Carbohydrate Research, 191 (1989) 105–116
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

RE-DETERMINATION OF THE CRYSTAL STRUCTURE OF NaBr·SUCROSE·$2H_2O$*

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(Received November 15th, 1988; accepted for publication, January 18th, 1989)

ABSTRACT

The NaBr·Sucrose·$2H_2O$ complex crystallizes in the $P2_12_12_1$ space group with cell constants of $a = 8.484(4)$, $b = 9.745(2)$, $c = 21.948(5)$ Å. The asymmetric unit consists of a Na–Br ion-pair, two water molecules, and one sucrose molecule. Inside the unit cell, there are four channels running along the b axis, which accommodate infinite arrays of iso-oriented Br^-–Na^+–$2H_2O$ units. This arrangement is not far from a van der Waals packing of sugar molecules in which neutral solvated NaBr moieties are embedded. Calculations of the electrostatic potential spanned by the sucrose and water molecules show that the electrostatic field of polyhydroxylated ligands can be modified to fit different ionic arrangements by a simple mechanism involving rotation of hydroxyl groups.

INTRODUCTION

It is well known that an important role of carbohydrates in biological systems is their cation-binding ability. Therefore, studies of the structure of complexes of polyhydroxylated ligands with inorganic salts are important for investigating the co-ordinative modalities of metal cations. We have reported[1] the crystal structure of the 3NaI·2Sucrose·$3H_2O$ complex, in which the cations and anions were shown to be segregated, and now report on the crystal structure of NaBr·Sucrose·$2H_2O$.

The crystal structure of NaBr·Sucrose·$2H_2O$ was determined first in 1947[2] by isomorphous substitution methods, but the precision was rather low compared to that of present standards. Accordingly, re-determination of this structure was undertaken.

An important point is that the complex contains a Na–Br ion-pair in spite of the presence of water of crystallization which usually hinders their formation in crystals and in solution[3]. On the other hand, the intrinsic instability of ion pairs in

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*Structural Aspects of Inorganic Salt–Carbohydrate Interactions, Part II, For Part I, see ref. 1.
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0008-6215/89/$ 03.50

water-containing environments has been justified theoretically[4] using Monte Carlo simulations, which show that the solvation energy becomes more negative with increasing separation of the ion pair and that this effect is more important in water than in other polar solvents.

A search of the Cambridge Crystallographic Database[5] revealed, as expected, that sodium–halogen ion-pairs are uncommon in the solid state.

EXPERIMENTAL

Preparation of the NaBr·Sucrose·2H$_2$O complex. — Slow concentration of a solution of NaBr (5 g, 0.48 mol) and sucrose (11.09 g, 0.32 mol) in water (50 mL) at room temperature gave good crystals.

Crystal structure determination. — Intensity data were collected on an Enraf–Nonius CAD4 diffractometer with monochromated MoK_α radiation and the $\omega/2\theta$ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 23 centered reflections in the range $11 < \theta < 14°$. Crystal data are reported in Table I. Intensities were corrected for Lorentz, polarization, and absorption (minimum transmission factor, 0.74). Scattering factors and anomalous

TABLE I

CRYSTAL DATA

Compound	NaBr·Sucrose·2H$_2$O
Mol. wt.	481.01
Crystal size (mm)	0.33 × 0.38 × 0.40
Space group	$P2_12_12_1$
Unit-cell parameters (Å)	8.484(3), 9.745(2), 21.948(5)
V (Å^3)	1814.6(8)
Z	4
F(000)	992
D_c (g.cm^{-3})	1.76
D_0 (g.cm^{-3})	1.70
μ (MoK_α) (cm^{-1})	23.2
Radiation	MoK_α
Monochromator	Graphite
θ_{min}–θ_{max}	2–27°
Standard reflections	3
Temp (°)	22
Independent reflections	2275
Reflections with $I \geqslant 2\sigma(I)$	1900
Variables (last cycle)	349
Final R_1, R_2[a]	0.024, 0.027
Final shift/error max.	0.16
Largest peak (eÅ^{-3}) in the final difference map (outside Br co-ordination sphere)	0.37
Weighting	$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
S = Error in an observation of unit weight	0.97

[a] $R_1 = \Sigma|\Delta F_o|/\Sigma|F_o|$; $R_2 = (\Sigma_w|\Delta F_o|^2/\Sigma_w|F_o|^2)^{1/2}$.

