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STUDY OF CONCEPTUAL KNOWLEDGE AND MODE OF REASONING RELATING TO THE CHARACTERISTICS OF COVALENT BONDS IN FUTURE ALGERIAN PHYSICS TEACHERS

Abstract: In this study we tried to analyse how future teachers of Ecole Normale Supérieure (ENS) school who are at the end of education have integrated the specifications of covalent bonds in the different bond orders in terms of symmetry, stability, length, localisation (in the case of structures of ethane, ethylene and acetylene) or delocalisation of electrons (case of benzene). The analysis of responses to a written questionnaire shows that the majority of students have only integrated some knowledge, which may be termed as procedural, on the structural elements of molecules such as stability and the length of bonds. Although possessing some conceptual knowledge, students tend to use an alternative way of reasoning arising from the mental representation that single and multiple bonds are independent entities: the single bond is a "σ bond" while the double bond is considered only as a "π bond".

Keywords: covalent bond, orbital overlap, stability of bonds, length of bonds, localised system, conjugated system

Introduction

During our teaching, we noticed that undergraduate students of physical sciences encountered difficulties in the interpretation of the reactivity of organic compounds and in particular in the prediction of the reactive sites and the interpretation of their reactivity in terms of the breaking and the formation of bonds. One of the characteristics of science is that it produces a network of highly interconnected and above all coherent knowledge [1]. In the case of teaching of organic chemistry, this knowledge network involves in particular the Lewis model and the quantum theory of the valence bond. Future teachers, at the end of their university studies, should have built an effective knowledge structure that best reflects the appropriation of the target knowledge set by the teaching. For example, the meaning of the different traits linking atoms in a Lewis scheme, the relative stability of σ and π bonds, the orbitals (atomic or hybrid) involved in their formation, the differences in the overlap of orbitals, the delocalisation of electrons in conjugated systems, area necessary knowledge to understand the reaction mechanisms in organic chemistry. Thus, among the learning

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objectives to be achieved at the end of the common core at Ecole Normale Supérieure (ENS) school at Kouba (i.e. at the end of the second year), it is necessary to possess the following knowledge:
- Describing the various OAs and p recovery methods.
- Indicating some characteristics of single and multiple bonds (mode of formation, free rotation or not, stability, symmetry, etc.).

In this work we will attempt to analyse to what extent ENS students at the end of their education have integrated the characteristics of single and multiple covalent bonds in terms of symmetry (provided or not with axial symmetry), stability (force), length, location (case of ethane, ethylene and acetylene structures) or electron delocalisation (case of benzene).

Theoretical framework of analysis

Chemical considerations

In organic chemistry, molecules are generally represented by their Lewis diagram. Atoms are connected by single, double or triple lines meant to represent the sharing of two, four or six valence electrons. To interpret the reactivity of a molecule, for example ethylene ($H_2C=CH_2$), it is necessary to consider that the two lines (or binding pairs) between the carbon atoms do not symbolise bonds of the same type. Two parallel ways of describing the bonds in a molecule are possible within the framework of the quantum model. The theory of the valence bond (electrons are located between atoms) and the theory of molecular orbitals (electrons are delocalised throughout the molecule). For the convenience of the problems to be solved, it is the Valence Bond theory (LV) which is generally used in organic chemistry to describe bonds, and which is the justification and quantum support of chemical writing in terms of Lewis structure" [1, 2]. It is based on the idea that atoms retain their identity within the molecule, that electrons are supposed to occupy atomic orbitals and that the chemical bond results from an increase in the presence of two electrons of opposite spin between the nuclei [3]. According to this theory, the pairs of electrons are localised, either between the atoms to form the bonds, or on only one (free pairs).

It will lead Pauling to introduce the notion of hybridisation of orbitals, an atomic wave function obtained by linear combination of the starting pure atomic wave functions (or atomic orbitals). To describe the bonds in the ethylene molecule within the framework of the LV theory, it must be considered that the two carbon atoms are in a state of sp^2 hybridisation, that one of the lines represents a σ bond resulting from the axial overlap of two hybrid orbitals (OH) sp^2 of carbon atoms, the other symbolises a π bond resulting from the lateral overlap of two atomic orbitals (OA) p of each carbon atom. The four C-H bonds can be described as resulting from the overlapping of four OH sp^2 from carbons and four OA s from hydrogens. These different connections resulting from different overlaps will therefore have different characteristics (energies, length, free rotation or not). This is how the notion of hybridisation makes it possible, for example, to say that:
- Energies of the hybrid carbon orbitals have average energies between those of the OA 2s and 2p and more or less high according to their s / p proportion [4]. As a result, the σ bonds formed from OH are as much stronger as the "character" s of these orbitals is higher (sp: 50% > sp^2: 33% > sp^3: 25%);
- The CH bond of an acetylene (OH sp overlap of C and 1s of H) is shorter and stronger than that of an ethylene (sp^2 - 1s overlap), it is itself shorter and stronger than that of an alkane (sp^3 -1s recovery).

