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## THE MAIN FACTOR DETERMINING THE LOW INVERSION BARRIERS OF N-SULFENYLIMINES

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The energy and electronic parameters of the nitrogen atom inversion in isoelectronic N-alkylimines and N-sulfenylimines ( $H_2C=NR$ , where  $R=Me, Et, SH, SMe$ ) have been calculated using DFT method (B3LYP/6-311+G(d,p)) in terms of NBO. It has been established that substitution of methylene group by sulfur atom does not lead to the decrease in the inversion barriers due to the  $nN \rightarrow \sigma_{S-H(C)}^*$  interactions, since total energies of the  $nN \rightarrow \sigma_{S-H(C)}^*$ ,  $nN \leftrightarrow \sigma_{S-H(C)}$  and  $nN \leftrightarrow n_sS$  interactions in the N-sulfenylimines and of the  $nN \rightarrow \sigma_{C-H(C)}^*$ ,  $nN \leftrightarrow \sigma_{C-H(C)}$  interactions in the N-alkylimines are almost equal. The interactions of the nitrogen lone pair with the Rydberg orbitals of the sulfur atom ( $nN \rightarrow RY_s^*$ ) promote the reduction of the inversion barriers of the N-sulfenylimines (by 28–33  $\text{kJ}\cdot\text{mol}^{-1}$ ) in comparison with the N-alkylimines. However, analysis of the total energies of all donor-acceptor and repulsive interactions between the nitrogen lone pair and the orbitals of neighboring atoms and bonds showed that they promote the increase in the inversion barriers of the N-sulfenylimines by 0.8–14.3  $\text{kJ}\cdot\text{mol}^{-1}$ . The  $n_sS \rightarrow \sigma_{C=N}^*$  and  $n_sS \rightarrow \pi_{C=N}^*$  interactions are the main factor that determines the decrease in the inversion barriers of the N-sulfenylimines relative to the N-alkylimines. These interactions, taking into account the corresponding interactions in the N-alkylimines, contribute to the barriers decrease of 64.5–71.7  $\text{kJ}\cdot\text{mol}^{-1}$ .

**Keywords:** imines, inversion barrier, intramolecular interactions, charge, natural bond orbital method.

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### Introduction

Configurational stability of imines is determined by the combination of electronic and steric effects of substituents at the  $C=N$  bond [1–4]. These effects cannot often be divided. The thermal isomerization of imines generally passes through the inversion mechanism [1], and the analysis of experimental data makes it possible to describe the effect of substituents on the values of the inversion barriers only qualitatively.

The inversion barrier increases when heteroatoms with higher electronegativity than the carbon atom and with at least one lone pair (LP) are attached to the nitrogen atom [1]. High configurational stability of hydrazones, oximes and

galoimines was explained by the increase of s-character of the nitrogen lone pair and the augmentation of the repulsion between nitrogen and N-substituent lone pairs [1]. These factors prevent reaching the transition state (TS) of the nitrogen inversion.

It was shown that the computed inversion barriers of imines  $H_2C=NXH_n$  (where  $XH_n=CH_3, NH_2, OH, F$ ) increase with the rise in electronegativity of N-substituents and with the decrease in hybridization degree of the nitrogen lone pair in the ground state (GS) of inversion [3]. Electronegativity of the  $XH_n$  substituent has the main influence on the inversion barriers and the s-character of the nitrogen LP in imines  $H_2C=NXH_n$  (where

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$\text{XH}_n=\text{H}$ ,  $\text{CH}_3$ ,  $\text{NH}_2$ ,  $\text{OH}$ ,  $\text{F}$ ,  $\text{SiH}_3$ ,  $\text{PH}_2$ ,  $\text{SH}$ ,  $\text{Cl}$ ) [5,6]. Intramolecular interactions are of secondary importance and promote the increase in the inversion barriers with the rise in electronegativity of the  $\text{XH}_n$  substituents containing elements of the second period (except C) and their decrease for the  $\text{XH}_n$  substituents containing elements of the third period (except Cl). The interactions of the X atom lone pairs with  $\pi^*$ -orbitals of the C=N bond ( $n\text{X}\rightarrow\pi^*_{\text{C=N}}$ ) make the main contribution to the change in the energies.

At the same time, the sharp decrease in the inversion barriers of N-sulfenylimines in comparison with N-alkylimines deserves special attention. For example, the experimentally determined inversion barrier of N-(methylsulfonyl)imine of mesoxalic ester ( $66.8 \text{ kJ}\cdot\text{mol}^{-1}$  [7]) is lower than the inversion barrier of corresponding isoelectronic N-ethylimine ( $101.7 \text{ kJ}\cdot\text{mol}^{-1}$  [8]) by  $34.9 \text{ kJ}\cdot\text{mol}^{-1}$ , despite the close electronegativities of sulfur (2.44) and carbon (2.5) atoms as well as the comparable volumes of N-substituents and the repulsion between the nitrogen and sulfur lone pairs. The observed decrease in the inversion barriers was a priori explained by the interaction of the nitrogen lone pair with the 3d-orbitals of the sulfur atom (the  $n\text{N}\rightarrow 3\text{dS}$  interaction or (p-d) $\pi$ -conjugation) and/or with the antibonding orbital of the S-Z bond (the  $n\text{N}\rightarrow\sigma^*_{\text{S-Z}}$  interaction) [9]. In the theoretical study of the electronic structure of N-sulfonylformaldehydes  $\text{H}_2\text{C}=\text{NSZ}$  (where  $\text{Z}=\text{H}$ ,  $\text{CH}_3$ ,  $\text{F}$ ,  $\text{Cl}$ ,  $\text{BH}_2$ ) [10], the presence of the  $n\text{N}\rightarrow 3\text{dS}$  and  $n\text{N}\rightarrow\sigma^*_{\text{S-Z}}$  interactions was confirmed and the conjugation of the sulfur lone pair with antibonding orbital of the C=N bond (the  $n_{\text{S}}\rightarrow\pi^*_{\text{C=N}}$  interaction) was found. These interactions increase in the TS of the inversion and supposedly lead to a reduction of the inversion barriers of N-sulfenylimines in comparison with corresponding N-alkylimines. However, there is no comparative analysis of the intramolecular

interactions in the isoelectronic systems in the mentioned work.

