

## Continuous Symmetry Numbers and Entropy

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**Abstract:** Traditionally, entropy changes are corrected for rotational permutability only if the molecule is perfectly rotationally symmetric. By this approach, only a small fraction of all known molecules *must* be evaluated in terms of symmetry numbers, while all other molecules are *totally exempt* of these considerations. A general approach which encompasses all molecules, symmetric or not, is proposed here. It is based on introducing the notion of continuity to symmetry numbers and on allowing noninteger values. In the first part of the account, we provide argumentation as to why continuity is needed and what difficulties one may encounter by adopting the “black-or-white” approach to symmetry. In the second part, we provide a working methodology of how to evaluate the symmetry number content of *any* molecule, symmetric or not. Finally, in the third part, we demonstrate the implications of this approach on entropy issues involving melting points, Jahn–Teller distortions (of fullerene) upon ionization, molecular distortion due to overcrowdedness, permutability of isotopes, and the structure of proton sponges. It is shown that continuous symmetry numbers provide entropy values, which better agree with experimental observations, and that they are capable of identifying correlations between symmetry and physical/chemical measurables.

## 1. Symmetry Numbers: Discrete and Continuous

**The Topic of This Study.** Symmetry numbers have been traditionally used to correct entropy values only for molecules which are perfectly rotationally symmetric (at least one  $C_n$  rotation element,  $n > 1$ ). Even the slightest deviation from a perfect  $C_n$  has led either to a discrete jump to a lower  $C_n$  resulting in abrupt change in the calculated entropy or, in the absence of an exact lower  $C_n$ , to the definition of the molecule as having no rotational symmetry whatsoever ( $C_1$ ) and consequently to an assumption of zero effect on entropy. The vast majority of the known  $\sim 23\,000\,000$  molecules either have no perfect symmetry axis at all or deviate to some degree from an obvious  $C_n$ , and thus either have been traditionally left out of the framework of rotational-symmetry entropy adjustment or treated in terms of a low  $C_n$ . We propose that the notion of a certain subgroup of molecules — the perfectly symmetric ones — which *must* be evaluated in terms of symmetry numbers, while regarding most other molecules as *totally exempt* of these considerations, may amount to a neglect of important elements in the rich library of stereochemistry and of their relation on entropy changes. This is particularly so because at ordinary temperatures the contribution to entropy changes from the translational, vibrational, electronic, and nuclear components tends in many instances to be small as compared to that from the rotational entropy component. Rotational symmetry is therefore a major factor in determining a large array of molecular properties,<sup>1–12</sup> and some central examples are listed below.

In this report, we propose a general approach and a general working methodology, which allows *all* molecules, symmetric or not, to be analyzed in terms of symmetry numbers and their contribution to rotational entropy. We do so by introducing continuity to symmetry numbers and by allowing noninteger values. Let us begin with the rationale of this proposition.

**The Necessity of Continuity in Symmetry Numbers.** We focus then on the entropy-change contribution,  $\Delta S_\sigma$ , to statistical effects, which is due purely to rotational symmetry as represented by the symmetry number,  $\sigma$ . We recall that  $\sigma$  is defined as the number of rotational operations which permute atoms in a molecule; that is, it is the order of the rotational-symmetry subgroup of the molecule, containing the rotational-symmetry operations (including the identity operation).<sup>13</sup> We also recall that it was introduced so as not to count more than once orientations that are indistinguishable by rotation.<sup>13,14</sup>  $\Delta S_\sigma$  and

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$\sigma$  are related through:<sup>1,15</sup>

$$\Delta S_{\sigma} = R \ln \frac{\sigma_B}{\sigma_A} \quad (1)$$

where the indices A and B refer to two species at equilibrium, B being the “product” and A being the “reactant”. For a particular species, one defines similarly:<sup>1,15</sup>

$$S_{\sigma} = R \ln \sigma \quad (2)$$

It is useful to recall that  $\Delta S_{\sigma}$  (eq 1) is subtracted from the rotational entropy change,  $\Delta S_R$  ( $\Delta S_R = \Delta S_{\text{therm}} - [S_{\sigma}(\text{B}) - S_{\sigma}(\text{A})] = \Delta S_{\text{therm}} - \ln[\sigma(\text{B})/\sigma(\text{A})]$ ; see ref 16 for details). It follows that for a chemical/structural change leading from a reactant A to a product B and eventually to an equilibrium between the two, the change in the symmetry numbers will contribute toward an increase of the total rotational entropy, if A is more symmetric than B (a positive  $[-\ln[\sigma(\text{B})/\sigma(\text{A})]]$  term; see ref 16 for a specific example).

As an introductory case, illustrating the need for continuity in eqs 1 and 2 is provided by the Jahn–Teller (JT) distortion of  $\text{C}_{60}$  fullerene, induced by its (reversible electrochemical) reduction<sup>17</sup> to the monoanion,  $\text{C}_{60}^{1-}$ . The icosahedral ( $I_h$ ) symmetry of the neutral  $\text{C}_{60}$  structure changes only very slightly (see below) upon the addition of one electron, and yet the current treatment of this minute change *requires* one to totally redefine the symmetry of the product, which in this case is  $D_{3h}$ . Let us evaluate how this jump in symmetry assignment affects the entropy change: Having  $\sigma = 60$  for  $I_h\text{-C}_{60}$  and  $\sigma = 6$  for the  $D_{3h}$  anion, one obtains from eq 1 ( $R = 8.314 \text{ J/K}\cdot\text{mol}$ ) an overestimated  $\Delta S_{\sigma}$  of  $-19.14 \text{ J/(K}\cdot\text{mol)}$ , which amounts to a  $T\Delta S_{\sigma}$  contribution to  $\Delta G$  of  $5.74 \text{ kJ/mol}$  at  $300 \text{ K}$  (!), an unrealistically huge value if one considers that it originates *only* from a minor shape change. Does not it make more physical sense to analyze the symmetry of the anion, which so slightly deviates from its original icosahedrality, in terms of its nearly icosahedral content? A method capable of doing so would introduce continuity to symmetry numbers, allowing one to identify a  $\sigma$  value between the extremes of 6 and 60, and if that

method reflects reality properly, the physically relevant  $\sigma$  output will be much higher than the  $\sigma = 6$  of  $D_{3h}$  and quite close to the  $\sigma = 60$  of  $I_h$ . This, in turn, would lead to a much more realistic estimation of  $\Delta S_{\sigma}$ ; that is, its value will be small, conforming with what the eye sees, that the anion is nearly icosahedral. We return to this introductory example in section 3.

