

MNDO CALCULATIONS OF THE MOLECULAR AND ELECTRONIC STRUCTURE OF THIONITROSO, DITHIONITRO AND RELATED COMPOUNDS*

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

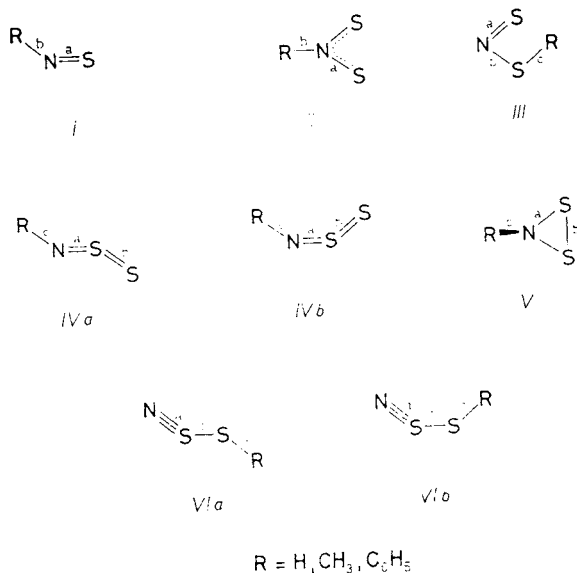
Compounds with the formulae RNS and RNS_2 (thionitroso *I* and dithionitro compounds *II*, dithionitrites *III*, N-thio-sulfinylamines *IV*, dithia-aziridines *V* and thiazylthiols *VI*, $\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5$) and the corresponding radical cations HNS_2^+ and anions HNS_2^- have been investigated by MNDO calculations with respect to their molecular geometries, relative stabilities, ionization and electron capture properties and dipole moments. For the simplest representatives ($\text{R} = \text{H}$) the infrared spectra have been calculated. The lengths of NS triple (in *VI*), double (in *I, III, IV*) and partial double (in *II, III*) bonds are predicted to be in the region of 147–150, 152–155 and 158–162 pm, respectively. Within these regions systematic shifts result from different substituents R. Contraction of NS bonds (1–6 pm) is observed in the case of ionization whereas electron capture causes bond elongation (2–6 pm). The MNDO sequence of stability deviates from that of *ab initio* calculations for compounds with tetravalent sulfur the stabilization effect of which is obviously underestimated by the MNDO approach. All compounds studied are characterized by negative non-vertical electron affinities suggesting vigorous reactivity with nucleophilic reactants. The patterns of infrared spectra enable recognition, discrimination and characterization of these mostly unknown compounds which might be accessible as short-living transients.

Rudolf Zahradnik's career in quantum chemistry started with the theoretical treatment of sulfur containing organic compounds by means of the simple Hückel model². The attractive power of this class of compounds runs like a red thread through his scientific life^{3–6}. His most eminent style to generate fascination and enthusiasm, his continuous support and his generous help for more than 25 years enable the author to devote the following paper thankfully to him as one of the most remarkable personalities in nowadays quantum chemistry.

This paper deals with some classes of sulfur-nitrogen containing compounds *I–VI* possessing basic functional groups which are either unstable and therefore scarcely known or still unknown so far.

* Part LV in the series MO-LCAO Calculations of Sulfur-Containing π -Electron Systems; Part LIV cf. ref¹.

Contrary to the carbon-analogue thioformaldehyde which is well investigated both theoretically and experimentally despite of its short lifetime^{6,7} compounds of type *I*, i.e. HNS and the whole class of organic thionitroso compounds have not



been isolated so far. This holds although extensive search of these compounds has been undertaken^{8,9} and first ideas about their molecular properties emerged from former theoretical investigations^{10,11}.

In the same way dithionitro compounds, *II*, and dithionitrites, *III*, were postulated as short-lived intermediates in certain chemical reactions¹² but their isolation failed and nothing is known about their physical and chemical properties. This is again surprising as the C-analogous dithiocarbonic esters have been synthesized and investigated in an overwhelming variety¹³.