Despite various assumptions about the reasons of the decrease in the inversion barriers of imines containing the sulfur atom – (p-d) $\pi$ -conjugation, the  $n_{\text{S}}\rightarrow\pi^*_{\text{C=N}}$  interaction, the negative hyperconjugation  $n\text{N}\rightarrow\sigma^*_{\text{S-X}}$  or other factors, which are not taken into account, nowadays there is no single standpoint on the considered problem. The relative or the mutual influence of these factors on the inversion barriers has not been practically discussed. The aim of the present work is to solve this problem.

#### Computational methods

All calculations were made using the DFT method (B3LYP/6-311+G(d,p) [11]) by means of the software package Firefly 8.2.0 [12]. Geometry optimizations were performed for all systems. The accordance of computed points to the minima and saddle points of the potential energy surface was confirmed by vibrational frequency calculations. Basis set 6-311+G(d,p) was used as sufficient for purposes mentioned above and for the better comparability with the results of previous studies and experimental structural data. The obtained wave functions were analyzed in terms of Natural Bond Orbital method using the program NBO 5.9 [13] which is implemented in the Firefly 8.2.0 package. The atomic charges and populations were obtained by means of natural population analysis (NPA).

#### Results and discussion

As the subject of the study, we selected N-alkylimines I, III and isoelectronic N-sulfenylimines II, IV (Table 1), in which the steric effect of the substituents at the nitrogen atom on the inversion barriers is minimal, and in the electronic interactions not only the orbitals of S-H and C-H bonds take place but also the orbitals of S-C and C-C bonds. This fact considerably expands the area of research.

Table 1

Energy parameters of imines  $\text{H}_2\text{C}=\text{NR}$ 

Imine	R	State	Energy, $\text{kJ}\cdot\text{mol}^{-1}$			
			$E^*$	$\Delta E_i^\ddagger$	$E(\text{nN})$	$\Delta E(\text{nN})$
I	$\text{CH}_3$	GS	-133.9855141	117.9	-932.76	405.32
		TS	-133.9406251		-527.44	
II	SH	GS	-492.8675073	89.6	-1154.17	495.72
		TS	-492.8333859		-658.45	
III	$\text{CH}_2\text{CH}_3$	GS	-173.3132320	115.7	-933.79	406.22
		TS	-173.2691625		-527.57	
IV	$\text{SCH}_3$	GS	-532.1954774	81.1	-1127.65	484.14
		TS	-532.1645939		-643.51	

Note: \* – absolute energy (a.u.).

The main energy parameters of imines I–IV are given in Table 1. The inversion barriers of the imines I–IV ( $\Delta E_i^\ddagger$ ) have been calculated as the difference between the energies of the transition and ground states. The decrease in the  $\Delta E_i^\ddagger$  values when replacing the methylene group with the sulfur atom at the nitrogen (by 28.3 and 34.6 kJ·mol<sup>-1</sup> for imines I, II and III, IV, respectively) agrees with the decrease in experimentally determined barriers for the single-type N-alkylimines and N-sulfenylimines [7–9].

The influence of intramolecular interactions on the inversion barriers in imines I–IV has been estimated using the approach given elsewhere [14].

All analyzed interactions were divided into 7 groups. Every group includes the alternative interactions of molecular orbitals of the same bonds (Table 2). They are the interactions of the nitrogen lone pair with orbitals of C(S)–C(H) bonds and with the sulfur lone pairs for the group 1; with the Rydberg orbital of atom attached to the nitrogen for the group 2; and with the methylene group orbitals for the group 3. They are the interactions of orbitals of N–C(S) bonds with the methylene group orbitals for the group 4; the interactions between orbitals of C=N and N–C(S) bonds for the group 5; the interactions between the orbitals of C=N and C(S)–C(H) bonds for the group 6; and the interactions between the sulfur lone pairs and orbitals of C=N bond for the group 7.

The energies of the donor-acceptor interactions, which stabilize the GS and TS, were taken with a minus sign and the energies of the repulsive interactions, which destabilize these states, were taken with a plus sign. The total energy of the interactions in each group ( $\Sigma E^i$ ) was calculated by adding the values of the donor-acceptor interaction energies and the repulsive interaction energies in the ground or the transition state. The resultant effect of the interactions on the inversion barrier in each group was found according to the formula  $\Delta \Sigma E^i = \Sigma E_{TS}^i - \Sigma E_{GS}^i$ . The negative values of  $\Delta \Sigma E^i$  indicate the decrease in the inversion barrier because of the considered interactions, while the positive values of  $\Delta \Sigma E^i$  indicate the increase in the inversion barrier. The relative influence of these interactions on the inversion barrier in the transition from N-alkylimines to isoelectronic N-sulfenylimines was determined by the formula  $\delta \Delta \Sigma E^i = \Delta \Sigma E^i$  (imine II (IV)) –  $\Delta \Sigma E^i$  (imine I (III)). The negative values of  $\delta \Delta \Sigma E^i$  denote the decrease in the inversion barrier of N-sulfenylimine compared to corresponding N-alkylimine because of the considered interactions, while the positive values of  $\delta \Delta \Sigma E^i$  denote the increase of the inversion barrier. The values of  $\Sigma E^i$ ,  $\Delta \Sigma E^i$  and  $\delta \Delta \Sigma E^i$  were

obtained by summation of corresponding values of  $\Sigma E^i$ ,  $\Delta \Sigma E^i$  and  $\delta \Delta \Sigma E^i$ .

