

Topology of Cyclooctane Energy Landscape: Supplementary Material

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Abstract

In Section 1, we give exact solutions in terms of torsion angle for five canonical conformations of cyclooctane (crown, boat, and chair). These conformations are derived using fixed bond angle, fixed bond length, and methods from distance geometry. In Section 2, we show that the cyclooctane conformation topology observed using torsion angles can also be seen in ring puckering coordinates.

1 Canonical conformations

1.1 Distance geometry

We use the loop closure constraints derived from the distance geometry model employed by Porta *et al.* [1]. In this model, we define the function

$$D(1, 2, 3, \dots, k) = \begin{vmatrix} 0 & r_{1,2} & r_{1,3} & \cdots & r_{1,k} & 1 \\ r_{2,1} & 0 & r_{2,3} & \cdots & r_{1,k} & 1 \\ r_{3,1} & r_{3,2} & 0 & \cdots & r_{3,k} & 1 \\ \cdots & \cdots & \cdots & \cdots & \cdots & 1 \\ r_{k,1} & r_{k,2} & r_{k,3} & \cdots & 0 & 1 \\ 1 & 1 & 1 & \cdots & 1 & 0 \end{vmatrix}, \quad (1)$$

where $r_{i,j} = \|\mathbf{p}_i - \mathbf{p}_j\|^2$, and \mathbf{p}_i is the position of an atom embedded in \mathbb{R}^3 . For cyclooctane, $k = 8$ (only ring atoms are considered).

Using D , we get a system of inequalities and equations which tell us whether or not a given conformation can be realized. These necessary and sufficient conditions are given by

$$D(1, 2) > 0, \quad (2)$$

$$D(1, 2, 3) < 0, \quad (3)$$

$$D(1, 2, 3, 4) > 0, \quad (4)$$

and for every pair (i, j) with $i, j = 5, \dots, k$ and $i < j$

$$D(\mathbf{R}, i) = 0, \quad (5)$$

$$D(\mathbf{R}, j) = 0, \quad (6)$$

$$D(\mathbf{R}, i, j) = 0, \quad (7)$$

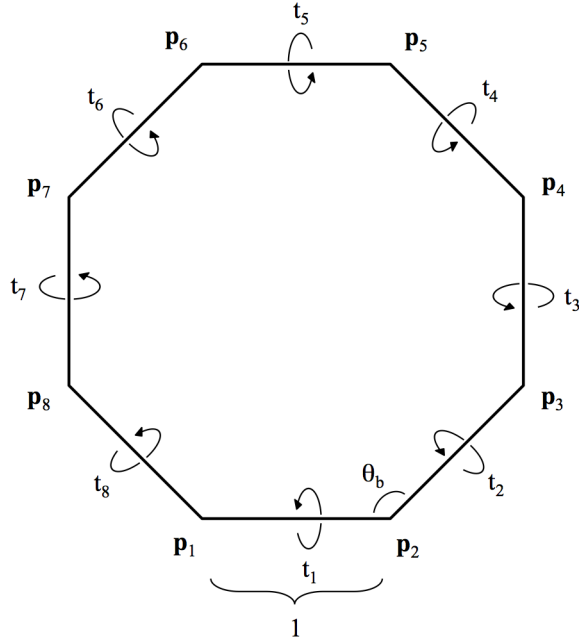


Figure S1: Variable definitions for cyclooctane conformation. We use \mathbf{p}_i for points in \mathbb{R}^3 representing ring atom positions, t_i for torsion angles using a right-handed system, and θ_b for the fixed bond angle.

where \mathbf{R} is used to indicate indices $1, \dots, 4$.

1.2 Distances from torsions

We use the distance model from Section 1.1 in combination with torsion angles. We derive quantities c , f and g which give us distances as functions of torsions. In deriving these quantities, we assume a constant bond angle θ_b and a constant bond length of 1. Our labeling of points and torsions are shown in Figure S1.

