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TEACHING STRUCTURAL PHYSICAL CHEMISTRY USING ADEQUATE STRATEGIES

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Abstract: *Within this study we propose a few examples of student-centred exercises to be used when applying in teaching and learning structural physical chemistry. These exercises imply to compute the bond orders using molecular orbitals method for σ homonuclear and heteronuclear bonds and for π polycentric bonds from organic conjugated systems. The values obtained for the diatomic molecules bonds and their cations and anions, metals from primary and secondary groups and organic compounds containing nitrogen atoms are further correlated with some properties and applications of these substances. These exercisesalso prove that structural and energetic indices, calculated by molecular orbitals method support acid, oxidant and electrophilic character of investigateddiazonium cations, and these static indices of reactivity underpin the description of stability of these compounds on which depend their uses in coupling reactions.*

Keywords: *conjugated systems; electrical conductibility; electronegativity; energy bands; stability; structural indices.*

Introduction

Chemistry, a central science field, is widely recognized by the majority students as being difficult. Many students perform poor in chemistry and more than that, structural physical chemistryis often considered by chemistry students as being abstract, unintuitive and among the most difficult field (Tsaparlis, 2007; Mammino, 2009; Adesoji, 2017; Partanen, 2018 and the references therein). This perception is usually due to their lack of familiarity with mathematics and also to their difficulty in passing from the understanding of the macroscopic world to the abstract thinking and understanding of the concepts and models used in the field of structural physical chemistry(Tsaparlis, 2007; Tsaparlis, 2016; Mammino, 2009).Consequently, most of the students are faced with learning difficulties in structural physical chemistry. They use memorization without understanding, which may result in school abandon.It conducts to the perception of lack of ability in chemistry (what is also called low self-efficacy in chemistry) resulting in unfavourable consequences for departments trying to increase enrolment and have adverse consequences on the financial viability of those departments (Dalgety&Coll, 2006). An analysis concerning the interest in chemistry of 495 students in Sweden revealed the importance of the teacher and the structure of lessons and the relevance for everyday life (Broman & Simon, 2015).

These contexts illustrate the need of designing adequate teaching strategies enabling the students to understand models and to facilitate the use of the concepts and procedures that are specific for structural physical chemistry,respectively to correlate them with the physical properties and practical applications of various materials. It underlines the importance of applying active-learning methods in teaching structural physical chemistry such as to form the students' ability to use the knowledge and to transfer it for use in new contexts.

In one of our previous studies, we have illustrated the application of the problem-based strategy to demonstrate to chemistry students that some physical and chemical properties of the hydrocarbons, of the acyclic and cyclic ions and of the heterocycles with nitrogen atoms have been correlated with static reactivity parameters, described by molecular orbitals method (Dascalu et al., 2018). Within this paper, we illustrate the use of important concepts specific to the field of structural physical chemistry for both inorganic (non-metals and metals) and organic compounds, and correlate the results with the physicochemical properties and practical applications of investigated compounds.

Methodology

A linked polyatomic system may actually exist if its bond order (b.o.), as a structural index, has a positive value. This structural index is correlated with the length of that bond and consequently with some properties of inorganic and organic substances (Coulson&Longuet-Higgins, 1947). According to quantum mechanics, formation of chemical bond consists in redistribution of wave functions of external electrons of the atoms which interact in the field created by several nuclei (Chiriac V. et al, 2003). Consistent with the molecular orbitals method (MOM), the molecular orbitals wave function (ψ_{MO}) is obtained by a linear combination of atomic orbitals (LCAOs) wave functions (ψ_{AO}) (Hanson, 2005). This mathematical procedure implies an algebraic sum of ψ_{AO} wave functions of the reactive atoms, each of them amplified by a contribution coefficient at ψ_{MO} functions. If at linear combination only two atomic orbitals (AO) with function (ψ_A, ψ_B) and their contribution coefficient (c_A, c_B) participate, two bicentric (localized) molecular orbitals (MO) will form because only two independent linear combinations are possible. The sum ($c_A\psi_A + c_B\psi_B$) represents bonding MO and the difference ($c_A\psi_A - c_B\psi_B$) is antibonding MO. If more than two AO are combining, a number of polycentric delocalized MO is forming, equal with the number of AO combined. The bicentric localized MOs are energetically different, according to the linear combination which generated them. It is also true for the polycentric molecular orbitals. It must be mentioned that the external electrons distribution on MO is more stable than the one from isolated atoms.

If a bonding MO is occupied with the same number of electrons as the corresponding antibonding MO, their effect is annulled and the electrons come to be under the influence of one nucleus. Hence they become non-bonding electrons and the orbitals on which they are located, are monocentric non-bonding MOs.

