



*Dedicated in memory of an excellent teacher, Prof. Zdeněk Friedl,
who died after a serious illness in July 2012*

The Relationship Between the Heats of Formation and the Molecular Electrostatic Potentials of Polyazaarenes

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Abstract: In order to characterize the explosive properties of high-nitrogen, energetic compounds, the heats of formation, either in the gas or the solid state, are often used as preliminary data. Their relationship to the number of nitrogen atoms involved is usually known, so exploring it cannot furnish any new information. However, the very promising, quantitative structure property relationship (QSPR) approach utilizes the molecular surface electrostatic potential $V(\mathbf{r})$. We have therefore performed calculations for 12 azines and 10 azoles by the DFT B3PW91/cc-pVTZ method, and constructed their gas phase heats of formation $\Delta_f H^\circ(298, \text{g})$ by means of the isodesmic reaction approach. The acquired gas phase heats of formation $\Delta_f H^\circ(298, \text{g})$ were correlated with the molecular surface electrostatic potentials $V_{S, \text{max}}$, $V_{S, \text{min}}$, and $V_{S(\text{ring})}$, which were calculated by the B3LYP/6-31G(d,p)//B3PW91/cc-pVTZ method. It is shown that the $V_{S(\text{ring})}$ electrostatic potential describes very precisely the structures of high-nitrogen N-heteroaromatics, with both consecutive and isolated nitrogen atoms, and their thermodynamic properties.

Keywords: high-nitrogen compounds, azines, azoles, heat of formation, molecular surface electrostatic potential

Introduction

In order to characterize the explosive properties of high-nitrogen energetic compounds, their heats of formation, either in the gas or the solid state, are commonly used. Their relationship to the number of nitrogen atoms involved

is commonly known, thus exploring this can not furnish any new information. However, the very promising quantitative structure property relationship (QSPR) approach utilizes the molecular surface electrostatic potential $V(\mathbf{r})$ that is created by the nuclei and electrons of a molecule in the surrounding space. The molecular electrostatic potential $V(\mathbf{r})$ has proven to be an effective guide for describing the molecule's reactive behavior. $V(\mathbf{r})$ is the potential that is created by the molecule's nuclei and electrons at any point \mathbf{r} , and is given rigorously by:

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

where: Z_A is the charge on nucleus A , located at \mathbf{R}_A , and $\rho(\mathbf{r})$ is the molecule's electron density. The value of $V(\mathbf{r})$ in a given region can be either positive or negative, and depends upon the dominating contributions of either nuclei or electrons. The molecular surface electrostatic potential is a fundamental property, which has an influence on the behavior of the whole molecule [1-3]. The features of the molecular surface electrostatic potential can be used to establish quantitative expressions for the heat of sublimation, thus permitting the gas phase heats of formation of high-nitrogen, energetic (and other) materials to be converted to the more useful solid phase values. Since these procedures are carried out computationally, they can be applied to the assessment of proposed target compounds as well as to those that have already been prepared [3].

Our research was focused on the characterization of the molecular surface electrostatic potential and gas phase heat of formation of 12 heteroaromatic azines and 10 azoles which are often important components of high-nitrogen, energetic materials [4-6].

Calculations

The gas phase enthalpies of formation $\Delta_f H^\circ(298, \text{g})$ (HOF) of the 12 azines and 10 azoles studied, whose structures and names are shown in Figures (1) and (2), were calculated by means of the SPARTAN'10 program [7].

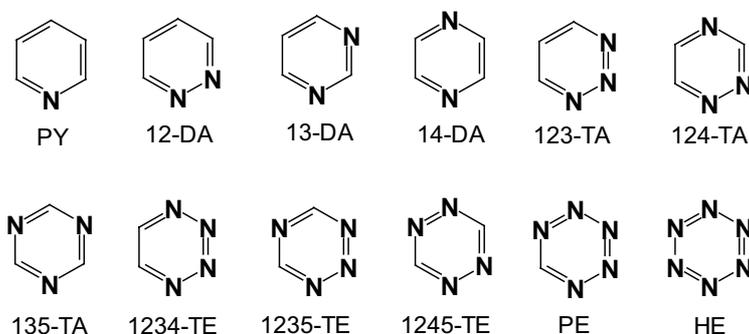


Figure 1. Structures and names of the azines studied.

