



# N-DERIVATIVES OF FORMALDIMINES: THE REASON FOR THE HIGH NITROGEN INVERSION BARRIERS IN N-METHYL- AND N-CHLOROIMINES

Yuliya A. Chertykhina<sup>[a]</sup>, Nataliya V. Kutsik-Savchenko<sup>[a]</sup>, Bohdan V. Murashevych<sup>[a]</sup>, Oleg S. Lebed<sup>[a]</sup>, Alexander V. Tsygankov<sup>[b]</sup>, Igor I. Melnik<sup>[b]</sup> and Alexander V. Prosyanyk<sup>[a]\*</sup>

**Keywords:** Imines, inversion barriers, intramolecular interactions, electronegativity, correlations.

The energy and electronic parameters of the nitrogen inversion in imines  $H_2C=N-XH_n$  ( $XH_n = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl$ ) have been calculated with the DFT method (B3LYP 6-311+G(d,p)) in terms of natural bond orbital. It has been established that the interactions of the nitrogen lone pair (LP) with the bond orbitals at the imino carbon atom are practically independent of the X atom and contribute to the decrease of the inversion barriers ( $\Delta E_i^\ddagger$ ). While  $nN \rightarrow \sigma_{X-H}^*$ ,  $nN \leftarrow \sigma_{X-H}$  and  $nN \leftrightarrow nX$  interactions substantially depend on the heteroatom type and promote the increase in the  $\Delta E_i^\ddagger$  values with the rise in electronegativity of the X atom. The contribution of the interactions of the nitrogen LP with the Rydberg orbitals of the C=N-X group atoms is small and they cannot be the main reason of the decrease in the  $\Delta E_i^\ddagger$  values when X atoms of the second period are replaced by atoms of the third period of the same group. The interactions of the LP of the X atoms and the X-H bond orbitals with the C=N bond orbitals have the main influence on the inversion barriers. The contribution of  $nX \rightarrow \pi_{C=N}^*$  interactions to the  $\Delta E_i^\ddagger$  values is dominant. The main reason of the “anomalous” inversion barriers of N-methyl- and N-chloroformaldimines is the destabilization of inversion transition states because of the reduction in the energies of  $\sigma_{X-H} \rightarrow \pi_{C=N}^*$  and  $nX \rightarrow \pi_{C=N}^*$  interactions and the rise in the energies of  $nN \leftrightarrow nCl$  interactions. The contributions of electronegativity of  $XH_n$  substituents and energies of intramolecular interactions to the  $\Delta E_i^\ddagger$  values have been determined.

\* Corresponding Authors

E-Mail [prosyanykav@gmail.com](mailto:prosyanykav@gmail.com)

[a] Ukrainian State University of Chemical Technology, Dnipro city, Ukraine

[b] National Technical University «Kharkiv polytechnic institute», Kharkiv city, Ukraine

period (except C) and increases for the  $XH_n$  substituents containing elements of the third period (except Cl).

The opposite vectors of changes in the energies of intramolecular interactions are mainly conditioned by the interactions of the X heteroatoms LP with the C=N bond orbitals;  $nN \rightarrow 3d$  interactions are insignificant and have practically no effect on the nitrogen inversion barriers. Compared to other formaldimines, the N-methyl- and N-chloroderivatives showed abnormally low orbital energies of the C-H  $\sigma$ -bonds of the methyl group and nitrogen LP. The absence of correlations between the charge on the imino carbon atom and other parameters has been noted.<sup>11,12</sup>

In general, quantum chemical computations of ordinary imines, primarily N-derivatives of formaldimines, allow accurate estimate of the impact of the electron factors and intramolecular interactions on their structure and properties, including nitrogen inversion barriers. This can be largely facilitated by analyzing the correlational equations between the calculated properties of the imines (inversion barriers, charges, orbital energies) and the empiric parameters of the substituents (for example, electronegativity and Hammett constants), which allow predicting the changes of the calculated magnitudes depending on parameters used.

The purpose of the current study is to find out the factors responsible for the abnormal properties of N-methyl- and N-chloroformaldimines, which are manifested in the correlations disorders between their inversion barriers with electronic parameters and intramolecular interactions, as well as to determine their relative contributions to the inversion barriers.

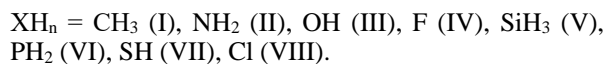
## INTRODUCTION

The nitrogen atom inversion is one of the classic problems of stereochemistry. Special attention is paid to the *Z,E*-isomerization process in imines occurring, as a rule, by an inversion. The energetic barrier of this inversion determines the electronic and steric effects of the substituents at the C=N-bond.<sup>1-3</sup> These effects are often hard to separate one from another, so in most cases only a qualitative description of the substituent's influence on the inversion barriers is possible. The quantitative influence of the substituents at imino-group and some intramolecular interactions on the nitrogen inversion barriers have been reviewed.<sup>4-12</sup> It has been established that the inversion barriers of the NH- and N-alkylamines decrease with the increase in electronegativity of the substituents on the carbon atom of the amino group, a positive charge on it and with a decrease in the population of the nitrogen lone pair (LP). The main influence on the inversion barriers is exerted by the interactions between the nitrogen LP and the bond orbitals of the imino carbon atom.<sup>4-10</sup>

In general, intramolecular interactions in N-substituted formaldimines reduce the inversion barriers. However, their contribution decreases with an increase in electronegativity of the  $XH_n$  substituents containing elements of the second

## COMPUTATIONAL METHODS

We have chosen isoelectronic N-derivatives of formalimine as the objects of the study in which the steric effect of the substituents on the imino-carbon atom on the inversion barriers is minimized:



All calculations have been made using the DFT method (B3LYP<sup>13,14</sup>) in the basic set of atomic functions 6-311+G(d,p) through the software package Firefly 8.2.0.<sup>15,16</sup> Geometry optimizations has been performed for all systems. The accordance of the computed points to the minima and saddle points of the potential energy surfaces has been confirmed by vibrational frequency calculations. Standard basis set 6-311+G(d,p) as has been used is sufficient for the purposes mentioned above and for the better comparability with the results of the previous studies and experimental data. The obtained wave functions have been analyzed in terms of Natural Bond Orbital method using the program NBO 5.9 G<sup>17</sup> implemented in the Firefly 8.2.0. package.