In a homonuclear molecule (A≡B) the simple bond (σ) is a pure non-polar covalent one. The functions ψ_A and ψ_B of the two atoms participate equally ($c_A=c_B=0.5$) to form bonding (σ) and antibonding (σ*) MO, and the charge densities of A and B atoms are equals (Simon, 1973). For a heteronuclear molecule, assuming that B atom is more electronegative than A $(\bar{X}_B > \bar{X}_A)$, the contribution coefficients (c_A, c_B) are unequal, and σ bond is always polar and acquires a percent of ionic partial character (Simon, 1973). Therefore, at the value of 0.5 of the contribution coefficient, a supplementary contribution $\left(\frac{0.5\,i}{100}\right)$ for ψ_B in bonding MO and for ψ_A in antibonding MO is added, where$i$ is the percent of the ionic character. In this situation, the electron cloud is not symmetrically distributed between the nuclei, but is concentrated close to the nucleus of the more electronegative atom. This gains a negative partial charge (-δ) and its partner will have a positive charge of the same value (+δ).

As stated by Pauling (Pauling, 1932), the electric moment (μ) of this dipole is calculated with the relation:

$$\mu = \delta \cdot e \cdot \bar{r} \quad (1)$$

where e is electron charge and $\bar{r}$ is the length of the covalent bond, determined with Schomaker-Stevenson relation, from the values of the atomic radii (r_A, r_B) and the electronegativity coefficients of the bonding atoms ($\bar{X}_A$, $\bar{X}_B$)

$$\bar{r} = r_A + r_B - 0.09\,(\bar{X}_B - \bar{X}_A) \qquad (2)$$

Interatomic (simple) bond is unitary in the sense that ionic and non-polar covalent bonds are limit states of polar covalent bond. It must be also emphasized that in polyatomic molecules, same as diatomic ones, σ bonding MO and σ* antibonding MO are always bicentric localized.

Localized π covalent bond, characteristic to multiple bonds, is formed in the cases wherein after the formation of σ bonds, non-bonded electrons are still remaining at both atoms. In contrast to σ bonding MO without nodal plane in the internuclear space (monolobar cylindrical symmetry), π bonding MO has a nodal plane which separates the two lobs where wave function has opposing signs. In the case of π* antibonding MO, there are two nodal planes, one being perpendicular on internuclear axis (Chiriac et al, 2003).

Analysis of E_2 systems (A≡B) (E being an element from period 2, with Z≥7) indicates the following energy succession for the 8 MO (2·4 external AO):

$$\sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_y} < \pi_{2p_x} \equiv \pi_{2p_z} < \pi^*_{2p_x} \equiv \pi^*_{2p_z} < \sigma^*_{2p_y} \qquad (3)$$

In the case of light elements from period 2, including C, for the E_2 molecules, the energy of molecular level is as follows:

$$\sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x} \equiv \pi_{2p_z} < \sigma_{2p_y} < \pi^*_{2p_x} \equiv \pi^*_{2p_z} < \sigma^*_{2p_y} \qquad (4)$$

The difference between the relations (3) and (4) is due to interelectronic rejections of the clouds with the same symmetry.

In inorganic and organic compounds with polycentric π bonds, electrons from delocalized π orbitals are extending on all the atoms that form the molecule, thus increasing its stability (Marcu et al, 1984). In order to calculate bond order (p_{pq} or π_{pq}) between *p* and *q* atoms of such molecules, theHückel MOM theory can be used (Pullman& Pullman, 1963).

For the elements with low electronegativity ($X_E < 2.1$) MOM considers the metallic bond as a covalent one strongly delocalized in the field of all nuclei. Bonding and antibonding MO being degenerated, they are merged in energy bands (Chiriac et al, 2003).

In the case of metals from main groups, which have in the valence shell 4 AO (1 AO type *s* and 3 AO type *p*), for *n* atoms from *4n* AO, *4n* MO are formed: *2n* bonding MO and *2n* antibonding MO.

In the case of transition metals, favourable orbitals to form metallic bonds are those of *s* type from the valence shell and the *5(n-1)d* orbitals that have energy close by the one of *ns* orbitals. Thus from the six AO of a number of *n* atoms *3n* bonding MO and 3 antibonding MO are formed (Notario, 2016). The strength of metallic bond depends on the degree of occupancy of bonding MO, which constitute valence band (V.B) of energy band. The electron pairs from the valence shell of metal represent bonding band from V.B, the rest of molecular levels of energy band being a conduction band. A higher metal bond order conducts to an augmented hardness, but the thermal and electric conductivity of the metal are lower(Notario, 2016).

