Analyzing the torquoselectivity through Fermi-Dirac's entropy: revealing the origin of the stereoselectivity

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Analyzing the torquoselectivity through Fermi-Dirac’s entropy: revealing the origin of the stereoselectivity

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Abstract This work analyzed the electrocyclic ring-opening reaction of the 3-cyanclobutene (3-CN-cyclobutene) through Fermi-Dirac’s entropy. This chemical reaction is linked to an important concept called torquoselectivity, our results show that beyond the bond-breaking process in this reaction, a specific atom is responsible for the stereoselectivity observed in this reaction.

Keywords Fermi-Dirac’s entropy · Torquoselectivity · Chemical Reaction.

1 Introduction

In the early 40s, Shannon published his now classic article entitled ‘A mathematical theory of communication’ [1], in his work the main interest of Shannon was to try to figurate how two systems can communicate, and as a consequence several questions arise, for example, what is information? how such systems can share information? the concept of information can be related to a physical aspect of the systems? In the beginning, information theory was restricted to the field of telecommunications; however, soonly several areas of the natural sciences adopt it and incorporated Shannon’s model, such as chemistry, physics, biology, mathematics, among others, in this regard, one can ask by self, how it is possible that this model can be related to these areas of the knowledge, in this context, for example, we can do the following question, what have in common the codes send from the international space station,

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with the DNA of a new species of coral reef recently discovered, and with a chemical reaction? The answer to this question is, information.

Information is the main concept of Shannon’s work, and the form that Shannon found to quantify it was through the following mathematical expression,

$$ S = - \sum_{i=1}^{n} p_i \log_2 p_i, \quad (1) $$

where $p_i$ is the probability to obtain a determinate symbol, and also fulfills $p_i \in (0,1], \sum_{i=1}^{n} p_i = 1$, the units of Eq. (1) depend on the basis of the logarithm, in this case, the units are bits, if we use log\(_{10}\) the units will be Hartleys and if we use log\(_{\ln}\) the units will be nats.

On the other hand, a remarkable aspect of Eq. (1) is that this equation has the same form as an equation discovered hundreds of years before, in the field of thermodynamics... the entropy, and for this reason, Eq. (1) is, currently known as informational entropy. In this vein, exists a famous story about a chat between Shannon and von Neumann, Why don’t you call it entropy, – von Neumann suggested– “In the first place, a mathematical development very much like yours already exists in Boltzmann’s statistical mechanics, and in the second place, no one understands entropy very well, so in any discussion you will be in a position of advantage.”

Although the first applications of Shannon’s model were in the field of telecommunications, it soon spread to the field of physics mathematics, thus in the 1950s started to appear several variations of Shannon’s entropy, for example, Rény’s entropy [5] Kullback-Leibler’s entropy [2], Jaynes’ entropy [3, 4], trigonometric entropy measures [6], Tsallis’ entropy [7] among others, see, for example, Ref. [8] and the included references for more information about the versatility of this concept.

In this vein, since the early 1970s informational entropies have been applied to the field of density functional theory, for example, Fisher’s entropy [9] which is an entropy that has the same form that the von Weizsäcker’s term [10] that is related to the kinetic energy of the systems, and it is one of the main ingredients of practically any density functional, in the case of Shannon’s entropy defined in terms of the electron density, Sen et al showed that its first derivative with respect to the number of electrons is related to the Fukui function [11]; in this regard, Shannon’s entropy has also been associated with other concepts of theoretical chemistry, such as electron correlation, chemical structure [12–26], and has also been used as a source for generating density functionals [27], With the above mentioned, informational entropies may be considered valuable tools that permit obtaining a description of the chemical systems since the perspective of the information, in this regard, for example, it has shown that one can obtain more information with the informational entropies than the traditional descriptors, such as electron energy, correlation energy, softness, hardness, among others [28–44].

Considering the above, in recent work [45], it was explored a new informational entropy called Fermi-Dirac’s entropy, this entropy emerges from the
Fermi-Dirac distribution,

\[ \tilde{n}_i = \frac{1}{\exp \left( \frac{\varepsilon_i - \mu}{k_B T + 1} \right) + 1}, \]  

(2)

where \( \tilde{n}_i \) is occupation of the particle \( i \) and it is subject to \( \tilde{n}_i \in (0, 1] \), \( k_B \) is the Boltzmann’s constant, \( T \) is the absolute temperature, \( \varepsilon_i \) is the energy of a single particle in the state \( i \) and \( \mu \) is the chemical potential, this distribution is normalized and fulfills that,

\[ \sum_{i=1}^{m} \tilde{n}_i = N. \]  

(3)

Form distribution (2), we can write the corresponding functional entropy,

\[ \tilde{n}S_{FD} = -\sum_{i=1}^{n} [\tilde{n}_i \ln \tilde{n}_i + (1 - \tilde{n}_i) \ln (1 - \tilde{n}_i)], \]  

(4)

in order to apply this last expression to the field of quantum chemistry, we have to recur to the occupation numbers, in this case, we choose the Natural Population Analysis, which are atomic occupation numbers and are subject to \( \lambda_i \in (0, 2] \) because of Pauli’s double occupation principle, and fulfill \( \sum_{i=1}^{n} \lambda_i = N \), where \( N \) is the electron number of the system, these numbers have the two main characteristics (i) They come from diagonalized one-center angular symmetry blocks of a density matrix, and (ii) They have no interatomic overlap [46].

