Classification of isentropic molecules in terms of Shannon entropy

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Abstract. Shannon entropy is widely used as a descriptor of molecular structure. Isentropicity of the molecules in terms of Shannon approach emerges in specific problems of physical and organic chemistry. In the present work, we consider the main classes of isentropic molecules, exemplify them, and provide their hierarchy.

1 Introduction

Shannon entropy (information entropy, \(h\)) is widely used as a structural descriptor in physical and organic chemistry. It allows assessing and comparing the complexities of the molecular structures [1–3]. For this purpose, a molecule is represented as disjoint subsets of atoms (atom types) made up with the chemically inequivalent atoms. The rules defining the inequivalence of the atoms in the molecule may vary but usually they are deduced from the analysis of the corresponding molecular graph [1–5]. In other words, the task of calculating Shannon entropy is based on counting the dissimilar atoms. The properties of this structural descriptor were deeply studied in previous works of the Bonchev and Basak groups (see their key papers [3,5]). In general, Shannon entropy provides numerical estimates of the molecules’ complexity, reflects their symmetry, and correlates with important physical and chemical properties (e.g., thermodynamic entropy or abundance) [2,3,5–9]. There are also works on the link between Shannon estimates and probabilities of chemical processes are discussed [9–13].

When molecules are treated in terms of the information-theoretic approach, the problem of comparison of may be emerged. Two marginal cases, when Shannon entropies are zero and maximal, were exhaustively discussed previously (\(h = 0\) and \(h_{\text{max}} = \log_2 N\), where \(N\) is the total number of atoms in the molecule) [1–3, 9,10]. Working on the Shannon entropy of mixing molecules [1], we came to the conditions of equal entropies of the molecules and found that this issue has not been studied. In the present work, we treat, classify, and exemplify some cases isentropic molecules.

2 Computational details

The details of the calculations have been previously presented [1, 14]. Their main idea is based on the partition of a molecule over \(N_i\) atoms of the 1\textsuperscript{st} type, \(N_2\) atoms of the 2\textsuperscript{nd} type, … \(N_n\) atoms of the \(n\)-th type, where \(n\) is the number of atom types and \(\Sigma N_j\) is the total number of atoms in the molecule. The Shannon entropy of the molecule in bits is introduced as a sum of the logarithms of the weights of each atom type \((N_j/\Sigma N_j)\):

\[
h = -\sum_{j=1}^{n} \frac{N_j}{\Sigma N_j} \log_2 \frac{N_j}{\Sigma N_j} \tag{1}
\]

Two molecules A and B are isentropic if their information entropies are equal (\(N_A\) and \(N_B\) are the total numbers of atoms in the molecules):

\[
\sum_{j=1}^{nA} \frac{N_{Aj}}{N_A} \log_2 \frac{N_{Aj}}{N_A} = \sum_{j=1}^{nB} \frac{N_{Bj}}{N_B} \log_2 \frac{N_{Bj}}{N_B} \tag{2}
\]

Here, \(N_i\), \(N_j\), \(N_A\), \(N_B\), \(n\), and \(m\) may be varied. Additionally, the partition of each molecule and the corresponding cardinalities of the subsets (\(N_i\) or \(N_j\)) are generally interdependent. Thus, we do not provide a general solution of Equation (2) and consider particular cases of the mentioned values when the condition of isentropicity is fulfilled.

3 Results and discussion

3.1 Zero-entropy molecules

If all atoms of the molecule belong to the single atom type, according to Equation (1), the Shannon entropy is zero. This is possible only under two simultaneous conditions:

(a) A molecule is homonuclear (\textit{i.e.} it is made up with the atoms of the one element).

(b) The three-dimensional molecular structure reveals a high symmetry (so that all atoms are chemically equivalent).

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3.2 Isotomic molecules

Two molecules partitioned over the same number of atom types \((n_A = n_B)\) in Equation (2) we call **isotomic** (from ἰσοτομή, ancient Greek ‘the same + partition’). Herewith, the molecular sizes \((N_A \times N_B)\) and cardinalities of the atom types \((N_{Aj} \times N_{Bj})\) may be either equal or different. The condition of the isotremicity of isotomic molecules relates to the proportionality of the weights of all atom types in A and B:

\[
\frac{N_{Aj}}{N_{Bj}} = \frac{N_A}{N_B} = k
\]

(3)

We consider separately the cases when \(k = 1\) and \(k \neq 1\) \((k\) is rational) in the subsections below.