The bond order between two atoms of a molecule or molecular ion is equal with half of the difference between the number of electrons (*n*) from bonding MO and the number of electrons (*n**) from antibonding MO (Chiriac et al, 2003).

We consider in this study 13 molecular species (diatomic molecules, derivative molecular cations and anions) of the elements from the first two periods and correlate their electronic configurations and the calculated bond order withthe diamagnetic and paramagnetic character.The strength of the corresponding homonuclear bonds and the stability of those compounds can be explained and also correlated with the internuclear distances, from the literature data (Rioux, 2001). We have also considered 10 heteronuclear bonds (Chiriacet al, 2003) and calculated the electrical dipole moments (μ) and the contribution coefficients (c_A, c_B) of the wave functions (ψ_A, ψ_B) to the wave functions of σ bonding MO and σ* antibonding MO. Furthermore, bond orders (b.o.) of the 14 metals from 4th period were calculated by dividing the number of electron pairs of the atomswithin the metal to the number of bonding MO of the system.The obtained results are used to interprettheir physical and mechanical properties.

As organic compounds with polycentric π bonds, aniline diazonium salts, p-dimethylaminoaniline and 2-naphtylamine were considered in this study. The calculations being made only for theπ electrons systems of the molecules (π

approximation), bond orders (p_{qp} or π_{qp}) correspond to the requests of the HMO method.Consequently, to compute the secular determinant of these compounds, the computational technique has been considered, using Streitwieserparameters (Streitwieser, 1961).

Employing the Hückel matrices, the eigenvectors, the π levels of energy ($\varepsilon_i=\alpha + \lambda_i \cdot \beta$) of the molecular orbitals, the coefficients of the atomic orbitals' contributions to them, the bond orders (p_{qp}) (equation 5) and the free valence indices (F_q) (equation 6) have been calculated (Isac et al, 1981 a). In assessing the energy (ε_i) of molecular orbitals (hence of their electrons) the following forms of energy are considered (Simon, 1973):

- α energy, representing the energy of the electron placed on a p orbital of an isolated sp^2 carbon;
- β energy, representing the energy of the electron in the vicinity of two sp^2 hybridized carbons placed at the appropriate distance and orientation (that enable the overlap of their orbitals) to form a π bond;

The relation used to calculate the reactivity index between atoms p and q is:

$$p_{qp} = \sum_i n_i \cdot c_{iq} \cdot c_{ip} \qquad (5)$$

where c_{iq} and c_{ip} are contribution coefficients of ψ_{AO} at ψ_{MO}, the sum index i going through all atomic orbitals (Coulson, 1947). For stable molecules, MO are occupied with 2 electrons (n_i=2) till a certain energy and the superior MOs are free (n_i=0). For radicals, the highest occupied MO (HOMO) has one electron (n_i=1) (Simon, 1973).

One measure of the reaction capacity of some positions within a molecule in radical and ionic mechanisms is the free valence index of the atom q (F_q) (Coulson, 1947).The p_{qp}values obtained from the HMO computation usedto find this structural index using the relation

$$F_q = 1{,}732 - \sum_{p\ vecini} p_{qp} \qquad (6)$$

The concepts specific to the field of structural physical chemistry presented here are used to illustrate the correlation of some structural indexes calculated by MOM with the properties of some di- and polyatomic compounds with homonuclear and heteronuclear bonds. In this regard, we expect that the increase of the bond order will result in a shorter bond, a higher dissociation energy and a displacement toward smaller wavelengths of the corresponding bands in the vibration spectra (Simon, 1973)

Results and Discussion

The calculations of the sequences of molecular orbitals, of their occupation with electrons and of the corresponding bond orders for the homonuclear and derivative molecular ions are revealed in Table 1.

Table 1. The sequence of the molecular orbitals, their occupation with electrons and bond order for diatomic molecules, molecular cations and anions, of the elements from the first two periods

