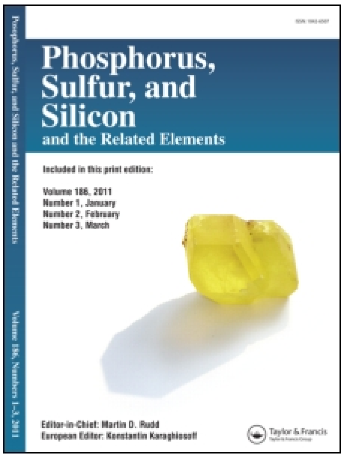

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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SOME EVIDENCE ABOUT THE MECHANISM OF FORMATION OF 5-(1-HYDROXYIMINOALKYL)-1, 2-DITHIOLE-3-THIONES

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To cite this Article Bertrand, H. O. and Burgot, J. L.(1994) 'SOME EVIDENCE ABOUT THE MECHANISM OF FORMATION OF 5-(1-HYDROXYIMINOALKYL)-1, 2-DITHIOLE-3-THIONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 97: 1, 103 — 111

To link to this Article: DOI: 10.1080/10426509408020733

URL: http://dx.doi.org/10.1080/10426509408020733

Phosphorus, Sulfur, and Silicon, 1994, Vol. 97, pp. 103–111
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SOME EVIDENCE ABOUT THE MECHANISM OF FORMATION OF 5-(1-HYDROXYIMINOALKYL)-1,2-DITHIOLE-3-THIONES

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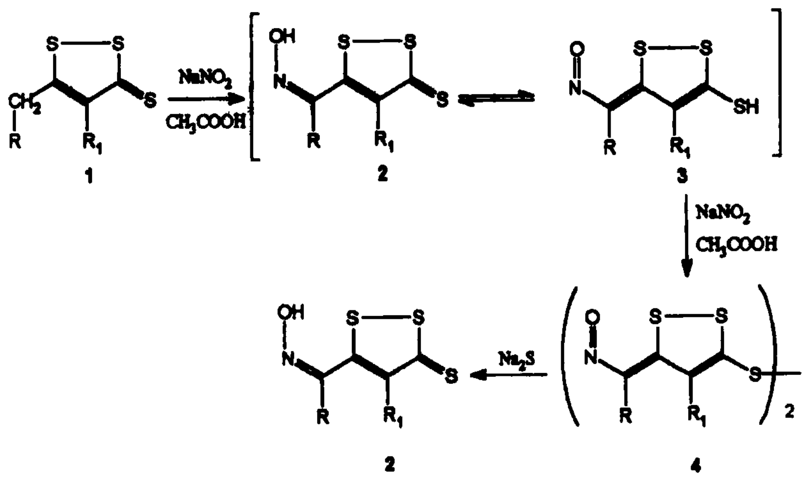
(Received July 21, 1994; in final form September 6, 1994)

Semi-empirical calculations (PM3 method) are used to check the possibility of an assisted addition of nitrosonium cation on 5-mercapto-1,2-dithiole-3-ylidene as a mechanism of formation of 5-(1-hydroxyiminoalkyl)-1,2-dithiole-3-thiones.

Key words: 1,2-dithiole-3-thiones, 5-(1-hydroxyiminoalkyl)-1,2-dithiole-3-thiones, nitrosation, no-bond resonance compounds, semi-empirical calculations (PM3 method).

We have described recently a general method of synthesis of 1,2-dithiole-3-thiones derivatives: 5-(1-hydroxyiminoalkyl)-1,2-dithiole-3-thione **2**.[1,2] We report, here, some evidence about the mechanism of formation of those compounds, on the grounds of semi-empirical calculations, which as far as we know are in agreement with experimental data.

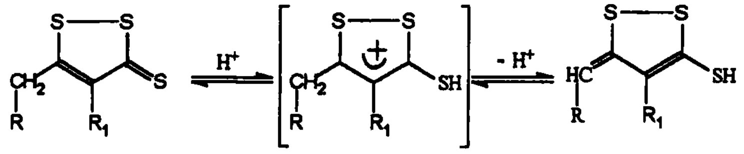
5-(1-hydroxyiminoalkyl)-1,2-dithiole-3-thiones **2** (dithiolethiones oxime) are easily synthesised by allowing 5-alkyl-1,2-dithiole-3-thiones **1** to react with sodium nitrite in acetic acid solution.[1,2] The compounds isolated are the disulphides **4** (Scheme I).