On the other hand, the isomeric N-thiosulfinylamines *IV* could be synthesized by reaction of sterically hindered arylamines and disulfur dichloride or from reaction of arylnitroso compounds and 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiophosphetane-2,4-bis-thioxide¹⁴ and characterized by X-ray studies¹⁵. Further isomers of RNS₂ are the dithiaaziridines *V* and the (*Z*)- and (*E*)-isomers of thiazylthioles *VIa* and *VIb* which are unknown, too.

Preparation, fixation and characterization of short-lived species can be undoubtedly promoted by theoretical predictive calculations. Along this line quantum chemical calculations become increasingly attractive and reliable tools due to the broad access of computers with increasing speed and storage capacity. For HNS, CH₃NS and several HNS₂ isomers first *ab initio* calculations with minimal or split

valence basis sets have been performed and partially published^{10,11,16,17}. In these studies first information about the ground state multiplicity (energy splitting of the S_0 and T_1 states) and the long wavelength absorptions of these structures have been given.

Recently a paper of Nakamura et al.¹⁸ presented a more profound *ab initio* study of the HNS_2 isomers *II–VI* by using a 4-31G* basis for geometry optimization supplemented by MP3/6-31G**//4-31G*// investigations for the order of isomer stability.

However, for RNS_2 compounds being of interest for organic chemists ($\text{R} = \text{CH}_3$, C_6H_5 , etc.) the model compounds HNS_2 are rather simple and the transferability of calculated properties to the organic analogues is by no means assured. On the other hand, *ab initio* calculations on the same level for larger compounds of this kind are still time-consuming or impossible.

This paper presents therefore MNDO calculations of compounds *I–VI* ($\text{R} = \text{H}$, CH_3 , C_6H_5) with the few experimental facts known and the *ab initio* calculations in refs^{17,18} as proper reference points in mind.

In detail the following objectives will be discussed: (i) Molecular geometries of neutral compounds *I–VI* and those of the radical cations and radical anions $\text{HNS}^{+(\cdot)}$ and $\text{HNS}_2^{+(\cdot)}$, respectively, in the ground state; (ii) vibrational spectra of all HNS_2 isomers as suited finger-prints for their recognition; (iii) vertical and non-vertical ionization potentials and electron affinities; (iv) electronic structure and dipole moments of the compounds; (v) availability of the MNDO method to reflect correctly the order of relative stabilities of the isomers *II–VI* even when octet expansion of the sulfur atoms can be supposed.

CALCULATIONS

The quantum chemical calculations were carried out by means of a modified and extended version (MNDO/VIB)¹⁹ of the original MNDO program²⁰ with original parameters^{21,22}. The new set of parameters for sulfur proposed recently²³ was tested²⁴ and found without significant influence on the results of importance.

RESULTS AND DISCUSSION

Table I collects molecular geometries of the most simple representatives of *I–VI*, HNS_n (in their ground and low-energetic triplet state), HNS_n^+ and HNS_n^- ($n = 1, 2$) obtained by minimizing the MNDO energies. Table II supplements molecular geometries of the neutral organic derivatives ($\text{R} = \text{CH}_3$, C_6H_5) *I–VI*. It is known that the MNDO approximation suffers from a systematic error concerning the X—S bond lengths^{22,24} ($\text{X} = \text{C}, \text{S}$). These bonds are always being underestimated in lengths by 1–10 pm. Unfortunately, this deficiency cannot be overcome by new

TABLE I

Bond lengths of the isomeric HNS_n ($n = 1, 2$) (S_0 , T_1) and their cation and anion radicals (D_0). Assignment of bonds cf. formulae on p. 2117

