

Electronic Spectra of Picoline-2-thiol *N*-Oxides

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The UV spectra of *N*-hydroxypicoline-2-thiones in ethanol and in solid state have been examined and compared with the results (transition energies, intensities) of modified INDO calculations in order to make the assignment of band allowed. The influence of substituents (CH₃ and SH groups) in molecule on λ_{\max} and ϵ_{\max} of spectral bands is discussed.

The chemistry of heterocyclic *N*-oxides has gained significance due to interesting biological activities of these compounds [1–5]. It has been suggested that the presence of nitro and thiol groups is very essential to any meaningful antifungal activity of these compounds [3, 4]. Ikeda [5] found some parallelism between the reduction potential and the fungicidal activity and assumed that the binding ability of fungicides with the SH group in the body of fungi may be the main factor determining the fungicidal activity.

The antifungal activity exhibited by some of 4-substituted pyridine *N*-oxides is discussed in terms of the nucleophilic frontier electron densities, super delocalizabilities, and electron acceptor properties [3].

Therefore it was thought worthwhile to investigate in detail the electronic structure of these *N*-oxides, in order to understand the mechanism of the antifungal activity of these compounds.

However, various researchers [1–3, 6–8] into the ultraviolet spectra have not dealt in their papers with calculated electronic spectra of methyl derivatives of pyridine-2-thiols and their *N*-oxides. This paper is devoted to the electronic structure of picoline-2-thiol *N*-oxides, to find out how the methyl group situated at various positions of the pyridine ring, as well as 2-thiol group, influence the degree of intramolecular charge transfer from oxygen of *N*-oxide group to the pyridine ring.

EXPERIMENTAL

The picoline-2-thiol *N*-oxides used in our tests were synthesized with the method described previously [9]. The absorption spectra of the title compounds in ethanol were recorded on a UV VIS spectrometer (Zeiss, Jena), using a quartz cell of 0.097 cm thickness (approximate concentrations being 10⁻⁴ mol dm⁻³), while the spectra of the compounds in solid state with Li₂CO₃ were recorded on a Hitachi Model 356 spectrometer.

Calculations of the electronic spectra and structure of picoline-2-thiol *N*-oxides and *N*-hydroxypicoline-2-thiones were performed within the framework of modified all-valence electrons INDO method [10] utilizing some of its modifications [10–14].

The ground-state geometry of the species was optimized using the semiempirical AM1 method [10].

RESULTS AND DISCUSSION

Excited State Properties of Picoline-2-thiol *N*-Oxide and *N*-Hydroxypicoline-2-thiones

Picoline-2-thiol *N*-oxides occur mainly in a thione form acting as an electron-acceptor group [15]. The observed and calculated energy of electronic transition and its intensity are shown in Table 1. Notwithstanding that AM1 calculations prefer the thiol form (thiol form: $\Delta H_0 = 174.47$ kJ mol⁻¹ – 3-CH₃; $\Delta H_0 = 167.74$ kJ mol⁻¹ – 4-CH₃; $\Delta H_0 = 167.61$ kJ mol⁻¹ – 5-CH₃; $\Delta H_0 = 173.47$ kJ mol⁻¹ – 6-CH₃ derivative; thione form: $\Delta H_0 = 210.58$ kJ mol⁻¹ – 3-CH₃; $\Delta H_0 = 202.46$ kJ mol⁻¹ – 4-CH₃; $\Delta H_0 = 204.35$ kJ mol⁻¹ – 5-CH₃; $\Delta H_0 = 210.25$ kJ mol⁻¹ – 6-CH₃ derivative) the experimental results (UV, IR spectra) [16] as well as calculated electronic spectra considered in this paper show better compatibility for the thione form. Therefore, further discussion will focus on the latter.

In case of *N*-hydroxy-3-methyl- and *N*-hydroxy-6-methylpyridine-2-thiones absorption bands (I) with moderate intensity ($\{\epsilon_{\max}\} = 3961$ and $\{\epsilon_{\max}\} = 4700$) are observed at $\lambda_{\max} = 350$ nm [16]. This band has not been observed for pyridine *N*-oxide derivatives containing electron-donating substituents in *meta* position [1]. However, the red shift of band I has been systematically observed according to the increasing donating substituent ability at *para* position. The intensity of band I of *N*-hydroxy-3-methyl- ($\lambda_{\max} = 342$ nm) and *N*-hydroxy-6-methylpyridine-2-thione ($\lambda_{\max} = 343$ nm) is very high due to participation of a π^*

