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Indazole, Pyrrole and 2-Pyrone Compounds as Corrosion Inhibitors for Mild Steel in Acidic Medium: DFT Analysis

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Abstract

In the present work we used density functional theory (DFT) with B3LYP/6-31G to study the reaction 6-Methyl-3-[1-(2-methyl-2H-indazol-6-ylamino)-ethylidene]-pyran-2,4-dione (R1), 3-[1-(2-Allyl-2H-indazol-6-ylamino)-ethylidene]-6-methyl-pyran-2,4-dione (R2) and 6-(2,5-Dimethyl-pyrrol-1-yl)-2-ethyl-2H-indazole (R3) were synthesized and examined as corrosion inhibitors for mild steel in 1.0 M HCl. It is noticed that R1 as more effective inhibitor than R3, this last as more effective inhibitor than R2. The theoretical calculation validate that these compounds can suck up on the mild steel surface by distributing the separate pair electrons of the hetero-atoms with iron atoms or by admitting electrons from the iron surfaces. The presence of the pyrrole group is assumed to be responsible for the elevated inhibition efficiency of R1. Determining the energies of the frontier molecular orbitals, chemical potentials, transfer charge quantities, and electrophilicity and nucleophilicity indices. We used the same method to calculate ionisation potentials, electronic affinities, hardness, softness, electrophilic Parr functions and the nucleophilic Parr.

Keywords: corrosion inhibitor, mild stee, DFT, electrophilic Parr, nucleophilic Parr, indazol.

1. Introduction

The investigation of corrosion inhibition of mild steel via organic inhibitors typically in acidic media is one of the most essential themes of modern study in diverse industries (van der Geer et al., 2010; Singh et al., 2014; Chafaa et al., 2014). In general inhibitors are used in these procedures to control the metal dissolutions. Hydrochloric acid is extensively used in the preserving of steel and different alloys. Most popular inhibitors are organic compound containing N, S, and O atoms. Organic compound containing functional electronegative groups and π electrons in triple or conjugated double bonds are usually good inhibitors (Rochdi et al., 2014; Sastri et al., 1998; Lagrenée et al., 2002; Florio et al., 2004; Zarrok et al., 2012). These organic inhibitors are usually adsorbed on the metal surface via formation of a coordinate covalent bond (chemical adsorption) or the electrostatic interaction between the metal and inhibitor (physical adsorption) (Traisnel et al., 2013; Goulart et al., 2013).

In this work, the corrosion inhibition efficiency of three novel organic compounds (El Ghozlani et al., 2016), 6-Methyl-3-[1-(2-methyl-2H-indazol-6-ylamino)-ethylidene]-pyran-2,4-dione (R1), 3-[1-(2-Allyl-2H-indazol-6-ylamino)-ethylidene]-6-methyl-pyran-2,4-dione (R2),

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6-(2,5-Dimethyl-pyrrol-1-yl)-2-ethyl-2H-indazole (R3) (Figure 1) on mild steel in 1M hydrochloric acid solution was studied using potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and atomic force microscope AFM. Effects of inhibitors concentration and temperature on inhibition action were investigated.



Fig. 1. Structures of R1, R2 and R3

2. Results Theoretical computation Computational method

DFT calculationwere carried out using the B3LYP functional (Yanai et al., 2004), together with the standard 6-31(d) basis set (Francl et al., 1982). The optimizations have been realized using the Berny analytical gradient. All computations have been shown with the Gaussian 09 suite of programs (Frisch et al., 1982). The global electrophilicity index (Liu et al., 1999) ω , μ and η , were given by the following expressions $\omega = \frac{\mu^2}{2\eta}$, $\mu = \frac{\epsilon_H + \epsilon_L}{2}$ and $\eta = \epsilon_L - \epsilon_H$, in terms of the electronic chemical potential μ and the chemical hardness η . Both quantities could be approached in terms of the one-electron energies of the frontier molecular orbital HOMO and LUMO, ϵ_H and ϵ_L , respectively.

Conceptual DFT essentially relies on the fact that the ground state energy of an N-electron system as given by the Hohenberg-Kohn theorem can be considered as depending upon the number of electrons N and the external potential v(r), which are themselves determined solely by the density, in other words $E[\rho_{(r)}] = E[N;v(r)]$. In this context, the responses of the system to changes of the number of its electrons, of the external potential or of both, provide information about its reactivity.

The E[N ;v(r)] derivatives with respect to N and v(r) constitute a first series of reactivity indicators, the electronic chemical potential μ , which is the opposite of the electronegativity χ , the chemical hardness , the Parr function P(r) and the two variables linear response function χ (r,r'), as shown in the diagram given in (Figure 2).



Fig. 2. First and second derivatives of E[N;v(r)] with respect to N and v(r)

Analysis of DFT reactivity indices of the reactants R1, R2 and R3

Quantum chemical calculations were conducted to understand the mechanism of inhibition of R1, R2 and R3 for mild steel in 303 K corrosion media. In particular, optimized geometric structures, electrostatic surface potential and frontier molecular orbital of R1, R2 and R3, including HOMO and LUMO electron density distributions for R1, R2 and R3 have been shown as (Figure 3). Then, the other parameters relating to quantum chemical calculation have been shown in (Table 1).



Fig.3. 3D representations of the frontier molecular orbital HOMO, LUMO and the electrostatic potential map of the three molecules

Table 1. Quantum chemical parameters for R1, R2 and R3 obtained in gaseous phase using the DFT at the B3LYP/6-31G level

Parameter	R1	R2	R3
EHOMO (eV)	-4.86374	-5.716277	-5.737774
ELUMO (eV)	-1.062396	-1.587062	-1.597403
Gap ΔE (eV)	3.801352	4.129215	4.140371
Dipole moment (µin Debye)	5.156800	5.694000	5.492600
Ionization potential (I in eV)	4.863748	5.716277	5.737774
Electron affinity (A)	1.062396	1.587062	1.597403
Electronegativity (χ)	2.963072	3.651669	3.667585
Hardness (ŋ)	3.801352	4.129215	4.140371
Electrophilicity index (ω)	1.154825	1.614676	1.624396
Fractions of electron transferred (ΔN)	0.779478	0.884349	0.885811

The highest occupied molecular orbital value, E_{HOMO} , of the three inhibitors R1, R2 and R3 are, -4.863748, -5.716277 and -5.737774 respectively, show that the tendency of inhibitors R1 to donate electrons through to the acceptor molecule with an empty, the energy orbital. E_{LUMO} of the three inhibitors R1, R2 and R3 are -1.062396, -1.587062 and -1.597403 indicates the tendency of the molecule R1 to accept electrons.

