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Distortions in Substituted Benzene Rings: Geometric Constraints on the Distortion of a Planar Ring

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Approximate, but relatively simple relationships among the angles and the lengths of the edges in a slightly irregular hexagon are given. The relationships are sufficiently accurate to describe the distortions normally found in benzene rings.

There is a growing number of structures in which the geometry of a benzene ring deviates from that of a regular hexagon beyond any question of experimental error. For a recent discussion of some of these deviations and a possible explanation see Domenicano, Vaciago & Coulson (1975*a*,*b*) and the references therein. Setting aside the reasons for the deviations, it seems worthwhile to set down explicitly some of the constraints on the distortions.

If we consider a planar hexagon in general, there are twelve coordinates required to define the hexagon. If two of these are taken to define the location of the center and a third to define the orientation, we are left with nine degrees of freedom. Thus, of the twelve variables, six lengths of sides and six angles, three are dependent on the other nine. We shall be concerned with finding simple expressions that define these constraints for the case of small deviations from a regular hexagon.

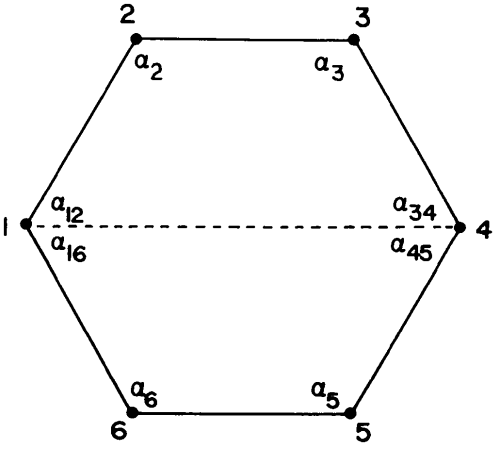

Fig. 1. Labelling of the hexagon.

The general case

We shall consider an irregular hexagon that is only slightly distorted from a regular hexagon and whose vertices are numbered from 1 to 6 (see Fig. 1). The interior angles are $\alpha_i = 2\pi/3 + \beta_i$; $\Sigma\beta_i = 0$ since $\Sigma\alpha_i = 4\pi$. (All angles will be expressed in radians unless explicitly labelled otherwise.) A diagonal divides α_1 into α_{12} and α_{16}, and α_4 into α_{43} and α_{45}; $\alpha_{ij} = \pi/3 + \beta_{ij}$. The lengths of the edges are $l_{ij} = 1 + \varepsilon_{ij}$, where the ε_{ij} are small compared with 1. If $\Sigma\varepsilon_{ij} = 0$, then the ε_{ij} are the fractional deviations from the average edge length, but this is not required. We can write the following independent relationships among the angles:

$$\beta_1 = \beta_{12} + \beta_{16} \tag{1}$$

$$\beta_4 = \beta_{43} + \beta_{45} \tag{2}$$

$$\beta_{12} + \beta_2 + \beta_3 + \beta_{43} = 0 \tag{3}$$

$$\beta_{45} + \beta_5 + \beta_6 + \beta_{16} = 0 \tag{4}$$

$$l_{12}\cos\alpha_{12} + l_{23}\cos(\beta_{12} + \beta_2) + l_{34}\cos\alpha_{43} = l_{45}\cos\alpha_{45} + l_{56}\cos(\beta_{45} + \beta_5) + l_{61}\cos\alpha_{16} \tag{5a}$$

$$l_{12}\sin\alpha_{12} + l_{23}\sin(\beta_{12} + \beta_2) = l_{34}\sin\alpha_{43} \tag{6a}$$

$$l_{45}\sin\alpha_{45} + l_{56}\sin(\beta_{45} + \beta_5) = l_{61}\sin\alpha_{16}. \tag{7a}$$