Molecular species	Electronic configuration of molecules	Bond order $\frac{n-n^*}{2}$
H_2	σ_{1s}^{2}	$\frac{1}{2}(2\text{-}0)=1$
H_2^+	σ_{1s}^{1}	$\frac{1}{2}(1\text{-}0)=\frac{1}{2}$
H_2^-	$\sigma_{1s}^{2}\sigma_{1s}^{*1}$	$\frac{1}{2}(2\text{-}1)=\frac{1}{2}$
He_2^+	$\sigma_{1s}^{2}\sigma_{1s}^{*1}$	$\frac{1}{2}(2\text{-}1)=\frac{1}{2}$
Li_2	σ_{2s}^{2}	$\frac{1}{2}(2\text{-}0)=1$
B_2	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\pi_{2p_x}^{1}\pi_{2p_z}^{1}$	$\frac{1}{2}(4\text{-}2)=1$
C_2	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\pi_{2p_x}^{2}\pi_{2p_z}^{2}$	$\frac{1}{2}(6\text{-}2)=2$
C_2^{2-}	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\pi_{2p_x}^{2}\pi_{2p_z}^{2}\sigma_{2p_y}^{2}$	$\frac{1}{2}(8\text{-}2)=3$
N_2	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\sigma_{2p_y}^{2}\pi_{2p_x}^{2}\pi_{2p_z}^{2}$	$\frac{1}{2}(8\text{-}2)=3$
O_2	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\sigma_{2p_y}^{2}\pi_{2p_x}^{2}\pi_{2p_z}^{2}\pi_{2p_x}^{*1}\pi_{2p_z}^{*1}$	$\frac{1}{2}(8\text{-}4)=2$
O_2^-	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\sigma_{2p_y}^{2}\pi_{2p_x}^{2}\pi_{2p_z}^{2}\pi_{2p_x}^{*2}\pi_{2p_z}^{*1}$	$\frac{1}{2}(8\text{-}5)=1.5$
O_2^{2-}	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\sigma_{2p_y}^{2}\pi_{2p_x}^{2}\pi_{2p_z}^{2}\pi_{2p_x}^{*2}\pi_{2p_z}^{*2}$	$\frac{1}{2}(8\text{-}6)=1$
F_2	$\sigma_{2s}^{2}\sigma_{2s}^{*2}\sigma_{2p_y}^{2}\pi_{2p_x}^{2}\pi_{2p_z}^{2}\pi_{2p_x}^{*2}\pi_{2p_z}^{*2}$	$\frac{1}{2}(8\text{-}6)=1$

Following correlations are resulting from data presented in Table 1:

- From the exemplified molecular configurations for σhomonuclearbonds result that the distribution of the electrons in MO follow the same rules as in the case of occupation of the electronic shell of the atom (the building up principle, the Pauli exclusion principle and the Hund's first rule);

- Electronic distributions of paramagnetic molecules ($H_2^+, H_2^-, He_2^+, B_2, O_2, O_2^-$) contain uncoupled electrons, while in diamagnetic compounds ($H_2, Li_2, C_2, C_2^-, N_2, O_2^{2-}, F_2$) only electron pairs exist;
- In gaseous phase, lithium exist as diatomic molecule (Li_2), in which atoms are bound by a bicentric σ bond, as in H_2 molecule;
- H_2^+şiH_2^- ions obtained by electrical discharges into rarefied hydrogen have the same bond order (1/2). In the cation molecule, density of bonding electronic cloud corresponds to one electron. In the anion molecule, the 3rd electron is in an antibonding orbital and,consequently, the binding effect of an electron from the molecular bonding orbital is cancelled;
- The internuclear distance (r_{AB})is $1.06\cdot10^{-10}$ m both in H_2^+ and in H_2^-.This distance is is higher compared to that observed in H_2 ($0.74\cdot10^{-10}$ m), thus the bonds of molecular ions are weaker.An H_2^{2-} anion molecule can't exist (b.o.=0) because the bonding effect of the two electrons from bonding orbital is cancelled by the two electrons from antibonding orbital. As a result the molecule breaks into two anions hydride;
- The decrease of bonding order from O_2 (2), O_2^- (1.5), O_2^{2-} (1) is correlated with an increase of the length of the covalent bond O_2 ($1.21\cdot10^{-10}$ m), O_2^- ($1.26\cdot10^{-10}$ m), O_2^{2-} ($1.49\cdot10^{-10}$ m). An O_2^+cation molecule (b.o.=2.5 and $r_{AB}=1.12\cdot10^{-10}$ m), more stable than the O_2 molecule, was observed only in electrical discharges into rarefied oxygen and not in binary combinations (Marcu et al, 1984).

Applying the relations (1) and (2) to the 10 σ bicentricheteronuclear bonds under consideration lead to the results presented in Table 2.