The tendency being often that the lower E_{LUMO} is the largest; the ability of these molecules to accept electrons is greater. The energy gap ΔE is an important parameter related to the reactivity of

the inhibitor molecule about the metal surface. The energy gap ΔE of R1, R2 and R3 are, 3.801352, 4.129215 and 4.140371 respectively, a high ΔE of the inhibitor R2 and R3 are associated with a lower tendency to reactivity, whereas a weak ΔE of the molecule R1 indicates a strong tendency to reactivity.

We note from (Figure 4) that the HOMO orbital and the LUMO orbital of the R2 and R3 molecules are distributed on the indazole and pyrone groups, in contrary the molecule R1, the HOMO orbital is very localized on the pyrrole group and the LUMO orbital is very localize on the indazole group. The map of the electrostatic potential shows that the pyrone group of the inhibitors R2 and R3 has a red color, which shows that the pyrone group is very negative, conferring the great values of the dipolar moments of these molecules $\mu_2 = 5.694000$ and $\mu_3 = 5.492600$. On the contrary, in the molecule R1, the two pyrrole and indazole groups have a red color, which indicates that these two groups carry electrons, this distribution over the entire molecule abbesses the dipole moment of this molecule $\mu_1 = 5.156800$.

Current studies indicate that the most favorable interaction is one that involves the interaction between the most electrophilic center of the electrophile and the most nucleophilic center of the nucleophile. Newly, Domingo (Domingo et al., 2016) exposed a new approach found on the electrophilic and nucleophilic Parr functions P_k^+ and P_k^- , respectively, which are found from the changes of spin electron-density take place from the nucleophile to the electrophile. This method demonstrates to be a dominant instrument for the study of the local reactivity. The maps of the ASD of these three inhibitors R1, R2 and R3 are given in (Figure 4).



Fig. 4. The ASD of the radical anion and the radical cations as well as the electrophilic Parr functions and the nucleophilic Parr functions of the three inhibitors R1, R2 and R3

The Parr Functions P(r)

In case an amount equivalent to one electron is transferred, the nucleophile becomes a radical cation, while the electrophile becomes a radical anion. Interestingly, analysis of the atomic spin density (ASD) at the radical cation and the radical anion gives a picture of the distribution of the electron density in the electrophile and the nucleophile when they approach each other along the reaction progress.

Based on these observations, in 2014, Domingo proposed the Parr functions P(r) (Chamorro et al., 2013), which are given by the following equations:

 $P^{-}(r) = \rho_{s}^{rc}(r)$ For electrophilic attacks. $P^{-}(r) = \rho_{s}^{ra}(r)$ For nucleophilic attacks

Each ASD gathered at the different atoms of the cation and the radical anion of a molecule provides the local nucleophilic P_k^- and electrophilic P_k^+ Parr functions of the neutral molecule. The values of nucleophilic Parr functions and the electrophilic Parr functions of these three

inhibitors R1, R2 and R3 are given in (Table 2). (Numbering atoms in (Figure 5)).

Table 2. The values of the electrophilic Parr functions and the nucleophilic Parr functions of the three inhibitors R1, R2 and R3

	Inhibitor R1		Inhibitor R2			Inhibitor I	R 3	
	P -	P +		P -	P +		P -	P +
C1	0.384	0.014	C1	-0.052	0.030	C1	-0.053	0.031
C2	-0.013	0.009	C2	0.270	-0.080	C2	0.276	-0.084
C3	0.156	-0.003	C3	-0.034	0.094	C3	-0.035	0.098
C4	0.293	0.019	C4	0.039	-0.035	C4	0.040	-0.036
N5	-0.068	-0.011	C5	0.028	0.123	C5	0.028	0.129
C8	0.050	0.288	07	-0.002	-0.009	07	-0.002	0.001
C9	-0.020	-0.077	08	0.032	0.068	08	0.032	-0.010
C10	0.013	0.072	09	0.129	0.021	09	0.133	0.071
C11	-0.022	-0.072	C10	-0.001	-0.012	C10	-0.001	-0.012
C12	0.002	-0.011	C14	-0.094	0.306	C14	-0.096	0.316
C13	0.049	0.267	C15	0.006	-0.026	C15	0.006	-0.027
C14	0.079	0.175	N19	0.160	0.011	N19	0.163	0.015
N8	0.091	0.153	C21	0.239	0.200	C21	0.234	0.202
N19	-0.021	0.189	C22	-0.060	-0.043	C22	-0.057	-0.043
C20	0.001	-0.015	C23	0.023	0.033	C23	0.025	0.028
C27	-0.016	0.009	C24	-0.034	-0.012	C24	-0.033	-0.009
C31	-0.024	0.0008	C25	-0.017	-0.032	C25	-0.019	-0.029
			C26	0.087	0.103	C26	0.086	0.097
			C27	0.109	0.041	C27	0.106	0.033
			N31	0.220	0.082	N31	0.211	0.080
			N32	-0.024	0.087	N32	-0.021	0.088
			C34	0.0002	-0.010	C34	-0.0004	-0.009
			37C	-0.001	0.004			
			C38	0.002	0.0000			
		1						



Fig. 5. Numbering atoms of the three inhibitors R1, R2 and R3

The computed values of the P_k^+ for the R1 inhibitor are mostly localized on the indazole ring (Table 2). Specifically the values of the centers C8, C13, C14, N8 and N19 are 0.288, 0.267, 0.175, 0.153 and 0.189 respectively, indicating that the these centers of the indazole ring are very favorite site for nucleophilic attack. The greatest values of the P_k^- for the R1 inhibitorare those carried by the atomsC1 (0.384), C3 (0.156) and C4 (0.293), indicating that these centers of the pyrrole ringare very favorite site for electrophilic attack.