Calculated values of the nitrogen inversion barriers in the formaldimines I-VIII ( $\Delta E_i^\ddagger$ ) have been defined as the difference between the energies of the transition (TS) and ground (GS) states (Table 1).

**Table 1.** Inversion barriers of the imines I-VIII ( $\text{H}_2\text{C}=\text{NXH}_n$ )

Imine	XH <sub>n</sub>	$\Delta E_i^\ddagger$ , kJ mol <sup>-1</sup>	$\chi^{18}$	$\sigma_i^{19}$
I	Me	117.9	2.55	0.01
II	NH <sub>2</sub>	141.8	3.12	0.08
III	OH	237.6	3.55	0.33
IV	F	311.7	4.00	0.45
V	SiH <sub>3</sub>	30.9	1.90	0.06
VI	PH <sub>2</sub>	47.3	2.17	0.09
VII	SH	89.6	2.65	0.30
VIII	Cl	194.4	3.05	0.42

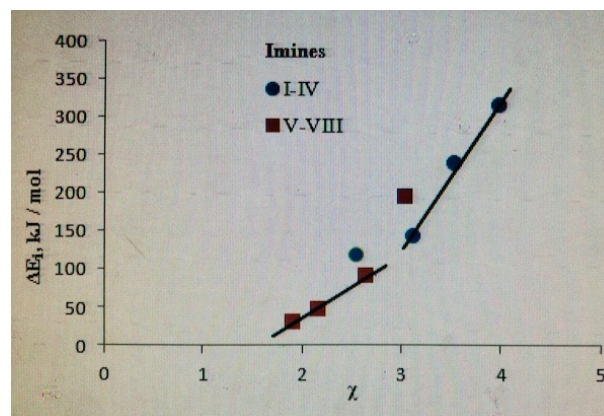
The influence of intramolecular interactions on the inversion barriers has been estimated using the approach described.<sup>7,10</sup> We have divided all analyzed intramolecular into 5 groups, composed, as a rule, based on alternative donor-acceptor and repulsive interactions of the same bonds (Table 2) i.e. the nitrogen LP with the orbitals of the methylene group on the imino carbon atom (group 1), with the orbitals of the X-H bonds and the LP of substituents X (group 2), with the Rydberg orbitals of the imino group (group 3), the X-H bond orbitals and methylene group of the imine fragment (group 4), the orbitals of the bonds C=N and X-H, as well as C=N, and the LP of the atom X (group 5).

Donor-acceptor interactions that stabilize the GS (TS) are taken with a minus (-) sign, and repulsive interactions that destabilize the considered states are taken with a plus (+) sign. The intramolecular interactions energies ( $E_i$ ) in the imines I-VIII are given in the article.<sup>11</sup> The influence of each interaction on the inversion barrier ( $\Delta E_i$ ) has been calculated as the difference between the energies of the transition and

ground states. The additivity of the contributions of the energies  $\Delta E_i$  to the changes of  $\Delta E_i^\ddagger$  is assumed a priori, i.e. regardless of the type of intramolecular interactions energies ( $E_i$ ) (donor-acceptor or repulsive) and the type of orbitals involved, any change in the energies  $\Delta E_i$  causes a proportional change in inversion barriers. The total effect of interactions on the inversion barrier in each group ( $\Delta\Sigma E_i$ ) has been obtained by the formula  $\Delta\Sigma E_i = \Sigma E_i(\text{TS}) - \Sigma E_i(\text{GS})$ . The values of  $\Sigma\Delta\Sigma E_{1-5}$  have been obtained by summation of the corresponding values of  $\Delta\Sigma E_i$  in all groups. Negative values of  $\Delta\Sigma E_i$  and  $\Sigma\Delta\Sigma E_{1-5}$  indicate a decrease of the inversion barrier due to the considered interactions, and positive ones indicate its increase.

## RESULTS AND DISCUSSION

The calculated values of the inversion barriers of formaldimines I-VIII satisfactorily correlate with the electronegativity of the substituents ( $\chi$ )<sup>18</sup> on the nitrogen atom (Table 3, Eqn. 1). With a separate consideration of the data for the imines I-IV, which contain elements of the second period on the nitrogen atom, as well as for the imines V-VIII, which contain elements of the third period, correlations deteriorate (Table 3, Eqns. 2, 3). Graphical analysis (Figure 1) shows that the correlations violate the data for N-methyl- (I) and N-chloroformaldimines violate (VIII), which have anomalously high inversion barriers. If these data are excluded, the  $\Delta E_i^\ddagger$  values of the imines II-IV and V-VII perfectly correlate with the values of  $\chi$ -constants of substituents (Table 3, Eqns. 4, 5). Since the equations obtained describe the dependence of the inversion barriers on the electronegativity of the substituents on the nitrogen atom, by substituting the values of the  $\chi$ -constants for the methyl group and the chlorine atom in them we can determine the theoretical inversion barriers for the imines I and VIII, which are conditioned only by the electronegativity of the substituents. The latter are respectively 36.1 and 120.2 kJ mol<sup>-1</sup>, which is 81.8 and 74.2 kJ mol<sup>-1</sup> less than the calculated values of  $\Delta E_i^\ddagger$  and  $\Delta E_{\text{VIII}}^\ddagger$ . Consequently, it is more correct to speak of the abnormally high values of the inversion barriers for imines I and VIII and not of their decrease, for example, when an S atom is introduced instead of a C atom at the nitrogen atom, basing on comparable electronegativities of S and C atoms.