On the other hand, in the case of multiple bonds (conjugated or not) the LV theory does not allow, unlike the theory of molecular orbitals, the determination of the energies of the bonds. The classification E (C–C) $<$ E (C=C) $<$ E (C≡C) proposed by Pauling stems from thermodynamic considerations. In the case of benzene, it is impossible to represent the actual electronic structure using a single Lewis diagram. We can use two, called mesomeric forms (Fig. 1).
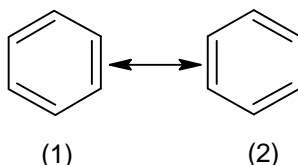

Fig. 1. Mesomeric forms of benzene

Within the framework of the LV theory, the hexagonal form of the benzene cycle finds its interpretation by the formation of 6 σ C–C bonds resulting from the overlap of the OH sp^2 of the 6 carbon atoms. We say that we have a conjugate system as a result of the alternation of single and double bonds in these diagrams. In such a system, the OA p$_z$ of the carbons remain unchanged and the 6 electrons which occupy them "move independently from atom to atom" (are delocalised on the 6 atoms of carbon) [4]. As a result, carbon-carbon bonds in benzene have intermediate characteristics (length and energy) to those of single and double bonds.

Didactic considerations

The connection of the binding or non-binding doublets of a Lewis scheme with the abstract concepts of quantum theory VB (electrons, atomic s and p orbitals, linear combination of atomic orbitals, hybridisation of atomic orbitals, symmetry of orbitals, overlap of orbitals respecting symmetry rules, σ and π bond, electron density, etc.) is a complex task. To carry it out successfully, students must, on the basis of the information received during the various courses, have achieved their "conceptual integration" by linking the various involved concepts and thus have built a structure of personal knowledge [5]. Conceptual integration is considered to be at the root of our ability to make sense [6]. According to Taber, conceptual integration is seen as "the structuring of knowledge that an individual has organised in such a way that there are strong relationships between different domains, and therefore, generally speaking, that there is consistency between different parts of an individual's personal knowledge". Different types of knowledge can constitute this personal knowledge that can be mobilised in the face of a given situation without requiring an integration of the theory from which it derives. This knowledge consists of the simple knowledge of the rules of action (codes and languages, representations, schemes). They have received the name of "procedural knowledge" [7] that cannot be only operational but also explained and justified by the learner. In this case, Orange [8] speaks of "working knowledge".

In this study we will seek to identify categories of knowledge constituting the structure of personal knowledge relating to the characteristics of the covalent bond integrated by the students.

Literature review

In the absence of a correct understanding of models and the meaning to be given to the representations associated with them, students will have difficulty perceiving the implications of structural aspects of molecules on the reactivity of chemical species [9, 10]. However, few studies have highlighted, on one hand, the difficulty encountered by students in constructing and manipulating Lewis structures [11, 12], and on the other hand using these structures to predict the physical and chemical properties of organic compounds [13]. For their part, Laszlo [14], Bhattacharyya and Bodner [15], Ferguson and Bodner [16] Kraft et al. [17] highlighted the difficulties that learners experience in describing reactivity or reaction mechanisms based on a Lewis structure by using curved arrows to track the movement of electrons. They are to be compared with the difficulties encountered in modelling at the nanoscopic scale of the chemical bond and the concepts related to it: polarity of bonds and molecules, formal charges, electron donor and acceptor sites, zones of strong or weak electron density [18-21].

This modelling of the covalent bond is based on theories of quantum mechanics. These latter are considered by various authors as the most difficult to learn and understand at all levels of learning of chemistry [22-31]. This has been confirmed by previous studies [32-37] where we have demonstrated, on one hand, that almost all of the students concerned by this research are not able to translate representations of single or multiple bonds of Lewis schemes using the concepts of OM or VB quantum theories (pure and hybrid atomic orbitals, overlap of orbitals, OM or σ or π bonds), and on the other, within the framework of the VB theory, they constructed an alternative conception of the concept of hybridisation. Regarding π bonds, students find it difficult to conceive of the delocalisation of electrons. This is how the circle used to represent the aromatic character of benzene is interpreted, either as a "reservoir of electrons within the cycle" [38], or as a mixture of single and double bonds which moves along the benzene ring [39].

Research questions and methodology

We will seek to answer the following questions:
- What is the knowledge relating to the characteristics of covalent bonds integrated by the students?
- Of what nature are they: can they be qualified as procedural knowledge (simple memorisation of the characteristics of the different links) or operative knowledge (the characteristics of the links are also justified by the student)?

Data collection

Students had to answer, in a 30-minute session, three questions: Q1 and Q2 relating to localised systems and Q3 corresponds to a delocalised system, benzene (see the Supplementary Material). In order to identify the nature of the knowledge assimilated for each question, learners must justify their answer. The conditions for answering the questionnaire were specified to students by the researcher (anonymity, not taken into account for the evaluation, personal conceptions). Questions were prepared after a discussion between the authors, and then submitted to two other chemistry teachers to assess whether students are able to answer these questions given the instruction received.

The questionnaire was then tested with a control group of 18 students to assess their interpretation of the meaning of the questions.