The calculated inversion barriers of the imines I–IV correlate with the  $\Sigma \Delta \Sigma E^{1-7}$  values according to the following equation:

$$\Delta E_i^\ddagger = 248.8 + 0.696 \cdot \Sigma \Delta \Sigma E^{1-7} \quad (r=0.988, s=2.9) \quad (1)$$

The satisfactory correlation is observed probably because of a little difference in electronegativities of the carbon and sulfur atoms as well as the comparable volumes of substituents at the nitrogen atom (conformational energies of Me-, HS-, Et- and MeS-group are equal to 7.1, 3.8, 7.35 and 2.9 kJ·mol<sup>-1</sup>, respectively [15]) and the minimal steric repulsion between the substituents at the imino-group. The correlation makes it possible to believe that the interactions, which have an effect on the change of the inversion barriers when varying N-substituents, were selected correctly and taken into account to the full. In this connection, the comparative analysis of the data from Table 2 must show the change of the energies of the intramolecular interactions in imines when replacing methylene group with the sulfur atom at the nitrogen and determine the relative influence of these interactions on the change in the nitrogen inversion barriers.

Difference between the energies of the nitrogen lone pairs in the transition and ground states (Table 1,  $\Delta E(nN)$ ) for imines I–IV also correlates with the  $\Delta E_i^\ddagger$  values according to the following equation:

$$\Delta E_i^\ddagger = 263.8 - 0.363 \Delta E(nN) \quad (r=-0.959, s=5.3) \quad (2)$$

The opposite direction of the change in the above-mentioned energy parameters attracts attention. The inversion barriers of N-alkylimines I, III are larger than the inversion barriers of N-sulfenylimines II, IV, whereas the  $\Delta E(nN)$  values are larger for the latter. Usually, these parameters change in one direction. Furthermore, the  $\Delta E(nN)$  values are 3.4–6 times more than the  $\Delta E_i^\ddagger$  values. Whereas the comparable electronegativities of the sulfur and carbon atoms as well as the close volumes of N-substituents (although the conformational energies of the sulfenyl substituents are even less than the alkyl substituents!), we have come to the obvious conclusion that the intramolecular interactions have the main influence on the decrease in the inversion barriers of the N-sulfenylimines.

Analysis of the data of group 1 shows the increase in the energies of the  $nN \rightarrow \sigma_{C-H(C)}^*$  and  $nN \rightarrow \sigma_{S-H(C)}^*$  interactions in the TS which contributes

Table 2  
Energies (kJ·mol<sup>-1</sup>) of the main interactions that affect the energetics of the nitrogen inversion process in imines I–IV