With these definitions, we obtain $c^2 = r_{1,3} = \|\mathbf{p}_3 - \mathbf{p}_1\|^2$, or

$$c^2 = 2(1 - \cos \theta_b) \quad (8)$$

from the law of cosines. We next obtain $f(t_2) = r_{1,4} = \|\mathbf{p}_4 - \mathbf{p}_1\|^2$, or

$$f(t_2) = (1 - 2 \cos \theta_b)^2 + 2 \sin^2 \theta_b (1 - \cos t_2). \quad (9)$$

Finally, we obtain $g(t_2, t_3) = r_{1,5} = \|\mathbf{p}_5 - \mathbf{p}_1\|^2$, or

$$g(t_2, t_3) = \left(c(1 - \cos \theta_b) - \sin \theta_b \sqrt{\frac{1 + \cos \theta_b}{2}} (\cos t_2 + \cos t_3) \right)^2 + \frac{c^2}{4} \sin^2 \theta_b (\cos t_3 - \cos t_2)^2 + \sin^2 \theta_b (\sin t_3 + \sin t_2)^2. \quad (10)$$

If we further assume that $\theta_b \in (0, \pi)$, we note that $c\sqrt{\frac{1 + \cos \theta_b}{2}} = \sin \theta_b$ so that

$$g(t_2, t_3) = c^2(1 - \cos \theta_b)^2 - 2(1 - \cos \theta_b) \sin^2 \theta_b (\cos t_2 + \cos t_3) + \sin^2 \theta_b \left(\frac{1 + \cos \theta_b}{2} \right) (\cos t_2 + \cos t_3)^2 + \frac{c^2}{4} \sin^2 \theta_b (\cos t_3 - \cos t_2)^2 + \sin^2 \theta_b (\sin t_3 + \sin t_2)^2. \quad (11)$$

Using c, f and g , we see that $D(1, \dots, 8)$ from Equation (1) assumes the general form

$$\begin{vmatrix} 0 & 1 & c^2 & f_2 & g_{2,3} & f_7 & c^2 & 1 & 1 \\ 1 & 0 & 1 & c^2 & f_3 & g_{3,4} & f_8 & c^2 & 1 \\ c^2 & 1 & 0 & 1 & c^2 & f_4 & g_{4,5} & f_1 & 1 \\ f_2 & c^2 & 1 & 0 & 1 & c^2 & f_5 & g_{5,6} & 1 \\ g_{2,3} & f_3 & c^2 & 1 & 0 & 1 & c^2 & f_6 & 1 \\ f_7 & g_{3,4} & f_4 & c^2 & 1 & 0 & 1 & c^2 & 1 \\ c^2 & f_8 & g_{4,5} & f_5 & c^2 & 1 & 0 & 1 & 1 \\ 1 & c^2 & f_1 & g_{5,6} & f_6 & c^2 & 1 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 \end{vmatrix}, \quad (12)$$

for cyclooctane ($k = 8$), where f_i denotes $f(t_i)$ and $g_{i,j}$ denotes $g(t_i, t_j)$.

1.3 Canonical crown conformation

Suppose now that

$$\begin{aligned} t_1 &= t_3 = t_5 = t_7, \\ t_2 &= t_4 = t_6 = t_8, \\ t_2 &= -t_1. \end{aligned} \quad (13)$$

In this case we should obtain the canonical cyclooctane crown conformation. If we let $u = t_1$ then

$$\mathbf{c}_r = (u, -u, u, -u, u, -u, u, -u)^T. \quad (14)$$

Using these constraints, we note that $f(t_i) = f(t_j) = f(u)$ for all i, j (since cosine is even) and g reduces to a function of a single variable

$$g(t) = \left(c(1 - \cos \theta_b) - 2 \sin \theta_b \sqrt{\frac{1 + \cos \theta_b}{2}} \cos t \right)^2, \quad (15)$$

such that $g(t_i) = g(t_j)$ for all i, j . The inequalities (2)-(4) are true in general for $\theta_b, t_2 \neq 0, \pm\pi, \pm 2\pi, \dots$ and $D(1, \dots, 8)$ further reduces to

$$\begin{vmatrix} 0 & 1 & c^2 & f & g & f & c^2 & 1 & 1 \\ 1 & 0 & 1 & c^2 & f & g & f & c^2 & 1 \\ c^2 & 1 & 0 & 1 & c^2 & f & g & f & 1 \\ f & c^2 & 1 & 0 & 1 & c^2 & f & g & 1 \\ g & f & c^2 & 1 & 0 & 1 & c^2 & f & 1 \\ f & g & f & c^2 & 1 & 0 & 1 & c^2 & 1 \\ c^2 & f & g & f & c^2 & 1 & 0 & 1 & 1 \\ 1 & c^2 & f & g & f & c^2 & 1 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 \end{vmatrix}, \quad (16)$$

where f and g are now functions of the dihedral angle u .