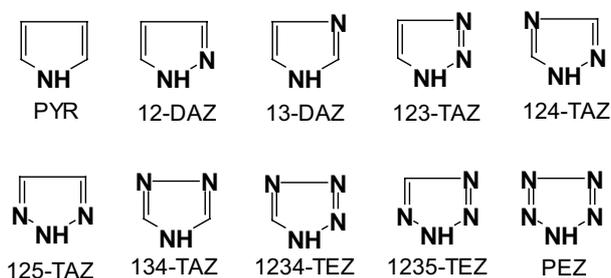


Figure 2. Structures and names of the azoles studied.

The DFT method was used with B3PW91 combination of the functional [8] and cc-pVTZ basis set [9]. The gas phase heats of formation $\Delta_f H^\circ(298, \text{g})$ were subsequently obtained (see the SPARTAN'10 program algorithm) by the isodesmic reactions approach [9] from theoretical B3PW91/cc-pVTZ reaction enthalpies $\Delta_r H^\circ(298)$ and experimental values [10] by:

$$\Delta_f H^\circ(298, \text{g}) = \Delta(\Delta_f H^\circ(298, \text{g}))_{\text{exp}} - \Delta_r H^\circ(298) \quad (2)$$

The molecular surface electrostatic potentials $V_s(\mathbf{r})$ (ESP) were calculated at the DFT B3LYP/6-31(d,p)// B3PW91/cc-pVTZ level and the molecular surface was taken to be the $0.001 \text{ e} \cdot \text{au}^{-3}$ contour of the electron density [11]. Values of the molecular surface electrostatic potentials were calculated in the following way: 10 values in the center of the heteroaromatic ring $V_s(\text{ring})$ were selected and then averaged [12-14]; they are shown in Table 1.

Results and Discussion

The gas phase heats of formation $\Delta_f H^\circ(298, \text{g})$ shown in Table 1 were calculated as described in the previous section by means of the isodesmic reactions approach [15-18]. These data confirm the general idea that increasing the number of nitrogen atoms causes a positive increase in the value of the HOFs. The N-N consecutive azines appear to be the most energetic compounds studied, which is apparent for example in the triazines, where 123-TA shows the highest HOF. The same applies even to the azoles, where 123-TAZ is the most energetic isomer.

The HOFs are the most used parameters for describing both the thermodynamic and the energetic properties of HNEMs. Nevertheless, additional descriptors are needed and the molecular surface ESP seems to be a very promising characteristic [1-3, 19, 20]. We calculated both positive $V_{S, \text{max}}$ and negative $V_{S, \text{min}}$ extrema, whose respective values are given in Table 1. Surprisingly, their correlations with the HOFs of azines and azoles proved to be nonlinear. Finally, we decided to use the ring molecular surface electrostatic potential $V_S(\text{ring})$, introduced by Politzer to describe its relationship with impact sensitivities of nitroaromatic and nitroheterocyclic molecules [12] or, more recently by other workers, for bond homolytic and disproportionation energies of polynitroaromatic compounds [13, 14].

Table 1. B3PW91/cc-pVTZ gas phase heats of formation $\Delta_f H^\circ(298, \text{g})$, B3LYP/6-31(d,p) maxima $V_{S, \text{max}}$, minima $V_{S, \text{min}}$, and ring $V_S(\text{ring})$ molecular surface electrostatic potentials of the azines and azoles studied [$\text{kJ} \cdot \text{mol}^{-1}$]

Name	$\Delta_f H^\circ(298, \text{g})$	$V_{S, \text{max}}$	$V_{S, \text{min}}$	$V_S(\text{ring})$
PY _(a)	140.2	71.6	-163.4	-42.1
12-DA _(b)	280.2	100.9	-182.8	-3.3
13-DA _(c)	188.9	93.4	-143.2	5.4
14-DA _(d)	206.3	70.5	-135.9	4.3
123-TA _(e)	403.3	130.0	-177.8	45.8
124-TA _(f)	339.0	110.5	-155.0	50.4
135-TA _(g)	229.9	77.1	-116.3	56.8
1234-TE _(h)	538.0	153.4	-149.1	98.1
1235-TE _(i)	455.7	110.9	-141.6	104.9
1245-TE _(j)	485.1	114.5	-118.4	93.5

Pe _(k)	669.5	152.8	-110.0	150.3
HE _(l)	868.6	207.0	-69.4	204.3
PYR _(m)	108.3	181.1	-115.5	-110.6
12-DAZ _(n)	183.4	186.5	-161.6	-69.2
13-DAZ _(o)	140.9	207.1	-193.2	-68.8
123-TAZ _(p)	276.4	224.5	-186.9	-28.7
124-TAZ _(q)	209.3	219.0	-162.0	-16.1
125-TAZ _(r)	259.7	198.4	-127.0	-28.4
134-TAZ _(s)	235.3	237.2	-204.8	-19.7
1234-TEZ _(t)	356.2	262.0	-173.0	20.3
1235-TEZ _(u)	346.3	242.2	-150.3	20.2
PEZ _(v)	480.0	284.2	-129.4	64.0

In order to scrutinize the relationship between the HOF and the ring ESP, we constructed the linear graphs shown in Figure 3 (for azines) and in Figure 4 (for azoles).