**Figure 1.** Dependence of the inversion barriers on the electronegativity of substituents X.

**Table 2.** The energies of intramolecular interactions in the imines I-VIII, kJ mol<sup>-1</sup> H<sub>2</sub>C=NXH<sub>n</sub>

Gr.	Interaction/XH <sub>n</sub>	Me(I)	NH <sub>2</sub> (II)	OH(III)	F(IV)	SiH <sub>3</sub> (V)	PH <sub>2</sub> (VI)	SH(VII)	Cl(VIII)
1	$\Delta\Sigma E_1^a$	-74.1	-50.5	-62.9	-65.8	-52.8	-50.2	-33.0	-49.3
2	$\Delta\Sigma E_2^b$	-21.5	-38.8	40.4	74.6	-31.7	-24.7	-21.0	72.4
3	$\Delta\Sigma E_3^c$	4.3	12.1	10.1	17.9	-2.5	-11.7	-23.1	-28.3
4	$\Delta\Sigma E_4^d$	-27.4	-37.0	-32.6	-23.4	-16.2	-14.3	-19.2	-14.5
5	$\Delta\Sigma E_5^e$	-50.0	-153.1	-115.4	-96.4	-11.8	-63.6	-115.5	-84.5
-	$\Sigma\Delta\Sigma E_{1-4}$	-118.7	-114.2	-45.0	3.3	-103.2	-100.9	-96.3	-19.6
-	$\Sigma\Delta\Sigma E_{1-5}$	-168.7	-267.3	-160.4	-93.1	-115.0	-164.5	-211.8	-104.1
5.1	$\Delta\Sigma E[nX(\sigma_{XH})\rightarrow\pi^*_{C=N}]$	-13.8	-152.6	-130.7	-78.4	-6.5	-28.9	-81.3	-53.3
5.2	$\Delta E[nX\rightarrow\pi^*_{C=N}]$	-	-160.5	-141.7	-78.4	-	-14.5	-81.3	-53.3

Note – following interactions have been considered<sup>11</sup>: <sup>a)</sup>nN→σ<sup>\*</sup><sub>C-H1,2</sub>, nN↔σ<sub>C-H1,2</sub>; <sup>b)</sup>nN→σ<sup>\*</sup><sub>X-H</sub>, nN↔σ<sub>X-H</sub>, nN↔nX; <sup>c)</sup>nN→RY<sup>\*</sup><sub>C=N</sub>, nN→RY<sup>\*</sup><sub>X</sub>; <sup>d)</sup>σ<sub>N-X</sub>→σ<sup>\*</sup><sub>C-H1,2</sub>, σ<sub>C-H1,2</sub>→σ<sup>\*</sup><sub>N-X</sub>, σ<sub>N-X</sub>↔σ<sub>C-H1,2</sub>; <sup>e)</sup>σ<sub>X-H</sub>→σ<sup>\*</sup><sub>C=N</sub>, σ<sub>X-H</sub>→π<sup>\*</sup><sub>C=N</sub>, π<sub>C=N</sub>→σ<sup>\*</sup><sub>X-H</sub>, σ<sub>X-H</sub>↔π<sub>C=N</sub>, σ<sub>X-H</sub>↔σ<sub>C=N</sub>, nX→σ<sup>\*</sup><sub>C=N</sub>, nX→π<sup>\*</sup><sub>C=N</sub>, nX↔σ<sub>C=N</sub>, nX↔π<sub>C=N</sub>.

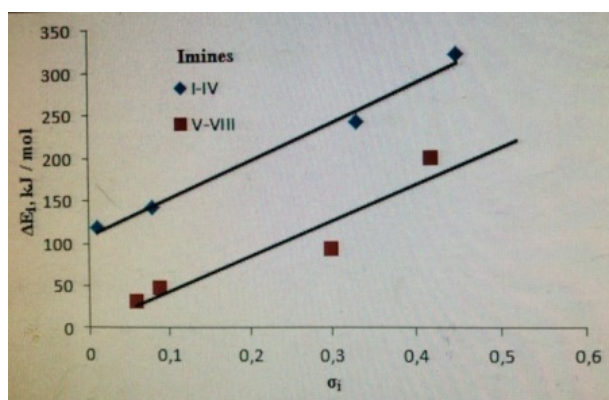
**Table 3.** Parameters of the dependence of the inversion barriers of the imines I-VIII on the χ- and σ<sub>i</sub>-constants of the XH<sub>n</sub> substituents and the energies of intramolecular interactions (Y=ρX+C).

