

A New Clathrate Featuring a Spiro-Type Ammonium Host. X-Ray Structure of the Inclusion Compound with Chloroform[★]

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Abstract

A new onium salt host molecule **1** featuring a spiro-type ammonium backbone was synthesized and shown to form a crystalline inclusion compound with chloroform, **1**·chloroform (1:2), the crystal structure of which is reported. The host molecular interactions including C–H···Br, Cl···Cl and aromatic stacking contacts are typical of the packing structure.

Introduction

Various kinds of artificial macrocyclic quaternary ammonium salts with hydrophilic cavities have been designed and studied due to their strong preference for complexation of anionic guests [1]. Others were used as inclusion hosts for uncharged molecules in aqueous solution [2], as enzyme models [3] or for the construction of self-assembling systems [4] and supramolecular devices [5]. Compared with the cavity and cleft type ammonium salt receptors, the organic ammonium salt hosts not featuring a distinct cavity structure are less developed, although a number of compounds of different structure exist [6]. They have been found to form a variety of crystalline inclusion complexes (clathrates) with neutral organic guest molecules [7]. Nevertheless, a spiro type clathrate analogue where the ammonium nitrogen represents the spiro atom of the host molecule is not in the literature [6, 7].

Here we report on the first example of a respective compound which is the crystalline inclusion of **1** with chloroform (1:2).

Experimental

Synthesis

General. The melting points (uncorrected) were taken on a heating stage microscope (Rapido, Dresden). The NMR spectra (δ in ppm, J in Hz, Me₄Si as internal standard) were obtained with Bruker Avance DPX 400 (¹H: 400 MHz, ¹³C: 100.61 MHz). The mass spectrum (ESI) was determined on a Hewlett-Packard HP 59987 A instrument. All reagents were commercial products and were utilized without further purification. The solvents used were purified or dried by common literature procedures [8].

2,2'-Bis(bromomethyl)biphenyl was obtained by bromination of 2,2'-dimethyl-biphenyl with N-bromosuccinimide according to the literature [9] as colorless crystals (53%); m.p. 81–83 °C (from benzene-petroleum ether).

1,4-Dimethyl-1,4,7-triazacyclononane was prepared by detosylation of 7-*p*-tosyl-1,4-dimethyl-1,4,7-triazacyclononane with hydrobromic acid according to the literature [10] which yielded 81% colorless oil; b.p. 36–38 °C (0.5 Torr).

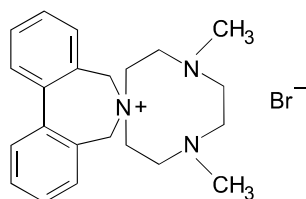
Spiro compound (**1**)

To a solution of 1,4-dimethyl-1,4,7-triazacyclonane (0.16 g, 1 mmol) and triethylamine (0.2 g, 1 mmol) in tetrahydrofuran (20 mL) was added in small portions

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2,2'-bis(bromomethyl)-biphenyl (0.34 g, 1 mmol), and the mixture stirred at room temperature for 1 d. The colorless solid which has formed was isolated, washed with tetrahydrofuran, and dissolved in methanol. Then sodium hydroxide (0.04 g) was added, stirred for 3 h, and the precipitate of sodium bromide filtered off (Celite). The solvent was evaporated under reduced pressure, and the solid subjected to vacuum (0.5 Torr) for several h to remove the triethylamine, which yielded 91% of product as a colorless solid; m. p. 138 °C; $^1\text{H-NMR}$ (CDCl_3) δ 2.41 (s, 6 H, CH_3), 2.53 (m, 4 H, $\text{N}^+\text{CH}_2\text{CH}_2\text{NCH}_3$), 2.58 (s, 4 H, $\text{CH}_3\text{NCH}_2\text{CH}_2\text{NCH}_3$), 2.66 (m, 4 H, $\text{N}^+\text{CH}_2\text{CH}_2\text{NCH}_3$), 3.39 (s, 4 H, ArCH₂), 7.53 (m, 2 H, Ar-H), 7.63 (m, 4 H, Ar-H), 7.86 (dd, $^3J = 7.6$ Hz, 2 H, Ar-H); $^{13}\text{C-NMR}$ (CDCl_3) δ 48.0 (NCH₃), 54.0, 58.4, 59.4 (NCH₂CH₂N), 63.4 (ArCH₂N), 126.8, 129.0, 131.1, 132.5, 140.6 (Ar); MS(ESI) $m/z = 336$ (M-Br⁻, 100%); calcd. for $\text{C}_{22}\text{H}_{30}\text{BrN}_3$: $M = 416.40$ (Scheme 1).