The calculated nucleophilic Parr functions at the reactive sites of the R1 inhibitor, the C2, O9, N19, C21, C27 and N31 centers atoms are the most nucleophile site possessing a 0.270, 0.129, 0.160, 0.239, 0.109 and 0.220 respectively, indicates that totality of the global nucleophilicity of R1 inhibitor is accumulated at the these centers and these sites are very preferred for electrophilic attack. Similarly, the calculated electrophilic Parr functions at the reactive sites of R1 inhibitor reveal that the most electrophilic centers in this species are the C5, C14, C21 and C26 atoms possessing a P_k^+ value of 0.123, 0.306, 0.200 and 0.103 respectively, we can conclude that these centers are very favored for electrophilic attack.

The presence of the methyl group in the molecule 3 decreases the values of the Parr functions in the Indazole ring and increases the values of the functions on the 2-pyronering and the values of the nucleophilic Parr functions grow to be C2 (0.276), O9(0.133), N19(0.163), C21(0.234), C27(0.106) and N31(0.211) and the electrophilic Parr functions become C5 (0.129), C14 (0.316), C21 (0.202) and C26 (0.097), The presence of the methyl group in the molecule 3 decreases inhibition efficiency of this inhibitor.

3. Conclusion

Both R1 and R3 at a concentration more than 0.8 mM can effectively prevent corrosion of mild steel from the acidic medium. In comparison with R2, however, R1 and R3 exhibits higher inhibition efficiency in the concentration range of this study. Although the three compounds can both adsorb on metal surface through the electron donation or acceptance between the hetero-atoms and iron atoms.

4. Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere.

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Clustering in Bismide Semiconductor Alloys

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Abstract

Interest in clustering in GaB^{v} -rich $GaBi_xB^{v}_{1-x}$ ($B^{v} = P$, As) highly lattice mismatched bismide alloys has recently grown. The main drawback associated with clusters is their heterogeneity. To resolve this problem, GaB^{v} -rich $B_xGa_{1-x}Bi_yB^{v}_{1-y}$ ($B^{v} = As$ or P) alloys are proposed. The internal strain energies due to isolated Bi atoms, 1B4Bi and 4B10Bi clusters are calculated. Formation of 1B4Bi and 4B10Bi clusters in $B_xGa_{1-x}Bi_yB^{v}_{1-y}$ decreases the internal strain and bond energies. The clustering conditions were calculated up to 800 °C. 4B10Bi clustering is more favorable than 1B4Bi one. The density of 4B10Bi clusters was obtained by minimization of the free energy. The cluster formation conditions were studied for $x \ge 5 \times 10^{-5}$ and $y \ge 0.5x$. The majority of boron atoms should be in 4B10Bi clusters if $x > 1 \times 10^{-4}$ and y > 4x. The binding energy of a hole bound to Bi tetrahedron in GaP is estimated. The obtained results demonstrate that GaB^{v} -rich $B_xGa_{1-x}Bi_yB^{v}_{1-y}$ alloys are promising semiconductors with 4B10Bi identical clusters.

Keywords: quaternary semiconducting bismuth alloys, nanomaterials, self-assembly, identical clusters.

1. Introduction

 $GaBi_xAs_{1-x}$ highly lattice mismatched bismide alloys are actively studied now (Zhang et al., 2018; Bushell et al., 2018; Valkovskii et al., 2018; Wilson et al., 2018). Such alloys are considered as perspective materials to fabricate a variety of electronic devices. However, high lattice mismatch between the constituent compounds leads to considerable alloy content inhomogeneity. It is a formidable obstacle to expending the use of these alloys.

For the first time, a way to reduce internal strains in $A^{III}B^V$ highly lattice mismatched alloys was described for GaAs-rich B_xGa_{1-x}Sb_yAs_{1-y} (Elyukhin, 2009). In such alloys the formation of 1B4Sb tetrahedral clusters with boron atoms in their centers is thermodynamically favorable. Boron and Sb atoms are smaller and larger than Ga and As atoms, respectively. Therefore, the presence of 1B4Sb clusters significantly reduces the internal strains. Further, the 4B10Sb cluster formation in GaAs-rich B_xGa_{1-x}Sb_yAs_{1-y} was also described (Elyukhin, 2011). 4B10Sb clusters are boron tetrahedrons surrounded by Sb atoms. The formation of them decreases internal strains more than that of 1B4Sb clusters. The internal strains also considerably decrease after an occurrence of 1B4Bi and 4B10Bi clusters in InAs-rich B_xIn_{1-x}Bi_yAs_{1-y} alloys (Elyukhin, 2018). GaB^vrich B_xGa_{1-x}Bi_yB^v_{1-y} (B^v = P, As) belong to the same class of alloys just as B_xGa_{1-x}Sb_yAs_{1-y} and B_xIn_{1-x} RBi_yAs_{1-y}. 1B4Bi and 4B10Bi clustering in GaB^v-rich B_xGa_{1-x}Bi_yB^v_{1-y} should also decrease the internal

* Corresponding author E-mail addresses: elyukhin@cinvestav.mx (V.A. Elyukhin) strains since boron and Bi atoms are, accordingly, smaller and larger than Ga and As (P) atoms. Therefore, 1B4Bi and 4B10Bi clustering in GaB^{V} -rich $B_xGa_{1-x}Bi_yB^{V}_{1-y}$ alloys seems highly probable.