TABLE II

POSITIONAL ($\times 10^4$ FOR NON-H, $\times 10^3$ FOR H) AND THERMAL PARAMETERS WITH E.S.D.'S IN PARENTHESES

Atom	x	y	z	B_{eq}/B
Br	2037.7(4)	5756.2(3)	6839.1(1)	2.200(5)
Na	1361(2)	2805(1)	6733.3(5)	2.40(2)
O-1	5598(2)	6484(2)	5785.8(9)	1.65(4)
O-2	4911(3)	4758(3)	4797.3(9)	2.24(4)
O-3	3931(3)	2390(2)	5444(1)	2.44(4)
O-4	4333(2)	2561(2)	6753.0(9)	2.09(4)
O-5	7394(2)	4872(2)	6160.9(9)	1.65(4)
O-6	8487(3)	2845(3)	6970(1)	2.68(5)
O-1′	6886(3)	9434(2)	4909(1)	2.89(5)
O-2′	7732(2)	7970(2)	5889.7(9)	1.69(4)
O-3′	3576(3)	8461(2)	6110(1)	2.07(4)
O-4′	5687(3)	10057(2)	6992.7(9)	2.19(4)
O-6′	8654(3)	7310(2)	7181(1)	2.29(4)
C-1	6608(3)	5393(3)	5637(1)	1.59(5)
C-2	5683(4)	4263(3)	5323(1)	1.62(5)
C-3	4577(4)	3538(3)	5762(1)	1.64(5)
C-4	5458(4)	3081(3)	6326(1)	1.63(5)
C-5	6352(3)	4270(3)	6614(1)	1.64(5)
C-6	7368(4)	3857(3)	7143(1)	2.10(6)
C-1′	6155(4)	8133(3)	4996(1)	1.85(6)
C-2′	6176(3)	7835(3)	5674(1)	1.51(5)
C-3′	5187(3)	8811(3)	6062(1)	1.53(5)
C-4′	6102(4)	8880(3)	6647(1)	1.59(5)
C-5′	7783(4)	8908(3)	6400(1)	1.58(5)
C-6′	9070(4)	8483(3)	6832(1)	1.92(5)
O-1W	167(3)	3597(3)	5721(1)	2.64(5)
O-2W	1703(3)	804(2)	6183(1)	2.62(5)
H(O-2)	418(4)	512(3)	488(1)	1.7(6)
H(O-3)	351(4)	202(3)	560(1)	2.8(8)
H(O-4)	465(4)	195(3)	681(1)	2.6(7)
H(O-6)	854(5)	222(4)	725(2)	6(1)
H-1	747(4)	567(3)	537(1)	2.6(7)
H-2	652(4)	362(3)	515(1)	1.9(7)
H-3	367(4)	418(3)	587(1)	2.1(7)
H-4	624(4)	235(3)	624(1)	1.8(7)
H-5	562(4)	496(4)	674(1)	2.9(8)
H-16	669(4)	351(3)	747(1)	2.3(8)
H-26	787(4)	467(3)	732(1)	2.9(7)
H(O-1′)	649(4)	983(3)	471(1)	1.9(7)
H(O-3′)	352(5)	766(4)	619(2)	5(1)
H(O-4′)	624(4)	1012(4)	729(2)	3.1(8)
H(O-6′)	893(4)	664(3)	703(1)	3.3(8)
H-11′	661(4)	748(3)	479(1)	2.5(8)
H-21′	512(4)	818(3)	487(1)	2.3(7)
H-3′	521(3)	969(3)	585(1)	1.1(6)
H-4′	600(3)	810(2)	683(1)	0.5(5)
H-5′	798(4)	991(3)	626(1)	2.3(7)
H-16′	1008(3)	843(3)	660(1)	0.8(6)
H-26′	923(4)	918(3)	709(1)	2.6(7)
H-11W	−57(6)	388(4)	586(2)	7(1)
H-21W	−28(4)	307(4)	542(1)	3.4(9)
H-12W	116(5)	64(3)	594(1)	3.4(8)
H-22W	214(5)	12(4)	625(2)	4.6(9)

dispersion parameters were taken from International Tables for X-Ray Crystallography[6]. The structure was solved by Patterson and Fourier methods. All H-atoms were located in the difference Fourier map. After a few cycles of isotropic refinement, the structure was refined by full-matrix least-squares using anisotropic temperature factors for all non-H atoms and isotropic ones for H-atoms. Weights for the last cycle were applied according to the scheme given in Table I. All calculations were done using the SDP system of programs[7]. Final positional and equivalent isotropic thermal parameters are given in Table II.

RESULTS AND DISCUSSION

The asymmetric unit consists of the Na^+–Br^- ion-pair, one sucrose molecule, and two water molecules, and the ORTEP[6] view is shown in Fig. 1, together with the complete co-ordination around the two ions and an additional ion-pair that is related to the first one by simple translation. Bond distances and angles are reported in Table III. The two ions are at a distance of 2.942(1) Å, which is significantly shorter than that [2.986(3) Å] found in the cubic NaCl-type NaBr crystal[9], where both Na^+ and Br^- are octahedrally co-ordinated. The ion pair is co-ordinated to the two water molecules (both bonded to Na^+) and four sugar molecules, one acting as tridentate, two as bidentate, and one as monodentate ligands (Fig. 2b). The Na^+ is surrounded by Br^-, three sugar hydroxyl groups, and two water

