

## Concerning the Structure of [18]Annulene

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Dedicated to Professor *Emanuel Vogel*

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A recent computational study of *Schleyer* and co-workers [1] is reviewed, which led these authors to the firm conclusion that [18]annulene has a localized structure with alternating single and double C,C bonds, contrary to earlier crystallographic analyses of X-ray-diffraction data favoring a delocalized non-alternating form. It is pointed out *i*) that deceptive orientational disorder phenomena in the crystal might be subject to experimental resolution in this case, and *ii*) that, in contrast to gas and solution phases, [18]annulene might possibly assume the non-alternating structure in the crystalline solid state.

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From a comparison of calculated and observed  $^1\text{H-NMR}$  chemical shifts, it has recently been firmly concluded by *Schleyer* and co-workers that [18]annulene prefers a structure with alternating ('localized') C,C single and double bonds, rather than a non-alternating ('delocalized') structure of maximum symmetry  $D_{6h}$  with more nearly equalized, but – for obvious symmetry reasons – not exactly equal, C,C lengths [1]<sup>1</sup>). The latter had previously been deduced from single-crystal X-ray-diffraction data [2][3]. In addition, the best computed structure of [18]annulene, an alternating, slightly non-planar potential-energy minimum of  $C_2$  symmetry, was calculated *ca.* 3 kcal mol<sup>-1</sup> energetically lower than the non-alternating  $D_{6h}$  form, reported as a transition state with the high imaginary frequency of *ca.* 1100i cm<sup>-1</sup> [1].

*Schleyer* and co-workers conclude from their results that the X-ray geometry of [18]annulene is not correct, and attribute this putative crystallographic failure to supposedly insurmountable disorder problems similar to those indicated previously for the related fundamental case of benzene [4]. In the following, we wish to point out that,

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<sup>1</sup>) The inner non-bonded H...H distances of [18]annulene are short and accordingly lead to unfavorable H...H repulsions. This strain may be partially released through C,C bond stretching, C,C,C bond angle opening, or non-planar molecular distortions. From purely geometric reasoning, the latter are not very effective, since large non-planar deformations are required in order to bring about sizable increases of the initially orthogonal H...H separations. However, a linear in-plane interrelation does hold for C,C bond length and C,C,C bond angle changes, which are thus influencing the inner H...H separations more effectively. Stretching of the outer (*cisoid*) 6 C,C bonds by  $\Delta l$  leads to a H...H increase by  $\Delta l$ , stretching of the inner (*transoid*) 12 C,C bonds is less effective leading to an increase of approximately  $\Delta l/2$ . This purely geometric effect, which is independent of the problem of bond alternation, at least partly explains the somewhat greater lengths of the outer C,C bonds, as consistently observed and calculated throughout. The respective length differences of the outer and inner C,C bonds are significant and amount to *ca.* 0.01–0.02 Å [1–3]. The C,C,C bond angles of [18]annulene are also noticeably expanded to further release non-bonded strain due to the congested inner H-atoms<sup>2</sup>). Beyond geometric factors, these angle openings are of course facilitated energetically by the smaller deformation constants involved, as compared to C,C stretchings.

in our opinion, this verdict is not entirely valid and would appear to require further substantiation.

In the crystal, the [18]annulene molecules reside on centers of symmetry (space group  $P2_1/a$ , 2 molecules per unit cell), and  $D_{6h}$  symmetry is closely approximated [2][3]. However, a non-alternating structure may not immediately be deduced from these observations, since we are dealing with time- and space-averaged atomic positions. A subtle orientational disorder phenomenon might interfere consisting of two superimposed alternating [18]annulene geometries of closely approximated  $D_{3h}$  symmetry, which are rotated with respect to each other by  $60^\circ$  around the threefold axis. Due to the small size of the atomic displacements involved, the resolution of this possible disorder might indeed be very difficult to deal with. However, the prospects that a careful experimental and theoretical analysis of the size and orientation of the anisotropic atomic temperature-factor tensors will lead to definite conclusions are at least better than in the still more-extreme and almost hopeless case of benzene (*Fig.*) [4][6].

Assuming, for example, a sensible difference of  $0.10 \text{ \AA}$  between the C–C and C=C bond lengths in the superposition disorder model of benzene, the positions of the superimposed C-atoms are only  $0.058 \text{ \AA}$  apart, leading to a disorder contribution of the anisotropic temperature motion of only  $0.0008 \text{ \AA}^2$  (*Fig. 1, a*) [4]. On the other hand, superposition of two likewise alternating [18]annulene  $D_{3h}$  geometries rotated with respect to each other by  $60^\circ$  around the threefold axis leads to positional separations of close to  $0.10 \text{ \AA}$  of the twelve outer C-atoms, while the six inner C-atoms virtually coincide (*Fig. 1, b*)<sup>2)</sup>. The temperature-factor contribution of the orientational disorder of [18]annulene in this model is thus expected to be close to  $0.0025 \text{ \AA}^2$  for the outer C-atoms, *ca.* 3 times higher than for benzene. A disorder effect of this size might indeed be detectable [6]. Ideally, variable-temperature neutron-diffraction experiments would be desirable necessitating, of course, the growth of rather large crystals. Unfortunately, [18]annulene is not comfortably amenable to synthesis and is chemically rather sensitive, such that an experimental commitment of this sort would demand a major effort. Moreover, it is to be noted that, in the crystals of [18]annulene, a second, seemingly experimentally established, more coarse orientational disorder phenomenon has been described: a minor molecular orientation generated by a

