

The Structure of the 1,4-Butanediol Clathrate of a Bis-Ammonium Salt of Azulene

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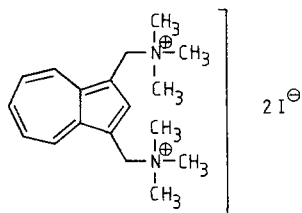
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Abstract. The X-ray structure of the 1,4-butanediol clathrate of *N,N'*-[1,3-azulenylenebis(methylene)]bis(trimethylammonium)-diiodide is described, and the differences as well as the similarities to the 1-butanol inclusion of the same host are discussed in detail. The unit cell data of further clathrates of this new type are quoted.

Key words: Inclusion, clathrate, clathrand, host/guest, X-ray analysis, onium compounds, azulene derivative.

Supplementary Data. Details of the crystal structure are available on request from the Fachinformationszentrum Energie-Physik-Mathematik, D-7515 Eggenstein, Leopoldshafen 2, by quoting the depository number CSD50482, the names of the authors, and the journal citation.

As we have recently reported, organyl-oligo ammonium salts belong to the most universal clathrate hosts of organic chemistry [1]. They are unique in their versatile inclusion ability and their adaptability to the geometry of the clathrated species [2]. Up to the present time, we have found more than 30 different stoichiometric inclusion compounds of the azulenylene-bis-ammonium host **1**; moreover, the modification of the host structure led to further 'clathrands' [3] of this type, with similar extensive inclusion capacities (cf. [1,2]).



(1)

As shown by the X-ray investigations of the **1**·iodomethane [1] and **1**·1-butanol clathrates [2], lattice inclusions are present. Apparently, the guest molecules are fixed sterically by the stable ionic host lattice, without specific host/guest interactions. The conformation of

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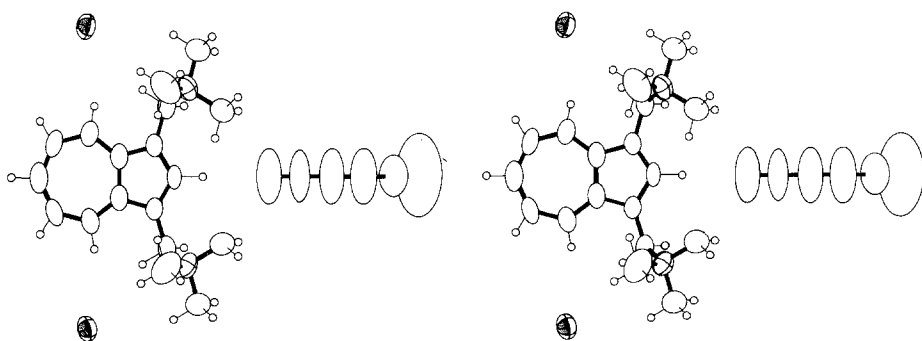


Fig. 1. Conformation of the host and guest molecules in the $1 \cdot 1,4$ -butanediol clathrate (stereoscopic illustration).

the host molecules **1** and their spatial arrangement in the clathrate lattice depend on size and structure of the incorporated guest molecules. Whereas, in the $1 \cdot$ iodomethane clathrate the two ammonium side branches are oriented to the same side (cisoid) of the azulene ring plane, one finds a transoid arrangement in the 1-butanol inclusion. Further differences exist in the type of the host cavities: iodomethane is encapsulated by several azulene units in a *cage* form, whereas 1-butanol is situated in oval-like extensions of *channels*. The butanol guests showed a specific head–tail disorder, which suggested that the oval-like extensions also offer sufficient space for 1,4-butanediol and would include it in a similar way. To our surprise, we obtained different cell parameters for the $1 \cdot 1,4$ -butanediol adduct by a single crystal measurement [2]. Therefore, it seemed to be interesting to examine the crystal structure of the $1 \cdot 1,4$ -butanediol inclusion compound by a complete X-ray analysis, and to point out the differences to the $1 \cdot 1$ -butanol clathrate.

