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Geometric Constraints on the Distortion of Planar Rings

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Abstract

Approximate but relatively simple relationships among the angles and the lengths of the edges in slightly irregular planar polygons are given. The relationships can be extended to polygons of any number of edges and are sufficiently accurate to describe the distortions usually found in molecular structures.

If we consider a planar polygon of n sides, there are $2n - 3$ degrees of freedom in defining the lengths of the sides and the interior angles. This means that there must be three constraints relating the n sides and the n angles. In a previous paper the case of the slightly distorted regular hexagon was considered in some detail and it was found that the three conditions could be expressed in a rather simple and symmetric way (equations 8–10 in Britton, 1977). Further consideration shows that similar conditions obtain for any slightly distorted regular polygon. These constraints have been recognized by vibrational spectroscopists as the problem of redundant internal coordinates: Califano & Crawford (1960) describe a general approach to the problem and give specific results for four- and six-membered rings; further discussion and the specific results for a three-membered ring are given by Gussoni & Zerbi (1966); the specific results for three-, four-, and six-membered rings are also given by Cyvin (1968). The question is considered again here for three reasons: (*a*) the existence of such constraints does not seem to be widely recognized by crystallographers; (*b*) specific expressions giving the solution for the constraints for any size ring do not appear in the earlier literature; (*c*) an analytical approach, different from the method of Califano & Crawford, has been used to derive the results.

The analytical approach

The problem can be approached from a purely trigonometric point of view in the following way. A fragment of an n-gon is shown in Fig. 1. The lengths of the sides are $l_{ij} = 1 + \varepsilon_{ij}$, and the interior angles are $\alpha_i = [(n-2)/n]\pi + \beta_i$. We are seeking three independent relationships between the l_{ij} and the α_i, or, equivalently,

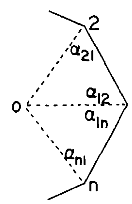

Fig. 1. Part of a nearly regular n-gon. The points 1, 2, ..., n are the vertices of the n-gon. The point o is the approximate centre. The angle α_1 (not shown) is the sum of α_{12} and α_{1n}.

between the ε_{ij} and the β_i. One of these relationships is always

$$\sum \beta_i = 0, \qquad (1)$$

which follows from the condition that $\sum \alpha_i = (n-2)\pi$. The corresponding relationship for the sides, $\sum \varepsilon_{ij} = 0$, is not required nor necessarily true, although we shall require that $\varepsilon_{ij} \ll 1$. We define (see Fig. 1) the radii, $r_{oi} = \frac{1}{2}[\sin(\pi/n)]^{-1} + \varepsilon_{oi}$, and the angles $\alpha_{ij} = [(n-2)/2n]\pi + \beta_{ij}$. For each triangle oij we use the law of cosines once to relate r_{oi}, r_{oj}, l_{ij}, and α_{ij}, and again to relate r_{oi}, r_{oj}, l_{ij}, and α_{ji}, to give $2n$ equations. These can be simplified by replacing the r's, l's, and α's with the corresponding expressions using ε's and β's, by making the approximations that $\cos\beta = 1$ and $\sin\beta = \beta$, and by keeping only first-order terms in the ε's and β's. We now have $2n$ linear equations in the ε's and β's. These can be reduced to n equations using the relationship $\beta_i = \beta_{i,i-1} + \beta_{i,i+1}$. These n equations relating the n ε_{ij}'s, the n ε_{io}'s, and the n β_i's take the form

$$\left(\cos\frac{\pi}{n}\right)\beta_i = -\left(\sin\frac{\pi}{n}\right)(\varepsilon_{i,i-1} + \varepsilon_{i,i+1}) - 2\left(\cos\frac{2\pi}{n}\right)\varepsilon_{io} + \varepsilon_{i-1,o} + \varepsilon_{i+1,o}.$$

Two of the ε_{io} can be arbitrarily set equal to 0 (provided the corresponding r_{io} are not collinear) to define the location of the origin, and the remaining $n - 2$ ε_{io}'s can be eliminated to yield the two equations we are seeking relating the ε_{ij} and the β_i. These equations can be expressed in a variety of ways, but after some