Eqns. No	Imines	X	Y	ρ	C	s	r
1	I-VIII	χ	ΔE <sub>i</sub> <sup>‡</sup>	134.5	-240.03	22.05	0.974
2	I-IV	χ	ΔE <sub>i</sub> <sup>‡</sup>	139.1	-257.49	24.48	0.962
3	V-VIII	χ	ΔE <sub>i</sub> <sup>‡</sup>	137.1	-244.34	22.65	0.951
4	II-IV	χ	ΔE <sub>i</sub> <sup>‡</sup>	192.8	-455.53	6.02	0.996
5	V-VII	χ	ΔE <sub>i</sub> <sup>‡</sup>	79.4	-121.96	2.20	0.996
6	I-IV	σ <sub>i</sub>	ΔE <sub>i</sub> <sup>‡</sup>	429.3	108.88	9.75	0.994
7	V-VIII	σ <sub>i</sub>	ΔE <sub>i</sub> <sup>‡</sup>	403.5	2.79	24.12	0.945
8	II-IV	ΣΔΣE <sub>1-5</sub>	ΔE <sub>i</sub> <sup>‡</sup>	0.968	398.43	3.96	0.998
9	V-VII	ΣΔΣE <sub>1-5</sub>	ΔE <sub>i</sub> <sup>‡</sup>	-0.604	-43.03	6.42	-0.966
10	II-IV	ΔΣE <sub>1</sub>	ΔE <sub>i</sub> <sup>‡</sup>	-10.10	-372.95	18.6	-0.964
11	V-VII	ΔΣE <sub>1</sub>	ΔE <sub>i</sub> <sup>‡</sup>	2.78	182.05	3.77	0.988
12	II-IV	ΔΣE <sub>2</sub>	ΔE <sub>i</sub> <sup>‡</sup>	1.448	193.60	10.5	0.989
13	V-VII	ΔΣE <sub>2</sub>	ΔE <sub>i</sub> <sup>‡</sup>	5.08	186.90	10.21	0.911
14	II-IV	ΔΣE <sub>3</sub>	ΔE <sub>i</sub> <sup>‡</sup>	13.93	44.17	52.1	0.663
15	V-VII	ΔΣE <sub>3</sub>	ΔE <sub>i</sub> <sup>‡</sup>	-2.88	20.08	4.62	-0.982
16	II-IV	ΔΣE <sub>4</sub>	ΔE <sub>i</sub> <sup>‡</sup>	11.81	596.61	18.86	0.963
17	V-VII	ΔΣE <sub>4</sub>	ΔE <sub>i</sub> <sup>‡</sup>	-9.62	-103.40	15.33	-0.785
18	II-IV	ΣΔΣE <sub>1-4</sub>	ΔE <sub>i</sub> <sup>‡</sup>	1.442	305.29	2.00	1.000
19	V-VII	ΣΔΣE <sub>1-4</sub>	ΔE <sub>i</sub> <sup>‡</sup>	8.606	917.64	1.47	0.998
20	I-IV	ΣΔΣE <sub>1-4</sub>	ΔE <sub>i</sub> <sup>‡</sup>	1.521	306.64	6.98	0.997
21	V-VIII	ΣΔΣE <sub>1-4</sub>	ΔE <sub>i</sub> <sup>‡</sup>	1.754	230.88	19.76	0.963
22	II-IV	ΔΣE <sub>5</sub>	ΔE <sub>i</sub> <sup>‡</sup>	2.93	587.02	7.95	0.993
23	V-VII	ΔΣE <sub>5</sub>	ΔE <sub>i</sub> <sup>‡</sup>	-0.566	19.91	6.09	-0.966
24	II-IV	ΔΣE <sup>a</sup>	ΔE <sub>i</sub> <sup>‡</sup>	2.131	487.25	20.94	0.954
25	V-VII	ΔΣE <sup>a</sup>	ΔE <sub>i</sub> <sup>‡</sup>	-0.789	25.25	0.54	-1.000

To determine the reasons for the inversion barrier increases in N-methyl- and N-chloroformaldimines, we have investigated the influence of electronic factors and intramolecular donor-acceptor and repulsive interactions.

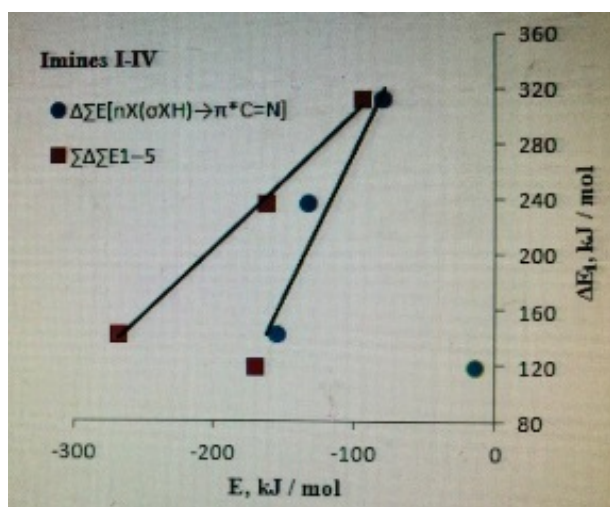
The ΔE<sub>i</sub><sup>‡</sup> values of the imines I-VIII do not show a direct dependence on the induction constants of the substituents (σ<sub>i</sub>),<sup>19</sup> although a certain correlation of values is observed (r = 0.765). With a separate consideration of imines containing elements of the second or third periods on the nitrogen atom, the values of ΔE<sub>i</sub><sup>‡</sup> correlate with σ<sub>i</sub>-constants of substituents (Table 3, eqns. 6, 7), forming two almost parallel straight

lines (Figure 2). Wherein, despite the comparable values of σ<sub>i</sub>-constants for the substituents, the central atoms X of which are in the same group, the inversion barriers for the corresponding imines differ a lot. The difference in the values of ΔE<sub>i</sub><sup>‡</sup> obtained from equations 6 and 7, is 106.1 kJ mol<sup>-1</sup> if σ<sub>i</sub> = 0, and 117.7 kJ mol<sup>-1</sup> if σ<sub>i</sub>=0.45. It may mean that the inversion barriers mainly depend on the electronegativity of the XH<sub>n</sub> substituents. The inductive effect has a subordinate impact. This fact indicates the incorrectness of the analysis of the imines inversion barriers values based on σ<sub>i</sub>-constants of the substituents containing elements X of different periods or groups.