Compound	Bond			Bond			Bond			Bond		
	a	b	c	a	b	c	a	b	c	a	b	c
<i>I</i>	149.1	101.3	—	148.6	99.2	—	143.0	101.4	—	156.5	101.4	—
<i>II</i>	154.6	101.9	—	157.3	99.9	—	— ^a	— ^a	—	158.3	100.2	—
<i>III</i>	149.6	160.5	131.7	149.3	159.9	131.5	145.0	154.8	133.3	155.4	164.6	131.1
<i>IVa</i>	153.7	182.9	100.6	158.8	191.2	100.7	152.1	191.5	101.6	159.4	186.9	100.8
<i>IVb</i>	152.0	182.9	100.4	160.9	186.9	100.3	152.2	189.1	101.2	158.0	187.3	100.1
<i>V</i>	168.0	195.0	101.3	155.8	228.8	—	170.0	190.0	102.2	164.3	226.2	102.1
<i>VIa</i>	145.7	198.2	130.4	153.3	195.0	130.6	144.5	199.7	131.0	147.2	210.4	129.5
<i>VIb</i>	145.4	197.7	130.3	153.1	195.1	130.8	144.9	198.8	130.5	147.5	207.0	129.5

^a No convergence achieved.

MNDO parameters for sulfur proposed recently²³. It seems however, that the errors can be compensated by a bond-specific correction term which must be added to the bond lengths obtained. For C—S, C=S, and S—S bonds these terms have been obtained statistically and amount to 3, 6 and 9 pm, respectively^{1,24}. In the case of NS bonds the situation is more complicated. For inorganic nitrogen-sulfur rings MNDO bond lengths for NS bonds agree satisfactorily with the experiment^{25,26}. Some organic heterocyclic compounds exhibit underestimation of NS bond lengths calculated by MNDO of 2 to 5 pm (refs^{27,28,29}). If we compare the MNDO results for HNS_n with *ab initio* bond lengths^{11,18} the deviation is found between 1 to 6 pm. It seems therefore reasonable to assume that an average correction of 3 pm will be necessary to approach the NS bond lengths to those which can be expected from experimental investigations for compounds *I–VI*. On the basis of these considerations the length of the NS double bond can be expected within the region of 152–155 pm, somewhat shorter than that of CS double bonds. Partial NS double bonds such as occurring in *II* and *III* (bond a and b, respectively) should be lengthened up to 158–162 pm. In thiazylthiols *VI* the partial triple bond character of NS bonds is reflected by their contraction to 147–150 pm. Generally NS bonds become slightly stretched if R is an alkyl or aryl group.

SS bonds in N-thiosulfinylamines *IV* are calculated to be considerably shorter than in normal disulfides. This might be a first consequence of *d*-orbital contributions to

TABLE II

Molecular geometries of RNS_n (*n* = 1, 2; R = CH₃, C₆H₅) isomers (in pm). Assignment of bonds cf. formulae on p. 2117

Compound	Bond			Bond		
	a	b	c	a	b	c
	R = CH ₃			R = C ₆ H ₅		
<i>I</i>	149.5	145.6	—	150.5	140.4	—
<i>II</i>	155.6	149.7	—	156.4	144.9	—
<i>III</i>	149.6	160.6	174.5	149.9	162.7	170.6
<i>IVa</i>	154.1	182.8	144.4	155.7	182.4	140.4
<i>IVb</i>	152.1	182.8	143.9	153.0 ^a	183.1	137.4
<i>V</i>	168.3	194.7	146.9 ^b	— ^c		
<i>VIa</i>	145.5	199.0	172.6	145.4	199.6	169.1
<i>VIb</i>	145.2	198.2	172.7	144.7	198.4	169.1

^a Experiment (on 2,4-di-tert.-butyl-6-methyl-N-thiosulfinylaniline)¹⁵: *a* = 154.8 pm, *b* = 189.8 pm; ^b dihedral angle of the CH₃ group: 67°; ^c no convergence achieved.