SCHEME I

Since compounds **4** are the disulphides of the 5-mercapto-1-oxa-6,6a-S^{IV}-dithia-2-azapentalenes **3** which are the tautomeric forms of dithiolethiones oxime **2**, compounds **4** can be considered as the result of a nitrosation of the starting dithiolethiones **1** followed by an oxydation by nitrous acid. Therefore, formation of disulphides **4**, is probably consecutive to the formation of the 5-mercapto heteropentalenes **3**. Otherwise, ketone-oximes are easily synthesised by allowing ketones to react with sodium nitrite, in acidic solutions.[3]

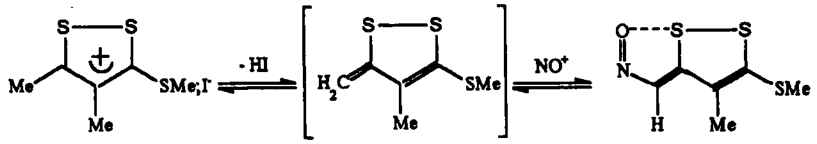
It is well known that the reaction of nitrosation occurs by addition of a nitrosonium ion on the corresponding enol.[4] So, in the first step of our reaction, the formation of 5-mercapto-1,2-dithiole-3-ylidenes **5** is highly probable, even if these latter forms have never been detected by NMR spectrometry in different solvents[2] (Scheme II).



1 **5**

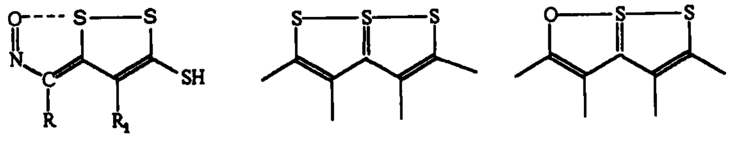
SCHEME II

This hypothesis is in agreement with some features of the chemistry of 1,2-dithiole-3-thiones. For instance, the easy dissolution of 1,2-dithiole-3-thiones in acidic conditions and particularly in sulphuric acid, provides good assumption for the protonation of the thione group.[5] Protonation of the thiocarbonyl group have been the matter of a theoretical interpretation.[6] Besides, the occurrence of 5-mercapto-1,2-dithiole-3-ylidenes **5** have already been proposed by Richter and Fanghanel in their explanation of the action of phenyl diazonium fluoroborate in acidic medium on 4,5,6,7-tetrahydrobenzo- and dihydro-5,6-cyclopenta-1,2-dithiole-3-thiones.[7] Moreover, we have synthesized 5-methylthio-4-methyl-1-oxa-6,6a-S^{IV}-dithia-2-azapentalene by action of nitrous acid on 3-methylthio-4-methyl-5-methyl-1,2-dithiolylium salt[8] (Scheme III).



SCHEME III

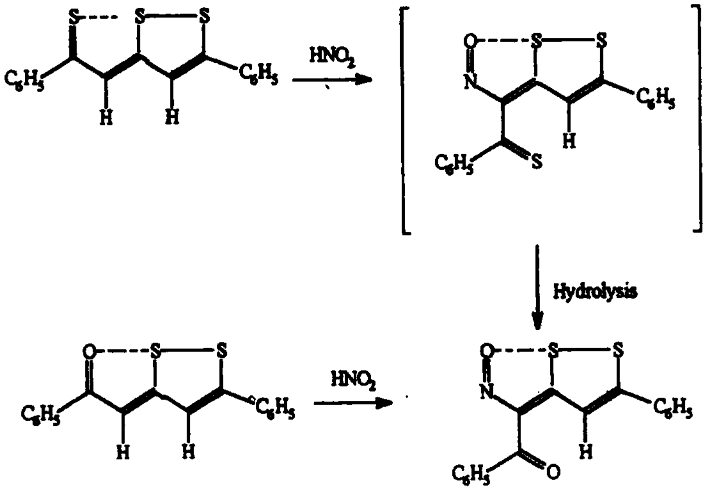
For the second step of our reaction, we must consider the particular structure of compounds **3** which are structural analogous of trithiapentalenes **6** and of their oxa-derivatives **7**[9] (Scheme IV).



