studies on this elusive molecule. To assist future characterization of the ground-state of C_2S_2, the predicted geometry, vibrational spectrum, rotational constants, heat of formation, ionization energy, and proton affinity are summarized in Table 3.

Table 3. Calculated properties for the C_2S_2 ground state ($^3\Sigma_g^-$).

Property	Value
geometry[a]	$r(\mathrm{C{=}C}) = 1.277$ Å, $r(\mathrm{C{=}S}) = 1.579$ Å
rotational constant[a]	$B_e = 1.5587$
IR spectrum[b]	2036 (0), 1198 (244), 561 (0), 364 (0), 175 $\mathrm{cm^{-1}}$ (0 $\mathrm{km\,mol^{-1}}$)
heat of formation	380.1 (ΔH^o_{f0}), 383.1 $\mathrm{kJ\,mol^{-1}}$ (ΔH^o_{f298})
ionization energy[c]	8.3 (adiabatic), 8.4 eV (vertical)
proton affinity[c, d]	731.8 $\mathrm{kJ\,mol^{-1}}$
dissociation energy[c]	$C_2S_2 \rightarrow CS(^1\Sigma_g^+) + CS(^1\Sigma_g^+)$: $\Delta E = 138.6\ \mathrm{kJ\,mol^{-1}}$ $C_2S_2 \rightarrow CS(^1\Sigma_g^+) + CS(^3\Pi)$: $\Delta E = 589.8\ \mathrm{kJ\,mol^{-1}}$

[a] QCISD/6-311 + G(2d)-optimized geometry. [b] QCISD/6-31G* values. Intensity values are given in parentheses. [c] G2//QCI[13] value. [d] The protonated C_2S_2 ion ($SCC(H)S^+$) has a singlet ground state. Proton affinity of SCCS ($^3\Sigma_g^-$) + $H^+ \rightarrow SCC(H)S^+$ ($^1A'$) = 812.1 $\mathrm{kJ\,mol^{-1}}$.

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Closure of the Cavity in Permethylated Cyclodextrins through Glucose Inversion, Flipping, and Kinking**

Thomas Steiner* and Wolfram Saenger*

*Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday*

Cyclodextrins (CDs) or cycloamyloses (CA) are macrocyclic oligosaccharides produced by enzymatic degradation of amylose; they can contain up to 100 or more $\alpha(1-4)$-linked glucose units.[1, 2] The well known smallest members with six to eight glucose residues called α-, β-, and γ-cyclodextrin are annular in shape (doughnut-form) reminiscent of a hollow, truncated cone. Their narrower side are formed by primary O6 hydroxyl groups and the wider side by secondary O2 and O3 hydroxyl groups. All the glucose residues are found exclusively in the $^4C_1$ chair form and are oriented *syn* about the glycosidic link so that all O2 and O3 hydroxyl groups are on the same side and connected by intramolecular $O2(n) \cdots O3(n-1)$ hydrogen bonds that stabilize the macrocyclic structures. The *anti* form with the O2 and O3 hydroxyl groups of adjacent glucose units on opposite sides has not yet been observed in any of the crystal structures of the common CDs.

Surprisingly, the solubility of the cyclodextrins in water increases manyfold if only O2 and O6 or all three of the hydroxyl groups of the glucose residues are methylated. Furthermore, the temperature coefficient of the solubility becomes negative, that is their solubility in water is lower at elevated temperatures and crystals can be grown by heating the solutions.[3] To shed light on these peculiar properties several partially and fully methylated CDs (that have practical importance as bioorganic host molecules) were crystallized from hot and cold water and analyzed by X-ray crystallography.[4–8]

Of particular structural interest are the fully methylated α-, β-, and γ-cyclodextrins hexakis-(2,3,6-tri-*O*-methyl)-α-, β-, and γ-CD (TRIMEA, TRIMEB, and TRIMEG, respectively) because intramolecular $O2(n) \cdots O3(n-1)$ hydrogen bonds cannot form. Crystals that have been grown from hot water include anhydrous TRIMEA,[6] TRIMEB monohydrate,[4] and TRIMEG dihydrate.[9] In all three cases the CD molecules adopt conformations characterized by greatly reduced cavity volumes. The remaining shallow cavities are only filled by O6 methyl groups of adjacent molecules and not by water, which occupies interstices in the crystal lattices of the hydrate forms. It is remarkable that the cavities are closed by three completely different structural mechanisms, which are discussed below. Because the molecular structure of

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1433-7851/98/3724-3404 $ 17.50+.50/0

TRIMEB monohydrate as reported by Caira et al.[4] is singular in the structural chemistry of CDs, we have repeated the study and fully verified the published results;[10, 11] this structure is discussed below only in points going beyond the original paper.

