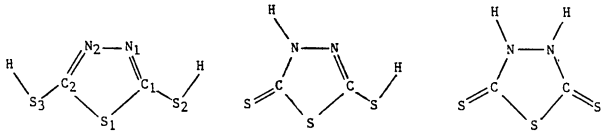
AM1 and CNDO/S Study of 2,5-Dimercapto-1,3,4-thiadiazole, the Mesoionic 1,3,4-Thiadiazolo[2,3-*b*][1,3]thiazine-2-thione and Its Dimerization Derivative

Giuseppe BUEMI
Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy
(Received October 23, 1989)

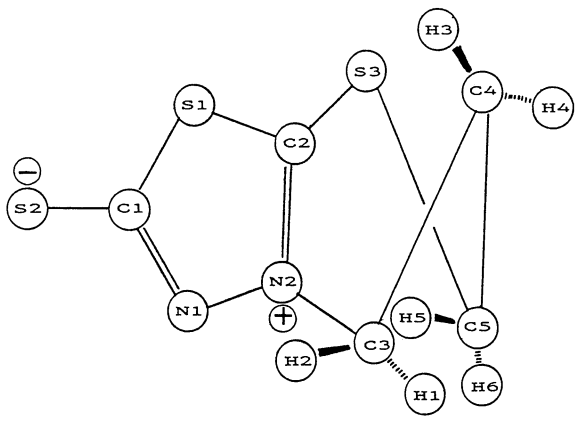
The molecular geometries of the mesoionic 1,3,4-thiadiazolo[2,3-*b*][1,3]-thiazine-2-thione (**II**) and its dimerization product, 1,10-dithia[4.4](3,5)-1,3,4-thiadiazolinophane-6,15-dithione (**III**) have been optimized by means of the AM1 method. Their electronic spectra, as well as those of the parent 2,5-dimercapto-1,3,4-thiadiazole (**I**), have been calculated at CNDO/S level. The analysis of the calculated electronic transitions and of the experimental UV absorption bands confirms the mixed thiolic-thionic structure of **I** as the most stable one, in agreement with 4-31G* prediction. The electronic transitions of compound **III** are practically coincident with those found for **I**; on the contrary, a band in the visible and a band in the UV region are predicted for compound **II**, so accounting for the yellow color of **II** and the lack of color of **III**.

Reaction of 2,5-dimercapto-1,3,4-thiadiazole (**I**) with 1,ω-dibromoalkanes, of general formula Br-$(CH_2)_n$-Br, in alkaline medium under high dilution conditions, gives rise to macrocyclic compounds containing 2,5-dithio-1,3,4-thiadiazole moieties connected by one or more methylene groups.[1,2] Since thiadiazole **I** can exist in the following three tautomeric forms, different cyclization modes are possible and, consequently, different macrocycles can be obtained.[2]



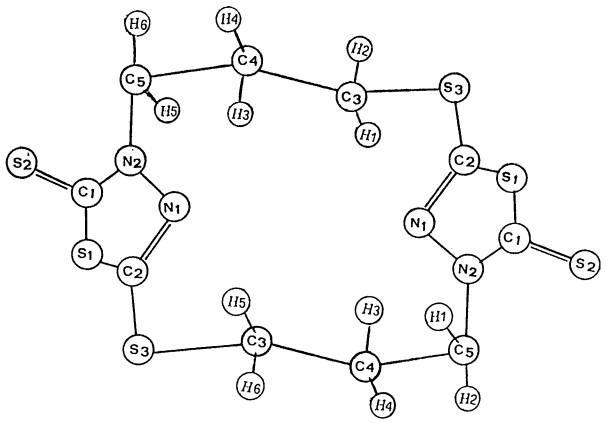
IA **IB** **IC**

Among these, 1,10-dithia[4.4](3,5)-1,3,4-thiadiazolinophane-6,15-dithione (**III**) (Fig. 2), derived from tautomer **IB**, is not the direct product of the reaction between the dipotassium salt of **I** and 1,3-dibromopropane but originates from thermal dimerization of the monomeric mesoionic 1,3,4-thiadiazolo[2,3-*b*]-[1,3]thiazine-2-thione (**II**) (Fig. 1), through ring opening in correspondence of the C_5-S_3 bond.[2,3]



II

Fig. 1. The mesoionic 1,3,4-thiadiazole[2,3-*b*][1,3]-thiazine-2-thione. Atoms C_4 and C_5 lie asymmetrically on the opposite sides of the plane defined by the remaining molecular framework.