Scheme 1.

Crystallography

Crystals suitable for X-ray investigations were grown by slow evaporation of a solution of **1** in chloroform. The intensity data, collected on a Bruker SMART CCD diffractometer using MoK α radiation and the ω - 2θ scan mode at 173 K was employed. Details of data collection and those of refinement procedure are given in Table 1. The structure was solved by direct methods using the SHELXS 97 [11] program package, and refined by anisotropic full-matrix least squares refinement [12]. The positions of the hydrogen atoms could be gained from the difference Fourier map.

Results and discussion

Synthesis

Compound **1** was synthesized as a colorless solid in 91% yield from 1,4-dimethyl-1,4,7-triazacyclononane [10] and 2,2'-bis(bromomethyl)biphenyl [9] in tetrahydrofuran in the presence of triethylamine. Recrystallization of **1** from chloroform yielded the corresponding inclusion

Table 1. Crystal data, experimental parameters and selected details of refinement calculations for **1**·chloroform (1:2)

Compound	1 ·CHCl ₃ (1:2)
Formula	C ₂₂ H ₃₀ N ₃ Br·2 CHCl ₃
Molar mass	655.14
Crystal system, space group	triclinic, <i>P</i> -1
Unit cell dimensions	
<i>a</i> (Å)	10.9173 (1)
<i>b</i> (Å)	10.9296 (1)
<i>c</i> (Å)	12.5705 (1)
α (deg)	99.577 (1)
β (deg)	100.336 (1)
γ (deg)	91.793 (1)
<i>V</i> (Å ³)	1452.13 (2)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.498
μ (mm ⁻¹)	1.986
<i>F</i> (0 0 0)	663
Data collection	
Radiation (Å)	0.71073
Temperature (K)	173 (2)
Approximate crystal size (mm)	0.60 × 0.60 × 0.40
No. of collected reflections	11341
within the θ -limit (deg)	1.67–30.25
No. of unique reflections	7556
Refinement calculations full-matrix least-squares based on all <i>F</i> ² values	
No. of refined parameters	435
<i>R</i> ₁ indices $\Sigma \Delta F /\Sigma F_0 $	0.0386
No. of <i>F</i> values used [<i>I</i> > 2 σ (<i>I</i>)]	6236
<i>wR</i> on <i>F</i> ²	0.0991
<i>S</i> (= Goodness of fit on <i>F</i> ²)	1.038

compound of composition **1**·CHCl₃ (1:2) which has been manifested by ^1H NMR integration.

Structural study

The 1:2 inclusion compound of the ammonium salt **1** with chloroform crystallizes in the space group *P*-1 with one host molecule in the asymmetric unit of the cell. The central nitrogen atom of the spiro cation exhibits a nearly tetrahedral binding environment with the C–N–C angles between 108.2 and 112.5°. Its C–N bond lengths (1.521–1.531 Å) are significantly longer than those of the methyl substituted nitrogen atoms (1.454–1.475 Å). The torsion angles of the nine membered ring may be grouped in three classes. Those which represent a +*gauche* conformation are given by the N–C–C–N sequences (53.5–73.7°). The C–N–C–C torsion angles involving the methyl substituted nitrogens are –101.7 and –109.2° (*anti-clinal*), whereas those of the remaining C–N–C–C sequences range between –73.8 and 78.9° (\pm *gauche*). These parameters which are summarized in Table 2 indicate a less strained conformation of the spiro cation.