These seven relationships among the ten angles (the α's and the β's are regarded as interchangeable) cannot be simplified in any rigorous fashion. For small distortions, however, the approximations $\sin\beta = \beta$ and $\cos\beta = 1$ are reasonable. Using these approximations and keeping only first-order terms, equations (5*a*), (6*a*), and (7*a*) become:

$$-\beta_{12} - \beta_{43} + \beta_{16} + \beta_{45} = (\sqrt{3}/3)(-\varepsilon_{12} - 2\varepsilon_{23} - \varepsilon_{34} + \varepsilon_{45} + 2\varepsilon_{56} + \varepsilon_{61}) \tag{5b}$$

$$-3\beta_{12} - 2\beta_2 + \beta_{43} = \sqrt{3}(\varepsilon_{12} - \varepsilon_{34}) \tag{6b}$$

$$-3\beta_{45} - 2\beta_5 + \beta_{16} = \sqrt{3}(\varepsilon_{45} - \varepsilon_{61}). \tag{7b}$$

We can now eliminate the angles β_{12}, β_{16}, β_{43}, and β_{45}, which are of no interest, and obtain three equations

relating the six sides and the six angles. These three relationships can be expressed in a variety of ways; a particularly nice set is:

$$\beta_1+\beta_2+\beta_3+\beta_4+\beta_5+\beta_6=0 \tag{8}$$

$$\sqrt{3}(\beta_2+\beta_3-\beta_5-\beta_6) = -\varepsilon_{12}-2\varepsilon_{23}-\varepsilon_{34}+\varepsilon_{45}+2\varepsilon_{56}+\varepsilon_{61} \tag{9}$$

$$2\beta_1+\beta_2-\beta_3-2\beta_4-\beta_5+\beta_6 = \sqrt{3}(-\varepsilon_{12}+\varepsilon_{34}+\varepsilon_{45}-\varepsilon_{61}). \tag{10}$$

In practice we would probably want to express three of the angles as functions of the remaining angles and the fluctuations in the bond lengths. Clearly, only one set of expressions is necessary, but three sets of solutions are tabulated since under various circumstances one might choose to fix angles 1, 2, and 3; or 1, 2, and 4; or 1, 3, and 5. If angles 1, 2, and 3 are chosen as independent

$$\left.\begin{aligned}\beta_4&=-\beta_1-2\beta_2-2\beta_3\\&\quad+(\sqrt{3}/3)(-\varepsilon_{12}-2\varepsilon_{23}-\varepsilon_{34}+\varepsilon_{45}+2\varepsilon_{56}+\varepsilon_{61})\\\beta_5&=2\beta_1+3\beta_2+2\beta_3\\&\quad+\sqrt{3}(\varepsilon_{12}+\varepsilon_{23}-\varepsilon_{45}-\varepsilon_{56})\\\beta_6&=-2\beta_1-2\beta_2-\beta_3\\&\quad+(\sqrt{3}/3)(-2\varepsilon_{12}-\varepsilon_{23}+\varepsilon_{34}+2\varepsilon_{45}+\varepsilon_{56}-\varepsilon_{61}).\end{aligned}\right\} \tag{11}$$

If angles 1, 2, and 4 are chosen as independent

$$\left.\begin{aligned}\beta_3&=-\beta_1/2-\beta_2-\beta_4/2\\&\quad+(\sqrt{3}/6)(-\varepsilon_{12}-2\varepsilon_{23}-\varepsilon_{34}+\varepsilon_{45}+2\varepsilon_{56}+\varepsilon_{61})\\\beta_5&=\beta_1+\beta_2-\beta_4\\&\quad+(\sqrt{3}/3)(2\varepsilon_{12}+\varepsilon_{23}-\varepsilon_{34}-2\varepsilon_{45}-\varepsilon_{56}+\varepsilon_{61})\\\beta_6&=-3\beta_1/2-\beta_2+\beta_4/2\\&\quad+(\sqrt{3}/2)(-\varepsilon_{12}+\varepsilon_{34}+\varepsilon_{45}-\varepsilon_{61}).\end{aligned}\right\} \tag{12}$$