It has long been known that isolated Bi atoms produce the localized states in GaP:Bi (Trumbore et al., 1966). The binding energy of holes bound to isolated Bi atoms in GaP:Bi is 0.04 eV (Phillips, 1969). However, the localized states formed by bismuth pairs in GaP:Bi were not observed (Christian et al., 2015). It is consistent with the theoretical results (Shen et al., 1990). The authors (Shen et al., 1990) demonstrated that different Bi pairs cannot form the localized states in the band gap of GaP due to the significant internal strains. But the estimates in (Shen et al., 1990) do not exclude the formation of the localized states caused by the larger isoelectronic impurity clusters reducing the internal strains in $B_xGa_{1-x}Bi_yP_{1-y}$. Therefore, the study of 1B4Bi and 4B10Bi clustering in GaP-rich $B_xGa_{1-x}Bi_yB^{V}_{1-y}$ would be important. The 1B4Bi and 4B10Bi clustering conditions in GaAs-rich $B_xGa_{1-x}Bi_yAs_{1-y}$ and GaP-rich $B_xGa_{1-x}Bi_yP_{1-y}$ alloys are considered here.

2. Theory

The internal strain energy of $B_xGa_{1-x}Bi_yB^{V_{1-y}}$ is presented as a sum of the internal strain energies due to boron and Bi isolated atoms and 1B4Bi, 4B10Bi clusters shown, accordingly, in Figures 1 and 2.



Fig. 1. 1B4Bi cluster in the GaB^V-rich matrix



Fig. 2. 4B10Bi cluster

The internal strain energies caused by isolated boron atoms in GaAs and GaP are available (Elyukhin, 2009a; Elyukhin, 2009b). The internal strain energies due to Bi isolated atoms and clusters of both types are the sums of two terms. The first term is the energies caused by the distortions of bonds and angles between bonds formed Bi atoms or clusters. This part is described

by using the valence force field model (Martin, 1970). The bond stretching and bond bending elastic constants of BBi and GaBi were taken from (Elyukhin, 2018; Elyukhin, 2019). The second terms of the sums are the deformation energies of GaB^V- rich matrix. The internal strain energies due to isolated Bi atoms, 4B10Bi and 1B4Bi clusters are equal, respectively, to $u_{Bi} = 29.29$ kJmol⁻¹, $u_{4B10Bi} = 254.88$ kJmol⁻¹ and $u_{1B4Bi} = 119.41$ kJmol⁻¹ in GaAs-rich alloys and $u_{Bi} = 51.19$ kJmol⁻¹, $u_{4B10Bi} = 587.53$ kJmol⁻¹ and $u_{1B4Bi} = 230.62 \times 10^5$ kJmol⁻¹ in GaP-rich alloys. All these deformation energies were obtained by the minimization method. The strain energies due to 4B10Bi and 1B4Bi clusters demonstrate a tendency to the formation of these clusters. In addition, the 4B10Bi cluster formation decreases the strain energy much more. It is due to the fact that only 2 bond/atom formed by boron or Bi atoms or both of them are in 4B10Bi clusters, but in 1B4Bi clusters there are 3.2 bond/atom. The formation of polyatomic boron or Bi clusters in GaB^V-rich alloys is improbable due to the high lattice mismatch of boron and Bi atoms. An occurrence of other boron and Bi clusters is also unlikely as it should lead to the larger internal strains than that of 1B4Bi and 4B10Bi clusters in the alloys with the same composition.

4B10Bi and 1B4Bi clustering is presented by 4B10Bi cluster order parameter α (4B10Bi COP) and 1B4Bi cluster order parameter β (1B4Bi COP). These parameters are the ratios between numbers of boron atoms in 4B10Bi and 1B4Bi clusters and total number of boron atoms, correspondingly. The alloys are considered in the boron and Bi dilute limits. In such a case, boron and Bi atoms are isolated in the alloys before clustering (disordered alloys). The internal strain energies of $B_xGa_{1-x}Bi_yB^{V_{1-y}}$ with clusters (cluster ordered alloy) and disordered alloy are, respectively,

$$u^{O(IS)} = u_{\rm B} x + u_{\rm Bi} y + (0.25u_{\rm 4B10Bi} - u_{\rm B} - 2.5u_{\rm Bi}) \alpha x + (u_{\rm 1B4Bi} - u_{\rm B} - 4u_{\rm Bi}) \beta x,$$
$$u^{D(IS)} = u_{\rm B} x + u_{\rm Bi} y,$$

where u_{B} , u_{Bi} , u_{4B10Bi} and u_{1B4Bi} are the strain energies due to isolated boron and Bi atoms and clusters of both types.

The 4B10Bi and 1B4Bi cluster formation in the disordered alloy decreases the entropy and it is favorable if the free energy of the disordered alloy reduces after an occurrence of the clusters. The entropies of the alloys with and without clusters, respectively, are

$$s^{O} = -RT(1-\alpha)x\ln(1-\alpha)x/(1-\alpha x) - RT(1-x)\ln(1-x)/(1-\alpha x)$$

- $RT(y-2.5\alpha x - 4\beta x)\ln\frac{y-2.5\alpha x - 4\beta x}{1-2.5\alpha x - 4\beta x} - RT(1-y)\ln\frac{1-y}{1-2.5\alpha x - 4\beta x}$
- $0.1RT\alpha x\ln 1.35\alpha x - RT(0.074 - 0.1\alpha x)\ln(1-1.35\alpha x)$
- $RT(1-\alpha-\beta)x\ln(1-\alpha-\beta)/(1-\alpha) - RT\beta x\ln \beta/(1-\alpha),$
 $s^{D} = -R[x\ln x + (1-x)\ln(1-x) + y\ln y + (1-y)\ln(1-y)].$

The entropy of the alloy with clusters is presented as a function of a number of atomic configurations. This number is a product of two factors. The first factor is a number of permutations of atoms when isolated boron and Bi atoms as well as 1B4Bi clusters are distributed randomly at a fixed location of 4B10Bi clusters. The second multiplayer is a number of the arrangements of 4B10Bi clusters. Such entropy corresponds to the alloys with the boron and Bi in the dilute limits. The entropy of the disordered alloy describes the random alloy.