III

Fig. 2. 1,10-dithia[4,4](3,5)-1,3,4-thiadiazoliphane-6,15-dithione.

Even if both **II** and **III** contain the 2,5-dithio-1,3,4-thiadiazole framework, their electronic structures are expected to be rather different, as it can be argued from the fact that **II** is yellow colored whilst **III** is practically colorless.

In order to elucidate the situation, a theoretical investigation was undertaken for calculating the electronic transitions of both molecules **II** and **III**, after a preventive optimization of the molecular geometries for determining the most stable conformations. The results are here discussed in connection with those of **I**, whose tautomeric equilibrium was widely studied some years ago at ab initio level.[4]

Calculations

The molecular geometries of **II** and **III** were optimized by means of AM1 method.[5] Since no out-of-plane deformation was observed (in agreement with

the experimental findings of **I** and **II**) the full planarity of the pentatomic rings was assumed also in **III**. For this latter compound various possible conformations were investigated, owing that the presence of three CH_2 units allows a wide molecular flexibility, even if its most stable structure is expected to have C_{2h} symmetry. Originally the old AM1 program (which utilizes MNDO parameters for sulfur) was used. The obtained minima were successively optimized again by means of the new AM1 program (version 2.1, announced by QCPE on November 1989, containing AM1 parameters for sulfur and other atoms).

The electronic transitions were calculated by means of CNDO/S method[6] with and without inclusion of doubly excited configurations. Calculations were carried out on a VAX-STATION 2000 and on a VAX-11-750 computers.

Results and Discussiom

a) Molecular Geometries. Ab initio results have shown that the stability order of **IA**, **IB**, and **IC** is strongly depending on the basis set adopted for calculations.[4] So **IA** was predicted to be the most stable

Table 1. AM1 Optimized Geometry of the Mesoionic 1,3,4-Thiadiazole[2,3-*b*][1,3]-thiazine-2-thione,[a] (**II**)

r	AM1[b]	Exp.	δ	AM1[b]	Exp.	ω	AM1[b]	Exp.
C1-S2	1.546(1.554)	1.682	S1-C1-S2	118.0(122.1)	121.1	C5-S3-C2-S1	−179.9(−174.3)	−168.4
C1-S1	1.833(1.789)	1.771	C1-S1-C2	91.2(90.9)	90.2	C5-S3-C2-N2	0.9(5.7)	11.6
S1-C2	1.678(1.686)	1.702	S1-C2-N2	110.3(110.8)	109.6	C2-S3-C5-C4	− 28.1(− 35.0)	− 46.1
C2-N2	1.372(1.360)	1.316	C2-N2-N1	117.2(117.0)	117.9	N1-N2-C3-C4	−151.8(−157.4)	−159.3
N2-N1	1.341(1.337)	1.375	N2-N1-C1	113.5(112.2)	111.0	C2-N2-C3-C4	29.5(22.6)	20.7
N1-C1	1.361(1.379)	1.311	N1-C1-S1	107.8(109.2)	111.4	N2-C3-C4-C5	− 57.7(− 53.7)	− 59.4
C2-S3	1.667(1.670)	1.718	S3-C2-N2	126.9(127.0)	127.0	C3-C4-C5-S3	57.1(60.9)	74.0
N2-C3	1.466(1.469)	1.489	C2-N2-C3	122.2(122.9)	126.9	H1-C3-N2-C2	86.5(80.5)	
C3-C4	1.526(1.525)	1.570	C5-S3-C2	104.2(103.4)	98.9	H2-C3-N2-C2	− 30.5(− 36.1)	
S3-C5	1.764(1.736)	1.846	C4-C3-N2	113.3(113.4)	109.0	H3-C4-C3-N2	64.8(69.0)	
C4-C5	1.504(1.505)	1.510	C5-C4-C3	112.3(112.5)	109.6	H4-C4-C3-N2	−178.8(−174.7)	
			S3-C5-C4	114.1(113.2)	107.7	H5-C5-S3-C2	95.1(87.5)	
						H6-C5-S3-C2	−149.5(−156.7)	

a) Bond lengths (*r*'s) in Å, bond (δ's) and dihedral (ω's) angles in degrees. b) Values in parentheses come from the old version of AM1 program, which utilized for sulfur the same parameters of MNDO method.

