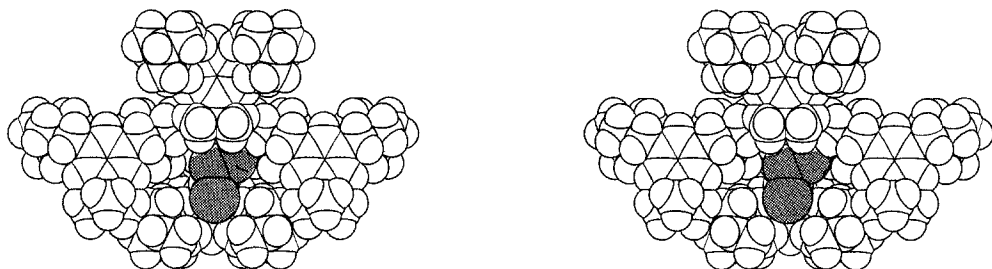


Fig. 3. Illustration of the propanol guest (marked by the dotted pattern) in the cage-type cavity (stereo figure).

3. Experimental

3.1. SYNTHESIS OF THE QUINUCLIDIUM BROMIDES (3)–(5)

General procedure. 1.0 mmol of the corresponding bis(bromomethyl) compound and 2.0 mmol of quinuclidine were refluxed in dry methanol (60 ml) for 8 h. After cooling and the addition of ether, colourless crystals were obtained (Table III).

Table III. Experimental data for the onium halides

No.	m.p. [°C]	Formula (mol. weight)	Elementary analysis			
			C	H	N	
(3)	– ^a	$C_{22}H_{34}Br_2N_2 \cdot \frac{1}{2}C_2H_5OH \cdot \frac{1}{2}H_2O^b$ (518.4)	Calcd	53.29	7.39	5.40
			Found	53.16	7.65	5.50
(4)	– ^a	$C_{26}H_{42}Br_2N_2 \cdot C_2H_5OH \cdot 2H_2O^b$ (624.5)	Calcd	53.84	8.39	4.48
			Found	54.32	8.11	4.67
(5)	– ^a	$C_{21}H_{33}Br_2N_3 \cdot 3H_2O$ (541.3)	Calcd	46.60	7.26	7.76
			Found	46.67	7.23	7.71
(6)	183	$C_{18}H_{28}I_2N_2 \cdot H_2O$ (544.3)	Calcd	39.72	5.56	5.15
			Found	39.44	5.56	5.13
(7)	200–202	$C_{18}H_{28}I_2N_2 \cdot H_2O$ (544.3)	Calcd	39.72	5.56	5.15
			Found	39.77	5.55	5.22
(8)	223–225	$C_{18}H_{18}Br_2N_2 \cdot \frac{3}{2}H_2O$ (459.3)	Calcd	47.07	6.80	6.10
			Found	47.38	6.82	6.05
(9)	– ^a	$C_{22}H_{30}I_2N_2$ (576.9)	Calcd	45.85	5.25	4.86
			Found	45.33	5.09	4.83
(10)	> 300	$C_{22}H_{30}I_2N_2$ (576.9)	Calcd	45.44	5.24	4.84
			Found	45.85	5.25	4.86
(11)	185–187 (dec.)	$C_{28}H_{40}I_3N_3 \cdot 2H_2O$ (835.4)	Calcd	40.26	5.31	5.03
			Found	40.24	5.22	4.96
(12)	– ^a	$C_{30}H_{45}I_3I_4$ (842.4)	Calcd	42.77	5.38	6.65
			Found	42.74	5.38	6.59
(13)	> 300	$C_{26}H_{34}I_2N_2$ (628.4)	Calcd	49.85	5.15	4.47
			Found	49.47	5.53	4.45
(14)	191–196	$C_{19}H_{28}I_2N_2 \cdot H_2O$ (556.3)	Calcd	41.03	5.44	5.04
			Found	41.28	5.45	4.81

^a The compound decomposes in a way that it is impossible to determine a definite melting range.

^b The salt could not be obtained without solvent.

3.2. SYNTHESIS OF THE TRIMETHYLAMMONIUM IODIDES (6), (7), (9)–(14)

General procedure. An excess of condensed dimethylamine was added to a solution of the corresponding benzyl bromide (2–30 mmol) in benzene or toluene (20–30 ml). After heating in a sealed tube for 12–15 h at 60–70°C, dimethylammonium bromide was filtered off and the solution is evaporated to dryness. The remaining oil is stirred with an excess of iodomethane in *ca.* 80 ml methanol at ambient temperature for several hours. Either the iodides precipitated during this time or upon the addition of ether. The salts (**11**) and (**14**) were obtained directly from the tertiary amines by methylation (Table III).

3.3. SYNTHESIS OF THE TRIMETHYLAMMONIUM BROMIDE (8)

Gaseous trimethylamine was passed into a refluxing solution of 1.0 mmol of 1,8-bis(bromo-methyl)naphthalene in 60 ml benzene for 0.5 h. During this time, the product precipitates (Table III).

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