If angles 1, 3, and 5 are chosen as independent

$$\left.\begin{aligned}\beta_2&=-2\beta_1/3-2\beta_3/3+\beta_5/3\\&\quad+(\sqrt{3}/3)(-\varepsilon_{12}-\varepsilon_{23}+\varepsilon_{45}+\varepsilon_{56})\\\beta_4&=\beta_1/3-2\beta_3/3-2\beta_5/3\\&\quad+(\sqrt{3}/3)(\varepsilon_{12}-\varepsilon_{34}-\varepsilon_{45}+\varepsilon_{61})\\\beta_6&=-2\beta_1/3+\beta_3/3-2\beta_5/3\\&\quad+(\sqrt{3}/3)(\varepsilon_{23}+\varepsilon_{34}-\varepsilon_{56}-\varepsilon_{61}).\end{aligned}\right\} \tag{13}$$

Symmetry restrictions

In most cases of interest there is some symmetry and, while the relationships in equations (11), (12), or (13) can be used, it is more convenient to have the equations simplified consistent with the symmetry. The various possibilities are as follows.

(*A*) *Twofold axis perpendicular to the ring*

There are three different lengths and three different angles. The angles are independent of the lengths. The only condition, which is rigorous, is

$$\beta_1+\beta_2+\beta_3=0. \tag{14}$$

(*B*) *Mirror plane through atoms* 1 *and* 4

There are three different lengths and four different angles. A fluctuation in l_{23} has no effect, to our degree of approximation, on the other lengths and angles. As in the general case we can choose the independent variables in several ways. If we fix β_1, β_2, and the ε_{ij},

$$\left.\begin{aligned}\beta_3&=-2\beta_1-3\beta_2+\sqrt{3}(-\varepsilon_{12}+\varepsilon_{34})\\\beta_4&=3\beta_1+4\beta_2+2\sqrt{3}(\varepsilon_{12}-\varepsilon_{34}).\end{aligned}\right\} \tag{15}$$

If we fix β_1, β_3, and the ε_{ij},

$$\left.\begin{aligned}\beta_2&=-2\beta_1/3-\beta_3/3+(\sqrt{3}/3)(-\varepsilon_{12}+\varepsilon_{34})\\\beta_4&=\beta_1/3-4\beta_3/3+(2\sqrt{3}/3)(\varepsilon_{12}-\varepsilon_{34}).\end{aligned}\right\} \tag{16}$$

If we fix β_1, β_4, and the ε_{ij},

$$\left.\begin{aligned}\beta_2&=-3\beta_1/4+\beta_4/4+(\sqrt{3}/2)(-\varepsilon_{12}+\varepsilon_{34})\\\beta_3&=\beta_1/4-3\beta_4/4+(\sqrt{3}/2)(\varepsilon_{12}-\varepsilon_{34}).\end{aligned}\right\} \tag{17}$$

If we fix β_2, β_3, and the ε_{ij},

$$\left.\begin{aligned}\beta_1&=-3\beta_2/2-\beta_3/2+(\sqrt{3}/2)(-\varepsilon_{12}+\varepsilon_{34})\\\beta_4&=-\beta_2/2-3\beta_3/2+(\sqrt{3}/2)(\varepsilon_{12}-\varepsilon_{34}).\end{aligned}\right\} \tag{18}$$

(*C*) *Mirror plane reflecting atom* 1 *into atom* 4

There are four different lengths and three different angles. If we fix β_1 and the ε_{ij},

$$\left.\begin{aligned}\beta_2&=-\beta_1/2+(\sqrt{3}/6)(-\varepsilon_{12}-\varepsilon_{23}+\varepsilon_{45}+\varepsilon_{56})\\\beta_5&=-\beta_1/2+(\sqrt{3}/6)(\varepsilon_{12}+\varepsilon_{23}-\varepsilon_{45}-\varepsilon_{56}).\end{aligned}\right\} \tag{19}$$