Table 2. AM1 Optimized Geometry of 1,10-Dithia[4,4](3,5)-1,3,4-thiadiazolinophane-6,15-dithione,[a] (**III**)

r	**III-A**	**III-B**	δ	**III-A**	**III-B**
N1-N2	1.340	1.337	C2-N1-N2	112.0	112.4
N1-C2	1.336	1.334	N1-N2-C1	117.0	116.8
C1-N2	1.412	1.415	N2-C1-S1	106.8	106.7
S1-C1	1.745	1.745	C1-S1-C2	91.0	91.2
C1-S2	1.554	1.555	S1-C2-N1	113.2	112.9
C2-S1	1.731	1.731	S1-C1-S2	124.8	125.0
C2-S3	1.671	1.673	N1-C2-S3	127.8	126.9
S3-C3	1.767	1.773	C2-S3-C3	107.5	111.0
C3-C4	1.507	1.504	S3-C3-C4	112.0	121.8
C4-C5	1.527	1.529	C3-C4-C5	111.8	111.9
C5-N2	1.463	1.463	C4-C5-N2	116.3	113.8
C-H	1.124	1.125	C5-N2-N1	122.8	119.8
			H-C3-S3	108.5	104.4
			H-C4-C5	109.2	110.3
			H-C5-N2	106.6	107.4
ω			ω		
N1-C2-S3-C3	20.9	−41.8	H1-C3-S3-C2	−133.1	−88.2
C2-S3-C3-C4	−106.1	34.9	H2-C3-S3-C2	−17.2	158.7
S3-C3-C4-C5	174.7	−61.8	H3-C4-C3-S3	−52.6	−61.6
C3-C4-C5-N2	−86.6	159.6	H4-C4-C3-S3	64.6	−176.7
C4-C5-N2-N1	21.5	−68.1	H5-C5-C4-C3	−153.0	80.2
			H6-C5-C4-C3	−34.5	−39.3
ΔH_f	141.07	146.39			

a) Bond lengths (*r*'s) in Å bonds (δ's) and dihedral (ω's) angles in degrees, ΔH_f in kcal mol^{-1}. The **III-B** geometry refers to the centrosymmetrical chair conformation. Bond lengths and bond angles of the nearly isoenergetic boat conformation are practically unchanged.

tautomer when STO-3G basis was used whilst adoption of more extended bases allowed to get **IC** (4-31G) or **IB** (4-31G* basis, 4-31G geometries) as the most probable conformer. UV,[7] IR,[7] and X-ray[8] studies suggested **IB** as prevailing tautomer (so supporting the 4-31G* findings) even if also **IC** seems to be present on the ground of IR measurements, especially in polar solvents.[7]

Table 1 shows the optimized and experimental geometries of **II**. The molecule was characterized as a zwitterion (see Ref. 3) and a possible limit structure is shown in Fig. 1. Two sligthly different geometries were calculated by the old and the new AM1 programs: version 2.1 of AM1 predicts **II** to be fully planar except C_5 (found about 0.65 Å out of the molecular plane); on the contrary, according to the geometry predicted by the old AM1 program, C_4 lies under and C_5 lies over the molecular plane (or vice versa, the two structures being energetically equivalent), but their positions are not symmetrical. This latter agrees with the experimental findings better than the former geometry. In any case, both of them produce nearly coincident electronic transitions.

The agreement between calculated and experimental data is satisfactory, especially if we bear in mind that theoretical values refer to gas phase and experimental ones to the solid state. However, the C_5-S_3 bond is not found to be the longest S-C bond, in contrast with the experimental datum.