 $B_xGa_{1-x}Bi_yB^{V}_{1-y}$ are alloys with B-Bi, B- B^{V} , Ga-Bi and Ga- B^{V} chemical bonds. The cluster formation leads to transformation of B- B^{V} and Ga-Bi bonds into B-Bi and Ga- B^{V} ones. This transformation may change the bond energy of the alloy. The bond energies of the cluster ordered and disordered alloys are, respectively,

$$u^{O(B)} = \Delta h_{B^{\vee}} (\alpha + \beta)(1 - y)x + \Delta h_{B^{\vee}} xy + h_{GaB^{\vee}} + (h_{BB^{\vee}} - h_{GaB^{\vee}})x + (h_{GaBi} - h_{GaB^{\vee}})y,$$

$$u^{D(B)} = h_{BBi} xy + h_{BB^{\vee}} x(1 - y) + h_{GaBi} (1 - x)y + h_{GaB^{\vee}} (1 - x)(1 - y),$$

where $\Delta h_{B^{\vee}} = h_{BBi} + h_{GaB^{\vee}} - h_{BB^{\vee}} - h_{GaBi}$ and $h_{GaB^{\vee}}$ is the enthalpy of GaB^{\vee} . The closeness of the values of the enthalpy and internal energy for condensed matter (Elyukhin, 2016a; Elyukhin, 2016b) was taken into account in the last formulae. The value of $\Delta h_{B^{\vee}}$ is equal to the negative value of a similar relation between the enthalpies of formation $\Delta h_{B^{\vee}}^{0f} = h_{BBi}^{0f} - h_{BB^{\vee}}^{0f}$.

 $h_{\text{GaBi}}^{0f} + h_{\text{GaB}^{V}}^{0f}$ since the enthalpies of the atoms and molecules involved in the enthalpies of formation are self-cancelled. The enthalpies of formation are available (Elyukhin, 2018; Elyukhin, 2019; Landolt-Börnstein, 1984; Dumont, Monteil, 2006). The calculated values of the relations between the enthalpies of formation $\Delta h_{\text{P}}^{0f} = -11 \text{kJmol}^{-1}$ and $\Delta h_{\text{As}}^{0f} = -57 \text{kJmol}^{-1}$ demonstrate the primary BBi and GaB^V bonding over the BB^V and GaBi one, respectively.

The values of COPs were obtained by minimization of the free energy of the alloys. The free energy is a sum of three terms $f^{O} = u^{O(B)} + u^{O(IS)} - Ts^{O}$. The first summand is the bond energy, the second item is the internal strain energy and the third item is the entropy term.

3. Results and discussion

 $B_xGa_{1-x}Bi_yAs_{1-y}$ epitaxial films with compositions x = 0.0022, 0.0044, 0.0089, 0.012 and y =0.016 were successfully grown at 320 °C via MBE (Beaton et al, 2012). The 4B10Bi cluster formation during the growth at 320 °C is improbable since it demands the boron and Bi selfdiffusion processes in the crystal lattice. Such processes in III-V semiconductors are very slow at such growth temperature. As it was shown (Kurtz et al., 2001; Müller et al., 2011), the thermal annealing of GaAs-rich In_xGa_{1-x}N_yAs_{1-y} epitaxial films at 670 °C - 700 °C during 15-30 min is an efficient method to change the arrangement of In and nitrogen atoms over long distances. B_xGa₁- $_{x}Bi_{v}B^{v}_{1-v}$ belong to the same type of the alloys just as $In_{x}Ga_{1-x}N_{v}As_{1-v}$. That is why the temperature range from 0 °C to 800 °C was considered. The small decrease of the bond energy and considerable diminution of the internal strain energy are two causes of clustering. The fulfilled estimates for B_xGa_{1-x}Bi_yB^V_{1-y} demonstrate that all or almost all boron atoms should be in 4B10Bi clusters up to 800 °C if $x > 1 \times 10^{-4}$ and y > 4x. However, the fraction of boron atoms in the clusters in the GaPrich alloys has to be smaller than that in $B_xGa_{1-x}Bi_vAs_{1-y}$. It is due to the favorable BBi and GaB^v bonding over the BB^v and GaBi one in GaP-rich alloys is five times less than in GaAs-rich ones $(\Delta h_{\rm P}^{0f} = -11 \rm kJmol^{-1}$ and $\Delta h_{\rm As}^{0f} = -57 \rm kJmol^{-1}$). 1B4Bi clustering also decreases the free energy but less than that of 4B10Bi clusters. Such clusters can be formed earlier than 4B10Bi clusters at a thermal treatment since an occurrence of 1B4Bi clusters demands the redistribution of the smaller number of atoms. Cooling of the alloys with 1B4Bi clusters will lead to the "frozen" atomic distribution as self-diffusion processes at RT are very slow. Accordingly, the last mentioned allovs can also be used for devices applications.

The other cluster formation conditions for the boron and Bi contents in $B_xGa_{1-x}Bi_yB^{v}_{1-y}$ were studied for $x = y = 1 \times 10^{-4}$, 7.5×10^{-5} , 5×10^{-5} and $x = 2y = 1 \times 10^{-4}$, 7.5×10^{-5} , 5×10^{-5} . The temperature dependencies of 4B10Bi COPs for $B_xGa_{1-x}Bi_yAs_{1-y}$ with these contents are shown in Figures 3 and 4, correspondingly.