Problems of this type abound in chemistry. Basically, they are rooted in the conceptual inflexibility of the definition of the symmetry numbers which demands a “yes or no” answer<sup>18</sup> and which therefore bends the rich reality of stereochemistry to the dictates of a strict codex, behind which are hidden, first, the paradigm that exact symmetry is superior and therefore must set the rules and, second, the practical aspect that fully symmetric situations are easier to formulate theoretically. Of course, the treatment of molecules through the eyeglasses of perfect symmetry is responsible for some of the more important advancements in chemistry, and yet we believe that time has come to move ahead of the first-order perfect-symmetry approach, recognizing that much of chemistry beyond the atomic level is *not* symmetric.

The strict codex of perfect symmetry can become particularly devastating in the case of small deviations from symmetry which, according to the current approach, force a jump in the symmetry description, the magnitude of which is totally out of proportion from that deviation. In such cases, the drastic reduction in the symmetry numbers forces an artificially major change in entropy. Because so much in chemistry is dictated by small molecular conformational adjustments, the need for a realistic description of such changes cannot be underestimated. Some of the many questions in chemistry, which are associated inherently with symmetry numbers and for which continuity considerations may turn out to be beneficial, are as follows: How do molecular symmetry distortions affect physical reactivity properties? How does symmetry affect melting points? What is the concentration-ratio value of an equilibrium, which involves a rotational-symmetry change? How are symmetry-dictated concerted reactions affected by symmetry upon interaction? What is the rotational contribution to entropy changes upon molecular associations, clustering, and hydrogen bond formation? What is the correct symmetry number to be attached to fluxional molecules?

Let us take the last question as a second illustration for the need for continuity. Pitzer posed in 1939 the following problem:<sup>18</sup> “Ordinarily one would assign a symmetry number of three to pyramidal  $\text{NH}_3$  or six to a hypothetical planar  $\text{NH}_3$ ... If the pyramid is rapidly reversing itself the effective symmetry should also be six.” Two important issues are raised here: First, the value of symmetry numbers depends on the resolution of measurement, spatial or temporal. A fast camera will see here  $\sigma = 3$ , but a slow one will see  $\sigma = 6$ . Which then reflects the molecule? The second issue concerns the gradual transition from pyramidal to planarity. Because one end of this process has  $\sigma = 3$  and the other has  $\sigma = 6$ , what happens in the middle from the point of view of  $\sigma$  values? Again we propose that a gradual, continuous change in resolution of observation or in

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- (16) The rotational partition function,  $Q_R$ , is factorized into two terms,<sup>14</sup>  $Q_R = Q_R'/\sigma$  (I), where  $Q_R'$  is the partition function which is uncorrected for the symmetry effect. The rotational entropy is  $S_R = R \ln Q_R$  (II).  $S_R$  has therefore been factorized into  $S_R = R \ln Q_R' - R \ln \sigma$  (III). The first term in (III) is the thermal contribution to the rotational entropy,  $S_{\text{therm}}$ , and the second is the symmetry contribution:  $S_R = S_{\text{therm}} - S_{\sigma}$  (IV). From (IV) it follows that the more symmetric the molecule is, the lower is its rotational entropy. For instance, comparing the  $D_{6h}$  benzene with a  $D_{3h}$  trisubstituted benzene –  $\sigma$  values of 12 and 6, respectively – leads (eq 1,  $R = 8.314 \text{ (K}\cdot\text{mol)/J}$ ) to  $S_{\sigma}$  values of 20.66 and 14.90  $\text{J/(K}\cdot\text{mol)}$ , respectively; the rotational entropy is reduced to a larger extent in the more symmetric molecule. Following (IV), for a process leading from a reactant A to a product B until equilibrium is reached, the rotational entropy change is then:  $\Delta S_R = \Delta S_{\text{therm}} - (S_{\sigma}(\text{B}) - S_{\sigma}(\text{A}))$  (V) and  $\Delta S_R = \Delta S_{\text{therm}} - \ln[\sigma(\text{B})/\sigma(\text{A})]$  (VI). Returning to the  $D_{6h}/D_{3h}$  example, consider a (hypothetical) reaction inducing this change in symmetry, that is, an isomerization or a trisubstitution reaction of benzene (reactant A). The change in rotational entropy due to the change in the symmetry numbers is  $R \ln(6/12) = -5.76 \text{ J/(K}\cdot\text{mol)}$ . That is, in eq V, the entropic symmetry term adds (twice negative) to the total rotational entropy, reflecting the conversion to a lower symmetry (A to B).
- (17) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593 and references therein.

- (18) The first report recognizing the difficulties with the symmetry numbers in systems that change the symmetry is probably: Pitzer, K. S. *J. Chem. Phys.* **1939**, *7*, 251. See also: Pitzer, K. S., Ed. *Molecular Structure and Statistical Thermodynamics. Selected Papers of K. S. Pitzer*; World Scientific: Singapore, 1993; pp 189 and a comment on p 194.

conformation should be represented by a gradual, continuous scale of symmetry numbers. It is perhaps appropriate to recall here Carl von Linné's statement in his "Philosophia Botanica" (Stockholm, 1751) that "Natura non facit saltus," "Nature does not make jumps," which is indeed the motto of this study.

Several of the central issues raised here are treated with specific examples in section 3, following the layout of the continuous symmetry numbers methodology in section 2.

## 2. The Methodology of Continuous Symmetry Numbers

The following is a list of methodological questions to be addressed. (a) How does one construct a definition of a *continuous symmetry number*,  $\sigma_c$ , that will follow, in a continuous and gradual way, changes or deviations from exact symmetry, such that it will coincide with  $\sigma$  for a perfectly rotational symmetric structure but will decrease continuously as the structure deviates more and more from that symmetry? (b) To answer the first question, one should be able to evaluate quantitatively the deviation from rotational symmetry. How should this task be carried out? (c) In an imperfect symmetry structure, what are the relevant imperfect rotational axes to be analyzed? In other words, what is the relevant reference structure representing perfection? (d) The counting procedure of the symmetry number is straightforward: Each of the  $k - 1$  perfect (and only perfect) rotation operations contributes to  $\sigma$  the counting value  $r_k = 1$  (as does the identity operation):

$$\sigma = \sum_k r_k \quad (3)$$

Imperfect axes are not at all looked at; that is, in practice they are counted as  $r_k = 0$ . Under the continuous approach, after the relevant axes have been identified, what should be the counting value,  $r_k$ , of a specific imperfect axis? (e) Once one has the counting values,  $r_k$ , for all relevant (perfect and imperfect) axes, how should they be accumulated toward the total continuous symmetry number,  $\sigma_c$ ? (f) Finally, having a  $\sigma_c$  value at hand, how should it relate to the symmetry-number entropy,  $S_\sigma$ ?