Table 1. Comparison of the Computed and Experimental Spectra of Picoline-2-thiol *N*-Oxides and *N*-Hydroxypicoline-2-thiones

Compound	Tran- sition	Sym.	Calculated			Compound	Tran- sition	Sym.	Calculated			Experimental		
			Energy eV	Oscillator strength	Dipole moment <i>D</i>				Energy eV	Oscillator strength	Dipole moment <i>D</i>	<i>E</i> /eV in solid state	<i>E</i> /eV in etha- nol	$\epsilon \cdot 10^{-3}$ mol ⁻¹ · cm ⁻¹ · dm ³
3-Methyl- pyridine- 2-thiol <i>N</i> -oxide	($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow n$)	A' A' A' A' A'' A' A'' A' A' A' A''	0 3.94 3.99 4.07 5.49 5.57 5.82 6.02 6.85 7.04 7.67	0.000 0.045 0.181 0.735 0.002 0.913 0.005 0.015 0.261 0.000	4.49 5.53 0.14 1.03 2.94 7.55	<i>N</i> -Hydroxy- 3-methyl- pyridine- 2-thione	($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$)	A'' A' A' A'' A' A'' A' A' A'' A'' A'	0 2.759 3.781 4.296 4.591 5.995 6.147 6.387 6.715 7.260 7.378	0.000 0.402 0.274 0.001 0.478 0.006 0.312 0.274 0.001 0.000	6.33 1.63 0.61 2.13 7.61 5.59	3.60 4.36 5.84	3.62 4.22 5.36	4.70 11.50
4-Methyl- pyridine- 2-thiol <i>N</i> -oxide	($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow n$)	A' A'' A' A'' A' A'' A' A'' A' A'' A''	0 3.960 4.002 4.080 5.528 5.530 5.894 6.105 6.677 7.115 8.020	– 0.054 0.000 0.271 0.004 0.743 0.789 0.044 0.043 0.222 0.002	4.78 0.72 5.93 1.39 7.14 2.95	<i>N</i> -Hydroxy- 4-methyl- pyridine- 2-thione	($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$)	A'' A' A' A'' A' A'' A' A'' A' A'' A'	0 2.757 3.783 4.388 4.615 6.039 6.120 6.698 7.282 7.832 8.606	0.000 0.356 0.296 0.000 0.743 0.012 0.194 0.000 0.000 0.003	6.88 1.21 0.61 2.04 7.49 6.84	3.63 4.28 5.25	4.36 5.79	22.50 9.63
5-Methyl- pyridine- 2-thiol <i>N</i> -oxide	($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow n$)	A'' A' A' A' A'' A' A'' A' A'' A' A'' A''	0 3.941 4.003 4.077 5.518 5.583 5.890 6.002 6.714 7.031 8.042	– 0.000 0.049 0.228 0.726 0.001 0.866 0.005 0.093 0.142 0.001	4.68 5.63 0.56 1.15 2.18 7.47	<i>N</i> -Hydroxy- 5-methyl- pyridine- 2-thione	($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$)	A' A' A' A'' A' A' A' A' A' A'' A'	0 3.000 3.770 4.345 4.843 6.096 6.205 6.276 6.677 7.768 8.940	– 0.001 0.360 0.367 0.001 0.081 0.489 0.165 0.295 0.002 0.000	6.78 3.44 1.54 2.72 8.98 3.96	3.54 4.35 5.25	4.20 4.80	8.85 14.41
6-Methyl- pyridine- 2-thiol <i>N</i> -oxide	($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow n$)	A' A' A' A' A'' A' A'' A' A'' A' A'' A''	0 3.89 3.96 4.06 5.41 5.48 5.86 6.07 6.83 7.04 7.38	– 0.000 0.056 0.169 0.746 0.002 0.832 0.005 0.037 0.338 0.000	4.46 5.74 0.37 1.28 2.19 7.38	<i>N</i> -Hydroxy- 6-methyl- pyridine- 2-thione	($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow \pi$) ($\pi^* \leftarrow n$) ($\pi^* \leftarrow \pi$)	A'' A' A' A'' A' A'' A' A'' A' A'' A'	0 3.05 3.74 3.37 4.78 5.98 6.17 6.39 6.72 7.33 8.30	– 0.000 0.372 0.331 0.000 0.444 0.007 0.363 0.229 0.001 0.005	6.87 3.56 0.98 2.64 8.76 7.29	3.54 4.33 5.84	3.61 4.21 5.30	3.96 14.02

The values μ can be recalculated to the multiples *D* using the relationship $1 D = 2.33564 \times 10^{-30}$ C m.