Group	Energy parameter	H <sub>2</sub> C=NCH <sub>3</sub> (I)		H <sub>2</sub> C=NSH (II)		H <sub>2</sub> C=NC <sub>2</sub> H <sub>5</sub> (III)		H <sub>2</sub> C=NSCH <sub>3</sub> (IV)	
		GS	TS	GS	TS	GS	TS	GS	TS
1	$E(nN \leftrightarrow \sigma_{C(S)-H(C)})^a$	50.0	81.2	31.9	54.4	54.5	88.9	32.7	55.8
	$E(nN \leftrightarrow n_{\sigma}S)^a$	–	–	5.1	19.8	–	–	6.2	24.7
	$E(nN \rightarrow \sigma_{C(S)-H(C)}^*)^{b,c}$	-32.4	-85.1	-9.8	-68.1	-27.8	-77.4	-7.7	-66.1
	$\Sigma E^1$	17.6	-3.9	27.2	6.1	26.7	11.5	31.2	14.4
	$\Delta \Sigma E^1 (\delta \Delta \Sigma E^1)$	-21.5		-21.1	(0.4)	-15.2		-16.8	(-1.6)
2	$E(nN \rightarrow RY_{C(H_2C)}^*)^{b,c}$	-20.1	-18.1	-23.7	-21.0	-19.6	-14.9	-24.6	-17.5
	$E(nN \rightarrow RY_{C(S)}^*)^{b,c}$	-12.1	-9.8	-10.5	-36.3	-11.1	-5.1	-9.4	-36.3
	$\Sigma E^2$	-32.2	-27.9	-34.2	-57.3	-30.7	-20.0	-34.0	-53.8
	$\Delta \Sigma E^2 (\delta \Delta \Sigma E^2)$	4.3		-23.1	(-27.4)	10.7		-19.8	(-30.5)
3	$E(nN \leftrightarrow \sigma_{C-H(H_2C)})^a$	73.2	121.6	59.5	122.2	72.0	122.1	60.5	115.8
	$E(nN \rightarrow \sigma_{C-H(H_2C)}^*)^{b,c}$	-68.6	-191.3	-49.0	-144.7	-68.0	-188.7	-49.3	-142.3
	$\Sigma E^3$	4.6	-69.7	10.5	-22.5	4.0	-66.6	11.2	-26.5
	$\Delta \Sigma E^3 (\delta \Delta \Sigma E^3)$	-74.3		-33.0	(43.3)	-70.6		-37.7	(32.9)
4	$E(\sigma_{N-C(S)} \leftrightarrow \sigma_{C-H(H_2C)})^a$	42.0	11.7	52.1	13.8	43.2	12.6	52.2	12.2
	$E(\sigma_{N-C(S)} \rightarrow \sigma_{C-H(H_2C)}^*)^{b,c}$	-16.9	0.0	-26.5	0.0	-16.4	0.0	-25.5	0.0
	$E(\sigma_{C-H(H_2C)} \rightarrow \sigma_{N-C(S)}^*)^{b,c}$	-28.8	-42.8	-40.9	-48.3	-26.9	-40.9	-36.8	-44.5
	$\Sigma E^4$	-3.7	-31.1	-15.3	-34.5	-0.1	-28.3	-10.1	-32.3
	$\Delta \Sigma E^4 (\delta \Delta \Sigma E^4)$	-27.4		-19.2	(8.2)	-28.2		-22.2	(6.0)
5	$E(\sigma_{C=N} \rightarrow \sigma_{N-C(S)}^*)^{b,c}$	-2.6	-13.9	0.0	-5.2	-3.0	-15.2	0.0	-5.1
	$E(\sigma_{N-C(S)} \rightarrow \sigma_{C=N}^*)^{b,c}$	-2.2	-15.3	0.0	-9.8	-2.5	-15.5	0.0	-9.8
	$\Sigma E^5$	-4.8	-29.2	0.0	-15.0	-5.5	-30.7	0.0	-14.9
	$\Delta \Sigma E^5 (\delta \Delta \Sigma E^5)$	-24.4		-15.0	(9.4)	-25.2		-14.9	(10.3)
6	$E(\sigma_{C=N} \leftrightarrow \sigma_{C(S)-H(C)})^a$	15.4	0.0	5.3	0.0	13.9	0.0	4.5	0.0
	$E(\pi_{C=N} \leftrightarrow \sigma_{C(S)-H(C)})^a$	48.7	47.4	0.0	0.0	49.8	48.2	0.0	0.0
	$E(\sigma_{C(S)-H(C)} \rightarrow \sigma_{C=N}^*)^{b,c}$	-15.2	-38.9	-8.9	-6.3	-14.0	-38.9	-7.1	-6.7
	$E(\sigma_{C(S)-H(C)} \rightarrow \pi_{C=N}^*)^{b,c}$	-29.9	-43.7	0.0	0.0	-24.1	-44.5	0.0	0.0
	$E(\pi_{C=N} \rightarrow \sigma_{C(S)-H(C)}^*)^{b,c}$	-27.1	-23.1	0.0	0.0	-25.6	-23.1	0.0	0.0
	$\Sigma E^6$	-8.1	-58.3	-3.6	-6.3	0.0	-58.3	-2.6	-6.7
	$\Delta \Sigma E^6 (\delta \Delta \Sigma E^6)$	-50.2		-2.7	(47.5)	-58.3		-4.1	(54.2)
7	$E(n_{\sigma}S \leftrightarrow \sigma_{C=N})^a$	–	–	3.1	2.8	–	–	4.9	2.2
	$E(n_{\pi}S \leftrightarrow \pi_{C=N})^a$	–	–	54.2	62.0	–	–	46.9	55.1
	$E(n_{\sigma}S \rightarrow \sigma_{C=N}^*)^{b,c}$	–	–	-3.6	-42.6	–	–	-4.3	-46.3
	$E(n_{\pi}S \rightarrow \pi_{C=N}^*)^{b,c}$	–	–	-64.9	-146.3	–	–	-72.4	-161.8
	$\Sigma E^7$	–	–	-11.2	-124.1	–	–	-24.9	-150.8
	$\Delta \Sigma E^7 (\delta \Delta \Sigma E^7)$	–		-112.9	(-112.9)	–		-125.9	(-125.9)
$\Sigma \Sigma E^{1-7}$	-26.6	-220.1	-26.6	-253.6	-5.6	-192.4	-29.2	-270.6	
$\Sigma \Delta \Sigma E^{1-7} (\Sigma \delta \Delta \Sigma E^{1-7})$	-193.5		-227.0	(-33.5)	-186.8		-241.4	(-54.6)	

Note: <sup>a</sup> – pairwise steric exchange energies  $dE(i,j)$ ; <sup>b</sup> –  $E(2)$  stabilization energies; <sup>c</sup> – were taken with a minus sign within the framework of our approach.

