# ΜΕΛΕΤΗ ΣΥΜΠΛΟΚΩΝ ΚΥΚΛΟΔΕΞΤΡΙΝΩΝ
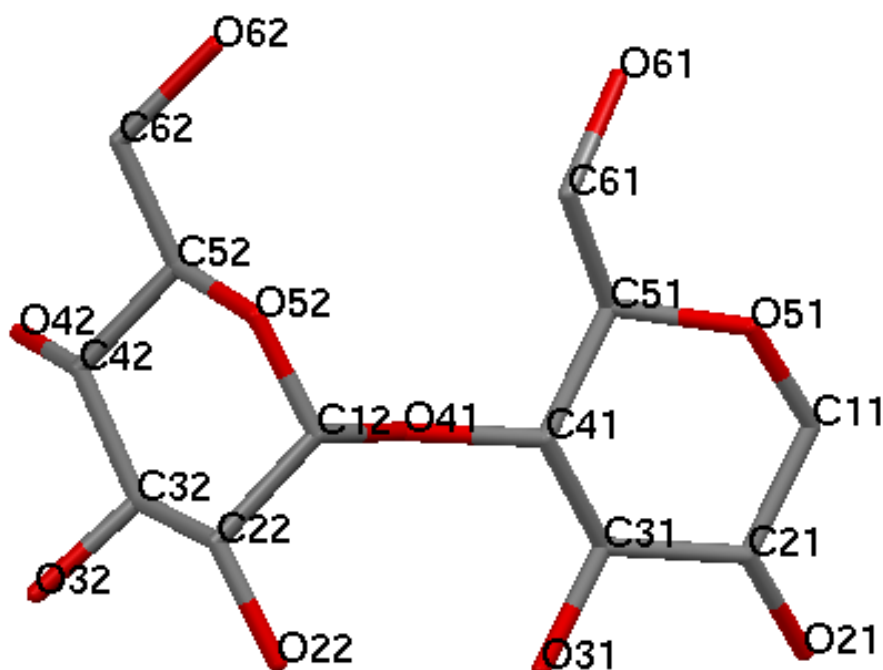
1) File --> open --> /.../4cpa.cif

2) Περιοχή: Structure Navigator --> Crystal Structures --> 4cpa
3) Περιοχή: Display options --> More Info
      Space group: .................
      ($^*$)Z:, Z′:

4) Παρατηρήστε τη θερμική κίνηση του μοντέλου επιλέγοντας:
   Style → Ellipsoid
      ή/και
   Colour → Atomic displacement

5) Ανοίξτε το 4cpa.cif με έναν text editor (π.χ. wordpad) και σβήστε τη θέση (Β) με αριθμό κατάληψης 36% (θα αναγνωρίσετε τα άτομα από το όνομα τους που περιέχει το Β αλλά και από τον αριθμό κατάληψης τους που είναι 0.36). Αποθηκεύεστε το αρχείο με διαφορετικό όνομα π.χ. 4CPA_A.cif και ανοίξτε με mercury το νέο αυτό αρχείο. Τώρα θα πρέπει να βλέπετε ξεκάθαρα μόνο μία θέση guest.

4) ΔΙΑΜΟΡΦΩΣΗ ΜΟΡΙΟΥ ΞΕΝΙΣΤΗ (β-κυκλοδεξτρίνη)



    i)   Ενδομοριακοί Υδρογονικοί δεσμοί;

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$^*$ http://www.xtl.ox.ac.uk/zprime.html
For many discrete-molecule materials, the molecules pack together to form crystals in a relatively simple way determined by the Space Group. Such materials are said to have Z'=1 (Z-prime). Increasingly, crystallographers are beginning to find crystals in which the basic building block is not just one molecule, but several molecules taken together. Such materials are said to have Z'>1.

| | Απόσταση (Å) | Γωνία (°) |
|---|---|---|
| O22 ... O31 | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

ii) Conformational characteristics of the ….-CD/…… complex

| Residue | n=1 | n=2 | n=3 | n=4 | n=5 | n=6 | n=7 |
|---|---|---|---|---|---|---|---|
| …….. | | | | | | | |
| $D$ (Å) | | | | | | | |
| $\Phi_h$ (°) | | | | | | | |
| $d$ (Å) | | | | | | | |
| $D_K$ (Å) | | | | | | | |
| $\tau$ (°) | | | | | | | |
| $\omega$ (°) | | | | | | | |
| Conformation (Παράρτημα Ι$^i$) | | | | | | | |