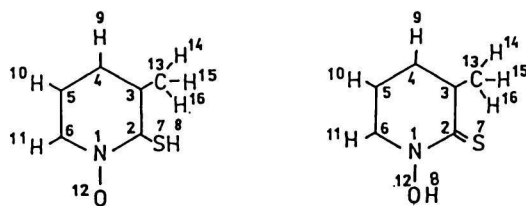
$\leftarrow n$ transition. Therefore, the above result may lead to the conclusion that band I has the nature of a $\pi^* \leftarrow \pi$ band.

Band II ($\lambda_{\max} = 253\text{--}294$ nm) comes from the $\pi^* \leftarrow \pi$ transition and is characteristic of aromatic tertiary amine *N*-oxides, where N—O and C=C create a conjugated system.

Band III ($\lambda_{\max} = 214\text{--}234$ nm) of the compounds

tested is ascribed to excitation of π -electrons of the aromatic system.

The spectra of *N*-hydroxypicoline-2-thiones exhibit a clear relationship between the position of methyl group and the intensity of band II or III. The highest intensity of band II ($\{\epsilon_{\max}\} = 22518$) of *N*-hydroxy-4-methylpyridine-2-thione results from the interaction between *N*-hydroxy and 4-methyl groups. The ab-

Table 2. The Values of the Net Electron Charges at the Atoms and HOMO, LUMO Energies of Picoline-2-thiol *N*-Oxides and of *N*-Hydroxypicoline-2-thiones in the Ground State (S_0) and the First (S_1) and the Second Excited State (S_2)

Atom	3-Methylpyridine-2-thiol <i>N</i> -Oxide			<i>N</i> -Hydroxy-3-methyl- pyridine-2-thione		
	S_0	S_1	S_2	S_0	S_1	S_2
N-1	0.574	0.300	0.514	0.232	0.104	0.197
C-2	0.101	0.053	0.114	0.311	-0.166	0.174
C-3	0.046	-0.008	-0.097	0.026	0.047	0.006
C-4	-0.040	-0.313	-0.028	0.021	-0.098	-0.207
C-5	-0.016	-0.062	-0.081	-0.084	-0.111	0.031
C-6	-0.008	-0.054	-0.160	0.101	0.078	-0.059
S-7	-0.118	-0.116	-0.010	-0.535	0.212	-0.094
H-8	0.129	0.128	0.128	0.258	0.258	0.257
H-9	0.030	0.032	0.030	0.018	0.019	0.018
H-10	0.009	0.014	0.009	0.013	0.013	0.013
H-11	0.008	0.008	0.008	0.005	0.007	0.005
O-12	-0.694	0.038	-0.402	-0.354	-0.353	-0.331
C-13	-0.081	-0.077	-0.077	-0.077	-0.076	-0.076
H-14	0.021	0.019	0.019	0.029	0.030	0.029
H-15	0.017	0.018	0.017	0.006	0.006	0.006
H-16	0.021	0.019	0.019	0.029	0.029	0.029
$E(\text{HOMO})/\text{eV}$				-9.995		
$E(\text{LUMO})/\text{eV}$				-1.192		
Atom	4-Methylpyridine-2-thiol <i>N</i> -Oxide			<i>N</i> -Hydroxy-4-methyl- pyridine-2-thione		
	S_0	S_1	S_2	S_0	S_1	S_2
N-1	0.575	0.302	0.531	0.221	0.115	0.200
C-2	0.132	0.095	0.123	0.342	0.015	0.227
C-3	-0.054	-0.120	-0.224	-0.077	-0.089	-0.124
C-4	-0.040	-0.314	-0.023	0.031	-0.230	-0.213
C-5	0.085	0.049	0.020	0.019	-0.028	0.138
C-6	-0.039	-0.093	-0.181	0.067	0.047	-0.091
S-7	-0.118	-0.116	-0.003	-0.529	0.249	-0.095
H-8	0.126	0.125	0.125	0.253	0.252	0.252
H-9	0.031	0.033	0.031	0.019	0.020	0.019
H-10	0.008	0.008	0.008	0.004	0.006	0.004
H-11	0.013	0.019	0.013	0.023	0.023	0.023
O-12	-0.693	0.037	-0.400	-0.347	-0.348	-0.330
C-13	-0.083	-0.079	-0.079	-0.080	-0.080	-0.077
H-14	0.017	0.017	0.017	0.013	0.013	0.013
H-15	0.021	0.020	0.021	0.020	0.018	0.026
H-16	0.020	0.020	0.021	0.020	0.018	0.026
$E(\text{HOMO})/\text{eV}$				-9.900		
$E(\text{LUMO})/\text{eV}$				-1.228		

sorption spectrum of *N*-hydroxy-5-methylpyridine-2-thione is red-shifted relative to 3-methyl and 6-methyl derivatives and characterized by a significant absorption coefficient of band III ($\{\epsilon_{\text{max}}\} = 14412$) due to complementarity of interaction (resonance effect) of thione group in position 2 with methyl group in

position 5. Good agreement between the calculated and observed parameters is obtained for lower excited states.