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2) It is noted that this disorder analysis of the alternating planar  $D_{3h}$  form of [18]annulene is not strictly exact, yet it holds to a good degree of approximation. Essentially, it implies that the two non-equivalent long C,C (single) bond lengths, the two non-equivalent short C,C (double) bond lengths, and the two non-equivalent endocyclic C,C,C bond angles each do not differ too much from one another, which is the case in sufficient measure. Geometrically, the C-skeleton of the  $D_{3h}$  form is a 6-parametric system [5]. Choosing the four non-equivalent C,C bond lengths as internal geometry parameters leaves us with two independent adjustable C,C,C angles. Since, of course, three non-equivalent C,C,C angles are present, a relation of constraint must hold between them; obviously the exocyclic C,C,C angle plus  $120^\circ$  is equal to the sum of the two different endocyclic C,C,C angles. To make more room for the inner six congested H-atoms, the C,C,C angles are widened beyond  $120^\circ$ , and it follows that the widening of the six exocyclic angles is about twice as large as that of the twelve endocyclic angles (*ca.* 8 and  $4^\circ$ , resp.; *Fig. 1, b*)<sup>1)</sup>. The C-skeleton of the  $D_{6h}$  form of [18]annulene is 3-parametric. Fixing the two different C,C lengths leaves one free C,C,C angle, and it may be easily seen that in this case the widening of the exocyclic angles is constrained by symmetry to *exactly* twice that of the endocyclic angles.