Table 2. Dipole moments (μ) and contribution coefficients (c_A, c_B) of the atomic wave function to the molecular wave functions (bonding MO and antibonding MO) of 10 heteronuclear bonds

Bond A-B	$(\bar{X}_B-\bar{X}_A)$ (Pauling)	i (%)	$\bar{r}$ ($\cdot10^{10}$ m)	μ ($\cdot10^{30}$ C· m)	Bonding MO		Antibonding MO	
					c_A	c_B	c_A	c_B
(01) H-O	1.40	39	0.974	6.08	0.30	0.70	0.70	0.30
(02) H-N	0.90	19	1.04	3.16	0.41	0.59	0.59	0.41
(03) -C	0.40	4	1.14	0.72	0.48	0.52	0.52	0.48
(04) e-O	1.70	51	1.84	15.01	0.24	0.76	0.76	0.24
(05) e-S	0.70	12	2.22	4.26	0.44	0.56	0.56	0.44
(06) l-C	1.00	22	1.86	6.55	0.39	0.61	0.61	0.39

(07) -F	1.50	43	1.36	9.35	0.28	0.72	0.72	0.28
(08) s-F	3.30	96	2.67	41.01	0.02	0.98	0.98	0.02
(09) g-Br	0.90	19	2.59	7.87	0.40	0.60	0.60	0.40
(10) g-I	0.60	9	2.80	4.03	0.45	0.55	0.55	0.45

Quantum-mechanics calculationspresented in the Table 2 lead to the following remarks:

- Bonds (04) and (08) are preponderant ionic ($\Delta\overline{X} \geq 1.7$), have permanent high dipole moments and strong electric polarization effects. The biggest difference of the electronegativity coefficients ($\Delta\overline{X} = 3.3$) is revealed by theCsF complex, but also in this case 4% of the electronic cloud is common.
- Iron bond in oxide (04) has a much more pronounced ionic character than the iron bond in sulfide (05), because $\overline{X}_O > \overline{X}_S$;
- The carbon-aluminum (06) and carbon-fluoride bonds (07) are preponderant covalent, but based on the data revealed in Table 2 relations regarding their ionicity can be established: i(C-F) ≅ 2i (C-Al); μ(C-F) ≅ 1.40 μ(C-Al);
- Regarding thebonds made by the C, N and O with hydrogen (bonds (03), (02) and (01)) their ionic character increases in correlation with the increase of$\overline{X}_B$, decrease of r_B and with the polarizability of the second atom in the molecule. Due to the weak ionic character, the bond (03) can be considered as non-polar covalent (standard in establishing + I and – I inductive effects of atoms and groups of atoms);
- The higher polarizability of iodine compared with the one of bromine results in an increase of the weight of the covalent bond from bond (09) to bond (10), both being responsible for the decrease of the solubility in water of the compounds containing them;
- The relationship between the contribution coefficients (c_A, c_B) of AO (calculated according to*i*) in MO formation shows that: AO of the more electronegative atom participates to a greater extent in the formation of the bonding MO, and AO of the less electronegative atom contributes more in formation of antibonding MO.
- The essential characteristics of the σ bonds are rigidity (the interatomic distances remain constants when the aggregation state modifies) and spatial orientation around the nuclei.

The examples with the 4th period metals (emphasized in Table 3), whose research dates back to Antiquity (Cu, Fe, Zn), 18th century (Ti, Cr, Mn, Co, Ni) and 19th century (K, Ca, Ga, Ge, V, Sc), are considered for applying the method of bonding orders in explaining some of their properties (Chiriac et al, 2001). For some of them, the graphical (symbolic) configuration of their metallic structure is included (Figure 1).

Table 3. The electronegativity of the metals of the 4th period of the Periodic Table of Mendeleev, computed using thescale established by Pauling in 1932

Group I		Group II		Group III		Group IV		Group V	Group VI	Group VII	Group VIII
A	B	A	B	A	B	A	B	B	B	B	B
K 0.8	Cu 1.9	Ca 1.0	Zn 1.6	Ga 1.6	Sc 1.3	Ge 1.8	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe Co Ni 1.8 1.8 1.8

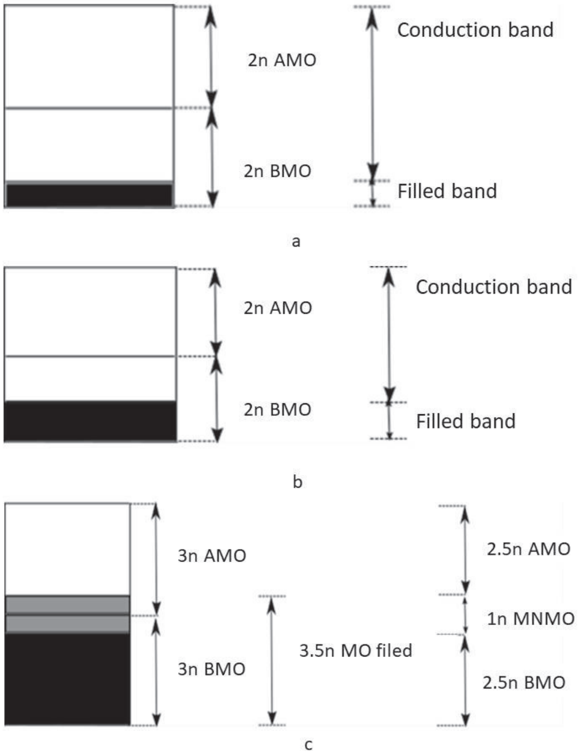


Figure1. The distribution of electrons in the energy band of potassium (a), calcium (b), manganese (c): AMO – antibonding molecular orbital, BMO – bonding molecular orbital, MNMO – monocentric nonbonding molecular orbital.