We were led by three guidelines in formulating specific procedures for answering these questions: minimalism in assumptions, simplicity in formalism, and adherence to the rationale that led to the classical equations. The details follow in the next sections.

### The Counting Value of an Imperfect Rotation Element.

We begin with the following question: Given an imperfect rotational axis, how should it be counted toward the total symmetry number,  $\sigma_c$ ? We generalize the counting value to

$$r_k = 1 - \text{Sy} \quad (4)$$

where Sy evaluates the degree of deviation of a specific rotation operation from perfectness. Sy has a value of 0 for perfect symmetry, grows continuously as the deviation increases, and reaches 1 for the maximal possible deviation. What then do noninteger  $r_k < 1$  values mean? While  $r_k = 1$  reflects perfect rotation, an  $r_k$  value of, say 0.96, indicates slight symmetry deviation,  $r_k = 0.54$  indicates a major deviation,  $r_k = 0.02$  casts doubt on the relevance of the selected axis, and  $r_k = 0$  reflects an absolutely irrelevant axis (e.g., a  $C_5$  symmetry element of a (distorted) hexagon). Our next task then is to evaluate Sy.

**The Evaluation of the Symmetry Content in an Imperfect Rotation Element.** The methodology for the evaluation of the

degree of symmetry on a continuous scale has been developed intensively since the early 1990's,<sup>19–24</sup> and has found useful applications including quantitative correlations between the degree of symmetry (and/or chirality) and a variety of chemical/physical/biochemical parameters which intimately relate to symmetry.<sup>25–27</sup> Basically, the continuous symmetry measure (CSM) is a distance function — an approach commonly employed in shape analyses<sup>28</sup> — but with a special feature: Sy is a general minimal distance function to *symmetry*, in contradistinction to the commonly used distance to a predetermined reference structure.<sup>28</sup> The task of evaluating Sy is demanding: Having a symmetry-distorted structure, the shape and coordinates of the ideal symmetry reference structure, the distance to which should be evaluated, are usually unknown. If, for instance, one wishes to evaluate the  $C_4$ -ness of a distorted tetragon, then, of course, the relevant reference shape is of a perfect square; but if one wishes to evaluate the  $C_2$  content of that tetragon, then there is an infinite number of  $C_2$ -symmetric structures (bent and two-dimensional (2D) parallelograms) which can serve as reference shapes. The SCM methodology identifies a specific  $C_2$ -symmetric structure, which provides the *minimal distance* from the tetragon. Thus, the distance function we shall employ has also the task of finding the structure to which the distance should be computed.

Formally, let M be a structure composed of  $n$  vertices (atoms) in an original configuration,  $Q_i$ , and let G be any symmetry point group. The amount of G-symmetry in M is then defined as

$$\text{Sy}(M,G) = \frac{1}{nD^2} \sum_{i=1}^n \|Q_i - P_i\|^2 \quad (5)$$

Here  $P_i$  are the searched corresponding points of the nearest G-perfectly symmetric configuration, and  $D$  is a size normalization factor (the rms of all distances from the center of mass to the vertices), making Sy size-invariant. The distance  $Q_i - P_i$  is squared to avoid sign limitations, as is a common practice in distance-function formulations. The bounds of Sy are 0 ( $Q_i$  coincides with  $P_i$ ; M is perfectly symmetric) and 1 (the nearest symmetric structure coalesces onto a center point, the distance to which is 1, as in the above-mentioned degree of  $C_5$ -ness of a perfect hexagon. Because most symmetry deviations which are of interest in chemistry are not of this form but are rather small, the 0–1 scale has been expanded in our previous experimental analyses publications to a 0–100 scale, for convenience of handling the Sy values, but this expansion is not applied here). Several algorithms were developed for the identification of  $P_i$ , and the interested reader is referred to refs 21–23 for details. When applied to a large array of symmetry related problems, Sy proved to be well behaved mathematically

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and capable, as mentioned above, of detecting many quantitative correlations with symmetry or chirality.<sup>22–27</sup>

Equation 5 has been used in all of our previous studies for the evaluation of deviation from a symmetry group,  $G$ , as a whole. However, for the evaluation of the symmetry number, the deviation of the studied structure from being symmetric toward each of the rotational elements of the rotational subgroup,  $G_{\text{rotat}}$ , is to be calculated separately;  $\text{Sy}(C_n^m)$  is to be evaluated for all  $n$ 's and  $m$ 's for all  $C_n^m$ 's of  $G_{\text{rotat}}$ . Equation 5 is directly applicable for that purpose as well (Appendix A). As an example of a relevant set of  $C_n^m$ 's, consider the following simple 2D “flatland” example (not to be confused with the 3D analysis of Figure 1), where one wishes to evaluate the 2D-symmetry number of a flat trapezoid with reference to a perfect  $C_4$ -square; one then needs to compute the Sy value of the four symmetry operations  $\{C_4, C_4^2, C_4^3, E\}$ . Here,  $\text{Sy}(C_4) = \text{Sy}(C_4^{-1}) = \text{Sy}(C_4^3)$ ; the distance to a perfect square (which supports  $C_4$  and  $C_4^3$ ) is searched. However,  $C_4^2 = C_2$ ; that is, for the evaluation of the symmetry measure of  $C_4^2$ , one searches for the nearest perfect parallelogram, the shape of which is a-priori unknown, and, finally,  $\text{Sy}(E) = 0$ . It is important to note that when  $\text{Sy}(C_4)$  is computed, the resulting nearest  $C_4$ -symmetric object is of course characterized also as being  $C_2$ -symmetric, and yet  $\text{Sy}(C_2)$  must be calculated separately for  $C_4^2$ , because the distance to  $C_2$  and  $C_4$  need not be the same (the latter is usually larger because the vertices adjustment to higher symmetry requires larger vertices motion). In general,  $C_n^k$  and  $C_n^{n-k}$  differ only in the direction of the rotation; and  $C_n^k C_n^l = C_n^{k+l}$  and  $C_{km}^k = C_m$ .

**Obtaining the Continuous Symmetry Number.** Having a method for estimation of Sy, we apply it for each of the relevant rotation operations (“relevant” is discussed below) and obtain for each a counting value,  $r_k$ , from eq 4. How should the resulting noninteger  $r_k$  values be accumulated toward  $\sigma_c$ , the continuous symmetry number? We follow the original definition, eq 3, and similarly accumulate the  $r_k$ 's according to

$$\sigma_c = \sum_k r_k = \sum_k (1 - \text{Sy})_k \quad (6)$$

where  $k = 1, 2, \dots, k$  are the relevant rotations.