We verified using the computer algebra system MuPAD (www.mathworks.com) that equations (5)-(7) yield a unique solution such that

$$g = 2c^2, \quad (17)$$

$$c^2 g = f^2 - 2f + 1. \quad (18)$$

Solving (17) and (18) gives

$$\cos(u) = \frac{1 - \sqrt{2} - \cos \theta_b}{1 + \cos \theta_b}. \quad (19)$$

1.4 Canonical boat conformation

For the canonical boat conformation, we assume

$$\begin{aligned} t_1 = t_3 = t_5 = t_7 &= 0, \\ t_2 = -t_4 = t_6 = -t_8. \end{aligned} \quad (20)$$

Letting $v = t_2$ this gives us

$$\mathbf{b}_1 = (0, v, 0, -v, 0, v, 0, -v)^T. \quad (21)$$

The same value of v suffices for

$$\mathbf{b}_2 = (v, 0, -v, 0, v, 0, -v, 0)^T. \quad (22)$$

In this case, we obtain

$$f_0 = f(0) = (c^2 - 1)^2 \quad (23)$$

and

$$\begin{aligned} g(t) &= (c(1 - \cos \theta_b) - \sin \theta_b \sqrt{\frac{1 + \cos \theta_b}{2}} (1 + \cos t))^2 \\ &\quad + \frac{c^2}{4} \sin^2 \theta_b (1 - \cos t)^2 + \sin^2 \theta_b \sin^2 t. \end{aligned} \quad (24)$$

Thus $D(1, \dots, 8)$ reduces to

$$\begin{vmatrix} 0 & 1 & c^2 & f & g & f_0 & c^2 & 1 & 1 \\ 1 & 0 & 1 & c^2 & f_0 & g & f & c^2 & 1 \\ c^2 & 1 & 0 & 1 & c^2 & f & g & f_0 & 1 \\ f & c^2 & 1 & 0 & 1 & c^2 & f_0 & g & 1 \\ g & f_0 & c^2 & 1 & 0 & 1 & c^2 & f & 1 \\ f_0 & g & f & c^2 & 1 & 0 & 1 & c^2 & 1 \\ c^2 & f & g & f_0 & c^2 & 1 & 0 & 1 & 1 \\ 1 & c^2 & f_0 & g & f & c^2 & 1 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 \end{vmatrix}, \quad (25)$$

where f and g are functions of v , and $f_0 = (c^2 - 1)^2$ from (23). Now equations (5)-(7) yield a unique solution such that

$$g = c^2 f - f - c^4 + c^2 + 1, \quad (26)$$

$$f = 2c^2 - 1. \quad (27)$$

Solving (26) and (27) gives

$$\cos(v) = \frac{\cos^2 \theta_b}{\sin^2 \theta_b}. \quad (28)$$

1.5 Canonical chair conformation

Finally, we assume

$$\begin{aligned} t_1 &= -t_3 = -t_5 = t_7, \\ t_2 &= t_6 = 0, \\ t_4 &= -t_8. \end{aligned} \quad (29)$$

If we let $\tilde{v} = t_1$ and $w = t_4$ we get the canonical chair conformation

$$\mathbf{c}_1 = (\tilde{v}, 0, -\tilde{v}, w, -\tilde{v}, 0, \tilde{v}, -w)^T. \quad (30)$$