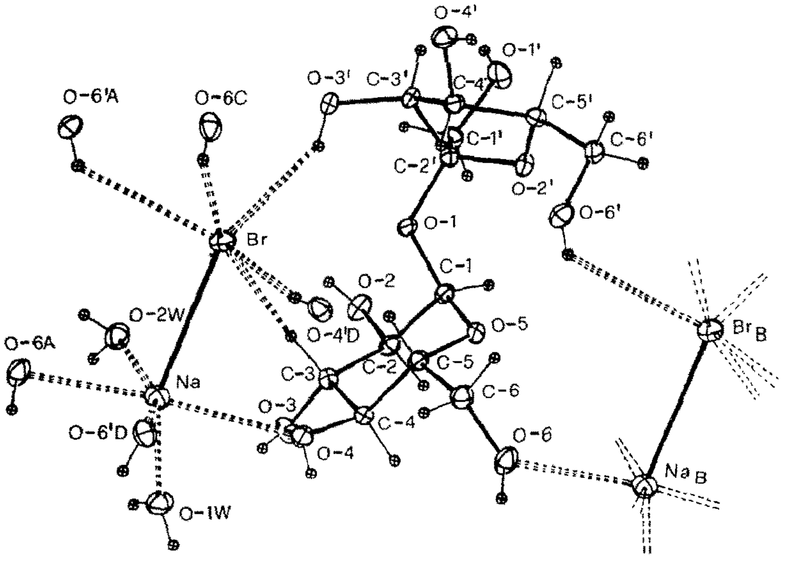

Fig. 1. ORTEP view of the asymmetric unit with complete co-ordination around the ion pair, showing the thermal ellipsoids at 30% probability. A [I; −1,0,0], B [I; 1,0,0], C [IV; 1,0,1], D [IV; 1, −1,1]. Symmetry operations: I, x,y,z; II, $1/2 - x$, $-y$, $1/2 + z$; III, $1/2 + x$, $1/2 - y$, $-z$; IV, $-x$, $1/2 + y$, $1/2 - z$.

oxygens in a distorted octahedral geometry, and Br$^-$ co-ordinates to Na$^+$, four sugar hydroxyl groups, and one C–H hydrogen in a distorted octahedron. Bond distances around the ion pair are collected in Table IV. The resulting shape of the polyhedron is that of two interpenetrating octahedra staggered around the Na–Br bond by an average angle of ~54°. The dihedral angle formed by the least-squares planes through the basal atoms [O-1W, O-4, O-6$_A$, and O-6'$_D$ or H-3, HO-6'$_A$, HO-4'$_D$, and HO-6$_C$ around Na$^+$ and Br$^-$, respectively] was 39.9(5)°.

The crystal packing along the *b* and *a* axes is shown in Figs. 2a and 2b, respectively. Inside one unit cell, there are four channels running along *b* (Fig. 2a), which accommodate infinite arrays of iso-oriented Br$^-$–Na$^+$ · 2H$_2$O units; the terminal water molecules are not connected to the next Br$^-$ ion but hydrogen-bonded to the surrounding sugar molecules (Fig. 2b). Each Na$^+$–Br$^-$ ion-pair is co-ordinated by four sugar molecules, and the arrangement is strengthened by a network of hydrogen bonds connecting sugar molecules directly or *via* one of the two water molecules. The complete list of hydrogen bonds is given in Table V. Thus, the

TABLE III

BOND DISTANCES (Å) AND ANGLES (°) WITH E.S.D.'S IN PARENTHESES

Br–Na	2.945(3)	O-4'–C-4'	1.421(4)
O-1–C-1	1.407(4)	O-6'–C-6'	1.422(4)
O-1–C-2'	1.428(4)	C-1–C-2	1.519(5)
O-2–C-2	1.412(4)	C-2–C-3	1.521(5)
O-3–C-3	1.428(4)	C-3–C-4	1.514(5)
O-4–C-4	1.431(4)	C-4–C-5	1.524(5)
O-5–C-1	1.424(4)	C-5–C-6	1.502(5)
O-5–C-5	1.456(4)	C-1'–C-2'	1.517(5)
O-6–C-6	1.423(5)	C-2'–C-3'	1.529(5)
O-1'–C-1'	1.426(5)	C-3'–C-4'	1.503(5)
O-2'–C-2'	1.411(4)	C-4'–C-5'	1.528(5)
O-2'–C-5'	1.447(4)	C-5'–C-6'	1.505(5)
O-3'–C-3'	1.415(4)		
C-1–O-1–C-2'	116.7(2)	O-6–C-6–C-5	111.4(3)
C-1–O-5–C-5	114.2(2)	O-1'–C-1'–C-2'	107.2(3)
C-2'–O-2'–C-5'	110.3(2)	O-1–C-2'–O-2'	110.6(3)
O-1–C-1–O-5	111.6(3)	O-1–C-2'–C-1'	109.9(3)
O-1–C-1–C-2	109.8(3)	O-1–C-2'–C-3'	106.8(3)
O-5–C-1–C-2	110.5(3)	O-2'–C-2'–C-1'	108.8(3)
O-2–C-2–C-1	111.3(3)	O-2'–C-2'–C-3'	105.8(3)
O-2–C-2–C-3	112.9(3)	C-1'–C-2'–C-3'	114.8(3)
C-1–C-2–C-3	111.7(3)	O-3'–C-3'–C-2'	115.1(3)
O-3–C-3–C-2	107.0(3)	O-3'–C-3'–C-4'	116.6(3)
O-3–C-3–C-4	111.0(3)	C-2'–C-3'–C-4'	102.6(3)
C-2–C-3–C-4	110.4(3)	O-4'–C-4'–C-3'	111.3(3)
O-4–C-4–C-3	108.0(3)	O-4'–C-4'–C-5'	114.0(3)
O-4–C-4–C-5	109.4(3)	C-3'–C-4'–C-5'	100.5(3)
C-3–C-4–C-5	111.2(3)	O-2'–C-5'–C-4'	103.6(3)
O-5–C-5–C-4	109.1(3)	O-2'–C-5'–C-6'	109.6(3)
O-5–C-5–C-6	106.7(3)	C-4'–C-5'–C-6'	116.9(3)
C-4–C-5–C-6	113.8(3)	O-6'–C-6'–C-5'	112.3(3)