Fig. 3. The temperature dependencies of 4B10Bi COPs in $B_xGa_{1-x}Bi_yAs_{1-y}$ with $x = y = 1 \times 10^{-4}$, 7.5×10⁻⁵, 5×10⁻⁵



Fig. 4. The temperature dependencies of 4B10Bi COPs in $B_xGa_{1-x}Bi_yAs_{1-y}$ with $x = 2y = 1 \times 10^{-4}$, 7.5×10⁻⁵, 5×10⁻⁵

As seen in Figure 3, the smaller concentrations decrease the fraction of boron and Bi atoms in 4B10Bi clusters at high temperatures. The reason is that the clusters decrease the entropy more if the boron and Bi concentrations are smaller. It may be seen also that the larger fraction of boron

atoms is in 4B10Bi clusters in $B_xGa_{1-x}Bi_yAs_{1-y}$ with $x = y = 1 \times 10^{-4}$ at high temperatures. The significant diminution of Bi atoms which might be in 4B10Bi clusters is in the alloys with $x = 2y = 1 \times 10^{-4}$, 7.5×10^{-5} , 5×10^{-5} at temperatures above 700 °C. Thus, if a small density of 4B10Bi clusters is desired then alloys with x > y could be used. However, in such a case, isolated highly lattice mismatched boron atoms will produce the considerable internal strains. 1B4Bi COPs should be insignificant in $B_xGa_{1-x}Bi_yAs_{1-y}$.

The temperature dependencies of 4B10Bi COPs for $B_xGa_{1-x}Bi_yP_{1-y}$ with $x = y = 1 \times 10^{-4}$, 7.5×10⁻⁵, 5×10⁻⁵ and $x = 2y = 1 \times 10^{-4}$, 7.5×10⁻⁵, 5×10⁻⁵ are shown in Figures 5 and 6, correspondingly.



Fig. 5. The temperature dependencies of 4B10Bi COPs in $B_xGa_{1-x}Bi_yP_{1-y}$ with $x = y = 1 \times 10^{-4}$, 7.5×10⁻⁵, 5×10⁻⁵

4B10Bi COPs in the GaP-rich alloys (shown in Figures 5 and 6) are smaller than those in the arsenides (Figures 3 and 4). It is also due to the small preference of BBi and GaB^{V} bonding in phosphides.



Fig. 6. The temperature dependencies of 4B10Bi COPs in $B_xGa_{1-x}Bi_yP_{1-y}$ with $x = 2y = 1 \times 10^{-4}$, 7.5×10⁻⁵, 5×10⁻⁵

4B10Bi COPs in the GaP-rich alloys shown in Figures 5 and 6 are smaller than those in the arsenides (Figures 3 and 4). It is also due to the small preference of BBi and GaB^v bonding in the phosphides. 1B4Bi COPs should be also insignificant in $B_xGa_{1-x}Bi_yP_{1-y}$.

The binding energy due to isolated Bi atoms in GaP:Bi (Trumbore et al, 1966) allows us to estimate the binding energy that may be caused by tetrahedral Bi cluster, by using the approach developed in (Goede, Hennig, 1983). The binding energy of a hole bound to Bi tetrahedron in GaP:Bi should be (Goede, Hennig, 1983)

$$\varepsilon_{4} = \frac{1}{2} T_{VB} \left[\frac{J}{T_{VB}} - \frac{7}{6} + \left(\frac{J}{T_{VB}} + \frac{1}{6} \right) \sqrt{1 + \frac{3T_{VB}}{2J}} \right]$$

where T_{VB} is an average energy related to the valence band and *J* is the Koster-Slater parameter (Koster, Slater, 1954). The average energy related to the valence band of GaP was estimated as $T_{VB} = -1.4$ eV (Baldereschi, Hopfield, 1972). The Koster-Slater parameter *J* is obtained from the experimental data on the binding energy of a hole bound to an isolated Bi atom and

calculated value of
$$T_{VB}$$
 by using the formula (Goede, Hennig, 1983) $\mathcal{E}_1 = J \left(1 - \frac{TVB}{4J} \right)^2$, where ε_1

= 0.04 eV is the binding energy of a hole bound to an isolated Bi atom. The calculated binding energy of a hole bound to Bi tetrahedron is ε_4 = 0.2598 eV. The binding energy of a hole that should be bound to an unstrained Bi dyad in GaP calculated by using the same approach is only ε_2 = 0.1222 eV. The fulfilled estimates show that the formation of the localized states due to 1B4Bi clusters in B_xGa_{1-x}Bi_yP_{1-y} cannot be excluded in spite of the internal strains. 1B4Bi clusters may be formed earlier than 4B10Bi clusters since the 1B4Bi cluster occurrence demands redistribution lesser number of atoms. Moreover, the self-diffusion processes at RT are very slow. Therefore, the considered alloys with 1B4Bi clusters may be also used for device applications.

4. Conclusion

To conclude, 4B10Bi clustering is favored thermodynamically in GaAs-rich $B_xGa_{1-x}Bi_yAs_{1-y}$ and GaP-rich $B_xGa_{1-x}Bi_yP_{1-y}$ alloys in the wide boron and Bi content ranges. The occurrence of 1B4Bi clusters is also favorable but less than 4B10Bi clusters. However, 1B4Bi clusters may occur earlier than 4B10Bi clusters since their formation demand smaller distances for self-diffusion processes. The alloys with 1B4Bi clusters should be in the "frozen" state at RT. The considerable compensation of the internal strains and favorable BBi and GaAs (GaP) bonding over BAs (BP) and GaBi one are the causes of clustering. The calculations demonstrate that the significant fraction of boron and Bi atoms should be in 4B10Bi clusters even at high temperatures. Therefore, the thermal treatment is offered as an effective way to reach the state of GaAs-rich $B_xGa_{1-x}Bi_yAs_{1-y}$ and GaP-rich $B_xGa_{1-x}Bi_yP_{1-y}$ alloys with the clusters. Thus, the studied semiconductors are promising candidates to obtain the identical polyatomic clusters in the Ga B^V -rich GaBi_x B^V_{1-x} ($B^V = P$, As) highly lattice mismatched bismide alloys.

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Toxicity of a Series of Molecules Derived from Anilides: DFT Study

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Abstract

The objective of our work was to study 7 molecules derived from anilides, which enabled us to determine their geometric, structural, electronic and optical properties. And other shares using calculated parameters: Energy of the orbital borders, electronic affinity, index of the global electrophile and electronic chemical potential. The results obtained showed that the toxicity of these molecules is influenced with different degrees by several descriptors. We find that 3 molecules out of 7 studied are more toxic has been studied within the density functional theory (DFT) at the B3LYP/6-31(d,p) computational level.