We note that $\tilde{v} = v$ since the first three entries of \mathbf{c}_1 are in fact identical to the first three entries of \mathbf{b}_2 , and hence the corresponding distance equations in (5) are identical. Thus we have

$$\mathbf{c}_1 = (v, 0, -v, w, -v, 0, v, -w)^T, \quad (31)$$

as well as

$$\mathbf{c}_2 = (v, -w, v, 0, -v, w, -v, 0)^T. \quad (32)$$

We now have $f_0 = f(0)$, $f_v = f(v)$, $f_w = f(w)$, $g_v = g(v, 0)$, and $g_{v,w} = g(v, w)$. Using (11) we know that

$$\begin{aligned} g(v, w) &= c^2(1 - \cos \theta_b)^2 - 2(1 - \cos \theta_b) \sin^2 \theta_b (\cos v + \cos w) \\ &\quad + \sin^2 \theta_b \left(\frac{1 + \cos \theta_b}{2} \right) (\cos v + \cos w)^2 \\ &\quad + \frac{c^2}{4} \sin^2 \theta_b (\cos v - \cos w)^2 \\ &\quad + \sin^2 \theta_b (\sin v - \sin w)^2. \end{aligned} \quad (33)$$

In this case, $D(1, \dots, 8)$ assumes the form

$$\begin{vmatrix} 0 & 1 & c^2 & f_0 & g_v & f_v & c^2 & 1 & 1 \\ 1 & 0 & 1 & c^2 & f_v & g_{v,w} & f_w & c^2 & 1 \\ c^2 & 1 & 0 & 1 & c^2 & f_w & g_{v,w} & f_v & 1 \\ f_0 & c^2 & 1 & 0 & 1 & c^2 & f_v & g_v & 1 \\ g_v & f_v & c^2 & 1 & 0 & 1 & c^2 & f_0 & 1 \\ f_v & g_{v,w} & f_w & c^2 & 1 & 0 & 1 & c^2 & 1 \\ c^2 & f_w & g_{v,w} & f_v & c^2 & 1 & 0 & 1 & 1 \\ 1 & c^2 & f_v & g_v & f_0 & c^2 & 1 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 \end{vmatrix}, \quad (34)$$

According to the previous remark regarding $\tilde{v} = v$, we can use (26) and (27) to obtain

$$f_v = 2c^2 - 1 \quad (35)$$

$$g_v = c^2 f_v - f_v - c^4 + c^2 + 1 \quad (36)$$

Using (35) and (36) in (34) we obtain

$$g_{v,w} = 1 + f_w. \quad (37)$$

Again using (34), the relation (37) yields

$$f_w = 6c^2 - c^4 - 3 \quad (38)$$

or

$$\cos w = \frac{3 \cos^2 \theta_b - 1}{\sin^2 \theta_b}. \quad (39)$$

2 Topology in puckering coordinates

2.1 Ring puckering coordinates

Cremer and Pople (1974) proposed a general coordinate system for quantifying ring pucker [2]. This system is based on locating a mean plane through the center of mass of a molecular ring and then computing the vertical displacements of the ring atoms from that plane. The displacements are used to compute puckering coordinates. Following Cremer and Pople, we denote the ring atom coordinates by $\mathbf{R}_j = (X_j, Y_j, Z_j)$ for $j = 1, \dots, N$, where N is the number of ring atoms. For cyclooctane, $N = 8$. If we define

$$\mathbf{R}' = \sum_{j=1}^N \mathbf{R}_j \sin(2\pi(j-1)/N), \quad (40)$$

$$\mathbf{R}'' = \sum_{j=1}^N \mathbf{R}_j \cos(2\pi(j-1)/N), \quad (41)$$

then the vector

$$\mathbf{n} = \frac{\mathbf{R}' \times \mathbf{R}''}{\|\mathbf{R}' \times \mathbf{R}''\|} \quad (42)$$

gives the normal to the mean plane, and

$$z_j = \mathbf{R}_j \cdot \mathbf{n} \quad (43)$$

give the displacements of the ring atoms from the mean plane. The ring puckering coordinates are then given by

$$q_m \cos \phi_m = \sqrt{\frac{2}{N}} \sum_{j=1}^N z_j \cos(2\pi m(j-1)/N), \quad (44)$$

$$q_m \sin \phi_m = \sqrt{\frac{2}{N}} \sum_{j=1}^N z_j \sin(2\pi m(j-1)/N), \quad (45)$$

for $m = 2, \dots, \lfloor (N-1)/2 \rfloor$ and

$$q_{N/2} = \frac{1}{\sqrt{N}} \sum_{j=1}^N z_j \cos((j-1)\pi), \quad (46)$$

if N is even, where $q_{N/2}$ can be either sign. For cyclooctane, we therefore have 5 ring puckering coordinates: $q_2, q_3, q_4, \phi_2, \phi_3$.