the SS bond in *IV* suggested also by the tetravalent sulfur in the Kekulé formula. The corrected MNDO values (192 pm) are somewhat longer than those obtained¹⁸ by *ab initio* SCF (188–190 pm) but agree also satisfactorily with the experimental results obtained by X-ray studies¹⁵ on 2,4-di-tert.-butyl-6-methyl-N-thiosulfinylaniline (189.8 pm). On the other hand, SS bonds in *VI* are slightly extended disulfide bonds (MNDO corrected: 206–207 pm, 4-31G*: 215–216 pm (ref.¹⁸)). SH bond lengths in *III* and *VI* are in good agreement to those found for thiols³⁰. Also the calculated NH and CN bond lengths correspond to experimental values measured for analogous compounds. Dithiaaziridine *V* should be nonplanar (dihedral angle 67° (R = H, CH₃)). Its geometrical parameters deviate from those of the other isomers due to the ring strain.

Excitation to the low-energy triplet state enhances the NS and SS bond lengths for 3–8 pm. Exceptions are *I*, *III*, and *V*. The latter system undergoes ring opening by excitation as it is indicated by the large increase of the SS bond (230 pm).

A general contraction of NS bonds accompanied with lengthening of SS bonds results from ionization of RNS_n compounds to the radical cations. On the other hand, electron capture causes extension of NS bonds for 2–6 pm and of SS bonds for 4–5 pm. Again *V* escapes the systematization and will probably be destroyed by the electron added (ring opening).

The infrared spectra of instable molecules being absorbed at argon matrices at low temperatures are very powerful tools for their characterization³¹. Theoretically vibrational frequencies are accessible via the second order derivatives of the energy to the coordinates using the harmonic approach. For thioformaldehyde the measured IR spectrum³² can be compared with the theoretical vibrational frequencies. Fig. 1 demonstrates the usefulness of *ab initio* calculations with different basis sets and the MNDO method for reproducing this IR spectrum⁶. Some systematic deviations from the experiment can be seen in all approaches. The errors due to the harmonic approach are roughly compensated by scaling all the frequencies³³ by 0.9. However, even when the semiempirical MNDO method is used the overall agreement is still satisfactory and the assignment of the corresponding vibrations to specific normal motions is possible. This encouraged us to calculate the vibrations of isomers *II–VI* (R = H) by means of the MNDO approach. The results are demonstrated in Fig. 2. It is evident that spectral characteristics for the different isomers are well distinguished so that they can be used as a fingerprint for different structures. This makes the IR spectra very promising for structure elucidation of HNS₂ isomers with short lifetimes. In Fig. 2 the 4-31G* results for the vibrational frequencies of *IVa* and *IVb* obtained in ref.¹⁸ are indicated by arrows. Besides of two band inversions in a narrow energy region ($\nu(\text{NS}) \leftrightarrow \omega(\text{HNS})$ and $\nu(\text{SS}) \leftrightarrow \tau$) the congruence of the two methods is still acceptable.

Six normal modes can be expected for HNS₂. Stretching vibrations $\nu(\text{NH})$ occurring in *II*, *IVa*, *IVb*, and *V* are found between 3 070 and 3 188 cm⁻¹. These values are

below the experiment for 200–300 cm^{-1} . S—H stretching frequencies were calculated at 2 680 cm^{-1} which is higher than usually found for thiols³⁴.

The SS stretching vibration for *VIa* and *VIb* at 530 cm^{-1} is in the expected region of disulfides³⁴. According to the geometrical relations the frequency will increase to 680 cm^{-1} for SS bonds in N-thiosulfinylamines. NS stretching modes are rather different for the various isomers and are real indicators for different bonding situations. The “true” $\nu(\text{N}=\text{S})$ is calculated at 1 270 cm^{-1} which corresponds approximately to the value of dithionitrous acid ($\nu(\text{N}=\text{S})$ 1 260 cm^{-1}). As expected the $\nu(\text{N}=\text{S}-\text{S})$ in *IV* and the $\nu(\text{N}\equiv\text{S}-\text{S})$ in *VI* are shifted to lower frequencies (1 105–1 170 and 1 200–1 220 cm^{-1} , respectively). Due to the coupling effect in *II* and *III* symmetric and antisymmetric $\nu(\text{N}-\text{S})$ can be observed (890–780 and 1 192–1 260 cm^{-1} , respectively). Among the three deformation modes two are in plane ($\delta(\text{NSS})$ and $\delta(\text{HNS})$) and one is out of plane (wagging or twisting motions). These bands are calculated in the low-energetic region between 300 and 600 cm^{-1} .