The molecular structures of anhydrous TRIMEA,[6] TRIMEB · H_2O,[10] and TRIMEG · $2H_2O$[9] are shown in Figure 1 (since the water molecules do not occupy the CD cavities they are not shown), and selected geometric parameters that define the molecular conformations are listed in Table 1. In anhydrous TRIMEA (Figure 1 a) the molecule is in a distorted "round" conformation and all the glucoses residues are *syn* oriented. The C6 sides of two diametrically opposed glucose residues are tilted inward so that the primary methoxy groups can form contacts across the cavity opening and hence close it.[6] The molecule is, therefore, not doughnut but bowl shaped.

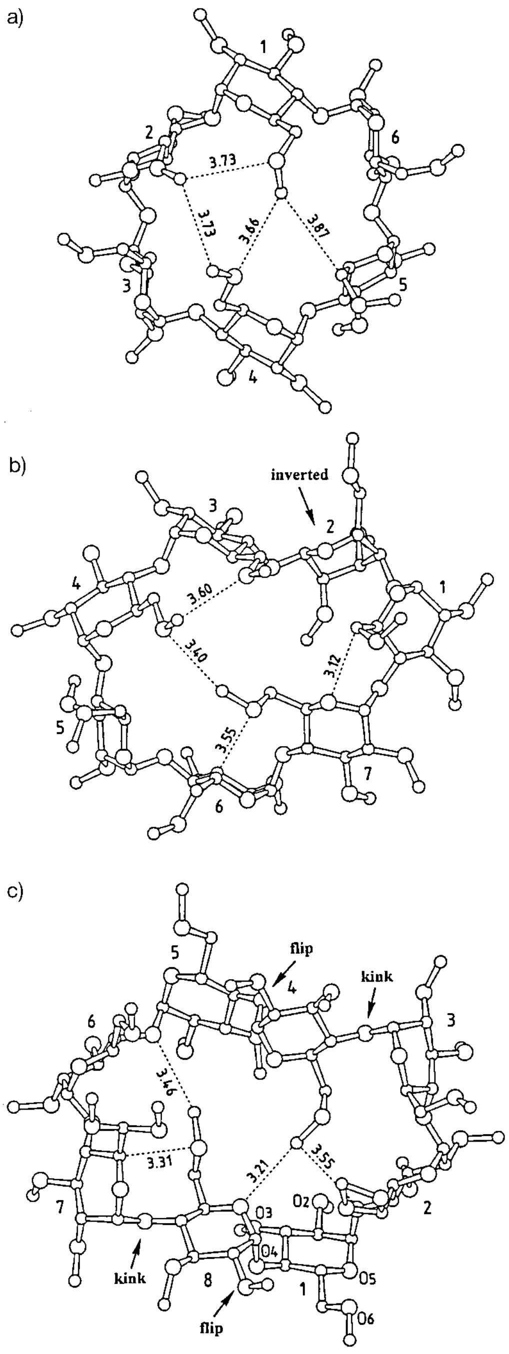

Figure 1. Molecular structures of permethylated cyclodextrins TRIMEA (a),[6] TRIMEB (b), and TRIMEG (c). Projection is on the least-squares plane through the O4 atoms. The short C ··· O contacts [Å] are indicative of C–H ··· O hydrogen bonding.

Table 1. Selection of geometric parameters for anhydrous TRIMEA,[6] TRIMEB monohydrate, and TRIMEG dihydrate (standard deviations are <0.5°. Flip sites are characterized by ψ angles of approximately −60°).

	Glucose residue							
	1	2	3	4	5	6	7	8
$\varphi = C4(n)\text{-}O4(n)\text{-}C1(n-1)\text{-}O5(n-1)$								
TRIMEA	91.6	115.7	97.7	94.8	110.9	97.7		
TRIMEB · H_2O	100.0	94.5	80.6	100.2	103.2	102.2	68.9	
TRIMEG · $2H_2O$	82.2	87.4	90.6	55.7	94.9	94.4	93.1	57.0
$\psi = C3(n)\text{-}C4(n)\text{-}O4(n)\text{-}C1(n-1)$								
TRIMEA	109.7	151.2	137.1	117.2	140.8	145.0		
TRIMEB · H_2O	151.5	175.5	109.9	125.6	141.5	144.8	85.5	
TRIMEG · $2H_2O$	−63.0	91.7	134.5	77.0	−56.5	89.4	112.3	80.2
$O4(n+1) \cdots O4(n) \cdots O4(n-1)$								
TRIMEA	117.6	122.8	117.4	116.1	122.0	116.1		
TRIMEB · H_2O	119.0	92.0	161.5	118.3	116.1	120.1	144.6	
TRIMEG · $2H_2O$	129.7	141.8	111.4	134.3	146.0	131.9	118.9	135.9