Study sample

The study was carried out with 3rd year undergraduate students of physical sciences of ENS school at Kouba (Algiers). Students are divided into 3 options (chemistry, physics, and technology) depending on the discipline and level of education (college or high school) they have chosen. All these students have followed the same course: teaching the concepts and theories of covalent bonding during the first two years of the common core and organic chemistry in the third year (i.e. in 2019-2020). It initially concerned 58 students of the chemistry option (in April 2019, that is to say 9 months after the end of the courses of the common core and 3 months after the end of organic chemistry teaching) having followed the course of organic chemistry of one of the researchers during 2019-2020 academic year (questions 1 to 3). Given the large number of non-responses to question 3 (on average 40 % for the 3 items), 32 additional students in the option of technology, having followed the same course as those in the option of chemistry, were submitted to question 3 only (non-response rate: 16 %). It should be noted, on one hand that these students gave their consent to participate in the study, on the other hand that they were taught in Arabic, that is the language used for data collection. Responses were then translated into English.

Data analysis

Given the received education, the expected justifications for the various questions are as follows:
- Q1a) σ bonds are more stable (strong) than π bonds because of the area covering orbitals, and therefore the electron density between nuclei, is greater in the case of σ bonds (characterised by axial symmetry) than in the case of π bonds (characterised by a nodal plane of symmetry).
- Q1b) Free rotation is allowed around a single link due to the axial symmetry of the σ link. This allows the two atoms to rotate relative to each other around the axis of the bond. It is not in the case of the double bond because of the lateral overlap of the two p orbitals of parallel axes leading to a π bond characterised by a nodal plane of symmetry.
- Q2a) The σ bonds formed from hybrid orbitals are as much stronger (stable) as the "s character" of these orbitals is higher. To discuss relative energies of single, double or triple bonds, it is necessary to take into account the number of σ bonds (axial overlap) and π bonds (lateral overlap) that constitute them. Therefore E (C–C) (axial overlap of two OH sp^3) $< E$ (C=C) (axial overlap of two OH sp^2 and lateral overlap of two OA p) $< E$ (C≡C) (axial overlap of two OH sp and two lateral overlaps of OA p).
- Q2b) The length of the link is linked to the link energy (therefore to the number of σ and π links and to the different overlap modes): the higher the link energy, the shorter the link, therefore: $l_{(CC)} > l_{(C=C)} > l_{(C≡C)}$.
- Q3) In the case of benzene, Lewis diagrams of the mesomeric forms translate a σ backbone resulting from sp^2 - sp^2 overlap of the OH of 6 carbon atoms and a π system where 6 electrons are delocalised on the molecule. The 6 carbon - carbon bonds are therefore identical and their characteristics are intermediate between those of single and double bonds.

The data were categorised, on the one hand by identifying expressions contained in the justifications given by the students who are close to those appearing in the expected answers above (justifications considered acceptable by the authors, highlighted in gray in Tables 1 to 8), on the other hand, after reading the answers, by grouping together in the same category related expressions appearing in the justifications given by several students. As a justification can contain keywords belonging to different categories, only one main reference has been retained per justification. The number of other references, which we arbitrarily qualify as secondary, is indicated in italics (and in brackets).

Results

Characteristics of σ and π bonds

Q1a: σ bonds are more stable (strong) than π bonds: Yes, 51; No, 3; No response, 4. Table 1 shows the different categories of justifications given by the students.

Table 1

Comparison of the stability of σ and π bonds

Reference		No. Yes	No. No
At overlap: axial / lateral	Mention of the difference in overlap area	4	
	Mention of the difference in overlap symmetries	21 (+3)	
To the ratio stability / breaking energy		14 (+4)	
To the ratio stability / reactivity		12	
To the order of bonds			3
No response		4	

Note: the numbers in brackets correspond to keywords appearing in other categories, No. - number of

About half of students who answered yes (28 out of 58) refer to the difference in axial / lateral overlap of the OA. Four of them mention the difference in overlap area / surface: "Yes, because the axial overlap area in the case of the sigma bond is greater than the lateral overlap area in the case of the π bond". The majority (24 students) mentioned the difference in overlap symmetries, either exclusively (21) or in addition to the stability / reactivity ratio (3):
- Without explaining explicitly what this difference consists of (16 students): "Because the σ bond is obtained from an axial overlap while the π bond is obtained from a lateral coverage".
- By limiting the axial overlap to the presence of hybrid orbitals (6 students): the σ bond is obtained from an axial overlap of two hybridised atomic orbitals (CC) (or from an axial overlap of two OA, one hybridised and the other pure) while the π bond is obtained by a lateral overlap of two unhybridised OAs. This excludes the axial overlap of two unhybridised atomic orbitals as for H2 or F2.
- By limiting the axial overlap to s and p orbitals and without mentioning the nature of the laterally overlapping OA (2 students): "Because the σ bond is obtained from an axial overlap of two atomic orbitals of the kind (s / s) or (p / p) while in the connection π the overlap is lateral".