The hierarchy upon the bond orders of the four metals from the main groups is as follows (A):

$$K\left(\frac{\frac{n}{2}}{2n}\right) < Ca\left(\frac{n}{2n}\right) < Ga\left(\frac{\frac{3n}{2}}{2n}\right) < Ge\left(\frac{2n}{2n}\right) \quad (7)$$

Taking into account equation (7), from K toward Ge, it is noted:

- the bonds between atoms become stronger;
- atomic radii (in Å) decrease in the order

K (1.96) > Ca (1.74) > Ga (1.26) > Ge (1.22) (8)

- electrical and thermal conductivities decrease;
- densities, hardness, melting and boiling temperatures increase.

The bands structures of the metals belonging to the second group (B) of the fourth period can also be correlated with the literature data. Such correlations are illustrated in Table 4.

Table 4. Population with electrons in the fundamental state of the transition metals of the fourth period

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electrons 3d	d^1	d^2	d^3	d^5	d^5	d^6	d^7	d^8	D^{10}	d^{10}
Total number of electrons (3d+4s) for an atom	3	4	5	6	7	8	9	10	11	12
Total number of electron pairs for n atoms	$\frac{3n}{2}$	2n	$\frac{5n}{2}$	3n	$\frac{7n}{2}$	4n	$\frac{9n}{2}$	5n	$\frac{11n}{2}$	6n
Bond order	$\frac{\frac{3n}{2}}{3n}=$	$\frac{2n}{3n}=$	$\frac{\frac{5n}{2}}{3n}=$	$\frac{3n}{3n}=1$	$\frac{\frac{5n}{2}}{3n}=$	$\frac{2n}{3n}=$	$\frac{\frac{3n}{2}}{3n}=\frac{1}{2}$	$\frac{n}{3n}=\frac{1}{3}$	$\frac{\frac{n}{2}}{3n}=\frac{1}{6}$	$\frac{n}{2n}=$
Number of electron pairs localized in non-bonding monocentric MO	-	-	-	-	n	2n	3n	4n	5n	5n
Number of electron pairs available for delocalization	$\frac{3n}{2}$	2n	$\frac{5n}{2}$	3n	$\frac{5n}{2}$	2n	$\frac{3n}{2}$	n	$\frac{n}{2}$	n

Taking into account the date presented in Table 4, the following points can be made:

- As the number of valence electrons of the metal increases, the electrons occupy a larger region of V.B;
- The binding order increases from the elements in the group III B (b.o.= 0.5) to those of group VI B, where it reaches the unit value;
- From the element of group VII B, the electrons also occupy the molecular antibonding orbitals of the energetic band. In this way, monocentric nonbinding molecular orbitals occur and are localized at the atomic cores placed in the nodes of the network. It is considered that the non-bonding electrons occupy the *np*vacant level, so that the energetic bandwidth does not change as long as the orbitals*d* arein the process of being occupied;

•The binding order between the manganese atoms is lower than that between the chromium atoms and decreases further with increasing the order number of element from the 3d series;

•For the elements belonging to groups I B and II B, the complete occupation of the orbital *3d* determines their stabilization. They become non-binding monocentric orbitals, located at the atomic cores. The energy band changes its structure, its "width" becomes *4n*, just as for the metals from the *block s*.

•The metals in the series: Sc, Co, Zn; Ti, Fe; V, Mn have the same binding orders.

In support of exemplifying by correlation some properties, we present (Macarovici, 1972):

•For vanadium and manganese:
- atomic radii V (1.34 Å), Mn (1.26 Å);
- densities V (6.1 g cm^{-3}), Mn (7.43 g cm^{-3});
- Brinell hardness V (264 kg mm^{-2}), Mn (210 kg mm^{-2});
- melting points V (1715 °C), Mn (1247 °C).

•For copper and iron to 0°C:
- specific electrical resistance ($\rho \cdot 10^6\ \Omega$) – Cu (1.692), Fe (8.8);
- thermal conductivity (cal.cm^{-1} s^{-1} $grad^{-1}$) – Cu (0.94), Fe (0.21).