#### The Continuous Symmetry Number Relation to Entropy.

As for the correlation of  $\sigma_c$  with  $S_{\sigma(c)}$ , again we follow eqs 1 and 2:

$$S_{\sigma_c} = R \ln \sigma_c \quad (7)$$

For an equilibrium which is built from A (reactants) to B (products):

$$\Delta S_{\sigma(c)} = R \ln [\sigma_c(\text{B})/\sigma_c(\text{A})] \quad (8)$$

As noted above for the classical use of eqs 1 and 2, here too one should recall<sup>16</sup> that  $\Delta S_{\sigma(c)}$  is *subtracted* from the rotational entropy change,  $\Delta S_R$ . The outcome is similar to that of the classical treatment, but on a continuous scale: If A is less symmetric than B, the change in the continuous symmetry numbers will contribute toward a decrease of the total rotational entropy.

**Selection of the Relevant Rotation Elements.** Three conceptual novelties are introduced in this paper, all of which are interconnected. One is the continuity in symmetry numbers, which we addressed in section 1. In this section, we address

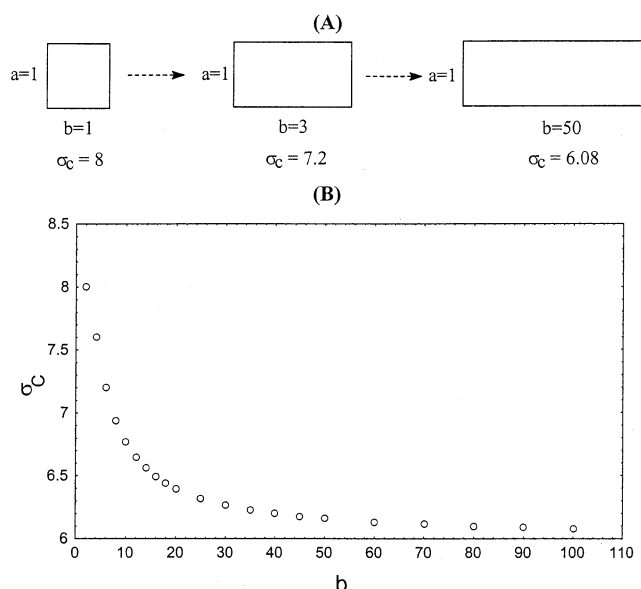
the two other new concepts, which relate to the methodological question we raised above: In an imperfect symmetry structure, what are the relevant (imperfect) rotational axes to be analyzed? In other words, what is the relevant reference structure representing perfection? As we shall see shortly, the answer we propose to this question has consequences not only for symmetry-imperfect structures but for structures of perfect symmetry as well and therefore on the classical discrete approach.

Returning to our flat trapezoid example, is the reference perfect 2D-rotational symmetry that of a parallelogram (a rectangle) with  $\sigma = 2$  or that of a perfect square with  $\sigma = 4$ ? In other words, should one evaluate for this case only  $\text{Sy}(C_2)$ , searching for the nearest rectangle, or should one also evaluate the distance to a perfect square to evaluate  $\text{Sy}(C_4)$  (and  $\text{Sy}(C_4^3)$ )? Indeed, the two options seem to be open, and, in studying the symmetry content of an object, the various Sy values illuminate characteristic features of the structure.

However, the link between the symmetry number and entropy requires a unique selection of ideality out of the possible options. That unique selection must be, in our view, the following: Given an (imperfect rotationally symmetric)  $n$ -vertices structure, the relevant rotational operations to be evaluated and counted toward the symmetry number are those which belong to the highest rotationally symmetric structure obtainable from the same number of vertices, retaining the same connectivity.

The new concept here is that even for a perfect 90° 2D-parallelogram, the relevant  $\sigma_c$  is not 2, but  $2 < \sigma_c < 4$ ! What is the rationale for adopting this counting procedure? Consider a 2D-square ( $\sigma = \sigma_c = 4$ ), which we begin to elongate gradually into a rectangle. After 0.01% of elongation, although barely detectable, we already have a rectangle. The classical  $\sigma$  jumps down to 2, but it is obvious that the tetragon is much more a square than a rectangle, and this will be reflected in the continuous approach by, say,  $\sigma_c = 3.99$ . It has been our claim, as detailed above, that from the point of view of entropy, the fact that this very slightly elongated square is strictly a rectangle is much less relevant than the fact that rotating it by 90° will practically leave the rotation unrecognized. This argument follows continuously with the continuation of the elongation. In particular, while  $\sigma$  is incapable of following this process and reports all rectangles, regardless of their elongation, as having a constant  $\sigma = 2$ ,  $\sigma_c$  will gradually decrease with the elongation, departing more and more from 4. In other words, we claim that all rectangles carry a “memory” of being squares to a certain degree.

Our proposition to replace the “yes/no” detection with graduation leads to the following change in the classical approach to the correction of entropy due to symmetry: Remaining with the same example, while the discrete approach to the  $S_{\sigma}$  term recognizes only the contribution of two rotational operations (those of the rectangle) — even if a rectangle is very near to a square — we propose that the correction *must* take into account the fact that there are two additional operations, which are capable of replicating the structure, at least approximately. Thus,  $\sigma_c$  for a rectangle contains contributions both from a perfect  $C_2$  operation ( $r_k = 1$ ) and from imperfect  $C_4$  and  $C_4^3$  operations ( $r_k < 1$ ). It follows that according to the continuous symmetry methodology, in general,  $\sigma_c \geq \sigma$ . Therefore, it also follows that the continuous approach leads to total entropies

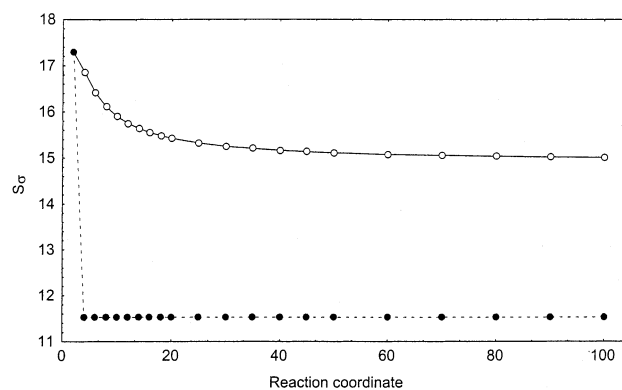


**Figure 1.** (A) Elongation of a planar square to a rectangle (the edges ratio,  $a/b$ , decreases). The symmetry numbers, from left to right, are 8, 4, and 4, respectively, but the continuous symmetry numbers,  $\sigma_c$ , are 8, 7.2, and 6.1. (B) The gradual change of the continuous symmetry number in (A) with the elongation ( $b$ ).

which are smaller as compared to values obtained by the classical approach. Because this, we acknowledge, is a major change over the classical discrete view, let us elaborate on this third novel concept with a specific example.