Relative stabilities of HNS_2 isomers obtained by *ab initio* calculations depend sensitively on the basis set and on the completeness of electron correlation effects taken into account. For example the stabilization energies resulting from MP2/6-31G** calculations differ from those obtained by MP3/6-31G** investigation for more than 50% (average value)¹⁸. However it is evident that inclusion of polariza-

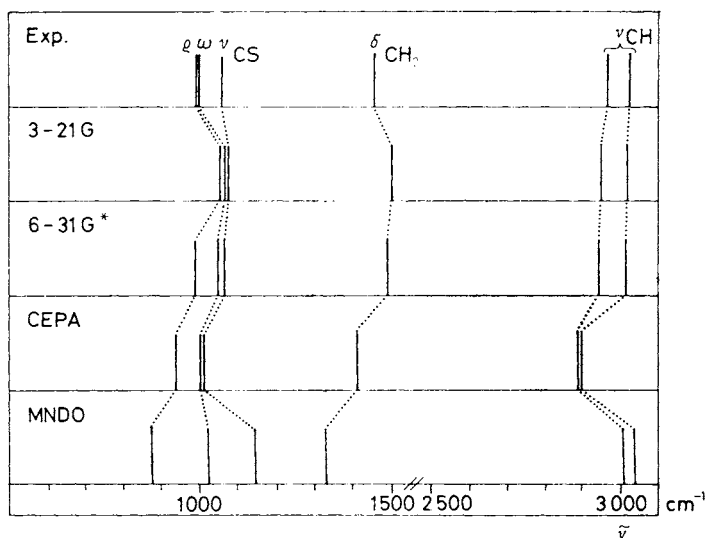


FIG. 1

Experimental IR spectrum of thioformaldehyde³² compared with the vibrational frequencies obtained by different⁶ *ab initio* and MNDO calculations

tion functions is essential and causes a considerable gain of stabilization particularly for structures *IV* and *VI*, i.e. compounds with formal tetravalent sulfur. This suggests that *d*-orbital effects cannot be neglected for these compounds and bring about a decisive stabilization effect. The order of stability derived from MP3/6-31G** calculations in ref.¹⁸ is $IVb > II > IVa \gg V > III \gg VIa > VIb$. The energy differences are rather small and require additional consideration of distribution functions: 4–17 kJ mol⁻¹ between *IVb*, *II* and *IVa*, 0.4 kJ mol⁻¹ between *III* and *V*, 6 kJ mol⁻¹ between *VIa* and *VIb*. However, the three groups are sufficiently discriminated from each other. The highest stability of *IVb* agrees qualitatively with the fact that this structure type alone could be isolated so far.

Contrary to this the MNDO method predicts (after inclusion of zero point energies) the sequence $V > III > II \gg IVb > IVa \gg VIb > VIa$ for R = H, $III > V \gg II \gg IVb > IVa \gg VIb > VIa$ for R = CH₃, and $III \gg IVb \approx II > IVa \gg VIb = VIa$ for R = C₆H₅. Clearly, the MNDO approach underestimates the stability