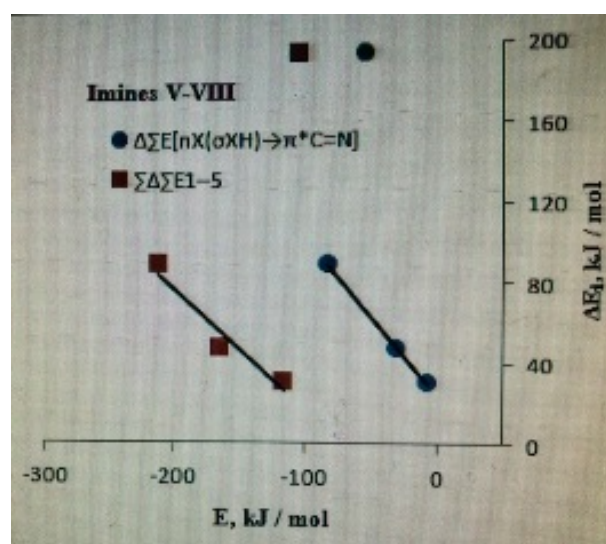


**Figure 2.** Dependence of the inversion barriers on the induction constants of substituents X.

The values of  $\Delta E_i^\ddagger$  do not show any dependence on the sum of the energies of intramolecular interactions  $\sum \Delta \sum E_{1-5}$  either by joint consideration of imines I-VIII ( $r = 0.32$ ) or by separate consideration of the imines I-IV and V-VIII ( $r = 0.75$  and  $0.31$ , respectively). The correlations are observed only after exclusion of the data for the imines I and VIII (Figure 3, 4, Table 3, Eqns. 8, 9). At the same time, the change in the  $\sum \Delta \sum E_{1-5}$  values with an increase of the electronegativity of the substituents contributes to an increase of the inversion barriers of imines II-IV and their decrease for imines V-VII. Since the Eqns. (8) and (9) describe the dependence of the inversion barriers on the sum of the energies of intramolecular interactions  $\sum \Delta \sum E_{1-5}$ , by substituting the values of  $\Delta E_i^\ddagger$  and  $\Delta E_{\text{VIII}}^\ddagger$  into them it is possible to determine the theoretical values of the sums  $\sum \Delta \sum E_{1-5(i)}^{\text{theor}}$ , which would conform to the above correlations of the inversion barriers of the imines I and VIII. The corresponding values of  $\sum \Delta \sum E_{1-5(i)}^{\text{theor}}$  for them are to be  $-289.2$  and  $-395.7$   $\text{kJ mol}^{-1}$ , which is  $120.5$  and  $291.6$   $\text{kJ mol}^{-1}$  less than the calculated values ( $\Delta \sum \Delta \sum E_{1-5(i)} = \sum \Delta \sum E_{1-5(i)} - \sum \Delta \sum E_{1-5(i)}^{\text{theor}}$ ). Reductions in the stabilization of the inversion TS as a result of a change in the energies of intramolecular interactions may be the main reason for the observed increase in the inversion barriers of imines I and VIII.



**Figure 3.** Dependence of the inversion barriers on the intramolecular interaction energies of substituents X of the second period.



**Figure 4.** Dependence of the inversion barriers on the intramolecular interaction energies of substituents X of the third period.

To determine the intramolecular interactions responsible for increasing the calculated values of  $\sum \Delta \sum E_{1-5}$ , the analysis of changes in the  $\Delta \sum \Delta E_i$  values for groups 1-5 has been carried out based on their correlations with the inversion barriers of the imines II-IV and V-VII.

The interactions of the nitrogen LP with the bond orbitals at the imino carbon atom (Table 2, Group 1) generally reduce the inversion barriers. An increase in electronegativity of X atom for the elements of the second period (subgroup A) contributes to a decrease in the  $\Delta E_i^\ddagger$  values as a result of an increase in stabilization of the inversion TS, whereas for the elements of the third period (subgroup B), it contributes to an increase in the  $\Delta E_i^\ddagger$  values because of a decrease in the TS stabilization (Table 3, eqns. 10, 11). Slope opposition of the changes in the values of  $\Delta \sum E_1$  in subgroups A and B indicates the impossibility of a general correlation for them. In general, even though the interactions of group 1 contribute to a significant decrease in the inversion barriers, they do not have a significant effect on the change in the  $\Delta E_i^\ddagger$  values depending on the heteroatom X (the relative change in the  $\Delta \sum E_1$  values for subgroups A and B is  $23.6$  and  $19.8$   $\text{kJ mol}^{-1}$ , respectively).

With the increase in the electronegativity of the X atom, the interactions of the nitrogen LP with the orbitals of the X-H bonds and the X heteroatoms LP (Table 2, Group 2) contribute to the increase of the inversion barriers in both subgroups due to the dominant influence of repulsive intramolecular interactions destabilizing the inversion TS (Table 3, Eqns. 12, 13). The interactions of the 2-nd group largely depend on the type of heteroatom X and have a significant effect on the change in the inversion barriers (the relative change in the  $\Delta \sum E_2$  values for subgroups A and B is  $96.1$  and  $104.1$   $\text{kJ mol}^{-1}$ , respectively). It is necessary to note an explicit, by  $93.4$   $\text{kJ mol}^{-1}$ , change in the intramolecular interactions energy  $\Delta \sum E_2$  upon transition from *N*-sulfhydrylimine VII to *N*-chloroimine VIII, which is approximate to the change in the values of  $\sum \Delta \sum E_{1-5}$  for this pair of imines ( $107.7$   $\text{kJ mol}^{-1}$ ). Undoubtedly, the repulsive interaction of  $n\text{N} \leftrightarrow n\text{Cl}$  has a significant effect on increasing the inversion barrier of the *N*-chloroimine VIII. Based on

the  $\Delta E_i^\ddagger$  values found for imines I, VIII, and the correlational equations 12 and 13, the theoretical values of the intramolecular interactions energies  $\Delta \sum E_{2(i)}^{\text{theor}}$  should be  $-52.2$  and  $1.5 \text{ kJ mol}^{-1}$ , respectively, which are  $30.7$  and  $70.9 \text{ kJ mol}^{-1}$  less than the calculated ones ( $\Delta \Delta \sum E_{2(i)} = \Delta \sum E_{2(i)} - \Delta \sum E_{2(i)}^{\text{theor}}$ ). Thus, as a result of the intramolecular interactions of the 2-nd group, the inversion barriers of imines I, VIII must increase proportionally to the increase in the intramolecular interactions energies  $\Delta \sum E_{2(i)}$ . It should be noted that the influence of these interactions on the values of  $\Delta E_i^\ddagger$  was not practically taken into account before.