18 students refer to the difference in fracture energy, either exclusively (14) or in addition to the stability / reactivity ratio (4). The above 14 students do not explicitly justify the cause of this difference: "Because there is an inverse relationship between force (energy) and stability: the σ bond is more stable (less energy), the reverse is true, the π bond

is less stable (greater energy)". We can consider that this has a relation with the energy diagram of OMs: the lower the energy levels (in general for OM σ), the more "stable" the OMs are. But in fact, the energies being negative, the lower the levels are in the energy diagram, the higher the corresponding energies are in absolute value.

For 12 students (3 of whom mentioned the difference in the overlap of σ and π bonds), stability is linked to reactivity: "Yes, the σ bond is stronger than the π bond because the first is characteristic of saturated (stable) compounds unlike the second which characterises unsaturated compounds (more reactive)". The weakness of the π bond is equated with its ability to react quickly compared to the σ bond.

Students who answered in the negative refer to the order of links: "Because we observe the genus σ in single bonds while π is found in multiple bonds (double and triple) which makes it more stronger than σ". They thus seem to limit the existence of σ bonds only to single bonds. Multiple links are considered to be part of a "single entity". In fact, they compare the energy of the σ bond to the set of energies of the σ and π bonds in the multiple bond.

Comparison of single and double bonds concerning the possibility of free rotation

Q1b: Free rotation is allowed around a single bond and is not in the case of a double bond: yes, 51; no 3; No response 4.

Table 2 shows the different justifications of students categorised according to the reference to the key words used.

The majority of students who answered yes (44 students) refer to the existence of the π bond in the double bond as the main constraint preventing free rotation.

Table 2

Comparison of single and double bonds concerning the possibility of free rotation

Reference		No. Yes	No. No
To the π bond in a double bond	≠ of overlap symmetry between σ and π	13	
	Its presence	17	
	Its breaking energy	14	
The stiffness of the double bond		7	
The rotation of the whole molecule			3
No response		4	

Some (13 students) evoke in a relevant way the difference in overlap symmetry (lateral and axial) between σ and π: "As the rotation is only done around an axis, it is allowed in the simple connection, which has one (axial overlap) and is not in the double because of the π bond which does not contain any (lateral overlap)" or "It is the lateral overlap in the formation of the π bond that prevents the rotation". Others (17 students) simply report the presence of the π bond within the double bond without specifying the reasons for the impediment: "Free rotation is allowed around the single σ bond and is not around the double bond because of the π bond which prevents this rotation".

14 students refer to the breaking energy of the π bond, either in relation to its reactivity, "For the rotation to take place around the double bond it is necessary to break the π bond which is more reactive", or at the barrier of relatively greater energy in the case of ethylenic isomerism than in that of ethane to pass from one isomer to another, "the passage from the (cis) isomer to the (trans) isomer requires a relatively higher energy to break the π bond".

Finally, for 7 students, the prevention of rotation is due to the rigidity of the double bond: "The existence of the double bond gives the molecule a certain rigidity which prevents rotation".

Students who answered in the negative think that rotation is allowed around the double bond: Free rotation is allowed in both cases of bond (single and double): the two groups can rotate at the same time and in the same direction. For these students, the confusion seems to lie in the word "rotation". They do not think of the internal rotation of one atom relative to another due to the presence of axial symmetry, but of the rotation of the whole molecule.

Comparison of the characteristics of the different bond orders

Q2a: Classification of the stability (strength) of the different orders of bonds:
(C–C) > (C=C) > (C≡C): Yes 28; No 19; No response 11.

Table 3 shows the different justifications of students categorised according to the reference to the used keywords.

Table 3

Classification of the stability (strength) of the different bond orders: (C–C) > (C=C) > (C≡C)

Reference		No. Yes	No. No
To bonds σ and π	Their number of overlap symmetry	13	
	Their number		11
	Their stability number	8	
To energy: of bond / of break		(+5)	8(+11)
To the relationship stability / reactivity		7	
No response		11	

Note: numbers in brackets correspond to keywords appearing in other categories

Only 19 students consider the proposed ranking to be wrong. They all justify their point by referring to bond / break energy. Either only (8 students), "No, because the energy of the triple bond in acetylene is greater than that of the double bond in ethylene which is itself greater than that of the simple bond in ethane", or by associating this energy in a relevant way with the number of σ and π bonds constituting the different bond orders (11 students): "No, because the triple bond is made up (of a σ bond and 2 π bonds), and the double bond (of a σ + a π bond), hence the difficulty of breaking them unlike the single bond (a σ only) which requires less energy".

Regarding the justifications proposed by the 28 students agreeing with the proposed classification, it is first of all the difference in overlap symmetry of the orbitals that is mentioned by 13 students: "Yes, because the σ bonds are from an axial OH overlap. They are therefore stronger than the π bonds, which are formed from a lateral overlap of p-p OA". The idea that arises here is that an axial overlap of hybrid orbitals only occurs in the case of a single bond. Multiple bonds seem to be considered only as resulting from a lateral overlap of OA and thus assimilated to π bonds. We find an identical idea among the 8 students who refer to the difference in the stability of the σ and π bonds (of which 5 mention the bonding or breaking energy): "Yes, because the CC bond is of the type σ, this latter is more stable than the π bond". It therefore seems that for these 21 students, the multiple bond is considered as a "single entity" having the characteristics of the π bond.