Keywords: energy of the orbital borders, electronic affinity, index of the global electrophile and electronic chemical potential, DFT.

1. Introduction

Amide bonding is one of the most important chemical reactions. The usual routes to primary, secondary and tertiary amides mainly involve the treatment of activated acid derivatives, in particular acyl halides, acid anhydrides, esters, with ammonia or primary and secondary amines (Roughley, et al., 2011; Vogel et al., 1989). Starch is an important functional group and is an integral part of many pharmaceuticals, natural products, agrochemicals, refined chemicals and polymers, and the constituents of drugs (local anesthetics, antiarrhythmics, antivertiginous drugs, etc.). It is also the key binding fragment in the proteins and peptides of drug products (Pierrick et al., 2014; Jack et al., 2014; Carey et al., 2006; Humphrey et al., 1997).

Amides are divided into three classes according to the number of acyl groups carried by the nitrogen atom. Primary, secondary and tertiary amides are distinguished. Primary and secondary amides have higher melting and boiling points than tertiary amides, because in the first two types of amides there are intermolecular hydrogen bonds (Kevin et al., 2014).

As a result, many protocols have been developed for starch synthesis, including:

catalytic condensation of carboxylic acids and amines and triphenyl borate as catalyst. This protocol is applicable for the synthesis of a wide range of starches providing excellent yields up to 92 % (Ghorpade et al., 2014).

• catalytic condensation of carboxylic acid and amine (starch) with arylboronic acid has been reported as an organo-catalyst for amide synthesis (Maki et al., 2014).

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• hydration of nitriles catalysed by Ag (I) N-heterocyclic (Ag (I) -NHC) is one of the classic reactions of organic synthesis to produce primary amides (NS Thirukovela et al., 2019). Among the known amide synthesis methods, condensation of carboxylic acid and amine (amidation) giving starch as a product and water as a by-product is an ideal method that is greener and more economical (Katkar et al., 2011; Maki et al., 2007).

• conversion of carboxylic acid by a combination of ammonium thiocyanate and potassium carbonate has made it possible to synthesize primary amides in the presence of 2,4,6-trichloro-1,3,5-triazine (Jaita et al., 2018).

• Conventional condensation of ammonia (NH4SCN as a source of ammonia) with acyl chloride in the presence of an activator (Zhang et al., 2006).

• amidation of aldehydes with ammonium chloride or salts of amine hydrochloride has been developed for the synthesis of a wide variety of primary, secondary and tertiary amides with good yields, using cheap copper sulphate or copper oxide (I) as a catalyst (Ghosh et al., 2012).

• Most of these processes correspond to a reaction between an amine and an activated carbonyl compound and are similar to the method used to prepare esters.

The anilide derivatives naphthol-AS are synthesized following the coupling reaction between 2-hydroxy-3-naphthenic acid (Figure 1) and aniline derivatives (Table 1).



Fig. 1. Acide 2-hydroxy-3-naphtoïque

To address these problems related to the synthesis of amides, many new amide formation reactions have been developed (Esmaiel Eidi et al., 2016), such as primary amide transamidation (Tamura et al., 2012), oxidative amidation of aldehydes (Shie et al., 2003; Wang et al., 2008; Sarkar et al., 2010; Tillack et al., 2001; Muthaiah et al., 2010; Seo et al., 2010; Ghosh et al., 2012), catalytic acylation of amines with carboxylic acid (P. Tang. et al., 2010), haloarene aminocarbonylation (Dang et al., 2012), alkyne hydroamination (Chen et al., 2011), alcohol dehydrogenant starch (Gunanathan et al., 2007) and amidation of methylarenes with salts of amine hydrochloride, on magnetic nanoparticles (Nps) of CoFe2O4.

Amides are generally considered to be compounds with low solubility in water; they are much less soluble in water than acids and alcohols because of their non-ionic character, these compounds can give and accept both hydrogen bonds. Amides undergo hydrolysis at a slower rate than esters. The hydrolysis of the ester, when placed in an aqueous alcoholic solvent in the presence of a base, can be done within a few hours, under the same reaction conditions, it can take days (or more) for a structurally similar amide (Carey et al., 2006).

2. Methods of calculation

GAUSSIAN 09 (Gaikwad et al., 2015) and GAUSS VIEW 5.0.9 (Dong et al., 2018) are used as before for all calculations (Wan, et al., 2018). The structures were drawn in the GAUSSIAN software GAUSS VIEW 5.0.9 (Dong et al., 2018). The initial structures were cleaned several times to obtain a standardized geometry. For each product was then subjected to successive optimizations using semi-empirical methods (PM3), Hartree-Fock and DFT in conjunction with appropriate base sets. The final optimization of these molecules is carried out by the method DFT/B3LYP/ 6-311G (d, p).

The toxicity of 7 molecules derived from anilides is given in the Table 1 are following after the experimental work of S. A. Chicu et al (Chicu et al., 2011).

Molecules	Chemical Formula	Toxicity
1	OH N OH	5,44
2		5,47
3	OH H N O Br	3,65
4	OH N O	4,29
5	OH H N O F F	3,85





3. Results and discussions

3.1. Optimized geometry and structures of the studied molecules

From the optimized structures, we can determine all the parameters relating to the geometry of the molecules, namely: interatomic distances, angles, dihedral angles, torsion angles, etc. In this work, the geometries of the optimized structures were obtained using the corrected gradient functionality of Becke, Lee, Yang and Parr (B3LYP) (Parr et al., 1989) exchange and correlation with the base 6-311G (Castro et al., 1998).









Molecule 7



Fig. 2. Optimized structures of the studied molecules

3.2. Electronic properties of the studied molecules

The structures of all the compounds studied are optimized with the DFT method (Wan et al., 2018) using the software Gaussian 09 (Frisch et al., 2009), the function B3LYP (Becke et al., 1998) and the base 6-31G (d) (Castro et al., 1998), the results obtained are grouped in Table 2.