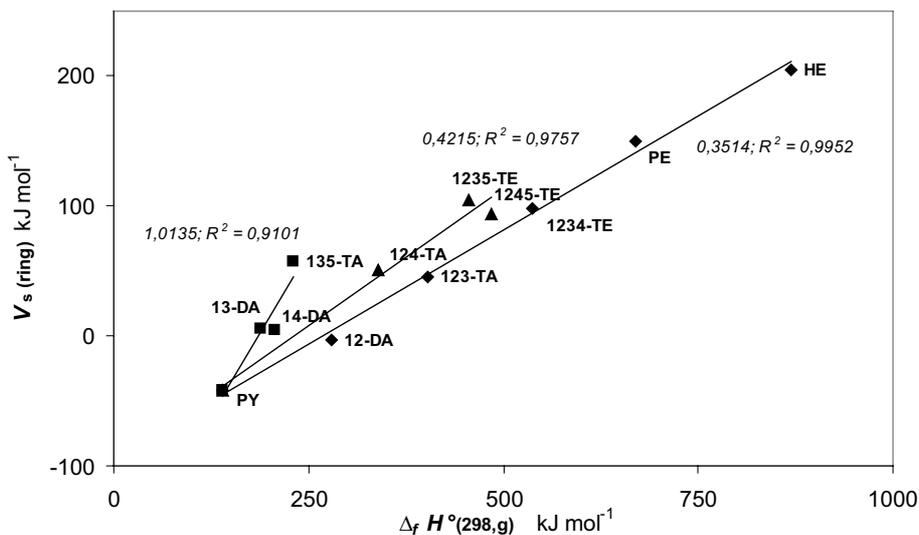


Figure 3. Relationships between the V_s (ring) ESPs and the gas phase HOFs of the azines studied.

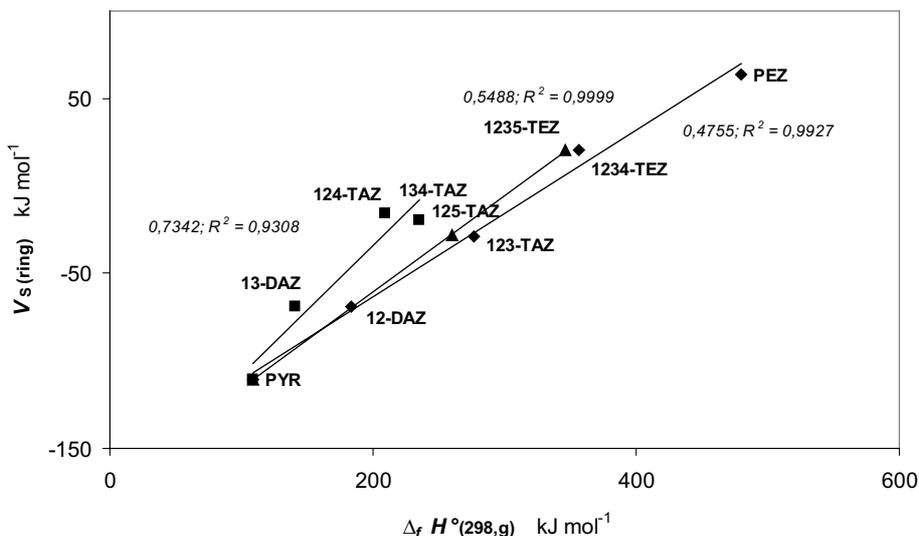


Figure 4. Relationships between the $V_S(\text{ring})$ ESPs and the gas phase HOFs of the azoles studied.