As can be seen from Figure 1, the bromide ion is not in close contact with the ammonium nitrogen *via* ion–

Table 2. Selected intramolecular distances (Å) and angles (deg) of **1** in **1**·CHCl₃ (1:2)

Atoms involved	Bond lengths (Å)	Bond angles	Torsion angles
N(1)—C(1)	1.521 (0)		
N(1)—C(7)	1.531 (1)		
N(1)—C(20)	1.522 (1)		
N(1)—C(6)	1.521 (0)		
N(2)—C(2)	1.463 (1)		
N(2)—C(3)	1.475 (1)		
N(2)—C(21)	1.456 (0)		
N(3)—C(4)	1.466 (1)		
N(3)—C(5)	1.454 (0)		
N(3)—C(22)	1.462 (1)		
C(1)—N(1)—C(6)		112.5 (2)	
C(1)—N(1)—C(7)		108.2 (2)	
C(1)—N(1)—C(20)		109.6 (2)	
C(6)—N(1)—C(7)		108.9 (2)	
C(6)—N(1)—C(20)		108.2 (2)	
C(7)—N(1)—C(20)		109.4 (2)	
N(1)—C(1)—C(2)—N(2)			53.5 (3)
N(1)—C(6)—C(5)—N(3)			73.7 (2)
N(2)—C(3)—C(4)—N(3)			69.7 (3)
C(1)—C(2)—N(2)—C(3)			78.9 (2)
C(2)—N(2)—C(3)—C(4)			-101.7 (2)
C(3)—C(4)—N(3)—C(5)			-109.2 (2)
C(4)—N(3)—C(5)—C(6)			58.7 (3)
C(5)—C(6)—N(1)—C(1)			-55.2 (2)
C(6)—N(1)—C(1)—C(2)			-73.8 (2)
C(8)—C(13)—C(14)—C(19)			42.9 (3)

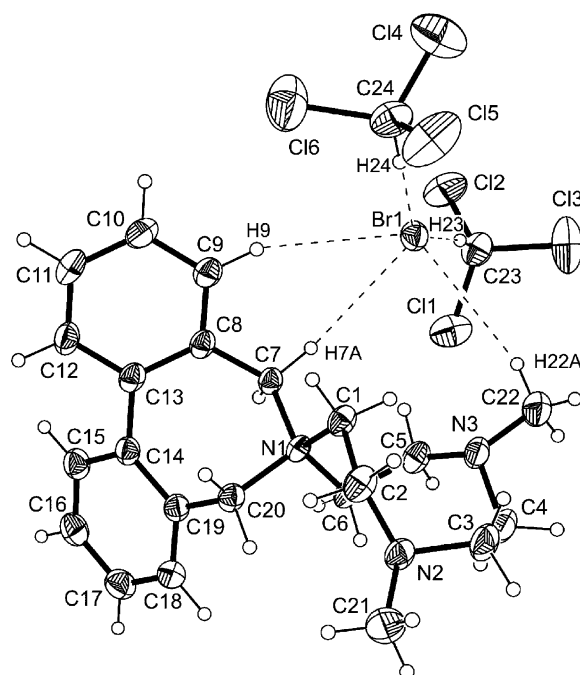


Figure 1. Perspective view of **1**·CHCl₃ (1:2) with the crystallographic numbering of the non-hydrogen sites. The displacement ellipsoids of the non-hydrogen atoms are drawn at 30% probability level. Dashed lines represent hydrogen bond type interactions.

ion interaction but is in a relationship of hydrogen bond type to H(7A), H(9) and H(22A) ($d = 2.78$ – 3.03 Å). Moreover, two stronger C—H...Br interactions around the bromide ($d = 2.58$ – 2.62 Å) are established by the chloroform molecules (Table 3).