The minimum energy conformation of **III** (Fig. 2), whose geometrical parameters are listed in Table 2, is centrosymmetric with a nearly overall rectangular shape (**III-A**) and the paraffinic chains in a roughly fully extended conformation (the torsion angle around C_3-C_4 is 174.7°). Other conformations, except the one having the $C_5C_4C_3S_3$ frameworks in chair (**III-B**) or boat forms are considerably less stable and therefore are not reported here.

b) Electronic Structure. The UV spectrum of 2,5-dimercapto-1,3,4-thiadiazole, in ethanol solution,[8] shows two absorption bands centered at 335 nm ($\log\varepsilon$=4.15) and 260 nm ($\log\varepsilon$=3.71). It is practically equal to the spectrum of 5-mercapto-3-methyl-1,3,4-thiadiazol-2(3*H*)-thione (λ_{max}=333, $\log\varepsilon$=4.11, and λ_{max}=260 nm, $\log\varepsilon$=3.82)[7] corresponding to the methylated **IB** or **IC** tautomers (compounds **B1** and/or **C1**). These bands shift towards the blue when one of the SH groups is forced into the enethiol form, as in the

Table 3. Electronic Transitions of the 2,5-Dimercapto-1,3,4-thiadiazole Tautomers.[a] CNDO/S Method, ab-initio (4-31G) Geometries[b]

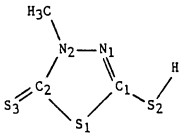
E[c]	λ[c]	f[c]	$\log\varepsilon$	Pol.	Sym.	Nat.[d]	MO's	
							εi	Nat.
			IA					
5.06(5.00)	245	0.	—	—	$^1A_2$	n	−12.90	π_2 (b_1)
5.14(5.15)	241	0.228	4.09	x	$^1B_2$	n	−12.84	n (a_1)
5.16(5.05)	240	0.	—	—	$^1B_1$	a	−11.26	π_1 (a_2)
5.99(6.01)	207	0.	—	—	$^1B_1$	c	−0.29	π_1* (b_1)
6.26(6.33)	198	0.005	2.39	y	$^1A_1$	d,b	+1.06	π_2* (a_2)
			IB					
2.91(3.21)	426	0.	—	—		n	−10.87	π_1
3.94(4.34)	315	0.282	4.19	−7[e]		a	−10.87	n
5.08(5.50)	244	0.	—	—		n	−1.04	π_1*
5.27(5.56)	235	0.100	3.74	76[e]		b	−0.27	π_2*
			IC					
2.88(3.10)	430	0.	—	—	$^1A_2$	n	−11.75	π_2 (b_1)
2.90(3.12)	427	0.	—	—	$^1B_1$	n	−11.58	n (a_1)
4.26(4.30)	291	0.519	4.45	x	$^1B_2$	a,e	−11.50	π_1 (a_2)
4.58(4.65)	271	0.050	3.44	y	$^1A_1$	b,d	−11.42	n (b_2)
5.40(5.62)	229	0.018	2.98	y	$^1A_1$	b,d	−1.63	π_1* (b_1)
5.62(5.67)	221	0.032	3.24	x	$^1B_2$	e,a	−1.43	π_2* (a_2)
			Experimental geometry[e]					
2.91(3.17)	427	0.	—	—		n	−12.62	π_2
3.82(4.18)	325	0.275	4.17	−2[e]		a,b	−10.84	n
4.74	261	0.	—	—		n	−10.77	π_1
4.89(5.21)	254	0.078	3.62	82[e]		b,a	−1.11	π_1*
							−0.46	π_2*

a) Experimental absorption maxima in EtOH solution: λ_{max}=335 nm, $\log\varepsilon$=4.15: λ_{max}=260 nm, $\log\varepsilon$=3.71.[8] b) Ref. 4. c) E (eV) and λ(nm) are the energy and wavelength, respectively, of the electronic transition; f is the related oscillator strength. Values in parentheses are the energies obtained when doubly excited configuration were omitted. d) The symbols in the column indicate the main configurations involved in the transitions according to the following: n: n→π^*; a: π_1→π_1^*; b: π_1→π_2^*; c: π→σ^*; d: π_2→π_1^*; e: π_2→π_2^*. e) Figure represents the angle between the transition moment and the x axis (x axis lies along the N-N bond). e) Ref. 9.