The regression lines in Figures 3 and 4 have very similar profiles. The closest correlation was achieved between the ring molecular surface electrostatic potentials $V_S(\text{ring})$ and the HOFs of N-N consecutive azines and azoles. The similarity between the electron density in both heterocyclic systems is further expressed by the close values of the corresponding slopes of the regression lines (azines 0.351 vs. azoles 0.476, respectively). An important feature of the ring electrostatic potential $V_S(\text{ring})$ is the ability to differentiate individual N isomers of azines and azoles. The cases of an N=N grouping with another N atom or another N=N segment in the *meta* position in a molecule (124-TA, 1235-TE and 1245-TE) is depicted in Figure 3, and, similarly, the grouping =N-NH-N= (125-TAZ and 1235-TEZ) in Figure 4. The series of isolated azines with all N atoms in *meta* (or *para*) positions given in Figure 3 (13-DA, 14-DA and 135-TA) constitutes the logical regression line with a slope of 1.014. The behavior of azoles with *meta* located NH amino groups and another N atom as shown in Figure 4 (13-DAZ, 124-TAZ and 134-TAZ) is similar to isolated azines with an appropriate regression line slope of 0.734. For the selected azines and azoles (see lines on the graphs), the graphs in Figures 3 and 4 show the dependence of the ring molecular electrostatic potential $V_S(\text{ring})$ on the number and positions of the nitrogen atoms. Generally, the ring molecular electrostatic potential $V_S(\text{ring})$ is influenced only by the number of nitrogen atoms. The positions of the $V_S(\text{ring})$

are depicted in Figures 5 and 6, showing maps of the molecular electrostatic potential $V_s(\text{ring})$ of the azines and azoles studied.

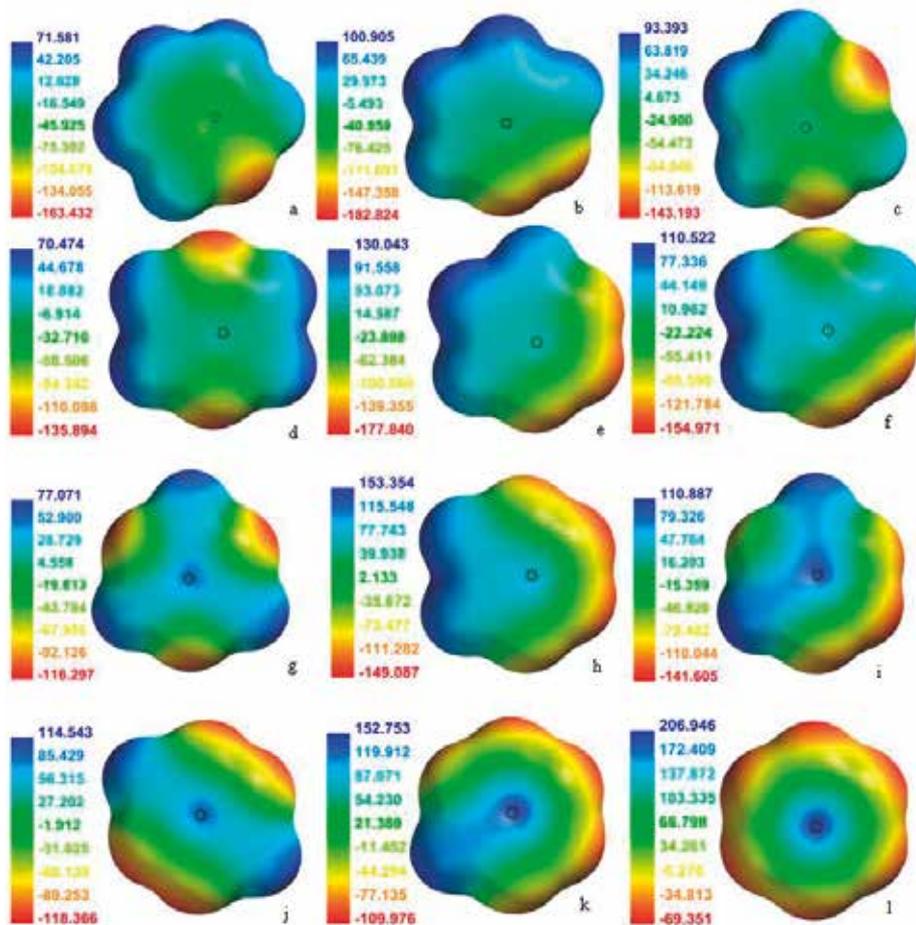


Figure 5. Maps of the molecular electrostatic potentials $V_s(\text{ring})$ of the azines studied.