For the metals, in MOM theory, the energy bands appear as a consequence of interactions of a very large number of particles placed in the nodes of crystalline network. The band width and the bond order are higher as the interaction between the particles is stronger. If this interaction is rather weak, there are not conduction bands.

By applying the algorithm to establish the polycentric molecule structure, for the three diazonium salts considered within this study, the data from Table 5 were obtained.

Table 5. The structures in conformity with MOM for the benzendiazonium cation (I), the p-dimethylaminobenzenediazoniummonocation (II) and the 2-naphthalene diazonium cation (III)

Compound	AO	MO	Number of electron pairs	antibonding MO		bonding MO		nonbonding monocentric MO
				σ*	π*	σ	π	
$\left.C_6H_5\text{—}N_2\right]^+$ (I)	37	37	19	13	5	13	5	1
$\left.(H_3C)_2N\text{—}C_6H_5\text{—}N_2\right]^+$ (II)	54	54	28	21	5	21	5	2
$\left.C_{10}H_7\text{—}N_2\right]^+$ (III)	55	55	28	20	7	20	7	1

The values obtained from the calculation for the binding orders (Figure 2) are correlated with the structure of these cations in terms of the simple, double and triple bond between atoms. Also, researches concerning their thermal and photochemical stability motivate their use in coupling reactions.

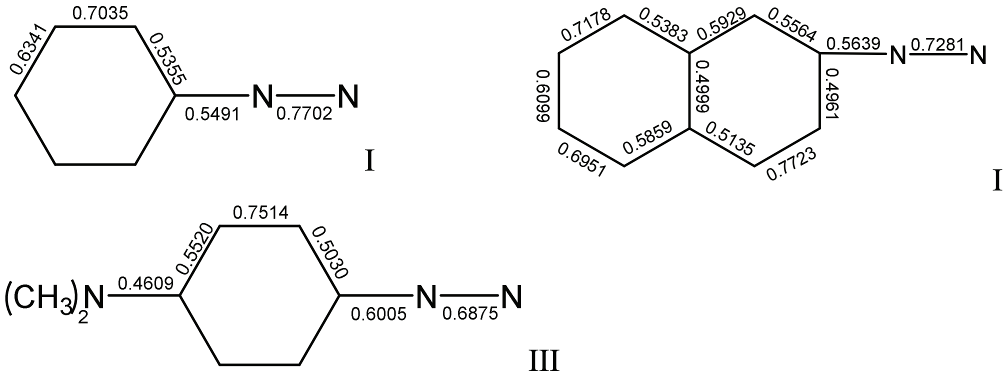
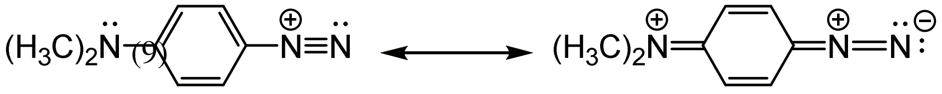


Figure 2. The bonding orders p_{qp} (the number near valences in the pictures) for the two mononuclear diazonium cations (I, II) and the polynuclear (III) cation.

Experimentally, it is found that, at room temperature, the thermal stability of compound II is relatively high (Isac et al, 1981 b). It is assumed that this stabilization is due to the resonance, which determines the increase of the order of the C-N bond (Barraclough, 1972).



Under these conditions, the photochemical effects on this diazonium salt can be easily distinguished, with applicability in the process of photocopying (diazotism). (Lee, 1961) The photo-reactivity of the compound II is due to its more extended conjugate system that displaces the maximum of absorption toward red, i.e. toward visible domain.

For compounds I and III, experimental literature data (Simon, 1967)correlated with the REPE index (Matito, 2007), *i.e.* the resonance energy (β) relative to the n_π delocalized electrons, sets the two diazonium salts upon stability in the relationship:

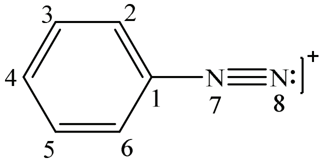
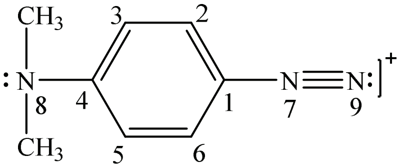
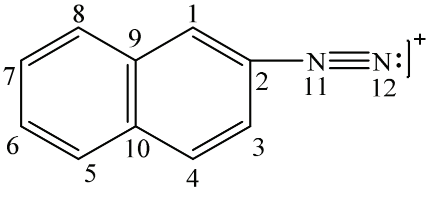
benzendiazonium cation (0.6392)>2-naphthylindiazonium cation (0.4280) (10)