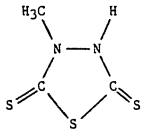
fully methylated **IC** tautomer, 5-methylthio-4-methyl-1,3,4-thiadiazol-2(3*H*)-thione (compound **B2**, λ_{max}= 320, log ε=4.13, and λ_{max}=243, log ε=3.63).[7]

If both the SH groups are forced into the enethiol arrangement (2,5-bis(methylthio)-1,3,4-thiadiazole, i.e. the methylated **IA** tautomer, compound **A1**) a further strong blue-shift of the longer wavelength absorption maximum (λ_{max}=288 nm, log ε=4.01) and the loss of the shorter wavelength band[7] are observed.

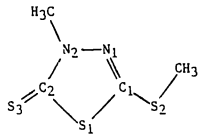
The electronic transitions calculated by adopting the 4-31G geometries of **I** are collected in Table 3.



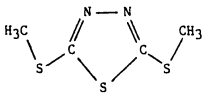
B1



C1



B2



A1

They indicate that the two above cited absorption bands originate from transitions $\pi \rightarrow \pi^*$ (accompanied by forbidden $n \rightarrow \pi^*$ transitions) involving the two highest occupied and the two lowest unoccupied π orbitals. The coefficient distribution of these and of the n orbitals of the title compounds are shown in Fig. 3. The MO's correlation diagram of **IA**, **IB**, and **IC** is shown in Fig. 4. The n and π_2 MO's of **IA**, as well as the n and π_1 MO's of **IB** and **IC**, are practically degenerate. In particular, the four highest occupied MO's of **IC** lie in a very narrow energy range and the two lowest vacant MO's differ from each other by only 0.2 eV. It is noteworthy that the n and π_1 orbitals of **IB** are nearly pure atomic orbitals of the S_3 atom and their calculated energy (−10.87 eV) is in good agreement with the sulfur ionization potential (10.36 eV).[9] Moreover, very remarkable energy differences exist between the lowest n orbital of the **IB** and **IC** tautomers and the corresponding n orbital of **IA** (about 2 and 1.4 eV, respectively). This is likely due to the fact that in the former structures the lone pairs of the lateral thionic S atom(s) are mainly involved, whilst in **IA** the n orbital is principally localized on the S atom of the ring. These differences are responsible for the different UV spectra of the three tautomers.

Theory predicts the $\pi \rightarrow \pi^*$ transitions of **I** (gas phase) at wavelengths lower than those of the experimental bands recorded in EtOH solution. The resulting red shift on passing from gas phase to solution is very likely due to solvent effect, even if somewhat an

