Steering of the Host Conformation and Host Lattice by Guest Molecules in Organic Ammonium Clathrates

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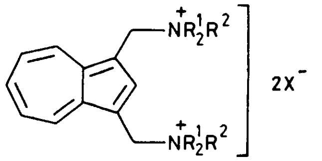
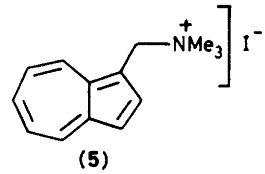
Systematic variations in the design of organic bis(ammonium) salts lead to a new, versatile host system with remarkable inclusion capacity; the *X*-ray structure analysis of the *N,N'*-(azulen-1,3-ylenedimethyl)bis(trimethylammonium) di-iodide (**1**)·butanol adduct, together with crystallographic data of further clathrates, demonstrates that the host conformation is essentially steered by the enclosed guest molecules, producing well adapted cavity proportions.

In a previous study, we have described the inclusion behaviour of the azulene-bis(ammonium) salt (**1**) with iodomethane and some other guest molecules.[1] The *X*-ray analysis of the (**1**)·iodomethane clathrate showed that the CH_3I molecules lay in *cage*-type cavities, enclosed by several azulene host units.

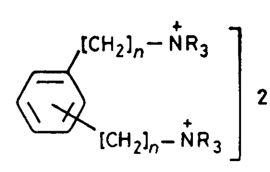
We have now examined the crystalline inclusion of butan-1-ol as a guest in the same host (**1**) and found that not only do the host molecules occur in a basically different *conformation*, but also the host *lattice* has changed, forming *channel*-type cavities, which incorporate the butanol guests, disorientated in a characteristic manner. As for the iodomethane inclusion, there is no evidence for strong binding interactions between host and guest molecules. Apparently, the guests are fixed sterically by the stable ionic host lattice. The determination of the cell parameters of other clathrates of (**1**) indicates that further crystal structures [(**1**)·CH_3NO_2 (1 : 1), (**1**)·$BrCCl_3$ (1 : 3), (**1**)·1,4-$C_4H_8(OH)_2$ (1 : 1)] with different cavity geometries exist.



(1) $R^1 = R^2 = Me, X = I$
(2) $R^1 = R^2 = Me, X = Br$
(3) $R^1 = R^2 = Me, X = I_3$
(4) $R^1 = Me, R^2 = Et, X = I$



(5)



	position	
(6)	*m*	R = Me, X = I, *n* = 1
(7)	*m*	R = Et, X = I, *n* = 1
(8)	*m*	R = Et, X = Br, *n* = 1
(9)	*o*	R = Me, X = I, *n* = 1
(10)	*p*	R = Me, X = I, *n* = 1
(11)	*m*	R = Me, X = I, *n* = 2

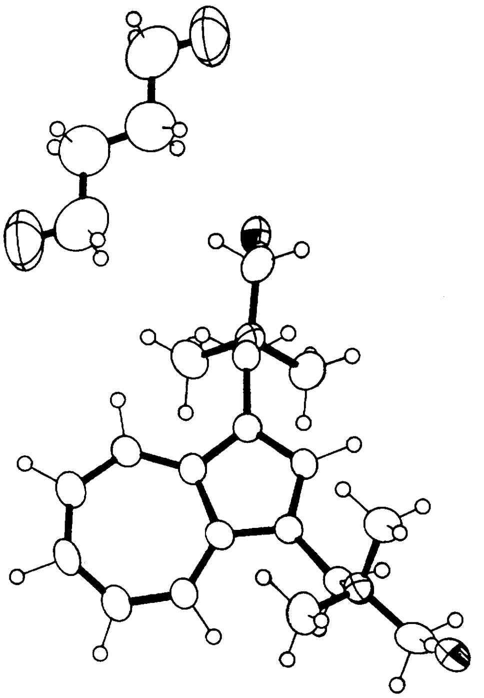


Figure 1. Perspective view of the clathrate **(1)**·C_4H_9OH.

In order to investigate the range and the limits of clathrate formation by hosts of this type, we synthesized the ammonium compounds **(1)**—**(11)**[2] and studied their inclusion capacities. On recrystallization from suitable solvents, a wide range of inclusion behaviour was found for the ammonium salts **(1)** and **(2)**, whereas the compounds **(3)** and **(8)** did not serve as hosts; the salts **(5)**, **(9)**, **(10)**, and **(11)** only gave adducts with iodoform[3] (Table 1).

On variation of the host anion, the change from the iodide **(1)** to the smaller bromide **(2)** causes a decrease in the inclusion capability; in the latter only some shorter chained guest molecules were enclosed and inclusion of alcohols was not observed. Chain lengthening [compound **(11)**] or ethyl substitution [compounds **(4)**, **(7)**, and **(8)**] also reduces the enclosing ability, probably because of the increasing flexibility of the ammonium side chains.

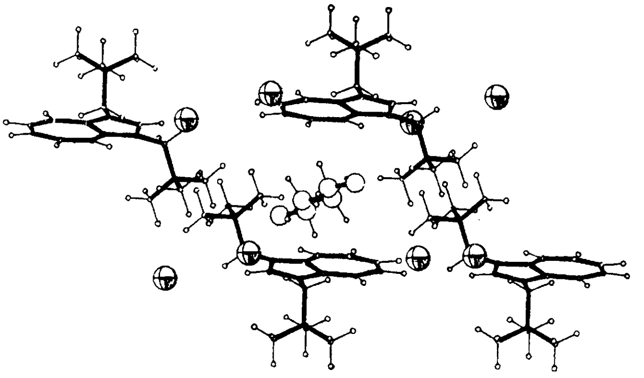


Figure 2. Illustration of the channel cross-section; view along the *a*–*b* diagonal (iodide ions with shaded octants).