From the optimized structures of each molecule, we directly determined the total energy Etot, the energy of the highest molecular orbital occupied E_{HOMO} , the energy of the lowest vacant molecular orbital E_{LUMO} .

In addition to these descriptors, we calculated: the Egap energy, the PCE chemical potential, the chemical hardness η , the global electrophile index, the global nucleophilia index N and the electronegativity.

3.3. Energy of boundary orbitals

According to the calculation we determined the energy of the orbital borders for each molecule. The following table shows the HOMO and LUMO energy for the 7 molecules.

COMPOUNDS	HOMO ENERGY (eV)	LUMO ENERGY (eV)
1	-0.2184	-0.0755
2	-0.2256	-0.073
3	-0.2239	-0.0842
4	-0.2194	-0.0774
5	-0.2268	-0.0886
6	-0.2258	-0.0902
7	-0.2316	-0.1166

Table 2. Energy of boundary orbitals (in eV) for different compounds

Therefore we have determined the HOMO/LUMO bondary orbital energy as illustrated in the following Figure 3.



Fig. 3. HOMO/LUMO boundary orbital energy

The molecule with a larger energy gap compared to others would be is more stable. HOMO/LUMO boundary orbitals play a special role (Hoffmann et al., 1969):

• HOMO translates the electro-donor character of the molecule. The higher the energy of this OM the more easily the molecule will yield electrons.

• LUMO translates the electroacceptor character of the molecule. The weaker the energy of this OM the more easily the molecule will accept electrons

The following table shows the geometrices and the energy of the molecules









We have computed adiabatic IP and adiabatic EA for seven Molecules presented in the following Table 5. Value deviates from the mean value are highlighted by underline. IP: Ionization potential, EA: Electron affinity, μ : Chemical potential, χ : Electronegativity, η : Chemical hardness, σ : Chemical softness (1/ η), ω : Electrophilicity index and Energy gap.

Molecules	μ (eV)	A (eV)	η (eV)	S (eV)	ω (Ev)	E gap (eV)
1	-0.0714	0.0755	0.1429	3.4989	0.0178	0.1429
2	-0.0763	0.0731	0.1526	3.2765	0.0190	0.1526
3	-0.0698	0.0842	0.1397	3.5790	0.0174	0.1397
4	-0.0711	0.0774	0.1421	3.5211	0.0177	0.1421
5	-0.0691	0.0886	0.1382	3.6179	0.0172	0.1382
6	-0.0678	0.0902	0.1356	3.6873	0.0169	0.1356
7	-0.0574	0.1166	0.1149	4.3493	0.0143	0.1149

Table 5. Electronic properties of the studied molecules

3.4. Energy gap

According to the graph analysis (Figure 4), molecule 2 has a higher gap energy than other molecules, so molecule 2 has a lower and more stable conductivity.



Fig. 4. Energy gap

3.5. Electronic chemical potential

The electronic chemical potential determines the direction of electron transfer during condensation between two molecules. According to the calculation of the chemical potential of the molecules (Figure 5), we observe that molecule 2 has a greater electronic potential than the other. This implies that the electron transfer will take place in molecule 2.



Fig. 5. Electronic chemical potential

3.6. Hardness and Softness

Hardness gives an idea of the relative duration of a molecule to store electrons in its environment. According to the curve (Figure 6) we have molecule 2 at a greater hardness compared to other molecules, so molecule 2 holds more electrons in its environment compared to other molecules. Softness (Figure 6) is the easiness with which the cationic A⁺ molecule can receive electrons, or anionic A-to lose electrons. So molecule 2 is difficult to receive or lose electrons.



Fig. 6. Hardness and softness

3.7. Index of the global electrophile

The index of the global electrophile of a molecule is the number of electrons it can acquire by an electrophile, if it is immersed in a cloud of free electrons. The value of the number of electrons acquired and the resulting energy stabilization would allow the electrophilic power of two species to be compared.

According to the curve (Figure 7), molecule 2 has a larger global electrophilic index value compared to other molecules, so it is more stable than the other molecules.



Fig. 7. The index of the global electrophile

3.8. Electronic affinity

Electronic affinity refers to the ability of a neutral atom or molecule to capture an additional electron. Molecule 2 has a lower electron affinity than other molecules, so this implies that molecule 2 is more stable (Figure 8).



Fig. 8. Electronic affinity

3.9. Thermodynamic parameters

We determined for each molecule the enthalpy H, entropy S and free enthalpy G.

- Enthalpy H is the sum of the internal energy of a system and the product of its pressure by its volume.

- Entropy S, it characterizes the degree of disorder or unpredictability of the information content of a system.

Molecule	ΔH (Cal/mol)	ΔS (Cal/mol/K)	ΔG (Cal/mol)
1	-939.138	138.585	-42237,468
2	-1089,268	152.428	-46509,812
3	-3434.073	136.080	-43985,913
4	-899.861	136.144	-41470,773
5	-1197.634	147.362	-45111,510
6	-1049.120	140.954	-43053,412
7	-1065.052	140.183	-42839,586

Table 6. Thermodynamic parameters

According to the free enthalpy calculation, the free enthalpy G-curve is plotted for each molecule (Figure 9).

We determined the enthalpy of 7 derived anilide molecules and we found that molecule 2 has a lower energy. This result means that molecule 2 is thermodynamically more stable.





5. Conclusion

This work has demonstrated the concordance between our results from quantum chemistry on the one hand and those of the team of Sergiu Adrian et al from experience.

In fact, our two teams found that 3 out of 7 molecules studied are more toxic. In addition, the two teams found the same rows of toxicity for these 3 molecules.

The parameters responsible for increasing toxicity are diversified: the energy of the highest molecular orbital occupied EHOMO, the energy of the lowest vacant molecular orbital E LUMO, the Egap energy, the ionization energy I, the electronic affinity A, the electronic chemical potential PCE, the chemical hardness n, the global electrophilic index, the global nucleophilic index N and electrolvte.

The quantum chemistry offers researchers and industrialists alike new horizons.

6. Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere.

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