The calculated electric dipole moments of ground and various excited states provide the measure of the electron transfer. The change of dipole moment dur-

Table 2 (Continued)

Atom	5-Methylpyridine-2-thiol <i>N</i> -Oxide			<i>N</i> -Hydroxy-5-methyl- pyridine-2-thione		
	S ₀	S ₁	S ₂	S ₀	S ₁	S ₂
N-1	0.527	0.260	0.466	0.190	0.079	0.153
C-2	0.149	0.111	0.168	0.349	0.021	0.232
C-3	-0.072	-0.133	-0.211	-0.094	-0.102	-0.112
C-4	0.008	-0.263	0.018	0.074	-0.193	-0.156
C-5	-0.071	-0.104	-0.123	-0.138	-0.190	-0.011
C-6	0.120	0.060	-0.061	0.221	0.199	0.038
S-7	-0.121	-0.118	-0.014	-0.541	0.245	-0.093
H-8	0.127	0.126	0.126	0.259	0.260	0.258
H-9	0.014	0.019	0.014	0.016	0.017	0.016
H-10	0.003	0.003	0.003	-0.0002	0.001	-0.0003
H-11	0.016	0.021	0.016	0.026	0.026	0.025
O-12	-0.698	0.021	-0.397	-0.354	-0.353	-0.334
C-13	-0.086	-0.082	-0.082	-0.098	-0.097	-0.097
H-14	0.036	0.033	0.032	0.033	0.032	0.027
H-15	0.012	0.014	0.012	0.024	0.024	0.024
H-16	0.035	0.031	0.031	0.034	0.033	0.028
<i>E</i> (HOMO)/eV				-9.950		
<i>E</i> (LUMO)/eV				-1.196		

Atom	6-Methylpyridine-2-thiol <i>N</i> -Oxide			<i>N</i> -Hydroxy-5-methyl- pyridine-2-thione		
	S ₀	S ₁	S ₂	S ₀	S ₁	S ₂
N-1	0.527	0.260	0.466	0.190	0.079	0.563
C-2	0.149	0.111	0.168	0.349	0.021	0.148
C-3	-0.072	-0.133	-0.211	-0.094	-0.102	-0.104
C-4	0.008	-0.263	0.018	0.074	-0.193	0.108
C-5	-0.071	-0.104	-0.123	-0.138	-0.190	-0.064
C-6	0.120	0.060	-0.061	0.221	0.199	0.010
S-7	-0.121	-0.118	-0.014	-0.541	0.245	-0.119
H-8	0.127	0.126	0.126	0.259	0.260	0.127
H-9	0.014	0.019	0.014	0.016	0.017	0.027
H-10	0.003	0.003	0.003	-0.0002	0.001	0.013
H-11	0.016	0.021	0.016	0.026	0.026	0.017
O-12	-0.698	0.021	-0.397	-0.354	-0.353	-0.699
C-13	-0.086	-0.082	-0.082	-0.098	-0.097	-0.082
H-14	0.036	0.033	0.032	0.033	0.032	0.015
H-15	0.012	0.014	0.012	0.024	0.024	0.020
H-16	0.035	0.031	0.031	0.034	0.033	0.020
<i>E</i> (HOMO)/eV				-9.930		
<i>E</i> (LUMO)/eV				-1.170		

ing electron excitation (the first excited singlet state) was calculated as 3.31–5.67 *D* (for the 3-CH₃, 4-CH₃, 5-CH₃, and 6-CH₃ derivatives as 5.30 *D*, 5.67 *D*, 3.34 *D*, and 3.31 *D*, respectively). *Tae Kyu Ha* [1] calculated that the change of dipole moment on electron excitation for pyridine *N*-oxide from the ground state to the first excited state was approximately 1 *D*.