For 7 students, it is the relationship between the stability and the reactivity of saturated / unsaturated compounds (bonds) that is put forward as justification: "Yes, the CC bond (σ) being a saturated bond, it is more stable (and less reactive) with a higher energy.

We generally classify the energy and the stability (and or reactivity) according to establishment degree".

Q2b: Classification of the length of the different bond orders:

$$(C–C) > (C=C) > (C≡C): \text{Yes } 42; \text{ No } 7; \text{ No response } 9.$$

In Table 4 are gathered the different students justifications categorised according to the reference to the key words used. If nearly ¾ of the students agree with the proposed classification, none gives a justification corresponding to the expected answer: the energy and the length of bonds depend on recovery mode, where the influence of the different hybridisation states play a role, and the stronger the binding energy the shorter the bond.

Table 4

Classification of the length of the different bond orders: $(C–C) > (C=C) > (C≡C)$

Reference		No. Yes	No. No
To σ and π bonds	Number and overlap symmetry	19	
	No calculate the link length	6	
To the single bond σ	Carbon hybridisation states (character s)	17	
	Its stability		4
To the volume occupied by the connections			3
No response		9	

There is no justification for the relationship between energy and link length. However, in some justifications (19) there appear relevant considerations which had not been taken into account to justify the proposed classification concerning the strength of the bonds: "Yes, taking into account the axial and lateral overlap in the formation of bonds (σ) and (π): (sp^3 / sp^3); $(sp^2 / sp^2, p_z / p_z)$; $(sp / sp, p_z / p_z; p_y / p_y)$. "Such a justification seems implicitly to mean that to compare the lengths of single, double or triple bonds, it is necessary to take into account the number of σ bonds (axial overlap and character s of hybrid OA) and of π bonds (lateral overlap) which constitute them.

But no mention is made of bond energies and their relation to lengths. Other students (17) relate only the length of the bond to the hybridisation state (s character) of the OH of the carbon which overlap to form the σ bond: "Yes, because the hybridisation state of the carbons (sp in acetylene), $(sp^2$ in ethylene) and $(sp^3$ in ethane) causes the length of the triple bond to be the shortest" or "Yes, as the character s in sp hybridisation increases $(C–C) > (C=C) > (C≡C)$, the length between the two atoms decreases". The contribution of the overlap of the OA p, therefore of the π bonds, seems to play no role on the energy and therefore the length of bonds, unless it is implicitly taken into account without being quoted. Finally, some students use a formula involving the number of links σ and π to compare the lengths of links: "Yes, knowing that the length of the link $l = (\sum\sigma – \sum\pi) / 2$, we notice that the single bond with $(l = 0.5)$ is the longest in comparison to the double and the triple bond with lengths $(l = 0$ and $–0.5)$". This is most likely a confusion between order (or link index $= ½ (n – n^*)$) and length (with an incorrect formula to calculate the order).

Indeed, the larger the order, the shorter the link. For 7 students, it is the reverse ordering that is correct $(C≡C > C=C > C–C)$. Two categories of justifications are proposed:
- The more stable the link is, the more shorter is (4 students): "… because the most stable link (σ) is the shortest". As the single bond σ is considered in this case to be the most stable, it is therefore the shortest. For these students, double and triple bonds are assimilated to less stable π bonds.

- A justification by comparing volumes occupied by bonds (3 students) "no, because the triple bond occupies a volume greater than that of the double, which is itself greater than that of the single bond", with as implied: the higher the volume is, the longer the connection is.

Characteristics of carbon - carbon bonds in the case of benzene (Q3)

The objective of this question is to identify the meaning given by students to the representation of benzene using Lewis diagrams of meso-mother forms. Do students consider all carbon - carbon bonds in benzene to be equivalent, justifying this equivalence, or do they attribute structural reality to the single and double bonds in these representations? We are aware that the formulation of questions is likely to orient students' answers towards structural reality, but if this is the case, it means that they have not integrated notions of mesomerism, conjugation or delocalisation of π electrons on the benzene cycle.

Analysis of responses

Remember that 58 students of chemistry option (average response rate to this question: 60 %) and 32 students of technology option (average response rate: 84 %) who constitute our study sample.

→ Q3a - stability (force, energy): (C–C) > (C=C): Yes 39; No 27

Table 5

Comparison of the stability / strength of bonds, in representations of benzene

Reference		No. Yes	No. No
To the lateral overlap of the OA p / π bonds			12
To the alternation of single and double bonds		(3)	5(+4)
To recoveries	Lateral of OA p only	9	
	Axial of sp² OH and lateral of p OA	13	
At bonds / electrons σ and π		22 (+5)	
To the mesomerism		8	
To the reactivity of double bonds		9	6
To the relative stability of compounds (stronger bonds in benzene)			4
No response		39	27