TABLE IV

BOND DISTANCES AROUND THE Na–Br IONIC COUPLE

Atoms		*Distance (Å)*	*Translational vector*
Na–Br	I[b]	2.942(1)	0,0,0
Na–O-4	I	2.533(3)	0,0,0
Na–O-1W	I	2.561(3)	0,0,0
Na–O-2W	I	2.312(2)	0,0,0
Na–O-6	I	2.493(3)	−1,0,0
Na–O-6′	IV	2.431(3)	1, −1,1
Br–H(O-3′)	I	2.66(4)	0,0,0
Br–H-3	I	2.97(3)	0,0,0
Br–H(O-6′)	I	2.81(3)	−1,0,0
Br–H(O-6)	IV	2.50(4)	1,0,1
Br–H(O-4′)	IV	2.48(4)	1, −1,1

[a]With e.s.d.'s in parentheses. [b]I, *x,y,z*; IV, −*x*, 1/2 + *y*, 1/2 − *z*.

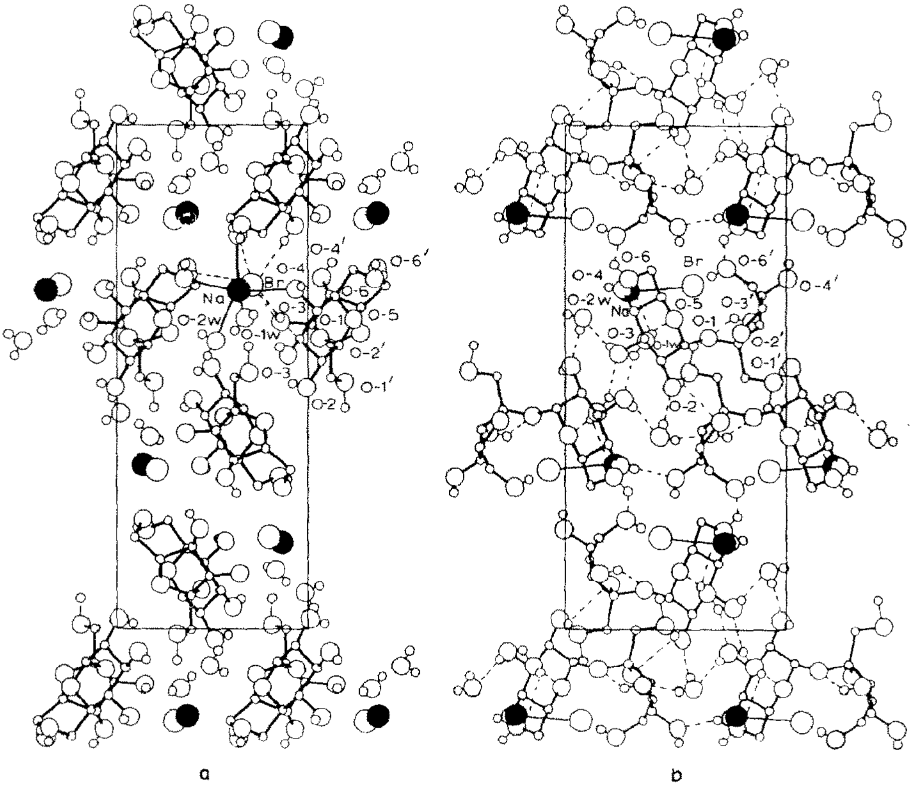

Fig. 2. (*a*) View along axis *b* of the packing in the unit cell. Around the central Na–Br ion pair, Na–O and Br–H contacts are represented by thin and broken lines, respectively; Na$^+$ ions are drawn as full circles. The labelled atoms are referred to the molecule at (1/2 + *x*, 1/2 − *y*, 1 − *z*). (*b*) View along axis *a* of the packing in the unit cell. The dashed lines represent the hydrogen bonds involving water and sucrose molecules.