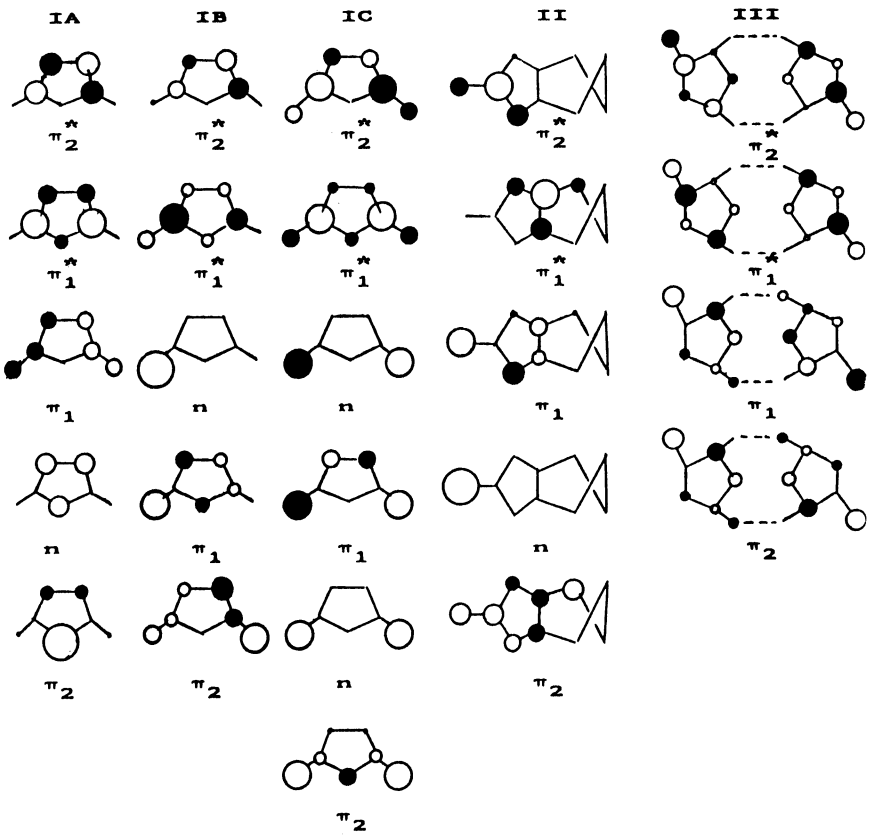


Fig. 3. Topology of the frontier orbitals of the title compounds (CNDO/S calculations). Sizes of Circles are roughly proportional to the coefficient values. The CH_2 chains in **III** are omitted.

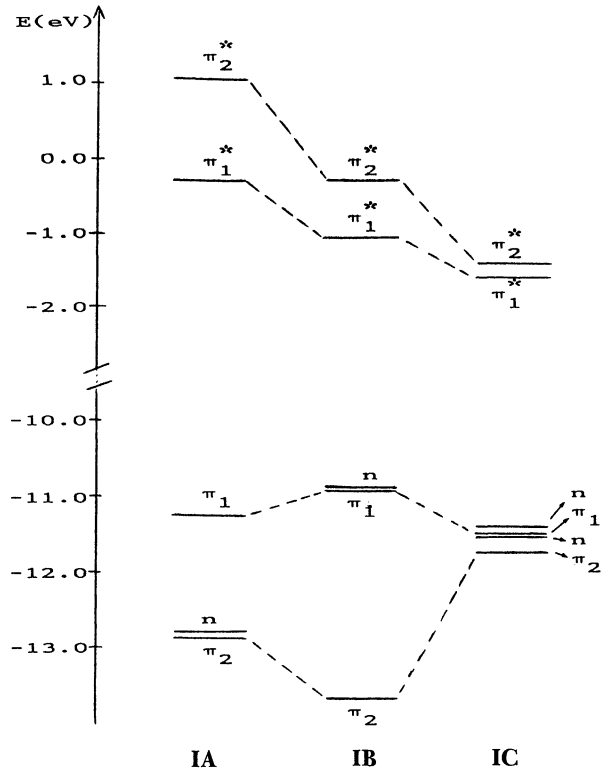


Fig. 4. Correlation diagram of the frontier MO's of the **IA**, **IB**, and **IC** tautomers (CNDO/S calculations).

Table 4. Electronic Transitions (eV) of Compounds **II** and **III**

E[a)]	λ[a)]	f	$\log\varepsilon$	Nature[a)]		MO's ε_i	MO's Nat.
			II[b)]				
2.55	486	$8\cdot10^{-4}$	1.65	n		−13.41	π_3
2.57	483	0.160	3.94	a		−13.39	n
3.46	358	0.	—	n		−13.14	n
4.36	285	0.224	4.09	b,c		−12.17	π_2
4.85	256	0.088	3.68	c,b		−9.82	n
5.16	240	0.	—	ps		−9.63	π_1
5.24	237	0.	—	n		−1.59	π_1*
5.69	218	0.002	1.97	ns		+0.73	π_2*
6.19	200	0.33	4.25	d		+1.36	σ*
			III-A[c)]				
3.14	394	$2\cdot10^{-4}$	1.06	n	^1B_g	−12.19	π_4 (b_g)
3.14	394	0.	—	n	^1A_u	−12.18	π_3 (a_u)
4.31	288	0.	—	b,c	^1A_g	−10.87	n (b_u)
4.33	287	0.836	4.66	a,e	^1B_u	−10.85	n (a_g)
5.14	241	0.463	4.40	f,g	^1B_u	−10.66	π_2 (a_u)
5.21	238	0.	—	h	^1A_g	−10.64	π_1 (b_g)
5.60	221	0.003	2.17	n	^1B_g	−0.87	π_1* (a_u)
5.65	219	0.	—	n	^1A_u	−0.87	π_2* (b_g)
6.00	207	0.023	3.10	m	^1B_u	−0.26	π_3* (b_g)
						−0.26	π_4* (a_u)