3 **6** **7**

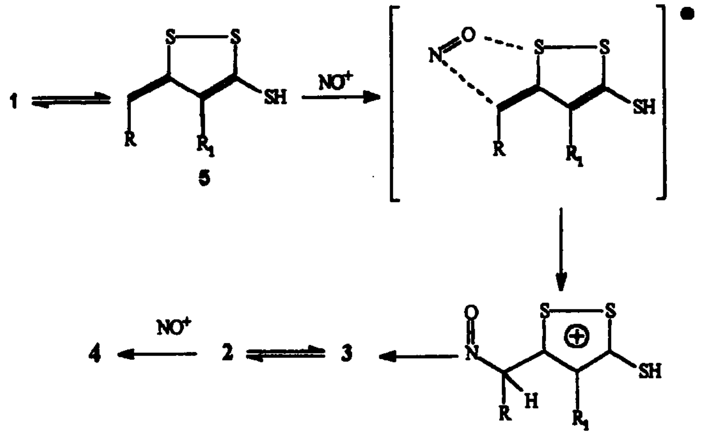
SCHEME IV

Indeed, according to their spectroscopic data, heteropentalenes **6** and **7** can be considered as no-bond resonance compounds or as bicyclic aromatic compounds with considerable Π-electron delocalization. This Π-electron delocalization confers them high stability. Likewise, compounds **3** are endowed with the same properties. An interesting proof of the particular stability of compounds **3** is the obtention of a compound of type **3** by nitrosation of 2,5-diphenyl-trithiapentalene or by nitrosation of its corresponding dithiolylidene-ketone by nitrous acid.[10] So, the obtained compound is undoubtedly more stable than the corresponding starting ones. Interestingly and from another standpoint, this reaction provides a new argument for the existence of the exocyclic double bond in the first step of the reaction (Schemes II and V).



SCHEME V

For all these reasons, the hypothesis, which is the object of this work, is that the reaction results from the addition of a nitrosonium ion on the exocyclic double bond of the tautomeric form **5** of the starting dithiolethione **1** with the assistance of the 2-thio atom of the dithiolethione nucleus (Scheme VI).



SCHEME VI

In this first account, semi-empirical calculations are used to check this hypothesis.

RESULTS AND DISCUSSION

For the sake of simplicity of calculations, the studied reaction is the one performed between the 5-mercapto-4-methyl-1,2-dithiole-3-ylidene **5a** ($R = H$; $R_1 = CH_3$) and nitrosonium ion.

Self-consistent-field molecular orbitals calculations were performed on personal computer and obtained from MOPAC 6.00[11,12] with the PM3 method.[13,14] This method was chosen because of the good fitting between experimental and calculated values of dipole moments for 1,2-dithiole-3-thiones in their ground state.[15] Starting files for MOPAC 6.00 were those obtained from Pro Chemist Model™ 4.02. The keywords were BONDS[11,12] for the calculations of the rotationally invariant bond orders between all pairs of atoms and VECTORS[11,12] for the calculations of molecular orbitals energy levels. It can be noted that molecular orbitals were treated like linear combinations of atomic orbitals. In some cases (nitrosonium ion and reaction path), the keyword CHARGE = + 1[11,12] was added. For all calculations, an RHF Hamiltonian was used.

Results of PM3 calculations for nitrosonium ion and 5-mercapto-4-methyl-1,2-dithiole-3-ylidene **5a** are summarized in Tables I and II.

As calculated and experimental[16,17] $\Delta H°f$ are identical for NO^+, PM3 can be considered as an accurate method for this system. Otherwise, it is worth noting that LUMO energy level for NO^+ is a degenerated one, where $\Phi_{2\text{LUMO}}$ is a Π pure molecular orbital. It can be noted also that Φ_{HOMO} for compound **5a** is a Π pure orbital.

TABLE I

PM3 results for nitrosonium ion

$\Delta H°f$: 238 kCal.mol-1

Highest occupied molecular orbital (HOMO)

.Calculated energy level :

-22.4 eV

.Analytical expression :

$\Phi_{\text{HOMO}} = 0.73\ s\,N - 0.23\ p_x N - 0.57\ p_y N + 0.10\ p_x N + 0.23\ p_y O$

Lowest unoccupied molecular orbital (LUMO)

.Calculated energy level :

-9.4 eV

.Analytical expression :

$\Phi_{1\,\text{LUMO}} = 0.73\ p_x N - 0.23\ p_y N - 0.54\ p_y O + 0.24\ p_y O$

$\Phi_{2\,\text{LUMO}} = 0.80\ p_z N - 0.59\ p_z O$

Calculated charges

N : + 0.69

O : +0.30

Calculated bond order

N-O : 2.81

TABLE II

PM3 results for 5-mercapto-4-methyl-3-ylidene-1,2-dithiole **5a**

$\Delta H°f$: 4 9.14 kCal.mol-1

Highest occupied molecular orbital (HOMO)

.Calculated energy level :

-8;39 eV

.Analytical expression :