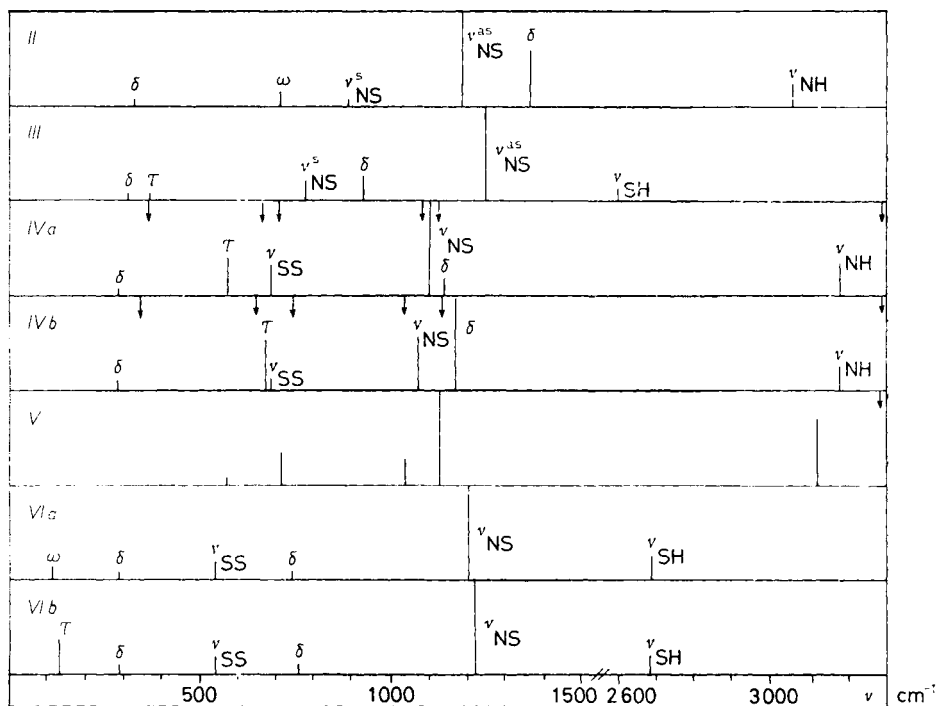


FIG. 2

MNDO vibrational frequencies of HNS₂ isomers and their assignment. The arrows mark the *ab initio* results¹⁸ for *IVa* and *IVb*

of compounds with tetravalent sulfur. This corresponds to deficiencies found for SO_2 and similar compounds^{23,24}. Energy difference between *II* and *IVb* is however strongly diminished in the case of phenyl derivatives (*IVb* is then by 8.5 kJ mol^{-1} more stable than *II*).

Common aspects of the nonempirical and semiempirical approach with respect to the order of stability are the following: (i) thiazylthiols *VIa* and *VIb* are obviously the most instable representatives of the whole series (independent of R); (ii) (*Z*)-configurations of *IVb* and *VIb* are favoured over (*E*)-configurations (in the case of *IVb* and the related sulfur diimides this is in agreement with the experiment^{15,35}); (iii) dithionitro compounds are of comparable stability to the known N-thiosulfinylamines, from this point of view there is no motive for their nonexistence; (iv) dithionitrites are of comparable stability to dithia-aziridines.

Ionization and electron capture properties are reflected approximately by the energies of frontier orbitals. For all molecules studied (with different R) these values are collected in Table III. The non-vertical first ionization potentials and electron affinities result from SCF energy differences between closed shell systems and the corresponding radical cations and anions, respectively. For HNS_n structures these values are contained in Table IV.