TABLE V

INTRA- AND INTER-MOLECULAR HYDROGEN BONDS (DISTANCES IN Å AND ANGLES IN DEGREES WITH E.S.D.'S IN PARENTHESES)

Atoms		$d_{O\text{-}H}$	$d_{O\text{---}O}$	$d_{H\text{---}O}$	*O-H–O*	*Translational vector*
O-3–H(O-3)---O-2W	I[a]	0.61(3)	2.931(3)	2.32(3)	174(4)	0,0,0
O-3′–H(O-3′)---O-1	I	0.80(5)	2.676(3)	2.28(4)	111(3)	0,0,0
O-1W–H-11W---O-5	I	0.75(5)	2.830(3)	2.09(5)	172(4)	−1,0,0
O-1W–H-11W---O-6	I	0.75(5)	3.175(3)	2.76(4)	118(4)	−1,0,0
O-4–H(O-4)---O-4′	I	0.67(3)	2.748(3)	2.08(3)	179(4)	0, −1,0
O-2W–H-22W---O-3′	I	0.78(4)	2.786(3)	2.05(4)	159(4)	0, −1,0
O-1W–H-21W---O-3	III	0.92(3)	2.926(3)	2.06(3)	157(3)	−1,0,1
O-2W–H-12W---O-2	III	0.72(3)	2.691(3)	1.97(3)	172(3)	−1,0,1
O-1′–H(O-1′)---O-1W	III	0.67(3)	2.779(3)	2.12(3)	165(3)	0,1,1
O-2–H(O-2)---O-1′	III	0.74(3)	2.761(4)	2.05(3)	163(3)	−1,1,1
O-2–H(O-2)---O-2′	III	0.74(3)	3.255(3)	2.80(3)	123(2)	−1,1,1
O-6–H(O-6)---O-6′	IV	0.87(4)	3.103(4)	2.69(4)	111(3)	2, −1,1

[a] I, x,y,z; III, $1/2 + x$, $1/2 - y$, $-z$: IV, $-x$, $1/2 + y$, $1/2 - z$.

situation is not far from a van der Waals packing of sugar molecules in which neutral solvated NaBr units are embedded, in contrast to the 3NaI · 2Sucrose · $3H_2O$ crystal[1] where the ligand and the solvent co-operate in segregating separately co-ordinated Na^+ and I^- ions.

The changes in conformation of the sucrose molecule due to complexation are small in comparison with the conformation in sucrose crystals[10]. Thus, the conformation of the glucose ring is the usual $^4C_1$ [calculated puckering co-ordinates[11] are: q = 0.553(3) Å, ϕ = −45.(6)° and θ = 177.01°], whereas that of the fructose ring is shifted slightly from $^4T_3$ to E_4 [puckering co-ordinates: q = 0.405(3) Å, ϕ = −76.4(4)°]. The relative position of the two rings is described by the values of the two torsion angles (O-5–C-1–O-1–C-2′) and (O-2′–C-2′–O-1–C-1) which are, respectively, 99.8(2) and −46.1(3)° and not far from those observed for sucrose [107.8(1) and −44.8(1)°]. The optimal sugar–ion co-ordination is achieved[1,12] by changing the conformations of the CH_2OH and OH groups. Table VI contains a selection of the corresponding torsion angles for sucrose in NaBr · Sucrose · $2H_2O$, in 3NaI · 2Sucrose · $3H_2O$, and in sucrose. Fig. 3 shows a projection of the sucrose molecule on the C-1–O-1–C-2′ plane (as in Fig. 1) in the last two crystals. All changes in torsion angles appear to be a function of the co-ordination of the cation or the ion pair (see below), with the exception of those involving the C-1′–O-1′ bond which change dramatically in the NaBr complex without being involved in the co-ordination. This situation is due to the fact that the O-1′–H---O-2 hydrogen bond present in sucrose is lost in the complex. For rotations around the C–OH bonds, in general, −*sc* and *ap* conformations correspond to lower-energy *staggered* arrangements, whereas the higher-energy *eclipsed* arrangements correspond to *sp* and −*ac* conformations. The data in Table VI show that only *staggered* confor-