#### Symmetry/Entropy Changes along a Reaction Coordinate.

Still with the square-rectangle example, let us now move to the 3D world and analyze a model of a  $[2 + 2]$  concerted reaction. We recall that it is a symmetry dictated photochemical process in which two ethylenes are allowed to interact only in a  $D_{2h}$  symmetry, ending up in a  $D_{4h}$  cyclobutane (which immediately relaxes to a diagonally bent  $C_{2v}$  structure, with bond length adjustments). For simplicity of argument, let us analyze the allowed reverse process of the gradual  $D_{2h}$  rectangular ring elongation of the  $D_{4h}$  cyclobutane (which leads eventually to ring rupture). According to the classical approach (Figure 1), the moment the  $D_{4h}$  cyclobutane begins to elongate, its  $\sigma = 8$  drops abruptly to the  $\sigma = 4$  of the  $D_{2h}$  rectangle, and this symmetry number remains constant along a  $D_{2h}$ -preserving reaction coordinate. The continuous approach offers a distinctly different picture (Figure 1): The symmetry number changes gradually along the reaction coordinate, decreasing continuously from  $\sigma_c = 8$ . All along the reaction coordinate, the symmetry number is composed *both* of the contribution from the constant rectangular background level of  $\sigma = 4$  and of the contribution from the decreasing similarity to a perfect square (leading to an asymptote of  $\sigma_c = 6$  for an infinitely thin rectangle;  $\sigma_c > 4$ , because the specific four points connectivity is retained even at infinity and thus some memory of perfect “squareness” persists even there, and specifically 6, because of the definition of eq 5). In other words, in the continuous approach, the symmetry number of a  $[2 + 2]$  ring opening is always larger than 4. In terms of entropy changes which accompany the reaction, while the classical approach requires an abrupt increase in entropy the moment the reaction begins and then stays at a constant low level which is dictated by  $\sigma = 4$  (Figure 2), our picture is first of a more ordered system than classically considered ( $8 \geq \sigma_c \geq 6$ ) and of a system of which the rotational



**Figure 2.** Entropy changes ( $J/K \cdot \text{mol}$ ) due to changes in rotational symmetry along the process coordinate of Figure 1: the classical treatment ( $\bullet$ ) and the continuous treatment ( $\circ$ ).

disorder is gradually being built as the reaction proceeds (Figure 2). Note that entropic relaxation of the reaction works fast at the beginning (we shall see the same behavior in other examples below) and that the residual  $D_{4h}$ -ness keeps the reacting system from going down to the level which has been based on the assumption of  $\sigma = 4$ . We propose here that this observation is of more general nature: Whenever rotational-symmetry changes along a reaction coordinate, more order is preserved along the process than was classically assumed. This conclusion should also have marked effects on the reaction free energy map. This then is the third important conceptual novelty of this report.

To what extent does the layout of section 2 reflect reality? To what extent are the assumptions and definitions justified? To answer these questions (section 4), we first provide several examples which demonstrate how the continuous symmetry methodology approaches some key problems in chemistry.

### 3. Examples

#### 3.1. Arbitrary Assumptions Made in the Literature Appear Natural in the Continuous Approach.

There are many examples in the literature where the discrete symmetry numbers approach had forced authors to make arbitrary assumptions, so that models and theories will conform to experimental results. Here are two examples which demonstrate that under the continuous symmetry numbers approach, such arbitrary assumptions become natural. We do not go into the specific details but just focus on the changes brought about by the continuous language.

##### 3.1.A. Molecules with Nonidentical Permutable Atoms:

**Isotopes.** East and Radom studied third law entropies of several molecules,<sup>29</sup> one of which was isotopically labeled  $\text{CS}_2$ ,  $^{34}\text{S}^{12}\text{C}^{32}\text{S}$ . A question arises: What is the symmetry number to be assigned to it? Is it 1 ( $C_{\infty h}$ ) or 2 ( $D_{\infty h}$ )? Each assumption leads, of course, to different rotational entropies, to 71.42 or 65.41  $J/(K \cdot \text{mol})$ , respectively. Classically, because the  $^{34}\text{S}-^{12}\text{C}$  and  $^{12}\text{C}-^{32}\text{S}$  bonds differ in length, one must take  $\sigma = 1$ , and yet the experimental result agrees with  $\sigma = 2$  (!). In an attempt to overcome this difficulty, East and Radom write that:<sup>29</sup> “One can see that the entropies for these two forms differ primarily by the  $-R \ln 2$  [factor],” and they solve this discrepancy in an arbitrary way “by including the  $-R \ln 2$  term,” by assuming that  $^{32}\text{S}^{12}\text{C}^{34}\text{S}$  does have a  $C_2$  axis. In our application, this assumption is a natural outcome: The  $^{12}\text{C}-^{34}\text{S}$  and  $^{12}\text{C}-^{32}\text{S}$

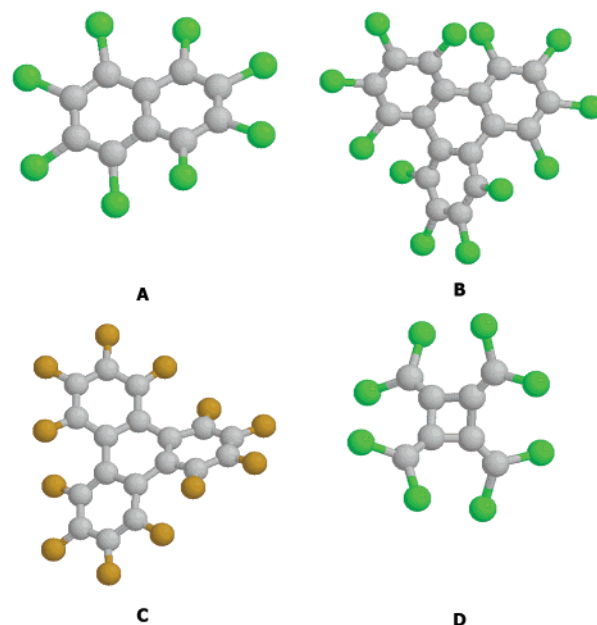
(29) East, A. L.; Radom, L. *J. Chem. Phys.* **1997**, *106*, 6655.

bonds are slightly different (approximately 3%, based on mass effects on vibrational amplitudes), and therefore the molecule is *nearly*  $C_2$ -symmetric, resulting in  $\sigma_c = 1.9988$  and in  $-R \ln(1.9988)$  as the symmetry correction factor, very close to the arbitrary correction factor of East and Radom.<sup>29</sup>

Thus, an outcome is that from the point of view of symmetry terms, isotopes are permutable. An interesting question follows (to be worked separately): To what extent then must permutable atoms be identical? Ortho/para hydrogen, polymorphs of crystals which impose different neighborhoods on same-type atoms,<sup>30</sup> and adsorption of molecules through one of otherwise identical atoms are additional examples of where this question is relevant. In most of these instances, the differently “labeled” atoms are also associated with (minor) variations in geometry and therefore are candidates for the continuous symmetry numbers analysis.