Note: numbers in brackets correspond to keywords appearing in other categories

66 students (73 %) gave an answer (Table 5). Among students who disagree with the proposed classification, 17 (26 % of responses) mention the identity of the carbon-carbon bonds (including 8 specifying: "intermediates between the single and double bonds") to justify the identity of their stability in the benzene cycle. Although the delocalisation of π electrons is not mentioned, it seems to be present implicitly through the formulations referring to the lateral overlap of the OA p, "No, in benzene, all the C–C bonds are the same. They are intermediate between the single and the double bond due to the lateral overlap of the OA p, "or π bonds:"… the stability of (C–C) = the stability of (C=C) because 3 single bonds alternate with 3 double bonds along the cycle through the lateral covering of the π bond". If the mention of the alternation of double and single bonds along the cycle can lead to confusion, the fact that it is accompanied by the overlap of the π bonds (4 students), or the reference to the two representations of Lewis (5 students), "No, the double bond is more stable than the single considering the energies, but since benzene

contains three double bonds which alternate along the cycle in the Lewis representations, these bonds, should have the same stability". It seems to show that the conjugation is present in the minds of these students and therefore a certain understanding of the representation using mesomeric formulas.

The majority of students (39 or 59 %) agree with the proposition that the stability (strength, energy) of bonds (C–C) is greater than that of bonds (C=C). The proposed justifications referring to lateral (of OA p: π bond) and axial (of OH sp^2: σ bond) overlaps - "Yes, ((C–C) > (C=C)) because the σ bond is obtained from an axial overlap (sp^2 / sp^2) while the π bond is obtained from a lateral overlap (p$_z$ / p$_z$)"- clearly show that these students consider that Lewis diagrams reflect a structural reality where alternate single and double bonds. They therefore do not seem to consider the existence of a delocalised π system leading to an intermediate bond between the single and the double bond. Here we also find the assimilation of the double bond to the single π bond.

Other students (8) refer to mesomerism: "Yes, because benzene which contains a mixture of single and double bonds which alternate along the cycle is stable due to mesomerism. However, because of the displacement of double bonds along the cycle, they become less stable than single bonds, hence the proposed classification". Such formulation reveals a rough understanding of delocalisation of electrons: a gain in stability, as this has already been pointed out by other authors [28, 34], the "displacement of a mixture single and double bonds along the cycle". But the stabilising element for these students seems to be the single bond (σ), localised. As the π bonds (assimilated here to the double bonds) are delocalised, they are less stable. Moreover, the use of the expression "mixture of single and double bonds" shows that these students have difficulty in conceiving the delocalisation of electrons as well as the concept of mesomerism.

In justifications referring to the reactivity of double bonds (15 students), it is mentioned that the single bond is more stable than the double bond. There are many justifications accompanying the choice of opposing answers. For those who answer yes (9 students), "the single bond is more stable than the double, because benzene always reacts with its double bonds", and for those who answer no (6 students), the σ bonds (being less reactive that the π bonds) should be more stable and have a lower energy: "No, the CC bond, characterised by low energy, is more stable than the C=C bond which is more reactive towards electrophiles and therefore having higher energy". We also find in these justifications the assimilation of the double bond to the π bond,

→   Q3b - length: (C–C) > (C=C): Yes 28; No 35

The number of students who responded is 63 % (or 70 %) (Table 6). While the percentage of negative responses (35 or 56 %) is predominant, only 18 students (or 29 %) mention the identity of the length of the carbon - carbon bonds. As with the previous question, the delocalisation of π electrons is not explicitly mentioned in the various justifications. It is the lateral overlap of the OA p which is the cause of this identity: "No, they have the same length because of the lateral overlap of the OA p", with sometimes the mention of the alternation of single and double bonds: "No, in benzene, all the C–C bonds alternate with the C=C bonds, they are therefore identical, due to the lateral overlap of the OA p".

For the other students (17) who answered no, the length of the double bond is greater than that of the single bond. It is mainly the mobility of the π bond or its "delocalisation" over the entire cycle, often in relation to the reactivity of the benzene ring (12 students), which makes the double bond (always assimilated to the π bond) less stable. It is therefore

longer than the σ bond, which remains fixed, located between the two carbons: "No, because of its mobility, the π bond makes the benzene ring very reactive and weakens the less stable double bond (due to mesomerism, specify 8 students)"; $L_{c=c} > L_{c-c}$: in benzene the double bond extends over the entire cycle in the form of a loop, while the single is located between two carbons. Mesomerism is thus considered as an invariance of the σ and a weakening of the double bond following the delocalisation of the "π bonds".

Table 6

Comparison of the lengths of "single" / "double" bonds in the representations of benzene

Reference	No. Yes	No. No
To the lateral overlap of the OA p	14	18
To the alternation of single and double bonds		(10)
To the conjugation	(7)	
To the mesomerism	(5)	(8)
To the reactivity of benzene		(12)
To the stability of the double bond	14	(12)
To relocation / mobility of π links		16
To the location of σ bonds		(4)
To the repulsion of electrons		1
No response	28	35

Note: numbers in parentheses correspond to keywords in other categories

We note in a student a particular conception of the role played by electrons in the formation of a chemical bond: "$L_{c=c} > L_{c-c}$ due to the repulsion of electrons between the two carbons. In the double bond there are 2 more electrons than in the single one which induces an increase in repulsion and therefore in length". In addition to attributing structural reality to Lewis schemes, it seems that this student limits binding to an interaction between charges. The more the number of negative charges increases, the more they tend to repel each other and therefore the more the bond length increases.