TABLE VI

A SELECTION OF TORSION ANGLES (°) IN THE PURE SUCROSE AND IN NaBr– AND NaI–SUCROSE COMPLEXES

Angle	*Sucrose*[10]		*NaBr·Sucrose*		*NaI·Sucrose*[1]			
O-5–C-5–C-6–O-6	−54.4	−*sc*	−62.4	−*sc*	61.3	+*sc*	56.9	+*sc*
C-4–C-5–C-6–O-6	64.4	+*sc*	57.9	+*sc*	−177.8	−*ap*	178.3	+*ap*
O-2′–C-2′–C-1′–O-1′	171.4	+*ap*	−53.1	−*sc*	172.7	+*ap*	−177.5	−*ap*
C-3′–C-2′–C-1′–O-1′	−72.1	−*sc*	65.0	+*sc*	−69.2	−*sc*	60.5	+*sc*
O-2′–C-5′–C-6′–O-6′	−69.6	−*sc*	−74.9	−*sc*	55.7	+*sc*	53.8	+*sc*
C-4′–C-5′–C-6′–O-6′	49.2	+*sc*	42.4	+*sc*	173.0	+*ap*	170.1	+*ap*
e.s.d.'s:	0.1		0.3		0.4–0.5			
C-1–C-2–O-2–H(O-2)	99.8	+*ac*	−80	−*sc*	150	+*ac*/*ap*	165	+*ap*
C-2–C-3–O-3–H(O-3)	−91.5	−*ac*	175	+*ap*	115	+*ac*	−101	−*ac*
C-3–C-4–O-4–H(O-4)	47.9	+*sc*	127	+*ac*	−56	−*sc*	−69	−*sc*
C-5–C-6–O-6–H(O-6)	64.4	+*sc*	−137	−*ac*	104	+*ac*	96	+*ac*
C-2′–C-1′–O-1′–H(O-1′)	−67.5	−*sc*	−136	−*ac*	159	+*ap*	126	+*ac*
C-2′–C-3′–O-3′–H(O-3′)	67.0	+*sc*	48	+*sc*	178	+*ap*	133	+*ac*
C-3′–C-4′–O-4′–H(O-4′)	134.4	+*ac*	−175	−*ap*	106	+*ac*	−100	−*ac*
C-5′–C-6′–O-6′–H(O-6′)	59.8	+*sc*	93	+*ac*	159	+*ap*	135	+*ac*
e.s.d.'s range:	0.2–0.4		2.0–3.0		4.0–5.0			

[a] Key: *s*, syn; *a*, anti; *c*, clinal; *p*, periplanar.

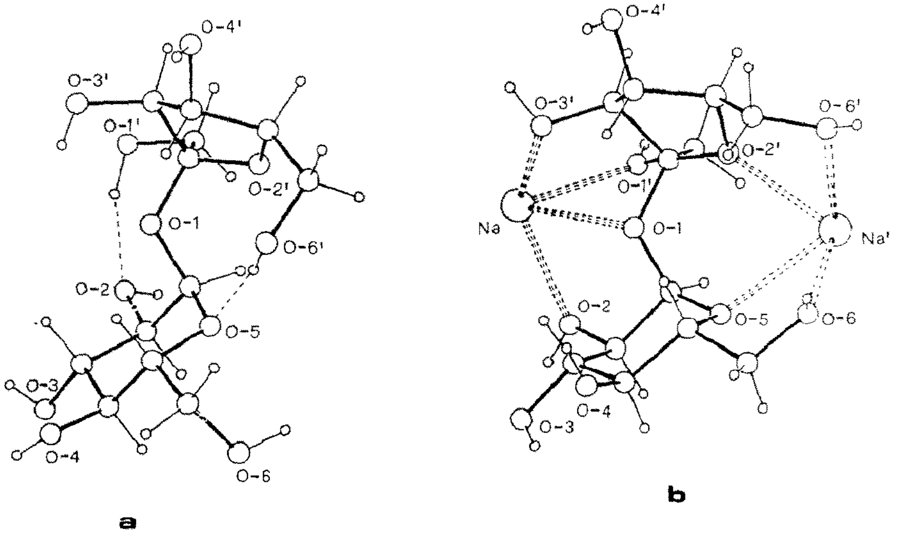

Fig. 3. Views of the sucrose molecule in (*a*) the sucrose crystal[10], and (*b*) the 3NaI·2Sucrose·3 H_2O complex[1] with the two directly coordinated Na^+ ions. The orientation of the molecules is as in Fig. 1.

mations are present in the sucrose crystal in spite of the formation of two intramolecular and several intermolecular hydrogen-bonds, whereas three of the eight conformations are eclipsed in the NaBr complex and there is no preference between staggered and eclipsed conformations in the NaI complex. The observed pattern of

C–O–H conformations is consistent with the idea that the energy needed to eclipse a proton is irrelevant or barely relevant in the NaI and NaBr complexes, respectively, whereas it is significant in the formation of simple hydrogen bonds, so that only staggered conformations occur in crystals of sucrose.