Thus Eq. (4), can be rewritten in terms of occupation numbers as,

\[ \lambda S_{FD} = -\sum_{i=1}^{n} [\lambda_i \ln \lambda_i + (1 - \lambda_i) \ln (1 - \lambda_i)], \]  

(5)

this expression is strictly positive overall space.

On the other hand, in chemistry one of the main interests is to investigate how different chemical species interact to form new species or how a specific molecule can change its structure, in this sense, we refer to stereoselectivity, in this area of chemistry there is an specific field called torquoselectivity, which is considered as the preference for inward or outward rotation of substituents in conrotatory or disrotatory electrocyclic reactions [47].

In this context, the electrocyclic reactions are arguably one of the most important reactions in very used by synthetic organic chemists. One of the most important characteristics is their ability to create regioselectively and/or stereoselectivity in unsaturated organic compounds [48–51]. These reactions are defined by the Woodward-Hoffmann framework as transformations in which the formation of a single bond between the terminal atoms of a linear conjugated system of π-electrons creates a compound of \((n-1)\) double bond through an intramolecular cyclization reaction or the inverse opening is produced (see figure 1) [52]. In this order of ideas the electrocyclic ring-opening reactions can have
two possible products, an open product can produce two different polyenes depending on if the reaction is conrotatory or disrotatoria (torquoselectivity).

In the case of the reaction studied 3-cyancyclobutene (3-CN-cyclobutene) [53] these electrocyclic reactions were performed thermally and are stereospecific. This reaction was studied by our research group in a previous study and the preferred way is by the Intrinsic Reaction Coordinate (IRC) through Transition State Outward Conrotatory (TSOC) [54]. It should be noted that the prediction of the activation energy agrees with the experimental data [52].

This reaction has been studied by the Frontier Molecular Orbital theory and the Transition States Theory, [55] but, occasionally, the application of classical theories disagrees with experimental results [56]. Our research group has published several papers where various methodologies have been applied that involve the Electron Localization Function (ELF), the main conclusion of this study indicated that the electronic reorganization in the thermal electrocyclic opening of trans-3,4-dimethylcyclobutene is not due to a pericyclic electronic reorganization postulated by Woodward–Hoffmann and therefore, could be considered as a pseudiodiradical \( \{2n + 2\pi\} \) process [57], maximum hardness, minimum electrophilicity and minimum polarizability principles [48], the natural bond orbitals have been obtained and the second-order perturbational theory analysis has been carried out to determine the main charge transfers due to delocalization [59] and Quantum Theory of Atoms in Molecules (QTAIM) and stress tensor frameworks, among others [60]. In such works the electronic reorganization agrees with the experimental data. Taking, into account these outcomes in this work has been analyzed the torquoselectivity through Fermi-Dirac’s entropy, with the main idea to seek new insights into molecular behavior for the Transition State Outward Conrotatory (TSOC) for the reaction of Figure (1).

![Fig. 1 Electro cyclic ring-opening reaction of the 3-cyancyclobutene (3-CN-cyclobutene) studied in by our research group following a way IRC of Transition State Outward Conrotatory (TSOC).](image)
2 Results

In this section, we present the results of the electrocyclic ring-opening reaction of the 3-cyanclobutene (3-CN-cyclobutene), this is a reaction in which the main process is the bond-breaking between the carbon atoms 2 and 3, see Figure (1). For our study, we performed an IRC calculation with 412 points using B3LYP/6-31+G**, and for each point, we calculated its corresponding population analysis (NPA) using the same functional and basis set, all calculations were done using Gaussian 09 [61].

In all figures we used, the variable $RX$ which is the reaction coordinate defined by Fukui in the 1970s who defined this concept as we tentatively define the reaction coordinate as a curve passing through the initial and the transition points and orthogonal to energy equipotential contour surface. A reaction coordinate, defined as such, may be called 'intrinsic reaction coordinate.' [62, 63].

In Figure (2(a)), we present the general behavior of the electron energy, and as is expected, this reaction is non-symmetric, and this trend has a maximum at $RX = 0$ which corresponds to the transition state structure, which is an unstable structure, in general, we cannot say too much about this reaction just based on the energy. In Figure (2(b)), is depicted the trend of the electron correlation energy, each point was calculated as the difference between the CISD and HF energies, and the energy values were obtained with the 6-31+G** basis set, as in the case of the electron energy, this trend does not appor enough information about this process, and just we can say that at $RX = 0$ this reaction has a minimum, this physically represents that in the transition state structure, the electron-electron interactions are minimum.

In Figures (2(c)) and (2(d)), we compare the electron energy and electron correlation energy with Fermi-Dirac's entropy, in these figures one can note that the trend of Fermi-Dirac's entropy has more structure than energy trends. In general, we observed that Fermi-Dirac's entropy has a change in its slope at $−2 < RX < −1$, then it presents a maximum at $RX \approx 0.9$, a minimum at $RX \approx 2.6$, and finally has a maximum at $RX \approx 4.1$, which suggest that some important changes occur in such zones of the reaction path; therefore, it is convenient to explore the changes in other parameters, in order to know if these changes in the entropy may be related to some physical changes.