Because of the larger ring size a more dramatic structural change is required to close the molecular cavity in TRIMEB monohydrate, (Figure 1 b). The glucose residues are still *syn* oriented relative to each other. One of them is inverted from the normal ${}^4C_1$ to the ${}^1C_4$ chair conformation,[4] which as yet has not been observed in any other cyclodextrin crystal structure. The consequences of this chair inversion are illustrated in Figure 2. The left half shows glucose units in the ${}^4C_1$ conformation: four of the five pyranose ring substituents are equatorial and one is in an axial orientation so that steric conflicts are minimized. Of the glycosidic oxygen

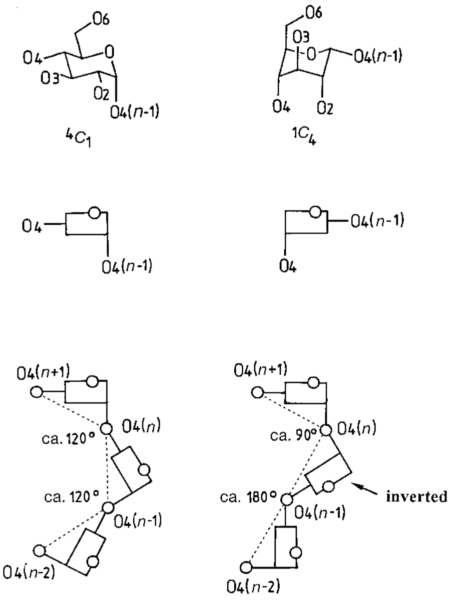

Figure 2. The consequence of the ${}^4C_1 - {}^1C_4$ chair inversion in a chain of α(1-4)-linked glucose residues.

atoms that link the residues O4(n) is equatorial while O4($n-1$), which belongs to the previous residue in the macrocycle, is axial. If glucose residues of this kind form a chain with the primary and secondary hydroxyl groups of neighboring residues in a *syn* arrangement a curved arrangement results with O4($n+1$)-O4(n)-O4($n-1$) angles of approximately 120°,[12] which can close to a cycle (as in the CDs) or form a helix (as in amylose). The right half of Figure 2 shows the effects of chair inversion to the $^1C_4$ conformation: four of the ring substituents are axial, which leads to severe steric conflits: in residue 2 of TRIMEB $\cdot$ H_2O, atoms O2 and O4 are 2.948(7) Å, apart and O3 and C6 3.27(1) Å. The glycosidic oxygen atom O4(n) is now axial, whereas O4($n-1$) is equatorial, that is, in a reversed situation as for "normal" $^4C_1$ glucose residues. If an inverted glucose unit is flanked by "normal" glucose molecules this leads to deviations from the regular curvature of the chain: O4(n) is now axial at both glucose residues to which it is bonded, which leads to a reduction of the O4($n+1$)-O4(n)-O4($n-1$) angle to about 90° (92.0(1)° in TRIMEB $\cdot$ H_2O). On the other hand, O4($n-1$) is now equatorial at both glucose residues to which it is bonded so that the O4(n)-O4($n-1$)-O4($n-2$) angle is opened to nearly 180° (161.5(1)° in TRIMEB $\cdot$ H_2O). Chair inversion of a single glucose residue in a cyclodextrin therefore leads to disruption of the "round" annular structure, and an "irregular" roughly elliptical shape is formed with partial closure of the molecular cavity. In addition, the axial O2 substituent of the inverted glucose residue is directed into the cavity and further reduces its volume (Figure 1 b).