**3.1.B. Melting Points.** Melting points analyses and the understanding of their trends are intimately linked with symmetry numbers.<sup>31</sup> While attempting to explain the “higher-than-expected melting points” of cycloalkanes (cyclohexane, in the example commented on here), Wei<sup>32</sup> noticed that the explanation he provides fails with the “standard assumption”, that “Cyclohexane has a symmetry number of  $\sigma = 6$  ( $D_{3d}$ ) at  $-100$  °C [where the molecule packs as a crystal] and  $\sigma = 12$  (the [liquid phase] “average planar”  $D_{6h}$ ) at room temperature.”<sup>32</sup> However, when he uses *arbitrarily* the “average conformer’s” value of  $\sigma = 12$  for the crystal form (instead of  $\sigma = 6$ ), then his specific explanation (see ref 32 for details) holds for the abnormal melting point. In the continuous symmetry approach, a value which is close to the arbitrary  $\sigma = 12$  comes naturally: Given the definition of relevant perfect symmetry –  $D_{6h}$  – the cyclohexane chair conformer has several perfect rotations (which belong to its  $D_{3d}$  subgroup symmetry) and several imperfect rotation elements with respect to  $D_{6h}$ . Accumulating the  $r_k$  values ((we use this case for a demonstration of specific  $r_k$  values; so as not to overload the paper, these are not given in the next case analyses) for the axes perpendicular to the molecular plane,  $r_k(C_6) = 0.899$ ,  $r_k(C_6^5) = 0.899$ ,  $r_k(C_3) = 1.000$ ,  $r_k(C_3^2) = 1.000$ , and  $r_k(C_2') = 0.899$ ; for the three  $C_2$  axes bisecting opposite vertices of the hexagon,  $r_k(C_2) = 0.899$ ; and for the three  $C_2$  axes bisecting opposed edges of the hexagon,  $r_k(C_2) = 1.000$ ), one arrives at a  $\sigma_c$  value of 11.394 (!), very close to Wei’s arbitrary assumption,<sup>32</sup> corroborating in a natural way his theory.

**3.2. The Symmetry Numbers of Sterically Strained Molecules.** When sterically overcrowded molecules distort to assume minimal-energy conformation,<sup>33,34</sup> entropy increases. Here we show that the contribution of entropy increase as a driving force for distortion has been grossly overestimated (leaving the burden mainly on enthalpy changes). Let us analyze several perhalogenated hydrocarbons which distort from planarity (for X-ray diffraction structures, see Figure 3): octachloronaphthalene (A) (which has been described as possessing one of the shortest intramolecular Cl...Cl distances, on the order of 300 pm between



**Figure 3.** The structures, as determined from X-ray diffraction data, of distorted molecules of Type I (see Table 1 for details).

the chlorine atoms in *peri* positions<sup>35</sup>), octachlorotetradialene (D) (described as “a severely distorted four-membered ring”<sup>36</sup>), dodecachlorotriphenylene (C) (which has a propeller-shaped structure<sup>37</sup>), and the fluorinated analogue (B) of the last molecule.<sup>38</sup> We determine now the change in the symmetry number from the hypothetically nondistorted molecules to the distorted ones. Classically, all are converted from a high symmetry number (see Table 1) to  $\sigma = 1$ ,<sup>39</sup> and these changes are translated to relatively high  $T\Delta S_\sigma$  terms (Table 1, fourth column). According to the continuous symmetry approach, the  $T\Delta S_{\sigma_c}$  values are much smaller because, as explained above, we treat the deviations not as a jump in symmetry but as a process which retains some of the original (hypothetical) full symmetry; the values, along with the symmetry measure of planarity (the degree of  $\sigma_h$ -ness of the molecule),<sup>19–21</sup> are collected in Table 1 as well.

While the set of four molecules just analyzed deviate upon distortion both from planarity and from rotational symmetry (Type I in Table 1), this need not always be the case. Thus, distortion from planarity can occur while preserving the rotational axes (Type II in Table 1 and Figure 4: tetrakis-(dimethylamino)ethene,<sup>40</sup> octamethylnaphthalene,<sup>41</sup> 1,10-diiodotriphenylene,<sup>42</sup> and octaphenyldibenzo[*a,c*]-naphthacene<sup>43</sup> ((A), (D), (B), and (C), respectively, in Figure 4)). In such cases,

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(37) Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A. *J. Org. Chem.* **1995**, *60*, 428.

(38) Hursthouse, M. B.; Smith, V. B.; Massey, A. G. *J. Fluorine Chem.* **1977**, *10*, 145.

(39) Sometimes symmetry higher than  $C_1$  is claimed for the distorted molecule, but detailed analysis shows that this is not the case. For instance, octachloronaphthalene has been reported to have  $D_2$  symmetry.<sup>35</sup> However, there are deviations from the three  $C_2$  axis resulting in nonzero values of  $Sy(C_2)$  for this molecule. Yet, even taking higher symmetries than  $C_1$  does not change the basic arguments of this section.

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(32) Wei, J. *Ind. Eng. Chem. Res.* **1999**, *38*, 5019.

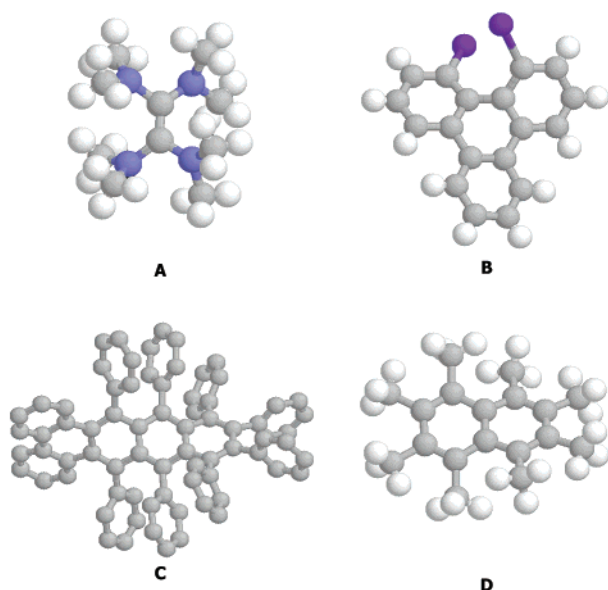
(33) Schastnev, P. V.; Schegoleva, L. N. *Molecular Distortions in Ionic and Excited States*; CRC Press: Boca Raton, FL, 1995.