The values for ionization energies are less scattered for the different isomers (less than 1 eV) than those of electron affinities (about 1.4 eV). Geometrical relaxation of the radical ions decreases the ionization energies for 0.2 to 0.9 eV. Because of the complete absence of experimental data for HNS_n types thioformaldehyde can be taken as a scaling example. The MNDO calculation yields -9.98 eV for the HOMO of thioformaldehyde, the experimental ionization energy amounts to 9.38 eV (ref.³⁶). It can be stated therefore that all isomers of HNS_n will be ionized between 9 and 10 eV. The values will be reduced for $0.15\text{--}0.3 \text{ eV}$ if $\text{R} = \text{CH}_3$ and for $0.5\text{--}1.5 \text{ eV}$ if $\text{R} = \text{C}_6\text{H}_5$. Contrary to the E_{HOMO} the E_{LUMO} values are only less affected by the substituent R and are found to be strongly negative in all cases. Likewise, the non-vertical electron affinities are predicted to be strongly negative and indicate a considerable stabilization of radical anions compared with the corresponding neutral compounds. Parallel calculations for butadiene, HNO, CH_2S , and $\text{C}_6\text{H}_5\text{NO}$ provide $+0.39$, -0.10 , -0.82 , and -0.88 eV for the LUMO energies and -0.00 , -0.52 , -1.14 , and -1.28 eV for the non-vertical electron affinities, respectively. It seems therefore in the light of experimental results found for similar compounds³⁷ that the MNDO approach overestimates the inclination of molecules to capture electrons. However, the negative values indicate at least that the electron capture is a favoured process for RNS_n compounds. Their inclination to undergo reactions with nucleophiles should be definitely more probable and more vigorous than for thiocarbonyl and nitroso compounds. The theoretical results imply therefore a recommendation to the experimentalist to avoid (if possible) the presence of bases and nucleophiles when the preparation of RNS_n compounds is intended.

The dipole moments resulting from MNDO calculations are slightly overestimated compared with the experiment. This is demonstrated³⁸ for thioformaldehyde again ($\mu_{\text{MNDO}} = 8.44 \cdot 10^{-3}$ C m, $\mu_{\text{exp}} = 5.50 \cdot 10^{-3}$ C m). If one assumes that at least the qualitative order is correct it can be suggested that the HNS_n compounds *I*, *III*, *IVb*, *V*, and *VIb* are less polar than thioformaldehyde whereas the dithionitro compound *II* is of comparable polarity. The dipole moments of (*E*)- and (*Z*)-configurations of *IVa*, *VIa* and *IVb*, *VIb* respectively are predicted to be proper tools for a configurative assignment. The dipole moments increase considerably for R = C₆H₅. For dithionitrobenzene and (*E*)-*N*-thiosulfinylaniline values of $17.18 \cdot 10^{-3}$ and $21.55 \cdot 10^{-3}$ C m were calculated, respectively. The high polarity of *IVa* results mainly

TABLE III

Frontier orbital energies of RNS_n compounds (in eV)

Compound	R = H		R = CH ₃		R = C ₆ H ₅	
	$-E_{\text{HOMO}}$	$-E_{\text{LUMO}}$	$-E_{\text{HOMO}}$	$-E_{\text{LUMO}}$	$-E_{\text{HOMO}}$	$-E_{\text{LUMO}}$
<i>I</i>	10.06	1.44	9.75	1.37	9.44	1.76
<i>II</i>	9.98	2.41	9.77	2.29	9.55	2.38
<i>III</i>	10.16	1.68	10.02	1.55	9.39	1.54
<i>IVa</i>	9.96	2.64	9.66	2.55	8.75	2.72
<i>IVb</i>	10.19	2.70	9.88	2.54	8.82	2.26
<i>V</i>	10.46	1.42	10.25	1.20	—	—
<i>VIa</i>	10.41	1.31	10.20	1.23	9.16	1.32
<i>VIb</i>	10.52	1.40	10.31	1.30	9.08	1.40

TABLE IV

Non-vertical ionization potentials, electron affinities and dipole moments of HNS_n compounds

Compound	IP^{NV} eV	EA^{NV} eV	$\mu \cdot 10^{-3}$ C m
<i>I</i>	9.55	-1.86	4.77
<i>II</i>	—	-2.79	7.87
<i>III</i>	9.30	-2.30	6.30
<i>IVa</i>	9.58	-3.07	13.98
<i>IVb</i>	9.98	-3.12	7.27
<i>V</i>	10.27	-2.12	5.17
<i>VIa</i>	10.13	-2.19	9.77
<i>VIb</i>	10.22	-2.23	2.23

from a strong charge alternation of the N—S—S group ($N^{\delta+}$ — $S^{\delta-}$ — $S^{\delta+}$). This effect will be certainly damped when the *d*-orbitals of sulfur are included.

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