Few examples of Na^+–X^- (X = Cl, Br, I) ion-pairs in crystals are known; three for Na–I[13a–c] and four for Na–Br[14a–d] have been reported[5]. All but one correspond to a specific binding situation where the Na^+ is encapsulated by a multioxygenated ligand, such as a crown ether or a tripode ligand, in an anhydrous environment, and the last co-ordination position is occupied by the halogen. Therefore, ion pairs in crystals seem to be associated only with non-protonated environments where the ion pair is protected in some way by an enveloping ligand. The Na–X distances in all of these compounds are systematically shorter than (or at least of the same magnitude as) the corresponding distance in the halide crystal. The only hydrate structure which is comparable to that of $NaBr \cdot$Sucrose$\cdot 2H_2O$ is a dibenzo-18-crown-6$\cdot NaBr \cdot 2H_2O$ complex[14d]. Inside the crystal there are two different environments around two independent Na^+ ions which are both co-ordinated to the six equatorial crown oxygens, whereas the axial positions are occupied by two water molecules or by a water molecule and a Br^- ion. The crystal contains infinite H_2O–Na^+–Br^-–H_2O–Na^+–chains and the Na–Br distance is 2.82(1) Å, which is slightly shorter than that in the $NaBr \cdot$Sucrose$\cdot 2H_2O$.

Because of the lack of structural data on ion pairs, it is of interest to investigate their co-ordination modalities by more general methods. As the bonding to Na^+ and Br^- is essentially ionic, a first approach can be made by the use of bond valence concepts[15] which assume that the total charge of the ion has to be saturated by $\Sigma_i s_i$, *i.e.*, the summation of the separated bond valences, s_i of each co-ordinated ligand atom i. The quantity $s = s_0\,(R/R_0)^{-N}$ can be calculated using the original parameters[16] for Na–O ($s_0 = 0.166$, $R_0 = 2.421$, N = 5.7) or H–O ($s_0 = 1$, $R_0 = 0.86$, N = 2.17). Parameters for Na–Br (or Br–Na) and H–Br are not available. However, a reasonably approximate estimate can be obtained, according to what was suggested by Brown and Altermatt[17] using, in the above equation for s, R values which are corrected for the difference of the ionic radii. For example, for the Na–Br interaction, the expression parametrized for Na–O can be used but with an R value equal to the actual Na–Br distance diminished by 0.62 Å, which is the difference between $r(Br^-) = 1.82$[16] and $r(0) = 1.20$ Å[1]. In the same way, s for H–Br interactions can be obtained by those for H–O, with the same correction of −0.62 Å for the actual H–Br distances. The calculated value of Σs turns out to be 0.98 for Na^+, which approximates quite well the theoretical value of 1. For comparison. Σs of 1.06 and 1.10 were obtained for the two Na^+ ions in the NaI complex[1], where the cations displayed co-ordination numbers (c.n.) of 7 and 8 and for which the average Na–O distances were 2.48[10] or 2.52[15] Å, respectively. For $NaBr \cdot$Sucrose$\cdot 2H_2O$, the average Na–O distance is 2.44[11] Å, showing that the same saturation of the charge on the cation can be achieved by an increasing number of ligand atoms situated, on average, at a longer distance, though without any definite geometrical regularity. Σs for Br^- is calculated to be 0.98 to which the short C–H---Br contact contributes 0.11, showing, as already observed[1], that aliphatic hydrogens, made more acid by geminal oxygens, can help to bind the anion. A similar situation was found[14d] in the NaBr crown complex noted above where seven C–H groups are used to complete, in a bond valence sense, the co-ordination sphere of the Br^- in the ion pair.

Moreover, as the co-ordination is of ionic nature, a better understanding of its modalities can be obtained by calculating the values of the electrostatic potential, V^{ES}, spanned by the constituent units, using q_i values calculated by the Gasteiger–Marsili method[19]. Such a method has been considered to give, in spite of its approximate nature, an estimate of the molecular potential accurate enough for semi-quantitative purposes. All calculations and graphical representations were carried out by the CHEM-X system of programs[20].

Fig. 2a shows the co-ordination of the ion pair, which is surrounded by three chelating sugar molecules, two water molecules (co-ordinated to Na^+), and a further sugar hydroxyl group linked to Br^-. The total electrostatic potential generated is -36 and $+7$ kcal.mol^{-1} at the Na^+ and Br^- positions, respectively, giving a total binding energy of 43 kcal.mol^{-1}. The interaction energy of the ion pair can be evaluated as $E_{Na-Br} = e^2/4\pi\varepsilon_0 r\ (1 - \rho/r_0)$, where e is the electron charge, ε_0 is the vacuum permittivity, r is the Na–Br distance, r_0 is the equilibrium Na–Br distance in the gas phase (2.502 Å)[9], and ρ is the empirical repulsion parameter[21] (0.35). The value of E_{Na-Br} is calculated to be 60.6 kcal.mol^{-1} with a total interaction energy of the two ions with the surroundings of 103.6 kcal.mol^{-1}. The comparison of this value with that (177.34 kcal.mol^{-1}) of the molar solvation enthalpy (ΔH°_{solv} of $Na^+(g) + Br^-(g)$[21] indicates that such classes of mixed crystals are unstable in non-concentrated solutions, as is shown by the difficulties encountered during their preparation. Another point concerns the relative importance of ion-pair and complexation energies in the formation of the crystal. Of a total of 103.6 kcal.mol^{-1}, only 43 kcal.mol^{-1} comes from complexation, of which 18 kcal.mol^{-1} arises from water complexation, as can be shown by recalculating the electrostatic potential after the removal of the two H_2O molecules linked to Na^+. This finding accords with what was noted previously, namely, that the crystal contains almost pure van der Waals packing of neutral ion-pairs, water, and sucrose molecules.