In the crystal structure of TRIMEG $\cdot$ 2 H_2O the molecular cavity is also closed as shown in Figure 3, but the associated structural changes are different compared to TRIMEA and TRIMEB. At two positions, diametrically opposed in the macrocycle adjacent glucose units are rotated by about 180° ("flip") and adopt *anti* orientations. Adjacent glucose residues are rotated by about 90° with respect to each other at the position preceding the flip site to form a "kink". The remaining glucose residues are in a *syn* arrangement (Figure 4) where the mutual orientation is drawn for all pairs of adjacent glucose residues. It should be noted that the flip is not local and does not involve one single glucose only; the amylose chain linked to it is also rotated, and hence the designation "chain-flip".[13] These structural features are reminiscent of the large crystalline cycloamyloses with 10 and 14 residues (CA 10, CA 14) where chain-flips and kinks also occur to relieve steric strain,[13] but they have never been observed before for a "normal" cyclodextrin with less than ten residues. As a consequence of such kink-flip sequences the "round" shape of a cyclodextrin becomes elliptical and the molecular cavity is narrowed. The glucose units of TRIMEG that are involved in the kink-flip sequence are strongly tilted, and their primary O6 methyl groups form van der Waals contacts across the molecular cavity, and thereby close it. These contacts are possibly associated with weak $C{-}H \cdots O$ hydrogen bonds that are formed by the terminal methyl groups, as is indicated by short $C \cdots O$ separations (Figure 1 c).[14]

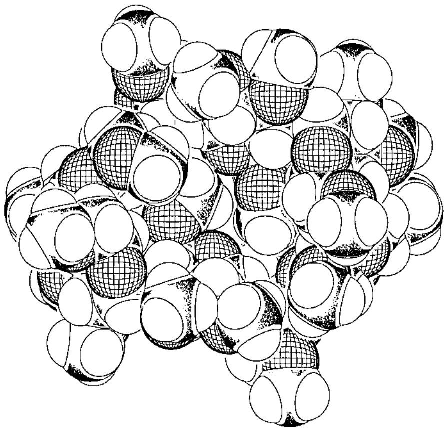

Figure 3. Space filling model of the TRIMEG molecule, drawn with the program PLUTON (A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34).

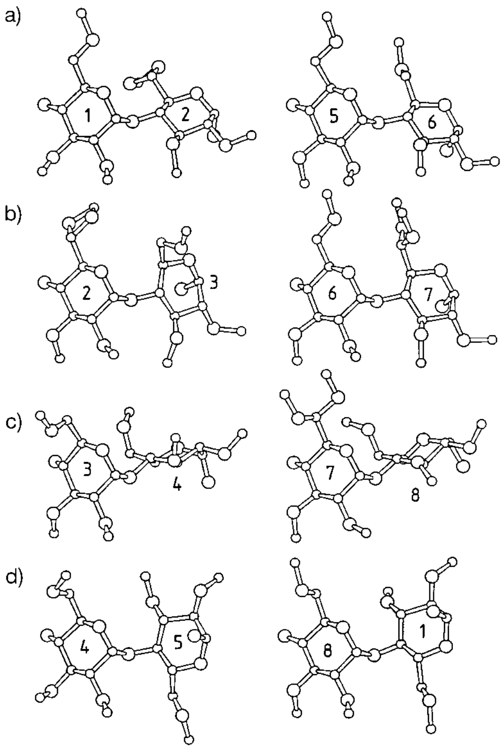

Figure 4. All pairs of adjacent glucoses in TRIMEG dihydrate, drawn in a common projection with respect to the left residue. a), b) regular orientation, c) kinks, d) flips. The primary methoxy groups of glucose units 2 and 7 are twofold disordered. The "regular" orientations are similar to those in anhydrous TRIMEA, or in crystalline complexes of TRIMEA and TRIMEB.

In the unmodified cyclodextrins O2(n)···O3($n-1$) hydrogen bonding between glucose units stabilizes the macrocyclic conformation. They adopt the "round" structure for α-, β-, and γ-CD; the next larger δ-CD is significantly distorted and from ε-CD (CA 10) on, chain-flips and kinks are introduced and the macrocycles become elliptical.[13] In the permethylated series the chain-flips and kinks are already found for TRIMEG, probably because there is no hydrogen bonding to stabilize the relative orientations of adjacent glucose residues. We assume that the mechanism of chain-flipping is associated with glucose units in the $^1C_4$ conformation similar to that found in TRIMEB. The $^1C_4$ form may be considered as a reaction intermediate because the O4(2)-O4(3)-O4(4) angle is 161.5° (Table 1)—instead of the average 128° in β-CD—and leads to an elliptical distortion of the macrocycle. Only a further slight rotation of the $^1C_4$ inverted glucose unit and revertion to the "normal" $^4C_1$ form would be required to complete the flip.