Students (28) who agree with the proposition that the length of bonds (C–C) is greater than that of bonds (C=C) seem to consider that Lewis representations reflect a structural reality where singles and doubles connections alternate. For example, the following justifications which refer, either to the lateral overlap of the OA p, "Yes, the length (C–C) is greater than the length (C=C), given the lateral overlap of the OA p", or to the stability of the double bond, "Yes, the length of the bond is a function of its strength, the stronger it is, the shorter it is. In benzene, double bonds are more stable and therefore shorter", they would be correct in a localised system. This stability is sometimes associated with conjugation and / or mesomerism, "Yes, conjugation makes the double bond always the shortest and most stable (due to mesomerism for 5 students)", but the delocalised π system benzene is not taken into account.

→ Q3c - Compare the average lengths of single (C–C) and double (C=C) bonds in ethane and ethylene with those of benzene and justify them.

• Q3c1: (C–C) ethane > (C–C) benzene: Yes, 21; No, 35
• Q3c2: (C=C) ethylene > (C=C) benzene: Yes, 21; No, 44

Of the 56 students who answered question Q3c1 (i.e. 62 %), 21 (i.e. 38 %) answered yes to the question. But the provided justifications are twofold (see Table 7).

Table 7

Comparison of the lengths of carbon - carbon bonds in benzene and ethane

Reference	No. Yes	No. No
To the alternation of single and double bonds	4	
To the conjugation	5	
To axial overlap sp^2 / sp^2 in benzene	12	
To axial overlap (σ bond) (sp^3 / sp^3) in both cases		12 (+9)
To the bond σ	(11)	14 (+18)
No response	21	35

Note: numbers in brackets correspond to keywords appearing in other categories

Nine students (16 %) refer to relocation explicitly, ”Yes the length (C–C) ethane is greater than that of benzene because of the conjugation”, or implicitly: ”Yes, in benzene the σ bonds are shorter than in ethane because they are intercalated with double bonds”. For the 12 others, it is the difference in the axial overlap of the hybrid orbitals which explains that the bond is shorter in benzene than in ethane: ”Yes, the length C–C in benzene is less than that of ethane because it is obtained by a sp^2 / sp^2 overlap”. It is possible that, by invoking sp^2 hybridisation in benzene, these students think of the delocalisation that bond formation allows, but another interpretation is possible if one considers another similar formulation: ”Yes, because the σ bond is obtained by an axial sp^3 / sp^3 overlap in ethane and a sp^2 / sp^2 axial overlap in benzene”. The mention of the difference between the OH leading to the formation of the σ bond also suggests that, as in the case of question Q2, it is the relation between the character s of the OH and the force, and therefore the length, of the bond σ which is in play: the higher the character s ($sp^2 > sp^3$), the stronger the bond, and therefore the shorter it is.

The answer no (35 students) is associated with the equality of σ bond lengths in ethane and benzene. Equality justified by the fact that these links always result from an axial overlap, ”the two lengths are equal, because the σ link is always obtained by an axial overlap” (21 students of which 12 specify: sp^3 / sp^3), or simply because the single C–C bond is a σ bond: ”Being a σ bond, the C–C bond has the same length in both molecules” (14 students). These students seem, on the one hand to attribute a structural reality to Lewis representations, on the other hand to consider that the delocalisation of π electrons on the whole of the benzene nucleus has no influence on the localised system characterising the σ bonds. Among the 65 students who answered question Q3c2 (Table 8) (72 %), the majority (68 %) gave a negative answer. However, only 13 % (or 20 %) made reference to the conjugation to justify their answer ”(C=C) ethylene < (C=C) benzene”.

Table 8

Comparison of carbon-carbon bond lengths in benzene and ethylene

Reference	No. Yes	No. No
To the conjugation	4	13
To the alternation of σ bonds and double bonds	15	
To axial and lateral overlap (sp^2/sp^2 and p / p)	(5)	17
To the double bond $\sigma + \pi$		(8)
To the identity of the lengths but < C - C		12
To a steric effect linked to the cyclic geometry of benzene	2	
To the repulsion of electrons		2
No response	21	44

Note: numbers in parentheses correspond to keywords in other categories

Among students who refer to conjugation, 10 do so explicitly. For example, 4 write: "No, the double bond in benzene has an intermediate length between double and single because of conjugation." For 3 other students, "The overlap of p atomic orbitals in the benzene cycle (circular shape) means that the C=C double bond is more compressed than in the open chain in ethylene, hence $L_{c=c}$ ethylene < $L_{c=c}$ benzene. This formulation, in which appears a contradiction, suggests that it is more to a steric effect than to the decrease in the probability of the presence of bond electrons following delocalisation that is due to the greater bond length in the benzene. This illustrates a certain misunderstanding of conjugated systems. As for question Q3b, the repulsion between bond electrons, which are more numerous in ethylene than in benzene, is also mentioned by two students to justify that (C=C) ethylene < (C=C) benzene: "the double bond in ethylene is lower than that of benzene due to the repulsion of π electrons".