$\Phi_{HOMO} = 0.60\ pz\ S_1 - 0.58\ pz\ S_2 + 0.14\ pz\ C_3 + 0.39\ pz\ C_{3'} - 0.26\ pz\ C_4 - 0.16\ pz\ C_5$

Lowest unoccupied molecular orbital (LUMO)

.Calculated energy level :

-2.11 eV

.Analytical expression :

$\Phi_{LUMO} = -0.66\ px\ S_1 - 0.65\ px\ S_2 - 0.15\ py\ S_{3'} - 0.10\ px\ S_{3'}$

Calculated charges

$S_2 = 0.05$

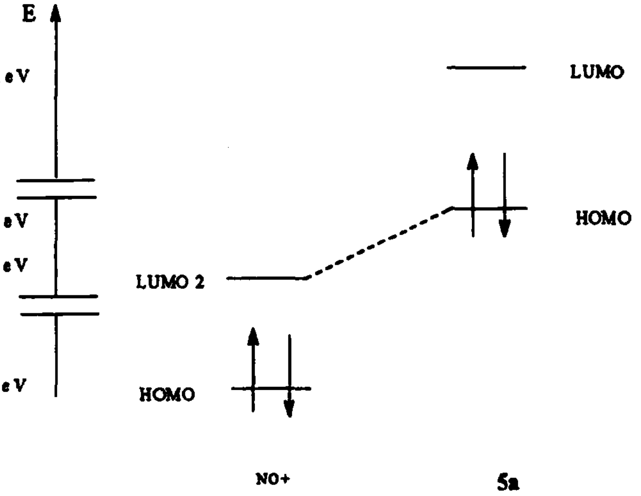
$C_{3'} = -0.09$

Calculated bond order

C_3-$C_{3'}$: 1.33

According to Klopman,[18] chemical reactions are either orbitals or charges controlled. In a frontier orbitals controlled reaction, the lower the difference between the interacting frontier molecular orbitals is, the easier the reaction is.

Frontier orbitals energy levels for the interacting species are given in Scheme VII.

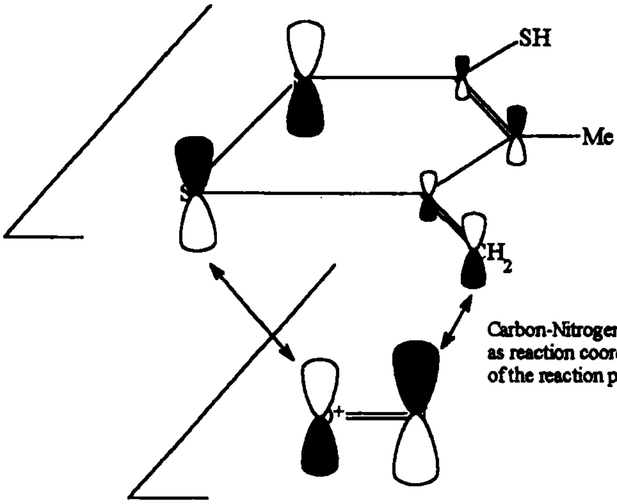


SCHEME VII

The interaction which minimises the energetic difference between the frontiers orbitals of NO^+ and compound **5a**, is an interaction between LUMO 2 of NO^+ and HOMO of compound **5a**. These two molecular orbitals which are a linear combination of pz atomic orbitals, are Π pure molecular orbitals. So, as it is indicated in Scheme VIII, the reaction results from through the overlap of pz atomic orbitals between sulfur and oxygen atoms on the one hand, and carbon and hydrogen on the other hand. It can be noted that the dithiolethione nucleus and the nitrosonium ion are lying in two parallel planes. Considering its analytical expression (Table I), $\Phi_{1\,LUMO}$ for NO^+ has been taken into account.

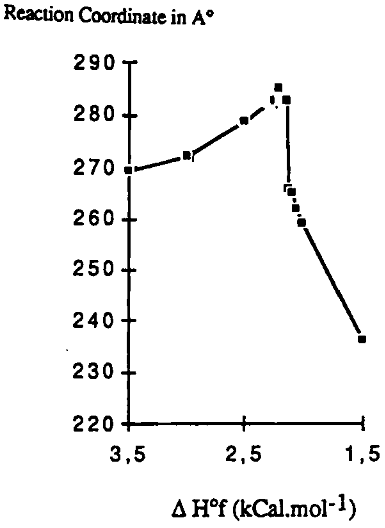
From another standpoint, charges on sulfur and oxygen and on carbon and nitrogen atoms are in agreement with this interaction.