*The main factor determining the low inversion barriers of N-sulfonylimines*

to the reduction of the inversion barriers of imines I–IV (Table 2). Actually, the differences between the energies of the  $nN \rightarrow \sigma_{C-H(C)}^*$  interactions in the transition and ground states for imines II, IV ( $\delta E$ ) are a little more than between the energies of similar  $nN \rightarrow \sigma_{C-H(C)}^*$  interactions for imines I, III (the  $\delta E$  values are  $-58.3$ ,  $-58.4$  and  $-52.7$ ,  $-49.6$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively). Therefore, the  $nN \rightarrow \sigma_{S-H(C)}^*$  interactions must lead to the decrease of the inversion barriers of imines II, IV as compared to imines I, III (the  $\Delta\delta E$  values are  $-5.6$  and  $-8.8$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively). The almost equal values of  $\Delta\delta E$  for imines II, I and IV, III indicate that the effect of the  $nN \rightarrow \sigma_{C-H}^*$  and  $nN \rightarrow \sigma_{S-H}^*$  interactions on the change in the inversion barriers of imine I relative to imine II and the effect of  $nN \rightarrow \sigma_{C-C}^*$ ,  $nN \rightarrow \sigma_{S-C}^*$  interactions on the change in the inversion barriers of imine III relative to imine IV are comparable. The substitution of methylene group by sulfur atom leads to the appearance of the  $nN \leftrightarrow \sigma_{S-H(C)}$  and  $nN \leftrightarrow nS$  interactions, instead of the  $nN \leftrightarrow \sigma_{C-H(C)}$  interactions, which rise in the TS and contribute to the increase in the inversion barriers. As a result, the total energies of the interactions of group 1 ( $\Delta\Sigma E^1$ ) for imines I, II and III, IV are nearly equal. Accordingly, interactions from group 1 do not affect the change in the inversion barriers of imines II, IV relative to imines I, III (Table 2,  $\delta\Delta\Sigma E^1$ ). Thus, the interactions of  $nN \rightarrow \sigma_{S-X}^*$  type cannot be the reason for the observed decrease in the inversion barriers of the N-sulfenylimines as compared to the N-alkylimines.

The interactions of the nitrogen atom LP with the Rydberg orbitals of adjacent atoms (Table 2, group 2) have a differently directed effect on the inversion barriers of imines I, III and II, IV. The interactions of the nitrogen atom LP with the Rydberg orbitals of the imino-carbon atom ( $nN \rightarrow RY_{C(H_2C)}^*$ ) and the N-alkyl carbon atom ( $nN \rightarrow RY_C^*$ ) decrease in the TS and contribute to the increase in the inversion barriers of the N-alkylimines. At the same time,  $nN \rightarrow RY_S^*$  interactions increase in the TS and contribute to the decrease in the inversion barriers of the N-sulfenylimines. In general, the resultant effect of the interactions of group 2 on the reduction of the inversion barriers of imines II, IV as compared with isoelectronic imines I, III is sufficiently large and is about  $-30$   $\text{kJ}\cdot\text{mol}^{-1}$  (Table 2,  $\delta\Delta\Sigma E^2$ ).

It is known, that the interactions of the nitrogen LP with the antibonding orbitals of  $\sigma$ -bonds of the imino-carbon atom ( $nN \rightarrow \sigma_{C-X(X_2C)}^*$ ) can lead to a reduction of the inversion barriers as a result of the TS stabilization [9]. At the same time, the influence of alternative repulsive intramolecular interactions ( $nN \leftrightarrow \sigma_{C-X(X_2C)}$ ), which contribute to the increase in

the inversion barriers was not taken into account. Analysis of data of group 3 (Table 2) shows that the energy of the  $nN \rightarrow \sigma_{C-H(H_2C)}^*$  interactions actually increases sharply in the TS, which promotes the decrease in the inversion barriers of imines I–IV. However, the energy of the  $nN \leftrightarrow \sigma_{C-H(H_2C)}$  interactions also increases. At the same time, the interactions of group 3 must lead to the decrease in the inversion barriers of N-alkylimines I, III relative to N-sulfenylimines II, IV (the  $\delta\Delta\Sigma E^3$  values are  $41.3$  and  $32.9$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively). This influence is mainly caused by the larger efficiency of the  $nN \rightarrow \sigma_{C-H(H_2C)}^*$  interactions in imines I, III because of the higher energies of the nitrogen LP (Table 1,  $E(nN)$ ). In other words, the interactions of group 3 should promote the increase in the inversion barriers of the N-sulfenylimines in comparison with isoelectronic N-alkylimines.

In general, the substitution of methylene group by sulfur atom at the nitrogen leads to the negligible change in the total energies of the donor-acceptor and repulsive interactions between the nitrogen lone pair and the orbitals of neighboring atoms and bonds (groups 1–3) for imines III and IV (the  $\Sigma\delta\Delta\Sigma E^{1-3}$  value is  $0.8$   $\text{kJ}\cdot\text{mol}^{-1}$ ). Furthermore, these interactions must lead to the rise rather than decrease in the inversion barrier of imine II relative to imine I (the  $\Sigma\delta\Delta\Sigma E^{1-3}$  value is  $14.3$   $\text{kJ}\cdot\text{mol}^{-1}$ ).

The change in the energies of all considered interactions (Table 2,  $\Sigma\Delta\Sigma E^{1-7}$  by  $1$   $\text{kJ}\cdot\text{mol}^{-1}$  causes the change in the inversion barrier by  $\sim 0.7$   $\text{kJ}\cdot\text{mol}^{-1}$  (Eq. (1)). Taking into account this fact, the total effect of the interactions from groups 1–3 on the increase in inversion barriers of the N-sulfenylimines in comparison with the N-alkylimines can be under  $10$   $\text{kJ}\cdot\text{mol}^{-1}$ .