Particularization on the construction of the Woodward Hoffmann molecular correlation diagram for the decomposition of compound I has used the HMO method of molecular orbitals (Isac et al, 1985). Correlations with literature data may be as follows:

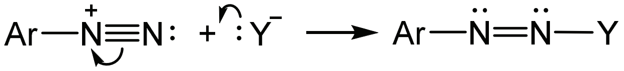
•The reaction allowed thermally and photochemically, with the purely thermodynamic activation energy (E_a=27.1 kcal mol^{-1}) without a barrier itself is explained by the higher stability of the diazonium cation by comparison to thatof the decomposition products. (De Tar, 1956)
•The pre-exponential coefficient ($A=5.10^{15}\ s^{-1}$) is increased because, when the C-N bond is broken, in the activated complex, the interaction of electrons of the diazonium group, especially of π electrons, with those of the remaining molecule will be weakened or even cancelled. (Simon&Bădilescu, 1967)

Using the values of the binding orders (Figure 2), we have computed the free valence indices (equation 6) of the atoms in the three investigated diazonium salts and resulting data are revealed in Table 6. Data in Table 6 reveal that the valence indices follow $F_N > F_C$ relationship, being in good agreement with the known electronegativity tendency (Putz, 2006). These diazonium cations are not strong electrophilic reactants due to the delocalization of their positive charges. The azo coupling of these compounds may occur only with strong nucleophiles (:Y^-) (Rys, 1996).

Table 6. The valence indices (Fq), calculated using the HMO method for the atoms of the conjugated systems I, II, III, with n_π delocalized electrons.

Molecule	n_π	F_q	
 (I)	8	$F_1 = 0.1119$ $F_2 = F_6 = 0.4930$ $F_3 = F_5 = 0.3944$	$F_4 = 0.4638$ $F_7 = 0.4127$ $F_8 = 0.9618$
 (II)	10	$F_1 = 0.1255$ $F_2 = F_6 = 0.4776$ $F_3 = F_5 = 0.4286$ $F_4 = 0.1671$	$F_7 = 0.4640$ $F_8 = 1.2711$ $F_9 = 1.0645$
 (III)	12	$F_1 = 0.5827$ $F_2 = 0.1156$ $F_3 = 0.4636$ $F_4 = 0.4452$ $F_5 = 0.4510$ $F_6 = 0.4270$	$F_7 = 0.4043$ $F_8 = 0.4759$ $F_9 = 0.1009$ $F_{10} = 0.1327$ $F_{11} = 0.4400$ $F_{12} = 1.0039$

As Lewis acids, cations I, II, III may participate in acid-base organic chemical reactions, demonstrating the ability to form covalent bonds between the marginal nitrogen (with high F_N) and nucleophilic agents (bases) (Isac et al, 2017). The generalization given by the chemical equation



$$Ar-\overset{+}{N}\equiv N: + :Y^{-} \longrightarrow Ar-\ddot{N}=\ddot{N}-Y$$

(11)

illustrates their character of oxidizing agents. In this respect, by referring to the energy index of the lowest MO free (ε_{LUMO}), it indicates the facility with which the molecule is reduced (Simon, 1973).

Based on the results obtained by the HMO method, the arrangement of the three cations after ε_{LUMO} is the following

$$\text{I}\ (\alpha + 0.1786\beta) < \text{III}\ (\alpha + 0.1685\beta) < \text{II}\ (\alpha + 0.1111\beta) \qquad (12)$$

As a consequence of the correlation between the chemical structures and practical applications, we give as example the use of cation I as the oxidizing agent for sodium bisulphite in the synthesis of arylhydrazine (Avram, 1995).

Conclusions

The information presented within this paper illustrates the role of science education theories and tools for the teaching and active learning of structural physical chemistry. We have selected a few examplesof student-centred exercises that may be used to emphasize the usefulness of the concepts specific to the field of structural physical chemistry for correlating the structural indices calculated by applying the MOM with the physicochemical properties and practical applications of 37 diatomic with homonuclear and heteronuclear bonds (both non-metals and metals) and 3 polyatomic compounds. The chosen examples illustrate the applicability of the problem solving method in teaching and learning structural physical chemistry. The teaching and learning task are to be successively solved (the degree of difficulty increases from one meeting to the other) by small groups of about 3–4 people with aid from teacher within 4 weeks and solutions are argued at the end of the meeting by every group. The discussions between the groups of students and the given arguments, give to the teacher the opportunity to notice the aspects of the student reasoning and to improve feedback quality. We expect an increase in students' motivation and understanding of the concepts of structural physical chemistry as a result of applying this strategy.

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