The **(1)**·butanol clathrate, obtained from methanol–butanol (1 : 1), forms compact, transparent, violet crystals with irregular shape. *Crystal data:* **(1)**·C_4H_9OH ($C_{18}H_{28}I_2N_2 \cdot C_4H_9OH$), $M = 600.36$, monoclinic, space group $C2/c$, $a = 1654.7(5)$, $b = 1227.1(2)$, $c = 1348.5(3)$ pm, $\beta = 109.94(2)°$, $U = 2.574$ nm^3, $Z = 4$. Final $R = 0.058$ ($R_w = 0.060$) for 3067 unique reflexions.

The structure was solved by the Patterson method and refined by full-matrix least-squares using weights $w = [1/\sigma^2(F) + 0.002\ F^2]$. Anisotropic temperature factors were employed for the I, C, N, and O atoms. The H atoms were included in the refinement with constraints (C–H: 108 pm) and a common isotropic temperature factor.†

The conformations of the host and guest molecules are shown in Figure 1. In contrast to the *cisoid* direction of the two ammonium side chains in the iodomethane inclusion (C_m-symmetry),[1] the ammonium groups in the butanol clathrate are located on opposite sides (*transoid*) of the azulene ring plane (C_2-symmetry). The azulene rings themselves are slightly twisted. The butanol guests are disordered in such a way that the 'head' and 'tail' of half the molecules are orientated in opposite directions, whereas the positions of the CH_2 groups are identical in both cases. Figure 1 could easily represent the clathrate if butane-1,4-diol were present, and suggests that the **(1)**·butane-1,4-diol clathrate might crystallize analogously.‡

A precise consideration of the packing scheme indicates that the host cavities are connected together, forming unidimensional tubes in the direction of the *a*–*b* diagonals of the unit cell. The top and bottom of the tubes are bounded by the azulene ring planes, which are arranged in layers, whereas the sides are bounded by the intermediary ammonium groups (Figure 2).

The location of the ammonium groups implies an alternating sequence of enlargements and narrowings, in the longitudinal direction of the channel. The butanol molecules take a slightly sloping position in the oval-like large cavities.

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† The atomic co-ordinates for this analysis are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ In fact, butane-1,4-diol is also enclosed by **(1)** with the same stoicheiometric ratio as butan-1-ol (1 : 1), but the cell parameters (determined from a single crystal by least-squares refinement of the positions of 25 reflexions) differ considerably [$a = 785.1(2)$, $b = 1750.0(3)$, $c = 970.0(1)$ pm, $\beta = 96.50(1)°$], so that different crystal structures must be presumed.

Table 1. Clathrates of the host compounds (**1**), (**2**), (**4**)—(**7**), and (**9**)—(**11**).[a]

Clathrand	Mole ratio of host : guest[b]	Guest molecules
(**1**)	1 : 1	1,3-$C_3H_6(OH)_2$; 1,4-$C_4H_8(OH)_2$; 1,5-$C_5H_{10}(OH)_2$; 2-ClC_2H_4OH; Pr^nI; Bu^nI; $EtNO_2$; Pr^nNO_2; $CH_2(CN)_2$
	1 : 2	HCI_3
	2 : 1	1,3-$C_4H_8(OH)_2$
(**2**)	1 : 1	MeBr; MeCN; Me_2CO; $HCONMe_2$; CH_2Cl_2; $MeNO_2$; $EtNO_2$; $PrNO_2$; $MeCO_2H$
	1 : 2	HCI_3
(**4**)	1 : 2	HCI_3
(**5**)	1 : 1	HCI_3
(**6**)	1 : 1	$CHCl_3$
	[c]	Dimethylformamide
	1 : 3	HCI_3
(**7**)	*ca.* 1 : 1	CH_2Cl_2, $CHCl_3$, $MeCO_2H$
	1 : 2	HCI_3
	[c]	MeCN
(**9**)	1 : 1	HCI_3
(**10**)	1 : 4	HCI_3
(**11**)	1 : 2	HCI_3

[a] Only the new guest inclusions of the hosts (**1**), (**4**), and (**6**) are listed (*cf.* ref. 1). [b] The mole ratios of host : guest were determined by multiple integration of the ^{1}H-n.m.r. spectra, employing [$^2H_6$]-dimethyl sulphoxide as solvent. [c] The ratio was not a stoicheiometric amount.

The narrowings represent nearly square openings with *ca.* 400 pm side length, which is comparable with the well known urea channel diameter of *ca.* 500 pm.

Based on these results, it can be concluded that these onium hosts offer an extraordinary adaptability to the geometrical requirements of the guest molecules. Apparently, the intramolecular distances of the ammonium side chains, as well as their mobility, play an important role in the enclosing ability and should therefore be considered in the design of further tailor-made onium hosts.

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3 To what extent the iodoform adducts can be considered as clathrates, or can be characterized as real charge transfer complexes, is being analysed thoroughly. *Cf.* R. D. Green and J. S. Martin, *J. Am. Chem. Soc.*, 1968, **90**, 3659; H. A. Creighton and K. M. Thomas, *J. Chem. Soc., Dalton Trans.*, 1972, **3**, 403.