a) E (eV) and λ (nm) are the energy and the wavelength, respectively, of the transitions; f (dimensionless) is the oscillator strength. The symbols in the column indicate the main configurations involved in the transition, according to the following: a: $\pi_1\rightarrow\pi_1$*; b: $\pi_1\rightarrow\pi_2$*; c: $\pi_2\rightarrow\pi_1$*; d: $\pi_3\rightarrow\pi_1$*; e: $\pi_2\rightarrow\pi_2$*; f: $\pi_2\rightarrow\pi_3$*; g: $\pi_1\rightarrow\pi_4$*; n: n→π*; h: $\pi_1\rightarrow\pi_3$*+$\pi_2\rightarrow\pi_4$*; m: $\pi_3\rightarrow\pi_2$*+$\pi_4\rightarrow\pi_1$*; ns: n→σ*; ps: π→σ*. b) Results coming from the AM1 geometry reported in parentheses in Table 1. Values obtained when the alternative geometry was adopted differ negligibly from the present ones. c) The electronic transitions of **III-B** coincide with those of **III-A**.

underestimation of the calculated values cannot be excluded. CNDO/S calculations reproduce in a satisfactory way the blue shift observed in the UV spectra of the methylated analogues on passing from **IC** to **IB** and to **IA** when doubly excited configurations are omitted (Table 3). Inclusion of bi-excitation terms improves the agreement with the experimental data but it shifts towards the red the lowest energy transition of **IB** with respect to the corresponding transition of **IC**. In any case, the loss of the absorption band at shorter wavelengths in **IA** is well accounted for since the corresponding $\pi\rightarrow\pi^*$ transition is calculated at an energy higher than 6 eV (i.e. in the vacuum UV region) with a very low oscillator strength.

The electronic transitions calculated for **II** and **III** are collected in Table 4. The π-system of the thiadiazole ring of **II** is certainly affected by the mesoionic character of the molecule and by its particular geometry. In fact, by comparing the frontier MO's (Fig. 5) one notes that the highest occupied orbitals of **II** (π_1 and n) are remarkably less stable than the corresponding orbitals of **III** and **IB**. The main peculiarity of the frontier orbitals of **II** with respect to those of **IB** is the presence of very large coefficients on S_2 and N_1 of HOMO (0.75 and −0.54, respectively) and on C_2 and N_2 of LUMO (0.77 and −0.46, respectively). By comparing the coefficient distribution of **II** and **IB** MO's, we observe somewhat a resemblance among the occupied orbitals of the two compounds. But the π_1* and π_2* enegy order appears to be reversed because the largest coefficients of π_1* of **II** correspond to the largest coefficients of π_2* of **IB** and the largest coefficients of π_2* of **II** correspond to those of π_1* of **IB**.

In **III** we find two degenerate π (and π*) orbitals and two degenerate n orbitals, whose energies are practically equal to those of π_1 and n orbitals of **IB**. Each pair originates from linear combination of the π_1 (or π* or n) orbital of each of the two cyclic frameworks. The very small energy lowering means that the two thiadiazole rings of **III** have the same electronic structure of the free tautomer **IB**, as, on the other hand, is expected, the two rings being separated by three methylene units which do not allow conjugation between the two π-systems.

These peculiarities are once again responsible for the different electronic spectra of **II** and **III**. In fact, apart from the feeble n→π* transitions, compound **III** shows two strong π→π* electronic transitions at 4.33 eV (287 nm) and 5.14 eV (241 nm), which correspond to those calculated for the **IB** tautomer of 2,5-dimercapto-1,3,4-thiadiazole at 3.94 and 5.27 eV.