The group 4 (Table 2) includes the interactions between the orbitals of  $\sigma$ -bonds of the nitrogen atoms with  $\alpha$ -atom of substituents ( $\sigma_{N-C(S)}$ ) and the orbitals of the C–H bonds at the imino-carbon atom ( $\sigma_{C-H(H_2C)}$ ). It should be noted, on the one hand, that the total effect of these interactions ( $\Delta\Sigma E^4$ ) on the inversion barriers of all considered imines is unexpectedly greater than the total effect of the interactions of the nitrogen lone pair from group 1 ( $\Delta E^1$ ). On the other hand, the interactions from group 4 promote the larger decrease in the inversion barriers of N-alkylimines I, III than N-sulfenylimines II, IV ( $\delta\Delta\Sigma E^4$ ), that is, they lead to relative increase in the inversion barriers of the latter.

The interactions of group 5 (Table 2) also promote the relative decrease of the inversion barriers of N-alkylimines I, III as compared to N-sulfenylimines II, IV (the  $\delta\Delta\Sigma E^5$  values are  $9.4$

and  $10.3 \text{ kJ}\cdot\text{mol}^{-1}$  for imines II, I and IV, III, respectively) and thus contribute to the relative increase in the inversion barriers of the N-sulfenylimines.

In general, the total effect of the interactions of groups 1–5 must lead to the increase in the inversion barriers of the N-sulfenylimines as compared to isoelectronic N-alkylimines (the  $\Sigma\Delta\Sigma E^{1-5}$  values are  $31.9$  and  $17.1 \text{ kJ}\cdot\text{mol}^{-1}$  for imines II, I and IV, III, respectively).

The interactions of groups 6 and 7 (Table 2) in a certain sense are analogous and antagonistic. There are the interactions between the orbitals of the C=N  $\sigma$ - and  $\pi$ -bonds and the orbitals of the C–H(C) and S–H(C) bonds of N-substituents in group 6. These interactions are insignificant in N-sulfenylimines II, IV. Whereas group 7 includes the interactions of the orbitals of the C=N bond with the sulfur lone pairs, that are not in N-alkylimines I, III. The interactions of group 6 because of the dominant stabilization of the transition states further the substantial decrease in the inversion barriers of N-alkylimines I, III in comparison with N-sulfenylimines II, IV. That is, they promote the relative increase of the inversion barriers of N-sulfenylimines (Table 2,  $\delta\Delta\Sigma E^6$ ). At the same time, the interactions of group 7 must contribute to the sharp decrease in the inversion barriers of the N-sulfenylimines (Table 2,  $\delta\Delta\Sigma E^7$ ). The interactions between the sulfur lone pair and antibonding  $\pi$ -orbital of the C=N bond make the dominant contribution to the  $\delta\Delta\Sigma E^7$  values. It is absolutely obvious that the contribution of the  $n_{\sigma}S \rightarrow \sigma_{C=N}^*$  and  $n_{\pi}S \rightarrow \pi_{C=N}^*$  interactions provides the decrease in the inversion barriers of N-sulfenylimines II, IV as compared to corresponding isoelectronic N-alkylimines I, III.

Relative equality of the changes in the inversion barriers and the total energies of the intramolecular interactions from groups 1–7 when replacing the methylene group with the sulfur atom (the  $\Delta\Delta E_i^{\pm}$  and  $\Sigma\delta\Delta\Sigma E^{1-7}$  values for imines II, I are  $-28.3$  and  $-33.5 \text{ kJ}\cdot\text{mol}^{-1}$  and for imines IV, III they are

$-34.6$  and  $-54.6 \text{ kJ}\cdot\text{mol}^{-1}$ ), in our view, can be a validation of the analysis of the intramolecular interactions effect on the decrease in the inversion barriers of N-sulfenylimines II, IV in comparison with isoelectronic N-alkylimines I, III.

Analysis of the intramolecular interactions from Table 2 enables to explain the observed change in the electronic parameters of imines I–IV (Table 3). The population of the lone pair of the nitrogen atom ( $N^{LP}$ ) increases with the decrease in the energies of donor-acceptor interactions of groups 1–3 that lead to the transfer of electron density from the nitrogen LP. The decrease in the  $N^{LP}$  values in the TS as compared with the GS, despite of the increase in effective electronegativity of the nitrogen atom in the transition from  $sp^2$ - into the  $sp$ -state, is due to the higher energies of the donor-acceptor interactions  $nN \rightarrow \sigma_{C(S)-H(C)}^*$  and  $nN \rightarrow \sigma_{C-H(H2C)}^*$ . These interactions promote the electron transfer from the nitrogen LP. The larger values of the  $N^{LP}$  for N-sulfenylimines II, IV than for N-alkylimines I, III are apparently caused by alternative transfer of the electron density from the sulfur atom, primarily because of the  $n_{\pi}S \rightarrow \pi_{C=N}^*$  interactions. The larger differences between the  $N^{LP}$  values in the TS and GS of N-sulfenylimines (the  $\Delta N^{LP}$  values are  $0.124$ – $0.126 e$ ) as compared to N-alkylimines (the  $\Delta N^{LP}$  values are  $0.103$ – $0.104 e$ ) are probably due to the larger change in the energies of the  $nN \rightarrow \sigma_{C(S)-H(C)}^*$ ,  $nN \rightarrow \sigma_{C-H(H2C)}^*$  and  $nN \rightarrow RY_{S(C)}^*$  interactions for imines II and IV ( $-58.4$  and  $-58.3$ ,  $-25.8$  and  $-25.8$ ,  $-95.7$  and  $-93 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively) than for imines I and III ( $-52.7$  and  $-49.6$ ,  $2$  and  $2.3$ ,  $-122.7$  and  $-120.7 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively).