On the contrary, the influence of the interaction of the nitrogen LP with 3d-orbitals of sulfur atoms and other heteroatoms of higher periods was intensively discussed. For example, it was pointed out that these interactions underlie the low inversion barriers of the sulfenyl-, sulfinyl-, and sulfonylimines.<sup>20-23</sup> The analysis of the interactions between the nitrogen LP and the Rydberg orbitals of the atoms of C=N-X group (Table 2, Group 3) shows that with an increase in electronegativity of X atoms in subgroup A, they contribute to a slight increase in the inversion barriers and their slight decrease in subgroup B (Table 3, Eqns. 14, 15). Moreover, upon the transition from the elements of the second period to the elements of the third period, the contribution of these interactions to the reduction of the inversion barriers for the IV-VII groups of the periodic system is relatively small and amounts to  $6.8$ ,  $23.8$ ,  $33.2$  and  $46.2 \text{ kJ mol}^{-1}$ , respectively. This is disparately insignificant in comparison with the observed change in the inversion barriers ( $87.0$ ,  $94.5$ ,  $148.0$  and  $117.3 \text{ kJ mol}^{-1}$ ). Consequently, these interactions cannot be the main reason for the decrease in the inversion barriers for the imines containing atoms of the third period.

The impact of interactions on the inversion barriers collected in the 4-th group has never been studied. Indeed, although these interactions contribute to decreasing of the inversion barriers (Table 3, Eqns 16, 17), they have insignificant effect on their change and, moreover, practically do not depend on the substituent at the nitrogen atom (the relative change in the  $\Delta \sum E_4$  values for subgroups A and B is  $13.6$  and  $4.9 \text{ kJ mol}^{-1}$ , respectively).

The sums of intramolecular interactions energies  $\Delta \sum E_{1-4}$  perfectly correlate with the values of  $\Delta E_i^\ddagger$  of the imines II-IV and V-VII (Table 3, Eqns. 18,19) and even more of the imines I-IV and V-VIII (Table 3, Eqns. 20, 21). This indicates a minor participation of these interactions in increasing the inversion barriers of N-methyl- (I) and N-chloroformaldimines (VIII) and reducing the energies  $\Delta \sum E_{1-5(i)}$  for them.

The interactions of the X-H bonds orbitals and the X atoms LP with the orbitals of the C=N bonds show the dominant impact on the change in the intramolecular interactions energies  $\Delta \sum E_{1-5}$  (Table 2, group 5). The energies of the intramolecular interactions of this group make the main contribution to the total energies of intramolecular interactions  $\Delta \sum E_{1-5}$  of the imines II-IV and V-VII. The values of  $\Delta \sum E_5$  correlate completely with the values of  $\Delta E_i^\ddagger$  of the imines II-IV and V-VII (Table 3, Eqns. 20, 21). In this case, the increase in electronegativity of the X atom in subgroup A contributes to the increase in the inversion barriers as a result of decreasing stabilization of the inversion TS, while in subgroup B it decreases the

values of  $\Delta E_i^\ddagger$  due to the increasing stabilization of the TS. Based on the values of  $\Delta E_i^\ddagger$ , found for the imines I, VIII, and the correlation equations 20 and 21, the theoretical energies  $\Delta \sum E_{5(i)}^{\text{theor}}$  should be  $-160.1$  and  $-306.1 \text{ kJ mol}^{-1}$ , respectively, which is  $110.1$  and  $221.6 \text{ kJ mol}^{-1}$  less than the calculated ones ( $\Delta \Delta \sum E_{5(i)} = \Delta \sum E_{5(i)} - \Delta \sum E_{5(i)}^{\text{theor}}$ ). Therefore, as a result of the intramolecular interactions of the 5-th group, the inversion barriers of imines I, VIII must increase significantly in proportion to the increase in the energies  $\Delta \sum E_{5(i)}$ .

In its turn, the dominant contribution to the change in the inversion barriers due to the interactions of the 5-th group is made by the energies of donor-acceptor interactions of electrons of the  $\sigma$ -bonds N-X and X heteroatoms LP with the  $\pi^*$ -orbital of the C=N bond (Table 2, Group 5.1), which are close to the total energies  $\Delta \sum E_5$  of the corresponding imines and correlate completely with the values  $\Delta E_i^\ddagger$  of the imines II-IV and V-VII (Table 3, Eqns. 24, 25). The similar values of the coefficients  $\rho$  in Eqns. 22 and 24, 23 and 25 indicate the dominant contribution of the interactions of group 5.1 to the total change in energies of the 5th group. The main contribution to the change in the values of  $\Delta \sum E[nX(\sigma_{XH}) \rightarrow \pi^*_{C=N}]$  is made by the interaction energy of the X atom LP with the  $\pi^*$ -orbital of the C=N bond ( $nX \rightarrow \pi^*_{C=N}$ , Table 2, group 5.2). Comparison of the dependences of the inversion barriers of imines I-IV and V-VIII on the  $\Delta \sum E_{1-5}$  and  $\Delta \sum E[nX(\sigma_{XH}) \rightarrow \pi^*_{C=N}]$  values (Fig. 3, 4, respectively) indicates the dominant influence of the latter especially clearly.