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manipulation, which becomes considerable as n increases, they can be written in the form (provided that we recognize $\varepsilon_{n,n+1} = \varepsilon_{n,1}$)

$$\sum \beta_i \cos\frac{(2i-2)\pi}{n} = -2\sin\frac{\pi}{n} \times \sum \varepsilon_{i,i+1} \cos\frac{(2i-1)\pi}{n}, \quad (2\text{-}n)$$

$$\sum \beta_i \sin\frac{(2i-2)\pi}{n} = -2\sin\frac{\pi}{n} \times \sum \varepsilon_{i,i+1} \sin\frac{(2i-1)\pi}{n}. \quad (3\text{-}n)$$

For a six-membered ring these equations are the same as equations (9) and (10) given in the earlier work (Britton, 1977). For three-, four-, and five-membered rings the explicit expressions are:

$n = 3$

$$2\beta_1 - \beta_2 - \beta_3 = \sqrt{3}(-\varepsilon_{12} + 2\varepsilon_{23} - \varepsilon_{31}) \quad (2\text{-}3)$$

$$\beta_2 - \beta_3 = \sqrt{3}(-\varepsilon_{12} + \varepsilon_{31}) \quad (3\text{-}3)$$

$n = 4$

$$\beta_1 - \beta_3 = -\varepsilon_{12} + \varepsilon_{23} + \varepsilon_{34} - \varepsilon_{41} \quad (2\text{-}4)$$

$$\beta_2 - \beta_4 = -\varepsilon_{12} - \varepsilon_{23} + \varepsilon_{34} + \varepsilon_{41} \quad (3\text{-}4)$$

$n = 5$

$$\beta_1 + \beta_2\cos(2\pi/5) + \beta_3\cos(4\pi/5) + \beta_4\cos(4\pi/5) + \beta_5\cos(2\pi/5) = 2\sin(\pi/5)[\varepsilon_{12}\cos(4\pi/5) + \varepsilon_{23}\cos(2\pi/5) + \varepsilon_{34} + \varepsilon_{45}\cos(2\pi/5) + \varepsilon_{51}\cos(4\pi/5)] \quad (2\text{-}5)$$

$$\beta_2\sin(2\pi/5) + \beta_3\sin(4\pi/5) - \beta_4\sin(4\pi/5) - \beta_5\sin(2\pi/5) = 2\sin(\pi/5)[-\varepsilon_{12}\sin(4\pi/5) - \varepsilon_{23}\sin(2\pi/5) + \varepsilon_{45}\sin(2\pi/5) + \varepsilon_{51}\sin(4\pi/5)]. \quad (3\text{-}5)$$

A group-theoretical approach

An alternative point of view is to regard the total distortion as a vector with components along symmetry coordinates of the regular polygon [for general background see Cotton (1971), Steele (1971) or Wilson, Decius & Cross (1955)]. The in-plane distortion can then be considered in terms of internal displacement coordinates, which are just the β_i and ε_{ij} of the previous treatment. A comparison of the representations of the Cartesian coordinates and the internal displacement coordinates in the point groups D_{nh} shows three redundant representations in the latter set; these are A_1' and E_1' if n is odd and A_{1g} and E_{1u} if n is even. These redundancies arise from the ring-closure conditions that the internal coordinates have to satisfy. An A_1 displacement involving ε_{ij}'s corresponds to a uniform expansion or contraction, a feasible distortion, whereas an A_1 displacement involving β_i's requires all the angles to increase or decrease simultaneously, which is a geometrical impossibility for a planar polygon. Thus $D_\beta(A_1) = n^{-1/2}\sum\beta_i = 0$, the same relationship as was given in equation (1).

The second redundancy arises because a given E_1 distortion of a polygon involves changes in both ε_{ij}'s and β_i's. In other words, $D_\beta(E_1)$ and $D_\varepsilon(E_1)$ must represent the same distortion, apart from a proportionality factor, which is $2\sin(\pi/n)$, the ratio of the side of the polygon to the radius of the circle through the vertices.

$$D_\beta(E_1) = 2\sin(\pi/n)\, D_\varepsilon(E_1). \quad (4)$$

The general equations (2-n) and (3-n) can be obtained from (4) by writing out the appropriate symmetry coordinates explicitly.

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