If we fix β_2 and the ε_{ij},

$$\left.\begin{aligned}\beta_1&=-2\beta_2+(\sqrt{3}/3)(-\varepsilon_{12}-\varepsilon_{23}+\varepsilon_{45}+\varepsilon_{56})\\\beta_5&=\beta_2+(\sqrt{3}/3)(\varepsilon_{12}+\varepsilon_{23}-\varepsilon_{45}-\varepsilon_{56}).\end{aligned}\right\} \tag{20}$$

(*D*) *Two mirror planes and a twofold axis as in A, B, and C combined*

There are two different lengths and two different angles. The angles are independent of the lengths. The only condition, which is rigorous, is

$$\beta_1+2\beta_2=0. \tag{21}$$

(*E*) *Threefold axis*

There are two different lengths and two different angles. The angles are independent of the lengths. The only condition, which is rigorous, is

$$\beta_2=-\beta_1. \tag{22}$$

(F) Threefold axis plus mirror planes through the atoms as in B

There are two different angles. All the lengths are equal. The only condition, which is rigorous, is that of equation 22.

(G) Threefold axis plus mirror planes between the atoms as in C

There are two different lengths. All the angles are equal.

(H) Sixfold axis with or without mirror planes

All lengths and angles are equal.

Discussion

As a sample check of the accuracy of the approximations we shall consider an equilateral ring distorted as in paragraph *B*. If we make $\beta_1 = 0°$ and $\beta_4 = -6°$, then we calculate $\beta_2 = -1{\cdot}50°$ and $\beta_3 = +4{\cdot}50°$ using equation (18). Exact calculation gives $\beta_2 = -1{\cdot}56°$ and $\beta_3 = +4{\cdot}56°$. A 6° distortion in a ring angle is about as large as is found and a change in β_1 in either direction from 0° makes the errors in β_2 and β_3 less. Thus, for the usual range of distortions the calculated angles are correct to within 0·1°.

If we wish to study the effects of substituents on bond lengths and interior angles, it would appear preferable to begin such studies with molecules having a rotational symmetry axis perpendicular to the ring since in all of these cases (*A* and *D* through *H*) the ring angles and the bond lengths are independent. In rings with only one mirror plane perpendicular to the ring or with no symmetry (except the mirror plane containing the ring) the angular deviations will be due in part to the effects of the inequalities in bond lengths and in part to intrinsic angular distortions. In order to correct the angles for the effects of the variations in the bond lengths a model that goes beyond the geometrical constraints is required. As an example of the difficulties that arise, if l_{12} and l_{61} are 1·442 Å and the remaining l's are all 1·400 Å, that is, l_{12} and l_{61} are 3·0% larger than the others, and if β_1 and β_3 are fixed at 0°, then $\beta_2 = -1{\cdot}0°$ and $\beta_4 = +2{\cdot}0°$ according to equation (16). Alternatively, if the angular distortions are distributed as evenly as possible over the six angles, then β_1 and β_2 are $-0{\cdot}75°$ and β_3 and β_4 are $+0{\cdot}75°$. The latter set of adjustments appears more reasonable, but the assumption of even distribution goes beyond the constraints of symmetry. A model including such assumptions will be discussed in a later paper.

One example along the lines of the previous paragraph might be mentioned. Domenicano, Vaciago & Coulson (1975*a*) found that in a number of monosubstituted benzene derivatives (substituted at atom 1) the conditions $\beta_1 = -2\beta_2$ and $\beta_3 = \beta_4 = 0$ are true to a good approximation. We can say from equation (15) that these conditions cannot be exactly true in an equilateral ring; if the ring is equilateral, then at most one independent angle can have $\beta = 0$. In the examples given by Domenicano *et al.*, the bond lengths are indeed unequal, although, as they point out, the apparent values may be seriously affected by thermal motion. If, as an example of the geometric constraints, we ask what changes would be required in l_{12} and l_{61} (the bonds adjacent to the substituent) to make the angular conditions exact, we find from equation (15) that for each degree β_1 is different from 0°, ε_{12} and ε_{61} must change by 0·5% (or 0·007 Å for a typical benzene ring) in the opposite sense.

It is intended to discuss the actual distortions in real molecules in the light of these conditions in a later paper.

References

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