(34) Bock, H.; Ruppert, K.; Nother, C.; Havlas, Z.; Herrmann, H.-F.; Arad, C.; Godel, I.; John, A.; Meuret, J.; Nick, S.; Rauschenbach, A.; Seitz, W.; Vaupel, T.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 550.

**Table 1.** Continuous Symmetry Numbers and Their Contributions to the Rotational Entropies of Highly Strained Molecules

molecule <sup>b</sup>	$\sigma_c(\sigma)^c$	$-T\Delta S(\sigma)^d$ (300 K) (J/mol)	$-T\Delta S(\sigma)^e$ (300 K) (J/mol)	$Sy(\sigma_h)^f$
Type I <sup>a</sup>				
octachloronaphthalene (A)	3.9721 (4)	17.45	3457.6	1.73
perfluorotriphenylene (B)	5.8428 (6)	66.22	4468.9	3.29
perchlorotriphenylene (C)	5.7416 (6)	109.80	4468.9	6.79
octachlorotetraradialene (D)	7.5408 (8)	147.47	5186.4	11.24
Type II <sup>a</sup>				
tetrakis(dimethylamino)ethene (A)	3.9953 (4)	2.74	3457.6	11.63
1,10-diiodotriphenylene (B)	1.9924 (2)	9.50	1728.8	2.77
octaphenyldibenzo[ <i>a,c</i> ]- naphthacene (C)	1.9962 (2)	4.74	1728.8	17.02
octamethylnaphthalene (D)	4.0000 (4)	0.00	3457.6	4.31

<sup>a</sup> Type I: Distortion of both planarity and rotational symmetry. Type II: Distortion of planarity while preserving the rotational axis. <sup>b</sup> For structures, see Figures 3 (Type I) and 4 (Type II). <sup>c</sup> Values in parentheses correspond to the hypothetical nondistorted molecules. <sup>d</sup> The continuous symmetry  $T\Delta S$  values. <sup>e</sup> Assuming the classical approach of total loss of symmetry upon distortion. <sup>f</sup> Continuous symmetry values of planarity (multiplied by 100).

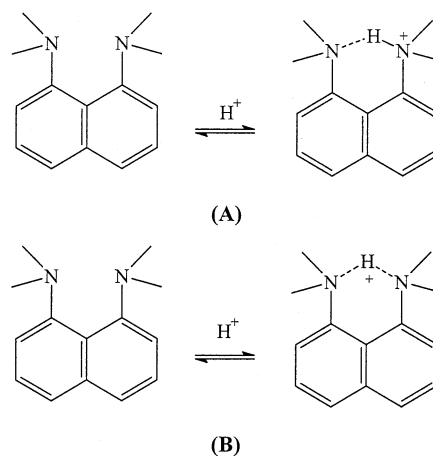
**Figure 4.** The structures, as determined from X-ray diffraction data, of distorted molecules of Type II (see Table 1 for details).

the rotational-entropy cost of distortion is low according to the continuous approach (third column, Table 1, Type II).

### 3.3. Changes in the Symmetry Number upon Reaction.

#### 3.3.A. Symmetry Changes upon Protonation: Proton Sponges.

Proton sponges are organic bases, very often diamines such as 1,8-bis(*N,N*-dimethylamino)naphthalene.<sup>44–47</sup> These bases are structurally distorted as a consequence of the strong repulsion of the neighboring unshared electron pairs of the nitrogen atoms. However, upon protonation which is facilitated by a strong intramolecular hydrogen bond (Figure 5), some of the steric strain is relieved. A major problem associated with the proton sponges has been where is the added proton located? The two extreme possibilities are demonstrated in Figure 5. In one, the proton is located exactly in the middle between the nitrogen

**Figure 5.** Two possible equilibria between a proton sponge and its protonated form. Bottom, the symmetric option B (see text); top, the nonsymmetric option A.

atoms (option B), and in the other (option A) the proton is attached covalently to one nitrogen and is hydrogen bonded to the other. Experimental methods, in particular X-ray crystallography, have been unable to distinguish between these two options.

In terms of the classical  $\sigma$  values, this difficulty translates into the need for a subjective  $\sigma$  assignment, either  $\sigma = 2$  or  $\sigma = 1$  for cations B and A, respectively. This, in turn, leads to a major difference in the assignment of the rotational-entropy change involved in the protonation equilibrium: It is either zero or  $-1.73$  kJ/mol (at 25 °C) for  $\sigma = 2$  and  $\sigma = 1$ , respectively. The 1.73 kJ/mol option is much too high, taking into account that the enthalpic differences between the two equilibria have been estimated to be only 2.7 kJ/mol in the gas phase and 2.1 kJ/mol in aqueous solution.<sup>46</sup> On the other hand, the zero option obviously neglects the changes in the symmetry content. We show now how the continuous symmetry approach addresses this problem.

For the unprotonated base, a value of  $\sigma_c = 1.9993$  is obtained from the available X-ray structural data,<sup>48</sup> indicating that this molecule belongs to the class which eases steric pressure by moving away from planarity while maintaining the rotational axes. Indeed, its measure of planarity is  $Sy(\sigma_h) = 5.24$ , a relatively high value. As for the protonated species, the  $\sigma_c$  values for the cations B and A, based on standard bond lengths, are 2.0000 and 1.9864, respectively,<sup>49–54</sup> leading to entropy changes of 0 and  $-16.04$  J/mol (at 25 °C). These values indicate that the nonsymmetric option has a very small rotational-entropy preference; in fact, the difference between 0 and  $-16.04$  J/mol is not enough for determining a real preference for one of the two options of protonation. This conclusion is in agreement with

(48) Einspahr, H.; Robert, J.-B.; Marsh, R. E.; Roberts, J. D. *Acta Crystallogr., Sect. B* **1973**, *29*, 1611.

(49) The structure for symmetric proton position was taken as the average of those determined by X-ray diffraction in refs 50 and 51. In the case of the asymmetric position, the structures of refs 52 and 53 were averaged. In all cases, the distances N–H–N computed by ab initio quantum chemical methods were taken into account as reported in ref 54.

(50) Kanters, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr., Sect. C* **1991**, *47*, 807.

(51) Bartoszak, E.; Jaskolski, M. *Acta Crystallogr., Sect. B* **1994**, *50*, 358.

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(47) Pozharskii, A. F. *Russ. Chem. Rev.* **1998**, *67*, 1.