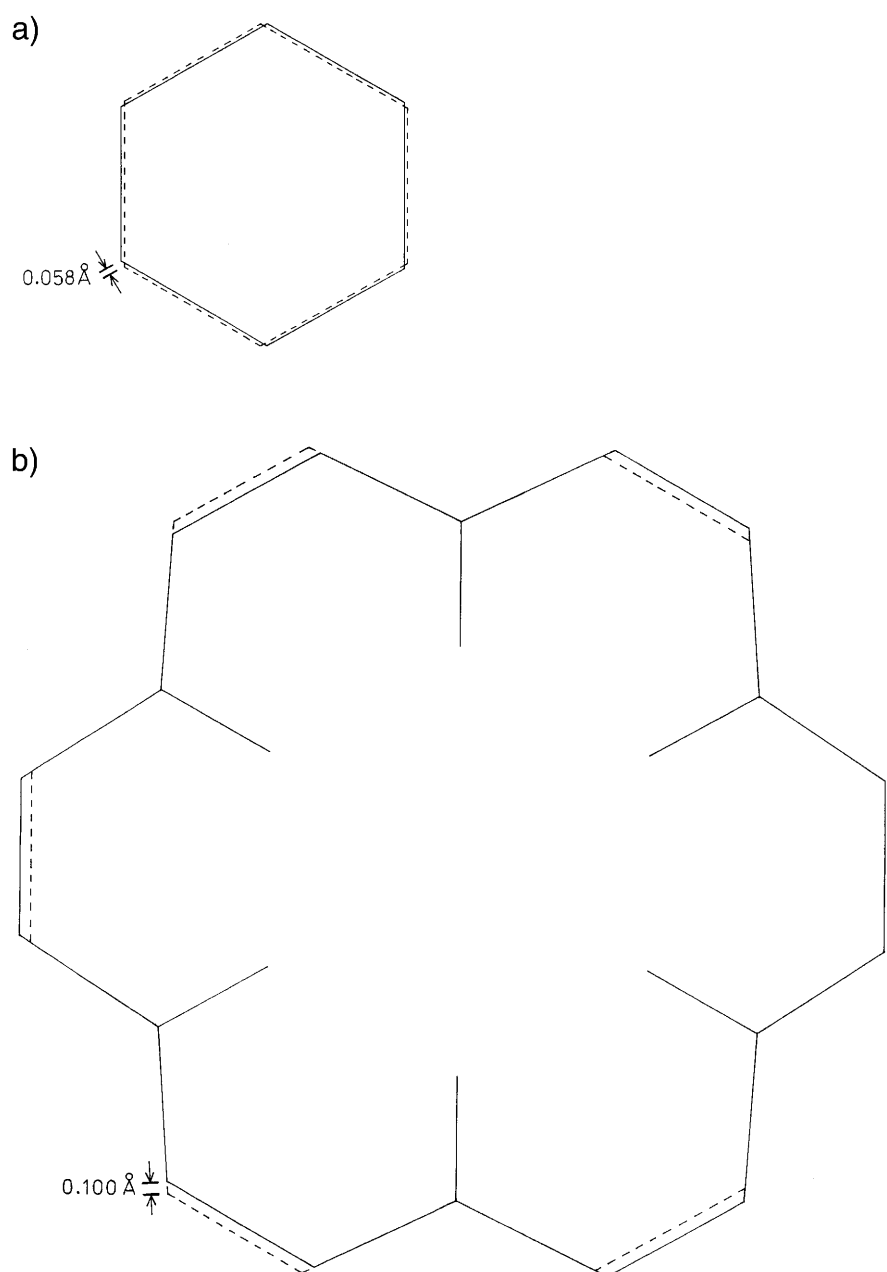


Figure. Solid-state orientational disorder models of alternating  $D_{3h}$  benzene (a) [4] and [18]annulene (b)<sup>2</sup> structures leading to averaged non-alternating  $D_{6h}$  forms. Both superimposed  $D_{3h}$  structures are rotated with respect to each other by  $60^\circ$  around the threefold axes; C–C and C=C bond lengths of 1.45 and 1.35 Å, resp., assumed; inner congested H-atoms of [18]annulene shown, others omitted.

rotation of *ca.* 30° around the approximate sixfold axis [3]. This might possibly impede matters further.

A second point of consideration concerns the rather intriguing question of whether [18]annulene indeed has the localized alternating structure in the crystal as tacitly supposed by *Schleyer* and co-workers [1]. Of course, their comparison of computed and experimental <sup>1</sup>H-NMR chemical shifts refers to the gaseous and solution states, respectively. Asking this question would appear well warranted, given the small calculated energetical advantage of the best alternating *C*<sub>2</sub> structure over the non-alternating *D*<sub>6h</sub> form of only *ca.* 3 kcal mol<sup>-1</sup> [1]<sup>3</sup>). Possible crystal-packing forces favoring the non-alternating structure could possibly overcome its energetic disadvantage in the gas phase. The overall symmetry of the supramolecular environment of the [18]annulene molecules in the crystal is centrosymmetric to a good degree of approximation, irrespective of what the fine details of the various possible disorder phenomena are. This could help to drive the structure of the [18]annulene molecules in the crystal towards centrosymmetric forms with non-alternating character. Furthermore, the intermolecular  $\pi$ - $\pi$  stacking interactions in the crystal could well benefit from a more evenly distributed molecular  $\pi$  electron density as prevailing in non-alternating [18]annulene forms. Finally,  $\pi$ - $\pi$  stacking energy may be expected to support molecular planarity, which would lead to a further energetical narrowing between alternating and non-alternating forms by up to *ca.* 0.5 kcal mol<sup>-1</sup> [1], in case the planar *D*<sub>6h</sub> form indeed represents the best non-alternating structure of [18]annulene<sup>3</sup>).

If C,C bond alternation would indeed vanish on crystallizing [18]annulene, this would admittedly represent a very unusual phenomenon and would, of course, also lead to significant consequences as regards nuclear magnetic properties in the solid state. Since this possibility, albeit speculative, cannot readily be dismissed in the present particular case, and because important issues of chemical bonding are at stake, further computational and experimental efforts should be rewarding, beyond the renewed crystallographic endeavors requested above. Obviously, reliable theoretical crystal calculations would appear indicated. As a first step, for example, the computational consideration of a supramolecular (laterally displaced) face-to-face  $\pi$  dimer of [18]annulene as cut out of the crystal structure might already furnish some insight, or, even better, a triple-decker [18]annulene trimer  $\pi$ -stacked as observed in the crystal with the two outer molecules more or less centrosymmetrically related. Thus, the

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<sup>3</sup>) From the comparatively high calculated imaginary frequency of *ca.* 1100i cm<sup>-1</sup> of the non-alternating *D*<sub>6h</sub> (transition) form of [18]annulene, *Schleyer* and co-workers infer a 'strong preference for C,C bond alternation' [1]. This conclusion is, however, not really convincing since this (improper) 'transition vibration' is associated with rather small atomic displacements. Thus, although it indeed corresponds to a sharp and narrow partial maximum of high (negative) curvature on the potential-energy surface, it is nonetheless of low height, *i.e.*, only *ca.* 3 kcal mol<sup>-1</sup>. Incidentally, it would have been desirable to also explicitly consider computationally the optimal centrosymmetric non-alternating [18]annulene forms of *D*<sub>3d</sub>, *S*<sub>6</sub>, and *C*<sub>i</sub> symmetry, which are not bound to strict planarity. If suitable trial structures of these symmetries indeed do converge to the planar *D*<sub>6h</sub> structure in the geometry-optimization process, this would better prove that the latter maximum-symmetry form definitely represents the most-favorable calculated non-alternating structure of [18]annulene. Else, the computed rather modest energetic gain associated with C,C bond alternation were to decrease still further. Even if only for completeness, it would finally also be reassuring if *Schleyer* and co-workers had confirmed that their computational tools reproduce the <sup>1</sup>H-NMR chemical shift of *D*<sub>6h</sub> benzene.

provocative question to be answered by this intriguing computer exercise would accordingly be: does the central  $\pi$ -sandwiched [18]annulene molecule of this supra-molecular triple-decker ensemble show a tendency to abandon C,C bond alternation?

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