The $1 \cdot 1,4$ -butanediol adduct is obtained by recrystallization of the ammonium salt **1** from 1,4-butanediol as solvent. It forms compact, violet, transparent crystals having a columnar shape. By heating to temperatures higher than 145 °C, the crystals gradually turn opaque due to the beginning of decomposition. Crystal data: $1 \cdot 1,4\text{-C}_4\text{H}_8(\text{OH})_2$, $[\text{C}_{18}\text{H}_{28}\text{I}_2\text{N}_2 \cdot \text{C}_4\text{H}_8(\text{OH})_2]$, $m = 616.36$, monoclinic, space group $P2_1/m$, $a = 785.1(2)$, $b = 1750.0(3)$, $c = 970.0(1)$ pm, $\beta = 96.50(1)^\circ$, $V = 1.324 \text{ nm}^3$, $Z = 2$. Final $R = 0.047$ for 2132 unique reflexions, using unit weights. The reflexions were measured on a four-circle-diffractometer CAD 4 (Enraf Nonius) using Mo- K_α -radiation and a graphite monochromator. No correction of the absorptions was made.

The position of the iodine atom of the asymmetric unit was determined by Patterson methods. All other atoms, including the hydrogen atoms of the host – but not of the guest – could be localized in the following difference electron density synthesis and the positions were refineable in the space group $P2_1/m$. Large anisotropic temperature factors and unacceptable bond distances and angles were found for the atoms of the guest. This suggests a statistical disorder of the butanediol molecules around the crystallographic symmetry plane.

Figure 1 shows the conformation of the host and guest molecules in detail. In conformity with the iodomethane inclusion [1], the two ammonium side branches of the host are arranged cisoid, which should be contrasted to the transoid orientation found in the 1-butanol clathrate [2]. The 1,4-butanediol has an *anti*-periplanar-like conformation.

The packing scheme of host and guest molecules in the lattice is displayed in Figure 2. Unlike the *channel-type* 1-butanol inclusion, a *cage-type* clathrate is present in this case.

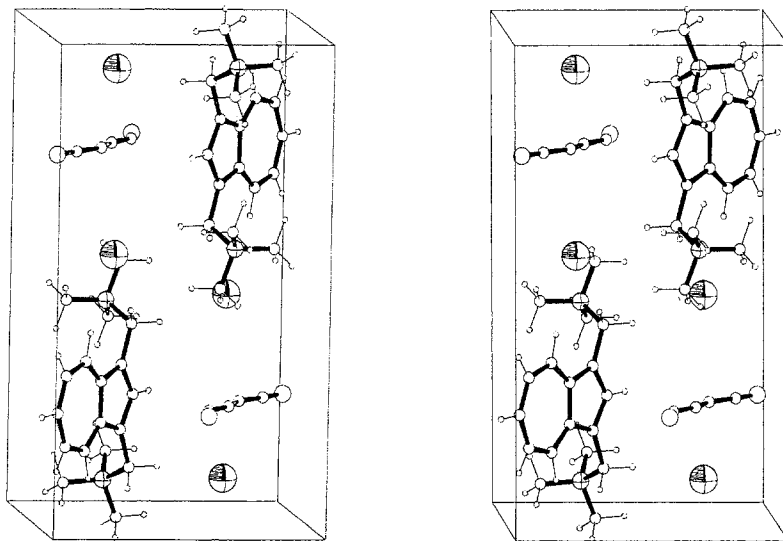


Fig. 2. Unit cell of the $1 \cdot 1,4$ -butanediol clathrate (stereoscopic illustration): view along the c -axis.

Although the conformation of the host molecules contrasts with that in the $1 \cdot 1$ -butanol clathrate, the size and the shape of the cavities are nearly equal: again the azulene rings are arranged in parallel planes forming the top and bottom sides of the cavities, and the lateral delimitation is given by the intermediary ammonium groups (Figure 3, cf. $1 \cdot 1$ -butanol in [2]).