**Table 2.** Classical and Continuous Symmetry Numbers of Fullerene Anions, Their Rotational Entropies, Structural Parameters, and Experimental Reduction Potentials<sup>a</sup>

anion	symmetry group	$\sigma$	$-\Delta S_{\sigma}$ (J/K mol)	$\sigma_c$	$-\Delta S_{\sigma_c}$ (J/K mol)	C=C (Å)	R (Å)	RP (exp., eV)
$C_{60}^{1-}$	$D_{3h}$	6	19.144	58.7295	0.1779	1.3997	3.5379	-1.37
$C_{60}^{2-}$	$D_{3h}$	6	19.144	58.7218	0.1790	1.4047	3.5419	-1.87
$C_{60}^{3-}$	$C_i$	1	34.040	58.7161	0.1798	1.4106	3.5469	-2.35
$C_{60}^{4-}$	$D_{5h}$	10	14.897	58.7158	0.1799	1.4160	3.5526	-2.85
$C_{60}^{5-}$	$D_{2h}$	4	22.515	58.7123	0.1804	1.4223	3.5592	-3.26

<sup>a</sup> Third and fourth column: the classical approach. Fifth and sixth columns: the continuous approach. Last columns: double bond lengths, radii, and reduction potentials.

the common view that the cation exists in fast tautomerism, as shown in Figure 5.<sup>47</sup>

**3.3.B. The Reduction of  $C_{60}$  Fullerene.** Our introductory example in section 2, illustrating the need for continuity, was provided by the JT distortion of  $C_{60}$  fullerene, induced by its reduction to the monoanion.<sup>17</sup> This reduction will also serve now as our final example: We analyze the reductive formation of the first six  $C_{60}$ -fullerene anions,<sup>17</sup> for which, as we shall now show, the difference between the discrete and continuous approaches is particularly evident. In section 1, we drew attention to the fact that, classically, the small structural change induced in  $C_{60}$  upon charging to  $C_{60}^{1-}$  is associated with an abrupt drop in symmetry from  $I_h$  to  $D_{3h}$ , which causes a drop from  $\sigma = 60$  to  $\sigma = 6$ , leading to a grossly overestimated  $\Delta S_{\sigma}$  of  $-19.14$  J/(K·mol) and to a  $T\Delta S$  of 5.74 kJ/mol (at 300 K). Similar abrupt changes without any reasonable order, as well as grossly overestimated values of rotational entropy changes, are also obtained for the rest of the consecutive reductions toward  $C_{60}^{6-}$ , as summarized in Table 2.<sup>55</sup> Note also that there is a smooth variation in the structural properties of the fullerene upon charging, which shows up, for instance, in the (calculated) lengths of the double bonds and of the radii, and that this is *not* reflected by the classical symmetry numbers approach. On the other hand, the continuous symmetry approach provides a natural solution to these problems (Table 2): The  $\sigma_c$  values are close to 60, reflecting the minor structural changes as compared to those of the uncharged molecule: they vary continuously with charge, the  $\Delta S_{\sigma}$  values are small, as they should be, and they correlate (nearly linearly) not only with the double bond lengths and radii but also with an experimental observable, the reduction potential,<sup>56</sup> and no correlation whatsoever is obtained with the classical symmetry numbers. Note that the main change in  $\sigma_c$  follows the first charging, but then upon additional charging, the variations are small, reflecting the very small structural changes.<sup>57</sup>

#### 4. Concluding Remarks

Our proposed continuous measure and its relation to entropy are not based on first principles. Yet, the objective of their introduction has been achieved: to put on the discussion table

(55) Data taken from ref 56; the molecular structures of the anions are after geometry optimization, using DFT calculations; the distortions were attributed there to the Jahn–Teller effect.

(56) Green, W. E.; Gorun, S. M.; Fitzgerald, G.; Fowler, P. W.; Ceulemans, A.; Titeca, B. C. *J. Phys. Chem. A* **1996**, *100*, 14892.

(57) The standard deviations are  $8.93 \times 10^{-3}$  for the C=C distances and  $8.46 \times 10^{-3}$  for the cage radii.<sup>56</sup>

the notion of continuity in symmetry numbers and to show that even on the empirical level practiced here, many literature observations fall in place, and values are corrected in the right direction. Thus, we have shown that graduality in physical and structural parameters, which is lost by the discrete approach, is reproduced by the continuous approach and that new correlations with symmetry are identified which otherwise have been blurred. The introduction of continuity gave rise to another important new concept: Because there is some degree of symmetry in any nonsymmetric object, there is more order – lower entropy change – than was previously assumed for nonsymmetric processes and systems.

Why does this measure, which has in it a degree of arbitrariness, represent reality so faithfully? We believe that this is due to two elements. First, no other definition for the distance function can be more minimalistic and natural than ours: The symmetry measure is the minimal distance to the desired symmetry. Second, in linking the measure to rotational entropy, we followed the least biased route: We applied the continuous symmetry number along the same footsteps as was practiced classically for the discrete symmetry number.

We hope we convinced the reader that even if details may change – for example, different definitions than those employed here – the concept of continuous symmetry is a natural extension of the classical treatment and is here to stay.

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#### Appendix: The Folding–Unfolding Procedure for $C_n^m$ Elements

The basic algorithm for obtaining the  $S(G)$  values was based on the “folding–unfolding” procedure, described in detail in refs 19 and 20. It was originally designed to evaluate the degree of G-ness as a whole. However, it is applicable in its original form for the evaluation of the deviation of specific symmetry elements from being perfect, including the  $C_n^m$  elements, which are relevant for this report. We exemplify the procedure for a 2D pentagon, from which one needs to evaluate each of the  $Sy(C_5^m)$  values (the degree of content of each of the  $\{E, C_5, C_5^2, C_5^3, C_5^4\}$  elements) to determine its continuous symmetry number. Denote the vertices of the pentagon by (clockwise) I, II, III, IV, V, and suppose one wishes to determine the deviation of the pentagon for being perfectly symmetric with respect to the  $C_5^2$  operation (a  $2\pi/5/2 = 4\pi/5 = 144^\circ$  rotation). The folding steps are carried out as follows (cf., ref 19):  $E$  is applied on vertex I, and it stays in place. Vertex II is rotated (clockwise) by applying the  $144^\circ$  rotation twice; vertex III is rotated by applying it four times; vertex IV is rotated by applying it once; and vertex V is rotated by applying it three times. A cluster of rotated vertices forms around vertex I, which is then averaged, and the averaged vertex is unfolded by applying the  $144^\circ$  rotation once (recreating vertex III), twice (recreating vertex V), thrice (for vertex II), and four times for vertex IV.

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