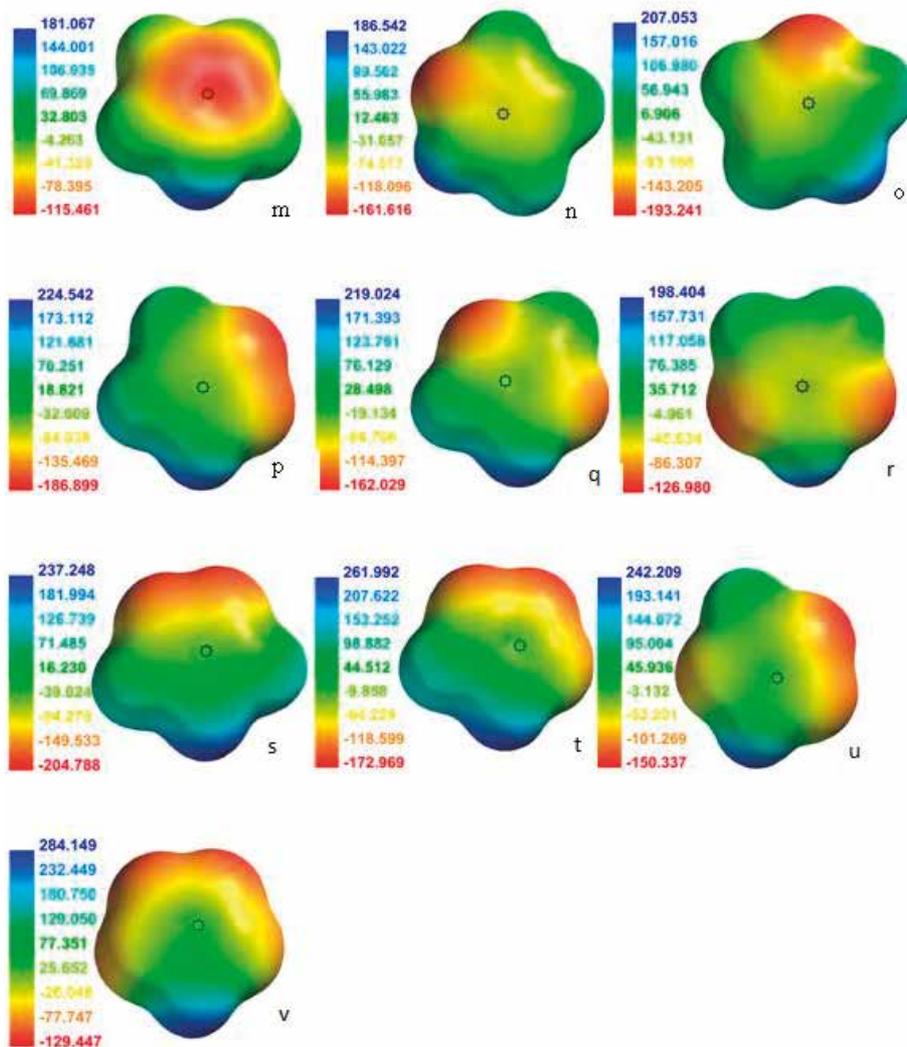


Figure 6. Maps of the molecular electrostatic potentials V_s (ring) of the azoles studied.

Conclusion

The gas phase HOFs of 12 azines and 10 azoles were calculated by the DFT B3PW91/cc-pVTZ method and, using the same geometry, the ring molecular

surface ESP was obtained by the DFT B3LYP/6-31(d,p) method. It is shown that the ring molecular electrostatic potential $V_s(\text{ring})$ is a very sensitive descriptor of the electronic structure and of the thermodynamic properties of N-heteroaromatics. It is therefore reasonable to assume that it may be used for the study of high-nitrogen energetic materials composed of azine and azole units. The ring molecular electrostatic potential $V_s(\text{ring})$ depends only on the number of nitrogen atoms, and not on their positions in the ring.