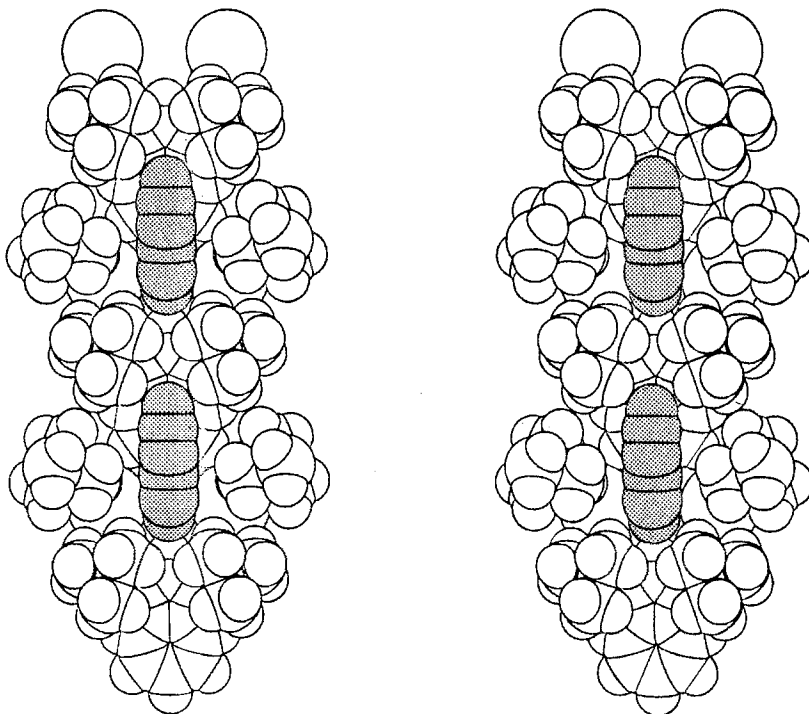


Fig. 3. Illustration of the butanediol guest (marked by dotted pattern) in the cavity (stereo figure): view perpendicular to the azulene-ring plane (space-filling drawing).

Table I. Crystal data of a few clathrates of the host **1**

Guest molecule	Molar ratio of host : guest	Space group	Crystal system	Z	Lattice parameters	Cell volume [nm ³]	Notes
1-C ₃ H ₇ OH	1 : 1	C2/c	monoclinic	4	<i>a</i> = 1647.6(13), <i>b</i> = 1217.4(9), <i>c</i> = 1352.5(13) pm, β = 109.55(6)°	2.556	isotype to 1 · C ₄ H ₉ OH
1-C ₄ H ₉ OH	1 : 1	C2/c	monoclinic	4	<i>a</i> = 1647.7(5), <i>b</i> = 1227.1(2), <i>c</i> = 1348.5(3) pm, β = 109.94(2)°	2.574	X-ray analysis [2]
2-C ₄ H ₉ OH	1 : 1	C2/c	monoclinic	4	<i>a</i> = 1650.3(6), <i>b</i> = 1213.3(4), <i>c</i> = 1366.4(5) pm, β = 108.26(3)°	2.598	isotype to 1 · C ₄ H ₉ OH
1,4-C ₄ H ₈ (OH) ₂	1 : 1	P2 ₁ /m	monoclinic	2	<i>a</i> = 785.1(2), <i>b</i> = 1750.0(3), <i>c</i> = 970.0(1) pm, β = 96.50(1)°	1.324	X-ray analysis
CH ₃ I	1 : 1	<i>Pnma</i>	orthorhombic	4	<i>a</i> = 1900.7(3), <i>b</i> = 1730.5(8), <i>c</i> = 755.5(3) pm	2.485	X-ray analysis [1]
BrCCl ₃	1 : 3	–	orthorhombic	8	<i>a</i> = 2413.3(30), <i>b</i> = 2652.3(20), <i>c</i> = 867.1(16) pm	5.550	–
CH ₃ NO ₂	1 : 1	–	triclinic	4	<i>a</i> = 760(6), <i>b</i> = 1763(14), <i>c</i> = 1930(8) pm, α = 88.3(5), β = 83.5(5), γ = 87.4(6)°	2.566	–

The cell data of a few clathrates of **1** (Table I), ascertained by single crystal measurements [4], indicate that the host **1** builds up further lattice structures with changed cavity proportions – depending on the enclosed species.

The similarity of the cell parameters of **1**·1-C₄H₉OH, **1**·2-C₄H₉OH and **1**·C₃H₇OH indicates that these clathrates are isotypes. The cell data of the other clathrates differ considerably, so that different crystal structure types must be inferred.

The versatile inclusion behavior of the clathrand **1** is probably caused by the conformational mobility of the ammonium side branches, whereas the high stability of the clathrates is conditioned by the ionic structure.

From the numerous oligo onium clathrates available, it is obvious that this host family offers a promising way to further specific guest inclusions.

References

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4. The lattice parameters were determined from single crystals by least squares refinement of the positions of 25 reflexions.