An interesting aspect of ion–sugar co-ordination concerns the modification of the electrostatic potential of the sucrose, by changing the torsion angles involving the hydroxyl groups. Fig. 4a shows the electrostatic potential map generated by a single sucrose molecule on the mean plane defined by the two Na–Br ion-pairs (not included in the calculations) almost in the same orientation as in Fig. 1, whereas Fig. 4b shows the potential spanned by an iso-oriented sugar molecule in the conformation in the sucrose crystal[11]. The comparison shows the remarkable changes of the overall potential needed for complexation and this is confirmed by the analogous V^{ES} maps of co-ordinated and non-co-ordinated sugar molecules on the

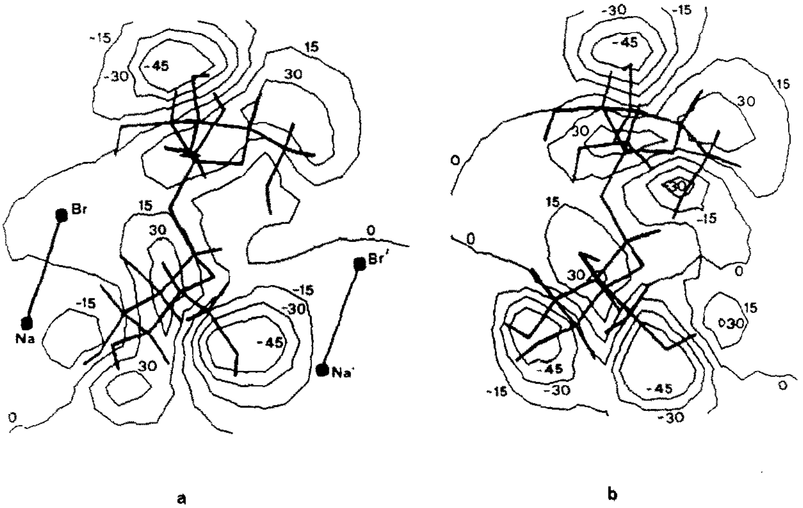

Fig. 4. V^{ES} (kcal.mol^{-1}) spanned by (*a*) a single sucrose molecule in the NaBr complex on the mean plane defined by the two Na–Br ionic couples, and (*b*) an iso-oriented sucrose molecule in the pure sucrose crystal on the same plane.

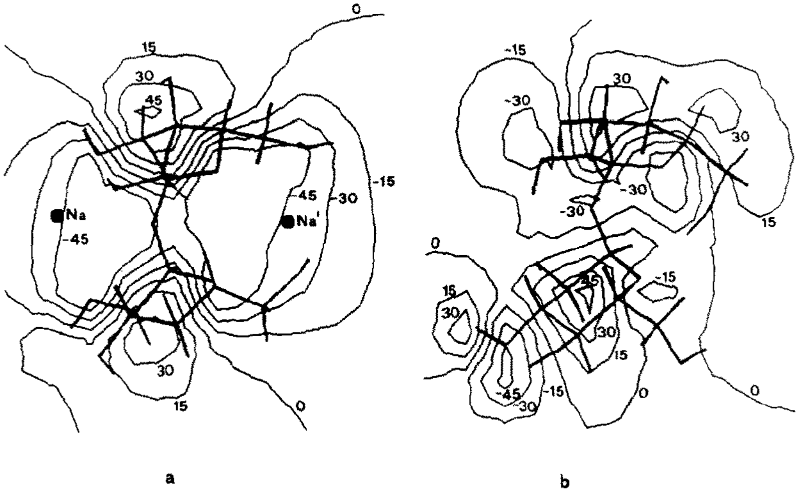

Fig. 5. V^{ES} (kcal.mol^{-1}) spanned by (*a*) a single sucrose molecule in the NaI complex on the plane passing through the Na^+ cations, and (*b*) an iso-oriented sucrose molecule in the pure sucrose crystal.

plane containing the third ion-pair (data not shown). A more dramatic modification of sucrose V^{ES} has been observed[1] in the only other salt–sucrose mixed crystal so far known, namely, $3NaI \cdot 2Sucrose \cdot 3H_2O$. In this complex, a single sugar molecule binds two different Na^+ ions on opposite sides, and Fig. 5a shows the rearrangement of V^{ES} which makes this co-ordination geometry possible together with the V^{ES} map spanned by the same molecule, in the same orientation, as found in crystals of sucrose (Fig. 5b).

In spite of the lack of data so far available, it may be concluded that one of the most remarkable properties of polyhydroxylated ligands is the facility for modifying, by hydroxyl rotations, their electrostatic field to allow binding to different ionic arrangements. This facility could play an important role in Nature.

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