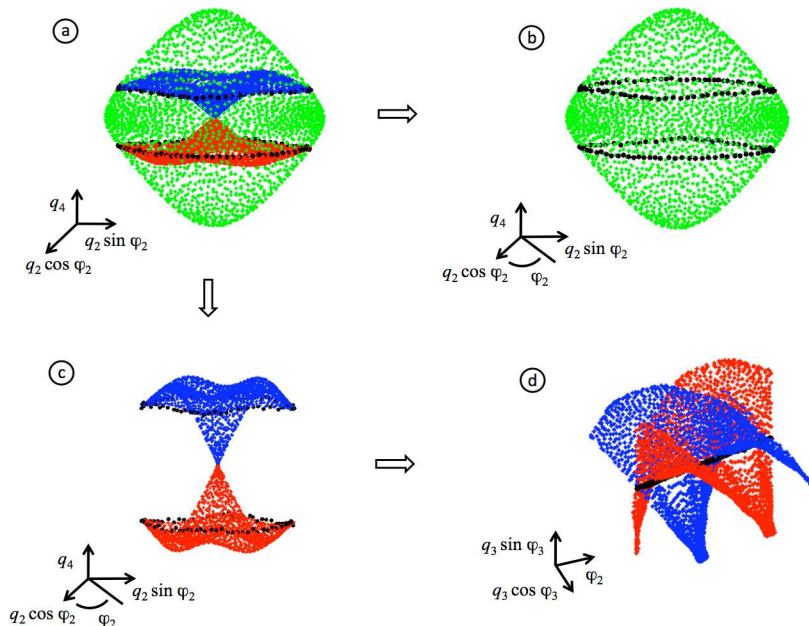


Figure S2: Puckering coordinates for cyclooctane. Here we show how the ring puckering coordinates can be used to visualize the topology of the cyclooctane conformation space, in analogy with Figure 3 in the main text. The entire space can be visualized using coordinates given by $(q_2 \cos \phi_2, q_2 \sin \phi_2, q_4)$, as shown in (a). We use green to represent the spherical component (b) of the conformation space and blue/red to represent the Klein bottle component (c). The intersection rings are shown using black. The Klein bottle component can be seen as two Möbius strips, apparent using $(q_3 \cos \phi_3, q_3 \sin \phi_3, \phi_2)$ coordinates (d), where ϕ_2 varies between 0 and 2π .

2.2 Ring puckering for cyclooctane

In work by Evans and Boeyens (1988), ring puckering coordinates were used to produce a map of the conformation space of cyclooctane [3]. This map was found to be a sphere intersecting a torus. In our work, we discovered a sphere intersecting a Klein bottle. It is our claim that Evans and Boeyens slightly misinterpreted the puckering coordinate representation, probably due to the fact that they were working with a very small sample of cyclooctane conformations. To substantiate this claim, we show that the cyclooctane topology observed using torsion angle (i.e. the sphere intersecting the Klein bottle) is also seen using ring puckering coordinates.

Using the 6,040 conformation dataset described in the main text, we computed the ring puckering coordinates for each conformation as described in Section 2.1. We used the puckering coordinates to obtain the

plots shown in Figure S2. The results are qualitatively identical to the results given in Figure 3 of the main text, thus supporting our claim. These results are in fact so similar that we are led to speculate that additional topological trends in cyclic alkanes (besides cyclooctane) might be easily observed by further exploiting the generic nature of the ring puckering coordinates.

References

- [1] J. M. Porta *et al.*, *Complete maps of molecular-loop conformational spaces*, J. Comput. Chem. 28 (2007), pp. 2170–2189.
- [2] D. Cremer and J. A. Pople, *A general definition of ring puckering coordinates*, J. Am. Chem. Soc. 97 (1974), pp. 1354–1358.
- [3] D. G. Evans and J. C. A. Boeyens, *Mapping the conformation of eight-membered rings*, Acta Cryst. (1988), pp. 663–671.