$D$ = O4$n$…O4($n$+1) distances;

$\Phi_h$ = O4($n$-1)…O4$n$…O4($n$+1) angles;

$d$ = deviations of the O4$n$ atoms from their least-squares plane;

$D_k$ = KA…O4$n$A;

$\tau$ = tilt angles between the optimum O4$n$ plane and the mean plane of the O4($n$-1), C1$n$, C4$n$, O4$n$ atoms;

torsion angles $\omega$ = O5$n$-C5$n$-C6$n$-O6$n$; conformation of the primary hydroxyls

iii) ΣΧΗΜΑΤΙΣΜΟΣ ΔΙΜΕΡΟΥΣ
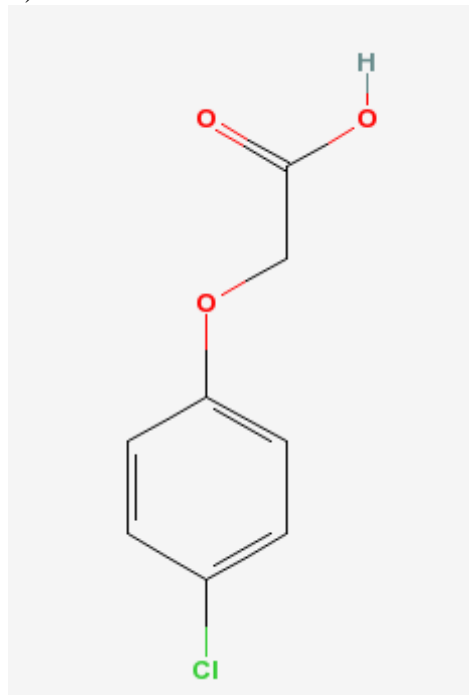Περιοχή: Display options --> Packing

(Menu) Calculate --> Packing/Slicing     -->   a: 0.4 - 0.6
                                                b: 0.4 - 0.6
                                                c: 0.0 - 1.0


Υδρογονικοί δεσμοί για σχηματισμό διμερούς συμπλόκων κατά τον άξονα b

|  | Απόσταση (Å) | Γωνία (°) |
|---|---|---|
| O31 ... O3′7 |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |


## 5) ΔΙΑΜΟΡΦΩΣΗ ΞΕΝΙΖΟΜΕΝΟΥ ΜΟΡΙΟΥ (4CPA)



5.1 Καρβοξύλιο (H-bonds με νερά έξω από cavity)

5.2 Etheric O

5.3 phenyl groups (pi-pi)
- Shortest inter-phenyl carbon-carbon distance (SICD) = 3.918 ( gia to C5A-C5A) [Hunter, 1990 rule 3.4<SICD<4.8]
- centroids distance = 4.502
offset(πυθαγορειο) = 1.68 (διαμετρος phenyl~2.78)

5.4 Cl (location: O2,O3 plane, H-bond entrapped water molecule)

## 6) ΑΛΛΗΛΕΠΙΔΡΑΣΕΙΣ ΞΕΝΙΣΤΗ – ΞΕΝΙΖΟΜΕΝΟΥ

CH-π interactions (ΠΑΡΑΡΤΗΜΑ II[ii])
=================

H: .............

C1: ............

C2: ............

ω = ............

θ = ............

Dpln= ..........

Dlin = ...........

Datm = ...........

Region = ..........

6) ΔΙΚΤΥΟ ΥΔΡΟΓΟΝΙΚΩΝ ΔΕΣΜΩΝ - ΝΕΡΑ

7) CRYSTAL PACKING

Glucose is a highly complex chemical compound because it can exist is many isomeric forms and each isomer is subject to rotational isomerism.