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References

- [1] Murray J.S., Politzer P., The Electrostatic Potential: an Overview, *WIRES Comput. Mol. Sci.*, **2011**, *1*, 153-163.
- [2] Bulat F.A., Toro-Labbé A., Brinck T., Murray J.S., Politzer P., Quantitative Analysis of Molecular Surfaces: Areas, Volumes, Electrostatic Potentials and Average Local Ionization Energies, *J. Mol. Model.*, **2010**, *16*, 1679-1691.
- [3] Politzer P., Murray J.S., Molecular Electrostatic Potentials in the Computational Characterization of Energetic Compounds, *New Trends Res. Energ. Mater., Proc. Semin.*, 9th, Pardubice, Czech Republic, **2006**, 65-74.
- [4] Singh R.P., Gao H., Meshri D.T., Shreeve J.M., Nitrogen-Rich Heterocycles, in: *High Energy Density Materials*, (Klapötke T.M., Ed.), *Struct. Bond.*, **2007**, vol. 125, pp. 35-83.
- [5] Klapötke T.M., New Nitrogen-Rich High Explosives, in: *High Energy Density Materials*, (Klapötke T.M., Ed.), *Struct. Bond.*, **2007**, vol. 125, pp. 85-121.
- [6] Steinhäuser G., Klapötke T.M., "Green" Pyrotechnics: A Chemist's Challenge. *Angew. Chem. Int. Ed.*, **2008**, *47*, 3330-3347.
- [7] SPARTAN'10 WinP 64 bit, Wavefunction, Irvine **2010**.
- [8] Politzer P., Lane P., Concha M.C.: Computational Approaches to Heats of Formation, in: *Energetic Materials, Part I. Decomposition, Crystal and Molecular Properties* (Politzer P., Murray J. S., Eds.), *Theor. Comput. Chem.* **2003**, *12*, 247-277.
- [9] Hehre W.J., *A Guide to Molecular Mechanics and Quantum Chemical Calculations*, Wavefunction, Irvine, **2003**.
- [10] *NIST Standard Reference Database*, Number 69, **2008**, NIST Chemistry Web Book <<http://webbook.nist.gov/chemistry/>>.
- [11] Bader F.W.R., Carroll M.T., Cheesman J.R., Chang C., Properties of Atoms in Molecules: Atomic Volumes, *J. Am. Chem. Soc.*, **1987**, *109*, 7968-7979.

- [12] Murray J.S., Lane P., Politzer P., Relationships between Impact Sensitivities and Molecular Surface Electrostatic Potentials of Nitroaromatic and Nitroheterocyclic Molecules, *Mol. Phys.*, **1995**, *85*, 1-8.
- [13] Pexa M., Friedl Z. : Relationship between Bond Disproportionation Energy and Molecular Surface Electrostatic Potential, *New Trends Res. Energ. Mater., Proc. Semin.*, 14th, Pardubice, Czech Republic, **2011**, 893-899.
- [14] Pexa M., Friedl Z., Relationships between Reactivity and Molecular Electrostatic Potential of Nitroaromatic Energetic Materials, *Chem. Listy*, **2011**, *105*, 944.
- [15] da Silva G., Moore E.E., Bozzelli J.W., Quantum Chemical Study of the Structure and Thermochemistry of the Five-membered Nitrogen-containing Heterocycles and Their Anions and Radicals, *J. Phys. Chem. A*, **2006**, *110*, 13979-13988.
- [16] Williams C.I., Whitehead M.A., Aromatic Nitrogen Heterocyclic Heats of Formation: a Comparison of Semiempirical and ab initio Treatments. *J. Mol. Struct. THEOCHEM*, **1997**, *393*, 9-24.
- [17] Matulis V.E., Ivashkevich O.A., Gaponik P.N., Elkind P.D., Sukhanov G.T., Bazyleva A.B., Zaitsau D.H., Theoretical Study of Gas-phase Formation Enthalpies and Isomerism for 4(5)-nitro-1,2,3-triazole and Its N-Alkyl Derivatives and Experimental Determination of Formation Enthalpy for 2-Methyl-4-nitro-1,2,3-triazole, *J. Mol. Struct. THEOCHEM*, **2008**, *854*, 18-25.
- [18] Abou-Rachid H., Song Y., Hu A., Dudiy S., Zybin S.V., Goddard III W.A., Predicting Solid-State Heats of Formation of Newly Synthesized Polynitrogen Materials by using Quantum Mechanical Calculations, *J. Phys. Chem. A*, **2008**, *112*, 11914-11920.
- [19] Murray J.S., Seminario J.M., Politzer P., A Computational Study of the Structures and Electrostatic Potentials of some Azines and Nitroazines, *J. Mol. Struct. THEOCHEM*, **1989**, *187*, 95-108.
- [20] Soscun H.J., Aray Y., Murgich J., Hinchliffe A., Ab initio Study of the Molecular Electrostatic Potential of Monocyclic and Bicyclic Azines, *J. Mol. Struct. THEOCHEM*, **1994**, *307*, 1-8.