The two phenyl groups contained in the seven membered ring of the cation adopt a torsion angle of 42.9° [C(8)—C(13)—C(14)—C(19)], thus allowing intermolecular aromatic stacking interactions with a mean distance of 3.74 Å between these groups (Figure 2). The packing structure of the compound also reveals that part of the chlorine atoms of the guest molecules are involved in weak Cl...Cl contacts (Table 3). These show angles of 122 – 145° [C—Cl...Cl] which do not correspond with the true angle characteristics of nucleophile or electrophile orientations of attack (near 90 and 180° , respectively [13]) but are in between these values [14]. Together with the mentioned H...Br interactions, they give rise to infinite supramolecular zigzag chains which run along the crystallographic a -axis. According to the orthogonal nature of the spiro cation, the internal structure of the host lattice can be characterized by formation of channel-like voids into which the incorporated guest molecules are arranged in such a manner that non-polar undulated layers are formed separating the ionic layers from one another.

Table 3. Distances (Å) and angles (deg) of hydrogen bond and Cl...Cl type interactions of **1**·CHCl₃ (1:2)

Atoms involved	Symmetry	Distances		Angle
		D...A	H...A	D—H...A
C(7)—H(7A)...Br(1)	x, y, z	3.701 (0)	2.78	164
C(23)—H(23)...Br(1)	x, y, z	3.518 (0)	2.58	171
C(24)—H(24)...Br(1)	x, y, z	3.529 (0)	2.62	162
C(9)—H(9)...Br(1)	x, y, z	3.845 (0)	3.02	150
C(22)—H(22A)...Br(1)	x, y, z	3.878 (0)	3.03	144
C(16)—H(16)...Cl(4)	x, y, z	3.637 (0)	2.90	138
			Cl...Cl	C—Cl...Cl
C(23)—Cl(3)...Cl(6)	$-1-x, -y, -z$		3.67	133
C(24)—Cl(6)...Cl(3)	$-1-x, -y, -z$		3.67	145
C(24)—Cl(4)...Cl(4)	$-1-x, -y, -z$		3.68	122

Hence, a first example of an onium salt crystalline host compound featuring a spirotype ammonium backbone is shown, inviting to structural modifications [7].

Acknowledgements

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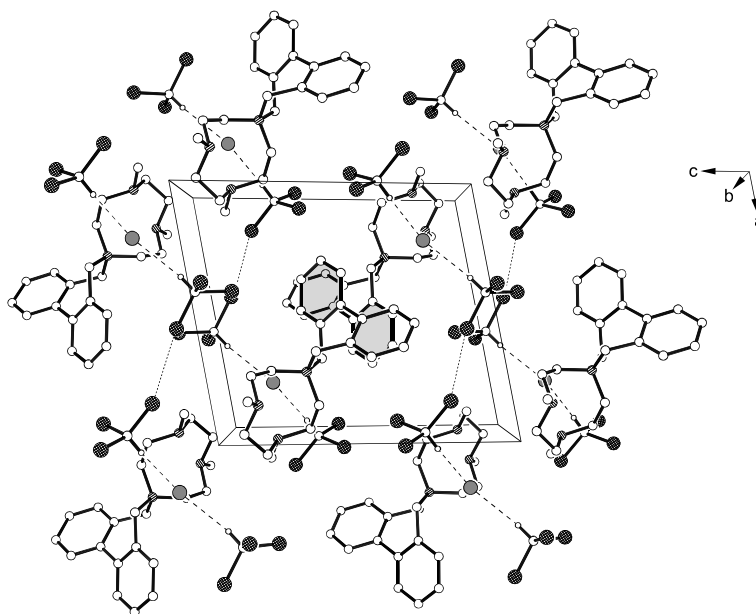


Figure 2. Packing illustration of $1 \cdot \text{CHCl}_3$ (1:2). Heteroatoms are shaded. Dashed and dotted lines represent hydrogen bond type ($\text{C}-\text{H} \cdots \text{Br}$) and $\text{Cl} \cdots \text{Cl}$ interactions, respectively. The aromatic stacking interaction is indicated by shaded phenylene rings.

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