Considerable increase in the negative charge on the nitrogen atom ( $q^N$ ) in N-sulfenylimines II, IV relative to N-alkylimines I, III is also the result of simultaneous decrease in the energies of the donor-acceptor interactions  $nN \rightarrow \sigma_{C(S)-H(C)}^*$  and  $nN \rightarrow \sigma_{C-H(H2C)}^*$  and increase in the transfer of the electron density to the nitrogen atom because of the  $n_{\pi}S \rightarrow \pi_{C=N}^*$  interactions. The larger  $q^N$  values in the TS compared

Table 3

Electronic and structural parameters of imines  $H_2C=NR$ 

Imine	R	State	$N^{LP}, e$	$q^N, e$	$q^C, e$	$q^{CH2(S)}, e$	$\theta_{C=N-R}^0$	%p	$l_{C=N}, \text{\AA}$
I	CH <sub>3</sub>	GS	1.910	-0.426	-0.044	-0.031	118.06	69.35	1.263
		TS	1.806	-0.471	0.034	0.035	179.31	100.00	1.236
II	SH	GS	1.942	-0.543	-0.070	0.156	117.45	59.33	1.270
		TS	1.818	-0.673	-0.033	0.368	175.84	99.75	1.254
III	CH <sub>2</sub> CH <sub>3</sub>	GS	1.909	-0.429	-0.041	0.145	118.25	69.21	1.263
		TS	1.806	-0.475	0.035	0.210	179.58	99.99	1.238
IV	SCH <sub>3</sub>	GS	1.937	-0.565	-0.068	0.364	118.73	60.21	1.272
		TS	1.811	-0.683	-0.048	0.553	176.73	99.76	1.257

*The main factor determining the low inversion barriers of N-sulfenylimines*

to the GS are caused by the increase in the nitrogen electronegativity because of the change in its hybridization (the transition from  $sp^2$ - into  $sp$ -state).

The larger negative charge on the imino-carbon atom ( $q^C$ ) of N-sulfenylimines II, IV in comparison with N-alkylimines I, III is seemingly a result of the transfer of the electron density from the sulfur atom to the C=N bond. The considerably less difference between the  $q^C$  values in the GS and TS for N-sulfenylimines than for N-alkylimines corresponds to the increase in the energies of the donor-acceptor interactions  $n_oS \rightarrow \sigma_{C=N}^*$  and, especially,  $n_\pi S \rightarrow \pi_{C=N}^*$ . These interactions are the cause of the larger positive charge on the sulfur atom ( $q^S$ ) than on the methylene group ( $q^{CH_2}$ ) at the nitrogen atom in N-alkylimines. In addition, they are the reason of the sharp increase in the  $q^S$  values in the TS relative to the GS of the N-sulfenylimines, as well as the elongation of the C=N bond ( $l_{C=N}$ ) of the N-sulfenylimines (Table 3).

It should be noted that for the considered imines any known relationship was not found between the value of the inversion barrier and following parameters: the valence angle at the nitrogen atom ( $\theta_{C=N-R}$ ) and p-character (%p) of the nitrogen LP in the GS, the difference between the nitrogen LP energies in the TS and GS (Table 3) [1,9]. The values of  $\Delta E_i^*$  are independent of the  $\theta_{C=N-R}$  values and rise with the increase in the %p values and with the decrease in the  $\Delta E(nN)$  values (Table 3).

### Conclusions

The decrease in the inversion barriers of the N-sulfenylformaldimines as compared with the isoelectronic N-alkylformaldimines (by 28.3–34.6  $\text{kJ}\cdot\text{mol}^{-1}$ ) is not a result of the  $nN \rightarrow \sigma_{S-H(C)}^*$  interactions, despite the fact that they promote the decrease in the inversion barriers of the N-sulfenylformaldimines (by 5.6–8.8  $\text{kJ}\cdot\text{mol}^{-1}$ ) relative to the alternative  $nN \rightarrow \sigma_{C-H(C)}^*$  interactions in the N-alkylformaldimines. The total energies of the donor-acceptor and repulsive  $nN \rightarrow \sigma_{S-H(C)}^*$ ,  $nN \leftrightarrow \sigma_{S-H(C)}$ ,  $nN \leftrightarrow n_oS$  interactions in the N-sulfenylformaldimines and the  $nN \rightarrow \sigma_{C-H(C)}^*$  and  $nN \leftarrow \sigma_{C-H(C)}$  interactions in the N-alkylformaldimines are nearly equal and therefore these interactions do not affect the change in the inversion barriers. The interactions of the nitrogen lone pair with the Rydberg orbitals of the sulfur atom ( $nN \rightarrow RY_s^*$ ) further the decrease in the inversion barriers of the N-sulfenylformaldimines (by 28.1–32.9  $\text{kJ}\cdot\text{mol}^{-1}$ ) in comparison with the  $nN \rightarrow RY_c^*$  interactions in the N-alkylformaldimines. However, the analysis of all donor-acceptor and repulsive interactions between the nitrogen lone pair and the orbitals of neighboring atoms and bonds shows that on the contrary, they