3.2.1 Isotomic molecules with the same size

When \(k = 1\), we deal with isotomic molecules having \(N_A = N_B\). Trivially, this case corresponds to the molecules with identical molecular graphs. Therefore, we call them **isographic**. For example, CH₄, CF₄, CCl₄, CBr₄, and CI₄ are isentropic as the original information-theoretic approach puts that atoms of different chemical elements equally contribute to the entropy. Other examples of the same-size isotremic molecules with \(N\) up to 4 are provided below accompanying with the \(h\) values in bits and conventional designations of the molecule’s partition [number of atom types]×[number of atoms within them]:

(a) all heteronuclear diatomic particles AB (e.g., HF, HD, and HO’) – \(h = 1\) (partition \(2\times1\));
(b) particles with general formulas AAA (e.g., O₃, N₃, and I₃) and ABA (e.g., H₂O, H₂S, and :CH₂) – \(h = 0.918\) (partition \(2\times1 + 1\times1\));

(c) ABC (e.g., HCN, HNC, and HOD) and AAB (e.g., N₂O) – \(h = 1.585\) (partition \(3\times1\));
(d) AB₁ (e.g., CH₃, NH₃, PCl₃, NO₃, and CO₂⁺) – \(h = 0.811\) (partition \(2\times1 + 1\times1\));
(e) ABBA (e.g., H⁺C=CH and H₂O₂) – \(h = 1\) (partition \(2\times2\));
(f) A₂BC (e.g., H₂C=O and H₂C=NC) – \(h = 1.5\) (partition \(1\times2 + 2\times1\));
(g) ABBC, ABCD, and ABBB (e.g., H⁺C=Cl, HCN, and HCN, respectively) – \(h = 2\) (partition \(4\times1\)).

Isentropic molecules of this class may be not isographic, i.e. have different molecular graphs but identical partitions (Figure 2). Consequently, within the same information-theoretic approach, their Shannon entropies are equal. To discriminate such molecules numerically, the approach should be modified to take into account connectivity of the atoms (see, e.g. [15, 16]). To do or not to do this depends on the task of a study. It is noteworthy that the partitions obtained at the used level of the structural detailing correspond to NMR patterns of the molecules [17]. Usually, it is sufficient to solve typical problems of physical organic chemistry.

Fig. 1. Zero-\(h\) molecules. The point symmetry groups are shown in parentheses.

All zero-\(h\) molecules are isentropic and this is regardless of their molecular size. This size-independent class involves such different molecules become isentropic as O₂, C₆₀, P₄, and S₈ (Figure 1).

3.2.2 Isotomic molecules with the different size

If \(k\) is rational and not unity, isotomic molecules reveal identical similarity in their molecular sizes \((N_A \times N_B)\) and the cardinalities of each atom types \((N_{Aj} \times N_{Bj})\). This case have been discussed in [3]. We provide here two pairs of such **similar** molecules as:

(a) ozone \(O₃\) (partition \(1\times1 + 1\times2\)) and ethylene \(C₂H₄\) (partition \(1\times2 + 1\times4\)) with \(k = 2\) and \(h = 0.918\) bits;
(b) benzene \(C₆H₆\) (partition \(2\times6\)) and acetylene \(C₂H₂\) (partition \(2\times2\)) with \(h = 1\) and \(k = 3\).

Notably, similar molecules with equal Shannon entropies have pronouncedly different structure (Figure 3). At the same time, formation of the ensembles of such molecules reveals zero Shannon entropy of mixing even when the molecules differ.
3.3 Allotomic molecules

We have occasionally found cases when two molecules with the same size and different partitions demonstrate equal Shannon entropies. For example, molecules with \( N_A = N_B = 8 \), partitions \( 4 \times 2 \) and \( 1 \times 4 + 4 \times 1 \) have \( h_A = h_B = 2 \) bits. The addition of another different atom to these molecular system leads to another pair of isentropic molecules: indeed, if \( N_C = N_D = 9 \), partitions \( 4 \times 2 + 1 \times 1 \) and \( 1 \times 4 + 5 \times 1 \), respectively, we have \( h_A = h_B = \frac{8}{9} - 2\log_23 \approx 2.281 \) bits. The next addition also produces the isentropic pair. We try to exemplify these two cases with ‘real’ chemical systems (Figure 4). Even when we call such system real, these remain quite exotic (but existing). Such particles could be united under the name allotomic (from \( \text{ἄλλος} + \tauομή \), ancient Greek ‘different + partition’) and the search for extending examples of such chemical particles we address to our further studies.

![Fig. 4. Two pairs of allotomic isentropic particles.](image)

3.4 Tree of isentropic molecules and general remarks

To summarize, we provide a tree of isentropic molecules, which slightly differ from the plot of this short paper (Figure 5). Indeed, one can see that the condition for zero Shannon entropy fits into Equation (2), so zero-\( h \) molecules are, in fact, isotomic and should not be allocated in a separate class.

We stress that this classification is valid within the original Shannon approach, in which the molecule is divided into atom types in line with the chemical equivalence of the atoms but the connectivity of the atoms does not directly influence on the calculated \( h \) values (but connectivity is used to discriminate the atoms over the atom types).

![Fig. 5. Classification of isentropic molecules with the distinctive properties of their structures.](image)

4 Conclusions

In the present work, we have considered the main types of isentropic molecules and constructed the corresponding hierarchical tree to visualize their classification. We think that this result will be fruitful for quantification of the similarity/dissimilarity of molecular objects and further development of the information-theoretic structural descriptors.

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