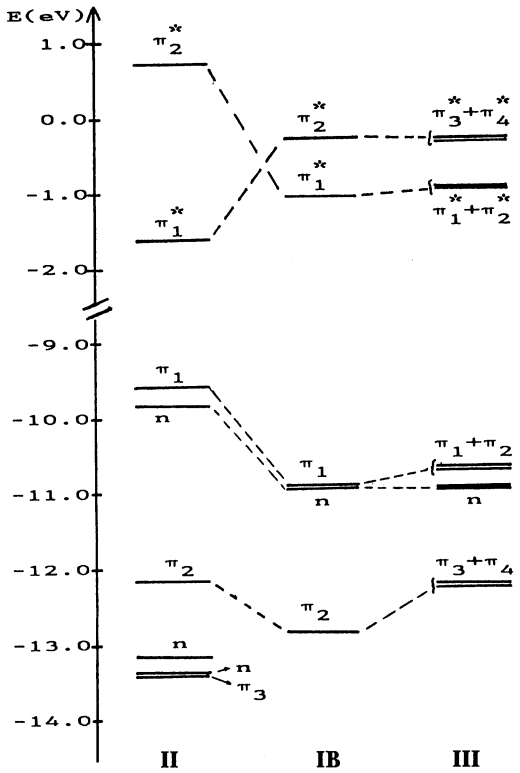


Fig. 5. Correlation diagram of the frontier orbital of **IB** and those of **II** and **III**.

On the contrary, the spectrum of the mesoionic compound **II** would show an absorption band, deriving from the HOMO→LUMO transition, lying in the visible region at 2.57 eV (483 nm), and a weaker band centered in the range of 4.36 eV (285 nm). Although the experimental UV spectra of **II** and **III** are lacking, the yellow color of **II** and the near absence of color of **III** confirm that the lowest energy absorption band of **II** lies in the visible region.

Conclusion

CNDO/S calculations reproduce in a satisfactory way both the electronic spectra of **I** and the blue shift observed in the absorption bands on going from **IC** to **IB** to **IA**. The electronic transitions calculated for **IB** agree with the experimental UV bands of **I** much better than those of **IA** and **IC**, so confirming **IB** as the most stable tautomer also in the gas phase.

The UV spectrum of **III** is predicted to be analogous to that of **I**, whilst for **II** it is expected one absorption band in the visible and one in the UV region. Since a substance is colored when it absorbs in the visible region (in particular absorption in the range 435—490 nm gives yellow or yellow-orange color),[10] the electronic transition calculated at 483 nm accounts for the yellow color of **II**. On the contrary, all the electronic transitions of **III** lie below 400 nm, in the UV region, and the molecule is colorless.

The author is very grateful to Prof. S. Pappalardo for the experimental geometrical data of compound **II** and for the useful discussion during the preparation of this work. Thanks are due to the Referees for their useful suggestions. Financial support from the Italian Ministero della Pubblica Istruzione is gratefully acknowledged.

References

1) S. Pappalardo, F. Bottino, and C. Tringali, *Heterocycles*, **22**, 1339 (1984).

2) S. Pappalardo, F. Bottino, and C. Tringali, *J. Org. Chem.*, **52**, 405 (1987).

3) F. Bottino, U. Chiacchio, F. R. Fronczek, and S. Pappalardo, *J. Org. Chem.*, **54**, 2024 (1989).

4) S. Millefiori and A. Millefiori, *J. Mol. Struct., Theochem.*, **151**, 373 (1987).

5) a) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985); b) QCPE Program No. 506, version 2.1 (1989).

6) H. Baumann, QCPE program No. 333 (1977), converted and modified by G. Buemi for running on IBM-PC and VAX computers; *QCPE Bulletin*, **9**, 38 (1989), program No. QCMP062.

7) C. D. Thorn, *Can. J. Chem.*, **38**, 1439 (1960).

8) J. W. Bats, *Acta Crystallogr., Sec. B*, **32**, 2866 (1976).

9) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electronic Affinities," ed by Edward Arnold, London (1966).

10) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," ed by Masson et Cie, Paris (1962), p. 450.