contribute to the increase in the inversion barriers of the N-sulfenylformaldimines (by 0.8–14.3  $\text{kJ}\cdot\text{mol}^{-1}$ ). Accordingly, the  $nN \rightarrow \sigma_{S-H(C)}^*$  and  $nN \rightarrow RY_s^*$  interactions that appear when replacing the methylene group with the sulfur atom cannot be the reason for the decrease in the inversion barriers of the N-sulfenylformaldimines relative to the N-alkylformaldimines. The interactions of the sulfur lone pairs with the antibonding orbitals of the C=N bond ( $n_oS \rightarrow \sigma_{C=N}^*$  and  $n_\pi S \rightarrow \pi_{C=N}^*$ ) have the main influence on the decrease in the inversion barriers of the N-sulfenylformaldimines as compared to the N-alkylformaldimines. These interactions taking into consideration the related interactions in the N-alkylformaldimines promote the barriers decrease of 64.5–71.7  $\text{kJ}\cdot\text{mol}^{-1}$ . The comparable difference between the inversion barriers of the corresponding N-sulfenyl- and N-alkylformaldimines and the sums of the energies of the intramolecular interactions is sufficient evidence of the present conclusions. Change in the population of the nitrogen lone pair, charges on the nitrogen atoms, sulfur atoms and the imino-carbon atoms as well as the elongation of the C=N bond in the N-sulfenylformaldimines relative to the N-alkylformaldimines agrees with the transfer of electrons due to the corresponding donor-acceptor interactions.

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## ОСНОВНИЙ ФАКТОР, ЯКИЙ ВИЗНАЧАЄ НИЗЬКІ БАР'ЄРИ ІНВЕРСІЇ N-СУЛЬФЕНІЛІМІНІВ

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Методом DFT (B3LYP/6-311+G(d,p)) в рамках NBO розраховані енергетичні та електронні параметри інверсії атома азоту в ізоелектронних N-алкіл- і N-сульфенілімінах ((H<sub>2</sub>C=NR, де R=Me, Et, SH, SMe). Встановлено, що введення атома сірки замість метиленової групи не приводить до зниження бар'єрів інверсії за рахунок внутрішньомолекулярних взаємодій nN→σ<sup>\*</sup><sub>S-H(C)</sub>, оскільки сумарні енергії взаємодій nN→σ<sup>\*</sup><sub>S-H(C)</sub>, nN↔σ<sub>S-H(C)</sub> і nN↔n<sub>s</sub>S в N-сульфенілімінах і nN→σ<sup>\*</sup><sub>C-H(C)</sub>, nN↔σ<sub>C-H(C)</sub> в N-алкілімінах є практично рівними. Взаємодії вільної електронної пари атома азоту з орбіталями Рідберга атома сірки (nN→RY<sub>s</sub>) сприяють зниженню бар'єрів інверсії N-сульфенілімінів у порівнянні з N-алкілімінами на 28–33 кДж/моль. Однак аналіз сумарних енергій всіх донорно-акцепторних і відштовхувальних взаємодій вільної електронної пари атома азоту з орбіталями сусідніх атомів і зв'язків виявив, що вони сприяють збільшенню бар'єрів інверсії N-сульфенілімінів на 0,8–14,3 кДж/моль. Основним фактором, який визначає зменшення бар'єрів інверсії N-сульфенілімінів у порівнянні з N-алкілімінами, є взаємодії n<sub>s</sub>S→σ<sup>\*</sup><sub>C=N</sub> і n<sub>s</sub>S→π<sup>\*</sup><sub>C=N</sub>, що сприяють, з урахуванням відповідних взаємодій в N-алкілімінах, зниженню бар'єрів на 65,4–71,7 кДж/моль.

**Ключові слова:** іміни; бар'єр інверсії; внутрішньомолекулярні взаємодії; заряд; метод натуральних орбіталей зв'язків.

## THE MAIN FACTOR DETERMINING THE LOW INVERSION BARRIERS OF N-SULFENYLIMINES

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The energy and electronic parameters of the nitrogen atom inversion in isoelectronic N-alkylimines and N-sulphenylimines (H<sub>2</sub>C=NR, where R=Me, Et, SH, SMe) have been calculated using DFT method (B3LYP/6-311+G(d,p)) in terms of NBO. It has been established that substitution of methylene group by sulfur atom does not lead to the decrease in the inversion barriers due to the nN→σ<sup>\*</sup><sub>S-H(C)</sub> interactions, since total energies of the nN→σ<sup>\*</sup><sub>S-H(C)</sub>, nN↔σ<sub>S-H(C)</sub> and nN↔n<sub>s</sub>S interactions in the N-sulphenylimines and of the nN→σ<sup>\*</sup><sub>C-H(C)</sub>, nN↔σ<sub>C-H(C)</sub> interactions in the N-alkylimines are almost equal. The interactions of the nitrogen lone pair with the Rydberg orbitals of the sulfur atom (nN→RY<sub>s</sub>) promote the reduction of the inversion barriers of the N-sulphenylimines (by 28–33 kJ·mol<sup>-1</sup>) in comparison with the N-alkylimines. However, analysis of the total energies of all donor-acceptor and repulsive interactions between the nitrogen lone pair and the orbitals of neighboring atoms and bonds showed that they promote the increase in the inversion barriers of the N-sulphenylimines by 0.8–14.3 kJ·mol<sup>-1</sup>. The n<sub>s</sub>S→σ<sup>\*</sup><sub>C=N</sub> and n<sub>s</sub>S→π<sup>\*</sup><sub>C=N</sub> interactions are the main factor that determines the decrease in the inversion barriers of the N-sulphenylimines relative to the N-alkylimines. These interactions, taking into account the corresponding interactions in the N-alkylimines, contribute to the barriers decrease of 64.5–71.7 kJ·mol<sup>-1</sup>.

**Keywords:** imines; inversion barrier; intramolecular interactions; charge; natural bond orbital method.

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