All *N*-hydroxypicoline-2-thiones show the same pattern: the lowest $\pi^* \leftarrow n$ transition followed by two $\pi^* \leftarrow \pi$ transitions. The lowest $\pi^* \leftarrow n$ transition, calculated at 2.76 eV to 3.05 eV above the ground state, is strongly forbidden, as the calculated value of oscillator strength equals 0 or almost 0. The second transition $\pi^* \leftarrow \pi$ (3.74–3.78 eV) is slightly above the

first $\pi^* \leftarrow n$. Two fifth (5.99–6.09 eV) and the seventh state $\pi^* \leftarrow \pi$ (6.28–6.70 eV) may be regarded as charge transfer states compared to the experimental spectra range (5.25 eV and 5.84 eV).

Electronic Structure of *N*-Hydroxypicoline-2-thiones

Comparison of the net charge density on oxygen atom for pyridine *N*-oxide [6] and *N*-hydroxypicoline-2-thiones in ground and excited states provides the quantitative measure of intramolecular charge transfer (Table 2). The highest positive charge of C-2 in all the compounds tested indicated that this position was the

most susceptible to nucleophilic substitution.

The position of methyl group in the ring of the compounds tested did not exert a great influence on excessive charge distribution during the excitation. As it can be seen in Table 2, transition from pyridine *N*-oxide to *N*-hydroxypicoline-2-thiones brought about an increase in HOMO energies (from -1.44 eV to $-(1.17-1.23)$ eV). Similarly to pyridine *N*-oxide, picoline-2-thiol *N*-oxides are characterized by the highest negative charge at the oxygen atom of *N*-hydroxy group among all atoms of these molecules.

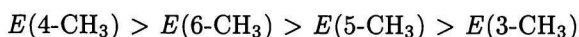
The HOMO energies were increasing in the order



but the LUMO energies were increasing in a bit different way



The value of difference between HOMO-LUMO energies points out that *N*-hydroxypicoline-2-thiones should react easier with soft nucleophiles [17] than with the hard ones. The values of HOMO energies of the compounds tested allow to predict the order of reactivity for nucleophilic substitution



The antifungal compounds are very good electron acceptors [3] and the value of LUMO energy is a measure of electron-accepting capacity of a molecule. The LUMO energies of *N*-hydroxypicoline-2-thiones ($-(1.17-1.23)$ eV) being too close to each other, it is not possible to account for the relative order of the antifungal activity.

The transition from the ground state to the excited one is connected with changes of the charge density in the molecule (Table 2). On passing from the ground

state to the first excited state in *N*-hydroxypicoline-2-thiones, the value of the negative charge at the oxygen atom decreases (from $-(0.347-0.354) \rightarrow -(0.348-0.353)$), increasing at position 4 (from $0.021-0.074 \rightarrow -(0.098-0.230)$). These results show that the π -electron transfer from the oxygen atom to the ring is much greater in the excited than in the ground state.

REFERENCES

1. Tae Kyu Ha, *Theor. Chim. Acta* 43, 337 (1977).
2. Cignitti, M. and Soccorsi, L., *Spectrochim. Acta, Part A* 41, 1287 (1985).
3. Kulkurni, G. V. and Ray, A., *Theochem, J. Mol. Struct.* 71, 253 (1981).
4. Edrissi, M. and Massoumi, A., *Microchem. J.* 16, 353 (1971).
5. Ikeda, N., *J. Pharm. Soc. Jpn. (Yakugaku Zasshi)* 75, 1073 (1955).
6. Puszko, A., *J. Crystallogr. Spectrosc. Res.* 1, 23 (1993).
7. Puszko, A., *Theochem, J. Mol. Struct.* 344, 1 (1995).
8. Leibovici, C. and Streith, M., *Tetrahedron Lett.* 1971, 87.
9. Puszko, A., *Prace Naukowe AE, Wrocław* 251, 151 (1984).
10. Lipiński, J., *Spectrochim. Acta, Part A* 45, 557 (1989).
11. People, J. A. and Beweridge, D. L., *Approximate Molecular Orbital Theory*. McGraw-Hill, New York, 1970.
12. Lipiński, J., Nowak, A., and Chojnacki, H., *Acta Phys. Pol., A* 53, 229 (1978).
13. Lipiński, J. and Leszczynski, J., *Int. J. Quant. Chem.* 22, 253 (1983).
14. Lipiński, J., *Theochem, J. Mol. Struct.* 201, 87, 295 (1989).
15. Yamakawa, M., Kubota, T., and Akazawa, H., *Theor. Chim. Acta* 15, 244 (1969).
16. Puszko, A., *Pol. J. Chem.* 68, 657 (1994).
17. Klopman, G., *Theochem, J. Mol. Struct. Suppl.* 103/12, 121 (1983).