Thus far, the common property of all partially and fully methylated CDs crystallized from hot water is that water is not located in their molecular cavities. It seems that the expulsion of water molecules from the cavity is a major driving force for crystallization of these substances. "Empty" cavities can only be obtained if the cavity volumes are either greatly reduced or if the cavities are totally blocked. This principle requires different structural changes for CDs of different sizes, and is always associated with the inward rotation of two or three O6-methyl groups to close the cavities. Since the three permethylated CDs are of different size this closure requires different structural changes, and ranges from a simple tilting of glucose units to inversion of the chair form, and flipping by about 180°. As shown by a number of X-ray structure analyses this does not occur if a guest molecule is added that can fill the cavity.[15]

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[9] Crystal structure of TRIMEG (Cyclolab, Budapest; crystallized as the dihydrate from water at approximately 80 °C, stable at ambient conditions). X-ray data were measured at room temperature on a Turbo-CAD4 diffractometer (Enraf–Nonius) with a FR571 rotating anode X-ray generator (Cu$_{K\alpha}$ radiation, $\lambda = 1.54176$ Å); $C_{72}H_{128}O_{40} \cdot 2H_2O$, $M_r = 1678.8$, crystal dimensions $0.75 \times 0.55 \times 0.20$ mm^3, orthorhombic, pace group $P2_12_12_1$ with $a = 16.730(13)$, $b = 16.875(8)$, $c = 32.172(14)$ Å, $V = 9083(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.228$ g cm^{-1}, 7404 reflections measured, of which 7368 unique, 4494 observed with $I > 2\sigma(I)$. The structure was solved with SIR 92 (A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined with SHELXL 93 (G. M. Sheldrick, *Program for crystal structure refinement*. University of Göttingen, Germany, **1993**). Hydrogen atoms were treated in the standard riding model with the methyl groups allowed to rotate. Two primary methoxy groups (at glucose residues 2 and 7) are twofold disordered. Four partially occupied water sites were located with a sum of occupancies of 2.01, water hydrogen atoms could not be located. $R = 0.081$, $R_w = 0.215$.[11]

[10] Crystal structure of TRIMEB (Cyclolab, Budapest; crystallized as the monohydrate at approximately 40 °C): Data collection and structure analysis were as for TRIMEG dihydrate. $C_{63}H_{112}O_{35} \cdot H_2O$, $M_r = 1445.5$, crystal dimensions $0.50 \times 0.25 \times 0.25$ mm^3, orthorhombic, space group $P2_12_12_1$ with $a = 14.823(5)$, $b = 19.382(3)$, $c = 26.534(5)$ Å, $V = 7623(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.259$ g cm^{-3}, 6225 unique reflections measured, 6214 observed with $I > 2\sigma(I)$. Methoxy groups are ordered. Water hydrogen atoms could not be located. $R = 0.053$, $R_W = 0.126$.[11]

[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101208. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] The angle O4($n+1$)-O4(n)-O4($n-1$) between the O4 atoms of consecutive glucose units is flexible, and allows some opening and closing. In α-CD the average angle is 120°, in β-CD it is 128°, and in γ-CD it is 135°.

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$Ca_5Cl_3(C_2)(CBC)$: A Compound with a Layer Structure and an Unusual Anion Combination**

Olaf Reckeweg and Hans-Jürgen Meyer*

Reports concerning "calcium monochloride"[1] inspired us some years ago to investigate reactions in and with melts of calcium chloride. The colorless "calcium monochloride" was found to be CaHCl,[2] the red one turned out to be $Ca_3Cl_2C_3$.[3] The synthetic potential of calcium chloride melts as a solvent for graphite or calcium metal is well known. When CaC_2 is dissolved in a melt of $CaCl_2$ the compound $Ca_3Cl_2C_3$ with the C_3^{4-} ion is formed. Reactions of calcium with certain combinations of the elements B, C, and N in calcium chloride melts yield compounds such as Ca_3Cl_2CBN with CBN^{4-} ions,[4] Ca_2ClBN_2,[5] and $Sr_3(BN_2)_2$[6] with BN_2^{3-} ions or the title compound $Ca_5Cl_3(C_2)(CBC)$.[7]

In attempts to synthesize "$Ca_4Cl_3BC_2$" with the help of a melt of calcium chloride, the new compound $Ca_5Cl_3(C_2)$(CBC) has been obtained which contains acetylide and dicarbidoborate ions. A characteristic feature of the structure of $Ca_5Cl_3(C_2)(CBC)$ is the puckered layers with the sequence Cl-Ca-Ca. The layered structure is reflected in the habitus of the crystals which occur as thin aggregates that are very often grown together. The C_2^{2-} and CBC^{5-} ions are sandwiched between double layers of calcium ions (Figure 1). The C_2^{2-} ions are coordinated by a distorted octahedron of Ca^{2+} ions.

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