Almost equal for the imines I and VIII values of the energies  $\Delta \sum \Delta \sum E_{1-5(i)}$  and the sum of energies  $\Delta \Delta \sum E_{2(i)}$  and  $\Delta \Delta \sum E_{5(i)}$ , which are  $120.5$  and  $140.8$  (imine I) and  $291.6$  and  $292.5 \text{ kJ mol}^{-1}$  (imine VIII), respectively, confirm the correctness of the above arguments. On the other hand, it points that abnormally high nitrogen inversion barriers in N-methylformaldimine I and N-chloroformaldimine VIII are mainly conditioned by the decrease in the interaction energies of the electrons of the  $\sigma$ -bonds XH and X heteroatoms LP with antibonding orbitals of the C=N bonds ( $\sigma_{X-H} \rightarrow \pi^*_{C=N}$  and  $\pi_{C=N} \rightarrow \sigma^*_{X-H}$  (imine I) and  $nX \rightarrow \pi^*_{C=N}$ ,  $nX \rightarrow \pi^*_{C=N}$  and  $nX \rightarrow \sigma^*_{C=N}$ ,  $nX \rightarrow \pi^*_{C=N}$  (imine IX)) and, to a lesser extent, by the increase in the interaction energies  $nN \leftrightarrow nCl$ . Therefore, we can assume that the calculated value of the inversion barrier of N-methylformaldimine I in the first approximation consists of the electronegativity of the methyl group ( $36.1 \text{ kJ mol}^{-1}$ ) and intramolecular interactions ( $81.8 \text{ kJ mol}^{-1}$ ). The electronegativity contributions of the chlorine atom and the intramolecular interactions for N-chloroformaldimine VIII are  $120.2$  and  $74.2 \text{ kJ mol}^{-1}$ , respectively. It is obvious that with the increase in the electronegativity of the  $XH_n$  substituent, its relative contribution to the nitrogen inversion barriers increases, and the contribution of intramolecular interactions decreases.

## CONCLUSIONS

The investigation of the correlation dependencies of the nitrogen atom inversion barriers in N-derivatives of imines on electronegativity and  $\chi$ -constants of substituents and intramolecular interactions has made it possible to establish that N-methyl- and N-chloroformaldimines have abnormally

high nitrogen inversion barriers. The main reason for such an increase of the barriers is a decrease in the stabilization of the transition states of the inversion as a result of a change in the energies of intramolecular donor-acceptor and repulsive interactions. The latter are mainly conditioned by the decrease in the energies of the interactions between the electrons of the  $\sigma$ -XH bonds and X heteroatoms LP and antibonding orbitals of C=N bonds ( $\sigma_{X-H} \rightarrow \pi_{C=N}^*$ ,  $\pi_{C=N} \rightarrow \sigma_{X-H}^*$  и  $nX \rightarrow \sigma_{C=N}^*$ ,  $nX \rightarrow \pi_{C=N}^*$ , respectively) and, to a lesser extent, by the increase in the interaction energies  $nN \leftrightarrow nCl$ . In general, the main contribution to the change in the energies of intramolecular interactions has been made by the interactions of X atoms LP with the  $\pi^*$ -orbitals of the C=N bonds ( $nX \rightarrow \pi_{C=N}^*$ ).

The magnitude of the inversion barriers depends on both the electronegativity of the substituents on the nitrogen atom and the energies of intramolecular interactions, and their relative contributions are 30–60 and 70–40 %, respectively. An increase in the electronegativity of substituents leads to the growth of its contribution to the barriers.

The interactions of the nitrogen LP with bond orbitals at the imino carbon atom contribute to the reduction of the inversion barriers, but they practically do not depend on the heteroatom X. On the contrary, the interactions of the nitrogen LP with the orbitals of the X–H bonds and the X heteroatoms LP significantly depend on the type of heteroatom. They have a great effect on the inversion barriers, contributing to their increase with the growth of electronegativity of the X atom as a result of the repulsive intramolecular interactions destabilizing inversion TS.

The interactions of the nitrogen LP with the Rydberg orbitals of the atoms of the C=N group promote an insignificant multidirectional change of the inversion barriers. The contribution of these interactions to the decrease of the inversion barriers in the transition from the elements of the second period to the elements of the third period for groups IV–VII is relatively small and cannot be the reason for their reduction in imines containing atoms of the third period.

The interactions of the orbitals of the X–H bonds and the X atoms LP with the orbitals of the C=N bonds have the main effect on the inversion barriers of N-substituted imines in comparison with other intramolecular interactions. An increase in electronegativity of X atoms for elements of the second period contributes to an increase in the inversion barriers resulting from a decrease in stabilization of the inversion TS; whereas, for the elements of the third period they decrease because of an increase in the stabilization of TS. The energies of donor-acceptor interactions of electrons of the N–X  $\sigma$ -bonds and X heteroatoms LP with the  $\pi^*$ -orbital of the C=N bond have made the dominant contribution to the change in the inversion barriers.