For the other students who answered no to the question (29 students, i.e. 45 % of the answers), lengths of links are equal. For 17 of them, the justification is based on the fact that in ethylene as in benzene: "… the double bond (σ + π) is always obtained by an axial (sp^2 / sp^2) and lateral (p / p) overlap… ". The delocalisation of electrons in the benzene cycle is therefore forgotten. For 12 other students, "(C=C) benzene have the same length as (C=C) ethylene but less than the single C–C bond". We can say that, for all of these students, the representation of single and double bonds in benzene formulas corresponds to a structural reality.

To justify their positive answer, "Yes, ((C=C) ethylene > (C=C) benzene)" (21 students), 15 students refer to the alternation of single and double bonds in the benzene cycle: "(C=C) benzene are shorter than (C=C) ethylene because they are intercalated with sigma bonds". Four others refer explicitly to conjugation: "The length of the double bond in benzene is equivalent to "one bond and ½" due to conjugation. It is therefore lower than the double bond in ethylene". It seems that these explanations, even if they implicitly or explicitly evoke conjugation, stick to the localised system. Indeed, the fact of speaking of a "bond and a half" between two carbon atoms can let suppose, as pointed out by Bucat and Mocerino [35], that for these students the six carbon atoms of the benzene cycle are connected by a connecting doublet; the other three doublets would be shared equally between the six bonds. The carbon - carbon bond in benzene would thus be equivalent to 1.5 conventional bonds (binder doublet). Its length would then be less than the double bond of ethylene, which would be equal to two binding doublets. The "conjugation" suggested by the representation of the limit formulas would thus be seen as a doublet sharing between the different bonds involved and not as a delocalisation of the π electrons on all six bonds.

Finally, we find in two students an explanation involving a steric effect in relation to the cyclic geometry of benzene: "the double bond in ethylene is greater than that of benzene because of the steric effect due to the cyclic geometry of this latest".

Discussion

At the end of their education of the 3rd year undergraduate degree in physical sciences, the majority of the questioned students seem to have only integrated knowledge that can be qualified as procedural relating to the characteristics of single and double bonds: σ bonds are more stable (strong) than π bonds; free rotation is allowed in the case of single bonds, it is not allowed in the case of double bonds due to the existence of the π bond; the

classification of the stability (force) and the length of the different bond orders is as follows (C–C) > (C=C) > (C≡C).

In the provided justifications, a high proportion of students appear to have a functioning pattern of reasoning already identified in previous studies [12, 32, 33, 39]:

- An axial overlap of atomic or hybrid orbitals, leading to the formation of a σ bond, only occurs in the case of a single bond;
- Double bonds are considered as a single entity resulting only from a lateral overlap of atomic orbitals: they therefore have the characteristics of a π bond.
  This operating diagram is accompanied by facets of alternative knowledge:
- Double bonds (characterised by the existence of a π bond) are weaker than the single σ bond;
- And as, the more stable / strong the bond is, the shorter it is, the single bond σ being considered as the most stable, it is therefore the shortest;
- The energy/stability of the σ bond is greater than that of the π bond because the σ bond is less reactive than the π bond ($E\,\sigma > E\,\pi$).

The analysis of responses relating to the characteristics of the carbon - carbon bonds in the case of benzene shows that the majority of students attribute a structural reality to the single and double bonds appearing in Lewis diagrams, which reflects a deficient conceptual integration of the notions of mesomerism, conjugation or delocalisation of π electrons on the benzene cycle:

- "Conjugation" is seen as a doublet sharing between the different involved bonds;
- The delocalisation on the whole of benzene nucleus has no influence on the localised system characterising the σ bonds;
- Mesomerism is considered as an invariance of the σ skeleton and a weakening of the double bond following the delocalisation of "π bonds".

Finally, students tend to use knowledge relating to localised system to explain the phenomena of relocation.

Conclusion

In conclusion, this study shows that many students at the end of their education are not able to justify characteristics of single or multiple covalent bonds using the concepts of LV quantum theory (atomic orbital, hybrid orbital, overlap of orbitals, σ bonds or π, localised or delocalised electrons). This is to be related to the lack of correct integration of covalent bonding and hybridisation models [12, 33]. The knowledge integrated by the majority of students cannot therefore be qualified as operative. They only integrated some knowledge, which can be qualified as procedural, concerning the structural elements of molecules such as stability (force) and the length of bonds. Their difficulty, even inability, to mobilise and network the concepts of Lewis and quantum models does not allow them to implement a systematic reasoning procedure making it possible to answer the asked questions. Although having certain knowledge, students tend to use an alternative mode of reasoning arising from the mental representation according to which single and multiple bonds are independent entities: the single bond is a "σ bond" while the double bond is assimilated only to a "π bond". This mode of reasoning seems to us to be favoured by teaching received in organic chemistry. As the interpretation of the reactivity of molecules and reaction mechanisms focuses on the movement of electrons from π bonds and nonbinding doublets, students forget the exact nature of a multiple bond.

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