Based on, the mentioned in the previous paragraph, and considering Figure (1), one might expect that will be the bond-breaking process, the main aspect of this chemical reaction, for this reason in Figure (3(a)) we compare the trends of the variation of the Electrostatic Potential Charge of atoms 2 and 3, which are the atoms involved in the bond-breaking process, un such figure we note that both trends have a maximum at $RX \approx −0.2$ and both decrease after this point, which indicates a decrease in their charges and also in their electron-electron interactions and at $RX \approx 2.2$ both trends have a minimum that can be interpreted physically as the end of the bond-breaking process.

Despite the interesting findings shown in Figure (3(a)), we analyzed the variation of the electrostatic potential charges of the rest of the atoms, and
we found that it is the atom 4, the atom that permits to carry out the bond-breaking process. In Figure (3(b)), we compare the trends of the Fermi-Dirac’s entropy with the variation of the Electrostatic Potential Charge of atom 4. Comparing the trend of the Electrostatic Potential (E.P.) of this atom with the trends of E.P. of atoms 2 and 3, we note that atom 4 has three maximums and three minimums along the path reaction, and in all cases, their location at the reaction coordinate, $RX$, corresponds to the zone in the bond-breaking is carried out, see Figure (3(a)), for this reason, we consider that the most important piece of this chemical reaction is atom 4, which is in charge of the most important changes that permit this reaction to proceed.

In this regard, in Figure (3(c)) we compared the trend of Fermi-Dirac’s entropy with the Kinetic Energy (K.E.), in this figure we note that this K.E. trend decreases in a pronounced way at $RX \approx -2$ and reaches its global minimum at $RX \approx -0.75$, and it increases to reach its maximum at $RX \approx 2.1$, and finally K.E. decreases and it presents a minimum. In this description worthwhile to note that while the variation of the K.E. decreases the entropy trend increases, which agrees with the maximum entropy principle.

Finally, in Figure (3(d)), we compare the trends of K.E. and P.E. of atom 4, in this figure we note that first the maximum of the E.P. decreases according to K.E., but it presents a local minimum, which apparently, does not have physical sense; nevertheless, if we observe Figure (3(c)), this minimum ties in with the variation of the slope of the entropy trend, finally both trends have variations and all of them have physical sense; notwithstanding, we can conclude that the steric effects that govern this reaction are because of the exquisite movement of this atom. In this sense, we conclude that Fermi-Dirac’s entropy may be a valuable tool that permits to find of some regions, in chemical reactions, in which the most important chemical and physical changes are carried out.
(a) General trend of the electron energy.  

(b) General trend of the electron correlation energy.

(c) Comparison between Fermi-Dirac’s entropy and electron energy.

(d) Comparison between Fermi-Dirac’s entropy and electron correlation energy.

Fig. 2 General trends of the electron energy, correlation energy, and Fermi-Dirac’s entropy.
(a) Variation of the Electrostatic Potential (E.P.) of the atoms 2 and 3, (see Figure (1)).

(b) Comparison between Fermi-Dirac’s entropy and the variation of the Electrostatic Potential Charge (E.P.) of atom 4 (see Figure (1)).

(c) Comparison between Fermi-Dirac’s entropy and the Kinetic Energy.

(d) Comparison between Kinetic energy and the variation of the Electrostatic Potential Charge (E.P.) of atom 4.

**Fig. 3** General trends of the electron energy, correlation energy, and Fermi-Dirac’s entropy.
3 Conclusion

Analyzing the trend of Figures 3(a)-3(d) for the electrocyclic ring-opening reaction of the 3-cyanclobutene (3-CN-cyclobutene) studied by our research group following a way IRC of Transition State Outward Conrotatory, we can reveal the origin of the stereoselectivity in this reaction and this analysis can be extrapolated in other electrocyclic ring-opening reactions. In this order of ideas, this study sheds light to understand the origin of the reaction products experimentally evidenced. Additionally, although the substituent effect falls on the C1 atom, the responsible for the stereoselectivity for the formation of the product is the behavior of the C4 atom. In organic chemistry, providing tools to understand the stereoselectivity of a reaction is very important, because it is possible to understand the high percentages of reaction for a certain product. Considering, that the selectivity arises from differences in steric and electronic effects in the mechanistic pathways leading to the different products. Stereoselectivity can vary in degree, but it can never be total since the activation energy difference between the two pathways is finite: both products are at least possible and merely differ in amount. However, in favorable cases, the analytical methods may not detect the minor stereoisomer. It should be noted that the two reaction trajectories Transition State Outward Conrotatory (TSOC) and Transition State Inward Conrotatory (TSIC) were studied for this reaction by our research group [59]. However, the reaction trajectory that agrees with the experimental reaction product is the TSOC and it was precisely on it that the present study was carried out.

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Conflict of interest

The authors declared that there is no conflict of interest.

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