## REFERENCES

- Lehn, J. M., Nitrogen inversion experiment and theory, *Top. Curr. Chem.*, **1970**, 15, 311-377.
- McCarty, C. G., *The chemistry of the carbon-nitrogen double bond*, John Wiley & Sons, NY., **1970**, 9, 363 – 464. <https://doi.org/10.1002/9780470771204.ch9>
- Kalinowski, H., Kessler, H., Fast Isomerizations About Double Bonds, *Top. Stereochem.*, **1973**, 7, 295-383. DOI: [10.1002/9780470147160.ch4](https://doi.org/10.1002/9780470147160.ch4)
- Blanco, F., Alkorta, I., Elguero, J., Barriers about Double Carbon-Nitrogen Bond in Imine Derivatives (Aldimines, Oximes, Hydrazones, Azines), *Croat. Chem. Acta.*, **2009**, 82, 173-183. <https://www.researchgate.net/publication/27221655>
- Shuhua, H., Ying, T., Xiuchan, X., Lijuan, Z., Yanzhi, G., Menglong, L., Anmin, T., Xuemei, P., Ning-Bew, W., Substituent effects on electronic character of the C=N group and trans/cis isomerization in the C-substituted imine derivatives: a computational study, *J. Mol. Struct., THEOCHEM*, **2010**, 951(1), 7-13. DOI: [10.1016/j.theochem.2010.03.029](https://doi.org/10.1016/j.theochem.2010.03.029)
- Prosyaniy, A. V., Kutsik-Savchenko, N. V., Kol'tsov, N. Yu., Yukhno, A. G., Konovalova, S. A., Avdeyenko, A. P., Thermal Z, E-isomerization of imines. VII. N-arylsulfonylimines of acetone, mesoxal ester and tetramethylurea, *Vopr. Khim. Khim. Tekhnol.*, **2012**(2), 14–24 (in Russian). [http://nbuv.gov.ua/UJRN/Vchem\\_2012\\_2\\_4](http://nbuv.gov.ua/UJRN/Vchem_2012_2_4)
- Kutsik-Savchenko, N. V., Lebed, O. S., Prosyaniy, A. V., NH- i N-alkylimines of formaldehyde: the electronic structure and inversion barriers of nitrogen atom, *Vopr. Khim. Khim. Tekhnol.*, **2014**(1), 15-23 (in Russian). <https://udhtu.edu.ua/public/userfiles/file/VHHT/2014/1/5.pdf>
- Kutsik-Savchenko, N. V., Lebed, O. S., Prosyaniy, A. V., The effect of C-substituents on the topomerization mechanism, inversion barriers and electronic character of C=N bond in N-alkylimines: A theoretical study, *Comput. Theor. Chem.* **2015**, 1072, 15-20. DOI: [10.1016/j.comptc.2015.08.019](https://doi.org/10.1016/j.comptc.2015.08.019)
- Kutsik-Savchenko, N. V., Lebed, O. S., Prosyaniy, A. V., Effect of substituents at the imine carbon on the nitrogen inversion barriers in the HN-imines, *Vopr. Khim. Khim. Tekhnol.*, **2015**(2) 45-52 (in Russian). <https://udhtu.edu.ua/public/userfiles//file/VHHT/2015/2/Kutsik-Savchenko.pdf>
- Kutsik-Savchenko, N. V., Lebed, O. S., Prosyaniy, A. V., The HN- and N-methylimines of formaldehyde, acetaldehyde and acetone: electronic structure and nitrogen inversion barriers, *Bull. Dnipropetrovsk Univ., Ser. Chem.*, **2015**, 23, 21-29 (in Russian). DOI: <https://doi.org/10.15421/081504>
- Chertykhina, Yu. A., Kutsik-Savchenko, N. V., Prosyaniy, A. V., N-Derivatives of formalimine: the effect of electronegativity of substituents and intramolecular interactions on the inversion barriers of the nitrogen atom, *Vopr. Khim. Khim. Tekhnol.*, **2017**(4), 37-45 (in Russian). <https://udhtu.edu.ua/public/userfiles/file/VHHT/2017/4/Chertihina.pdf>
- Chertykhina, Yu. A., Kutsik-Savchenko, N. V., Tsygankov, A. V., Prosyaniy, A. V., N-Derivatives of formalimine: the relationship between donor-acceptor intramolecular interactions and the electronic parameters of atoms, *Vopr. Khim. Khim. Tekhnol.*, **2018**(1), 57-66 (in Russian), <https://udhtu.edu.ua/public/userfiles/file/VHHT/2018/1/Chertihina.pdf>
- Koch, W., Holthausen, M. C., *A chemists guide to density functional theory*, Wiley-VCH, Weinheim (Germany), **2001**, 300, ISBNs: 3-527-30372-3 (Softcover); 3-527-60004-3 (Electronic)
- Schuchardt, K. L., Didier, B. T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Li, J., Windus, T. L., Basis set exchange: a community database for computational sciences, *J. Chem. Inf. Model.*, **2007**, 47(3), 1045-1052, DOI: [10.1021/ci600510j](https://doi.org/10.1021/ci600510j)
- Granovsky, A. A., Firefly version 8.2.0., <http://classic.chem.msu.su/gran/firefly/index.html>.
- Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S. J., Windus, T. L., Dupuis, M., Montgomery, J. A., General atomic and molecular electronic structure system, *J. Comput. Chem.*, **1993**, 14, 1347-1363. <https://doi.org/10.1002/jcc.540141112>

- <sup>17</sup>NBO 5.9/Gledening, E. D., Badenhop, J. K., Reed, A. E., Carpenter, J. E., Bohmann, J. A., Morales, C. M., Weinhold, F., Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2012**, <http://www.chem.wisc.edu/~nbo5>
- <sup>18</sup>Mullay, J., Atomic and group electronegativities, *J. Am. Chem. Soc.*, **1984**, *106*, 5842–5847. <https://doi.org/10.1021/ja00332a014>
- <sup>19</sup>Hansch, C., Leo, A., Taft, R. W., A survey of Hammett substituent constants and resonance and field parameters, *Chem. Rev.*, **1991**, *91*, 165–195. <https://doi.org/10.1021/cr00002a004>
- <sup>20</sup>Davis, F. A., Slegier, W. A. R., Kaminski, J. M., Sulfenimines: A new synthesis and barrier of stereomutation, *J. Chem. Soc., Chem. Commun.*, **1972**, *11*, 634–635. DOI: [10.1002/chin.197250210](https://doi.org/10.1002/chin.197250210)
- <sup>21</sup>Davis, F. A., Kluger, E. W., Chemistry of sulfur-nitrogen bond. 10. Barriers to planar inversion in *N*-(4,4-dimethylbenzophenylidene)arenesulfenamides and selenenamides, *J. Am. Chem. Soc.*, **1976**, *98*(1), 302–303. DOI: [10.1021/ja00417a084](https://doi.org/10.1021/ja00417a084)
- <sup>22</sup>Brown, C., Grayson, B. T., Hudson, R. F., Z-E isomerisation of *N*-sulphenylimines, *J. Chem. Soc., Perkin Trans. 2*, **1979**, 427–434. <https://pubs.rsc.org/ja/content/articlelanding/1979/p2/p29790000427>
- <sup>23</sup>Bharatam, P. V., Kaur, A., Kaur, D., Electronic structure of *N*-sulfenylimines, *J. Phys. Org. Chem.*, **2003**, *104*(3), 183–188. DOI: [10.1002/poc.592](https://doi.org/10.1002/poc.592)

Received: 22.02.2020

Accepted: 05.04.2020