Within the cyclic form of glucose, rotation may occur around the O6-C6-C5-O5 torsion angle, termed the $\omega$-angle, to form three rotamer conformations as shown in the diagram below. In referring to the orientations of the $\omega$-angle and the O6-C6-C5-C4 angle, the three stable staggered rotamer conformations are termed *gauche-gauche* (gg), *gauche-trans* (gt) and *trans-gauche* (tg). For methyl α-D-glucopyranose at equilibrium the ratio of molecules in each rotamer conformation is reported as

**57 : 38 : 5          gg : gt : tg.**

Kirschner, Karl N.; Woods, Robert J. (2001), "Solvent interactions determine carbohydrate conformation", *Proc. Natl. Acad. Sci. USA* 98 (19): 10541–45. This tendency for the $\omega$-angle to prefer to adopt a *gauche* conformation is attributed to the **gauche effect.** (The term "gauche" refers to conformational isomers (conformers) where two vicinal (In chemistry **vicinal** (from Latin *vicinus* = neighbor) stands for any two functional groups bonded to two adjacent carbon atoms) groups are separated by a 60° torsion angle).
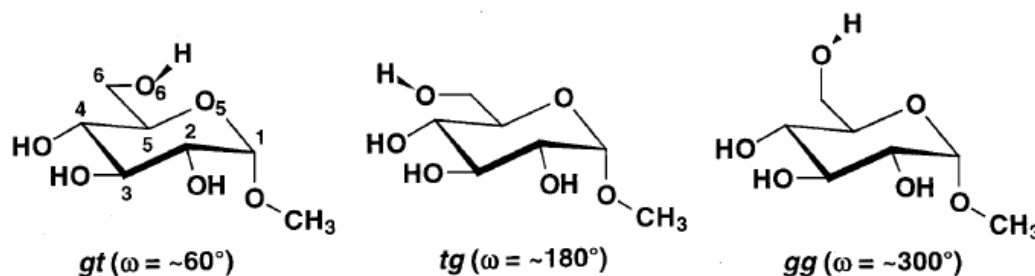


**Fig. 1.** The *gt, tg,* and *gg* rotamers of methyl α-D-glucopyranoside (1). Methyl α-D-galactopyranoside (2) differs from 1 in configuration at C4.

Rotation around the C-5/C-6 bond is described by the angle ω. Three possible staggered conformations possible; gauche-trans (gt), gauche-gauche (gg), trans-gauche(tg).

*Example*
Conformational characteristics of the α-CD/camphor complexes

| Residue | n=1 | n=2 | n=3 | n=4 | n=5 | n=6 |
|---|---|---|---|---|---|---|
| **R-αCD** | | | | | | |
| $\omega$ (°) | -59.7 a | 76.7 a | 75.2 a | 90.5 a | -77.4 a | 80.3 a |
| | -48.4 b | 60.4 b | 62.6 b | -37.5 b | -48.1 b | -52 b |
| | | | | 80.8 c | | 64.8 c |
| | *gg* | *gt* | *gt* | *gt* | *gg* | *gt* |
| Conformation | *gg* | *gt* | *gt* | *gg* | *gg* | *gg* |
| | | | | *gt* | | *gt* |

In stereochemistry, **gauche** interactions hinder bond rotation. For example, sighting along the C5-C6 bond, there are two possible relative potential energies. The conformational families about the $C_5$—$C_6$ bond display a bias for *gauche* orientations. In general a gauche rotamer (gg, -HO(6) points outwards the CyD cavity) is less stable than an anti-rotamer (gt - -HO(6) points inwards the CyD cavity).

# CH/p Interactions as Demonstrated in the Crystal Structure of Host/Guest Compounds. A Database Study

Hiroki Takahashi, Sei Tsuboyama, Yoji Umezawa, Kazumasa Honda and Motohiro Nishio

CH/$\pi$ interactions:
O: centre of plane.
$C^1$ and $C^2$: nearest and second nearest sp$^2$-carbons, respectively, to H.
$\omega$: dihedral angle defined by $C^1OC^2$ and H $C^1C^2$ planes.
$\theta$: angle $HXC^1$
$D_{pln}$: H/$\pi$-plane distance (H/I)
$D_{atm}$: interatomic distance (H/$C^1$)
$D_{lin}$: distance between H and line $C^1C^2$ (H/J)

$D_{max} = 3.005$ Å

| *Region 1* | *Region 2* | *Region 3* |
|---|---|---|
| $D_{pln} < D_{max}$ | $D_{lin} < D_{max}$ | $D_{atm} < D_{max}$ |
| $\theta < 60°$ | $\theta < 60°$ | $\theta < 60°$ |
|  | $90° < |\omega| < 130°$ | $50° < \varphi| < 90°$ ( $\varphi$: $HC^1I$) |