Reaction path and saddle point have been calculated by choosing $C_{3'}$-Nitrogen distance as reaction coordinate (Scheme VIII). For each reaction coordinate value,



Carbon-Nitrogen distance chosen as reaction coordinate in the calculation of the reaction path.

SCHEME VIII



SCHEME IX

TABLE III

Calculated ΔH°f and gradient of the reaction versus reaction coordinate

Reaction coordinate A°	Δ H°f k Cal.mol-1	Gradient k Cal A-1
3.50	269.26	-1.71
3.00	271.99	-9.34
2.50	278.73	-18.92
2.30	282.01	-12.48
2.28	282.25	-10.78
2.26	282.41	-10.04
2.24	282.53	-7.58
2.22	284.87	-5.92
2.20	282.79	-3.16
2.18	282.73	2.30
2.16	282.63	4.75
2.14	282.58	10.12
2.12	265.75	50.90
2.10	264.73	53.24
2.00	258.89	61.82

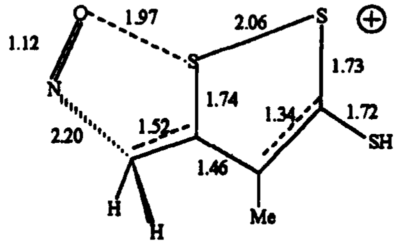
ΔH°f and the gradient of the super system [NO^+-**5a**] have been calculated. PM3 results of those calculations are summarized in Table III and Scheme IX.

The curve given in Scheme IX [ΔH°f = f (C.R.)] exhibits a maximum for a reaction coordinate lying between 2.24 and 2.18 A°. This zone corresponds to a saddle point, the calculated geometry and properties of which are given in Scheme X.

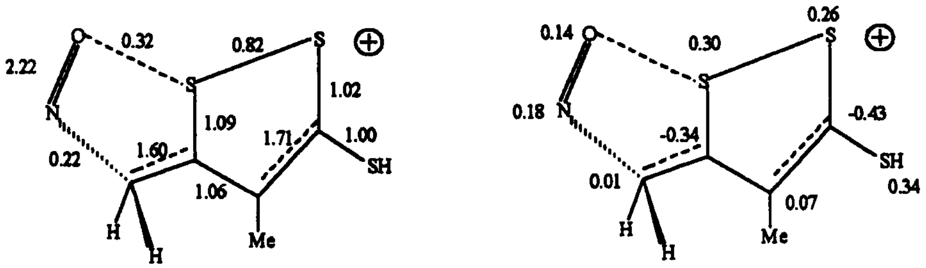
At the saddle point, bond orders provide an interesting argument for our hypothesis of the assisted addition. Indeed, it can be noted that the interaction is stronger between oxygen and sulfur than between carbon and nitrogen atoms.

As Scheme IX exhibits a maximum for the saddle point, it also exhibits a minimum for a reaction coordinate value of 1.49 A°. After the saddle point, the system is relaxed and yields to an intermediate cation. Calculated geometry and properties are given in Scheme XI. At this time, there exists a σ bond between carbon and nitrogen, and the interaction between oxygen and sulfur atoms persists (bond order = 0.31).

This intermediate cation yields then to compound **3a** which according to the calculations with the PM3 method shows the bicyclic resonant structure already discussed (Schemes IV and V). This is another argument of the accuracy of the method. Interatomic distances and bond orders are given in Scheme XII. Intera-



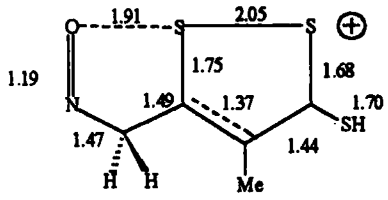
INTERATOMIC DISTANCES



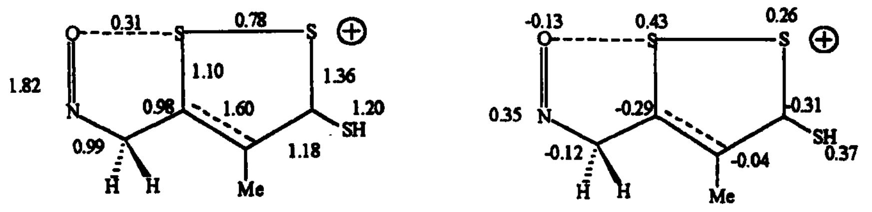
BOND ORDERS

CHARGES

SCHEME X



INTERATOMIC DISTANCES

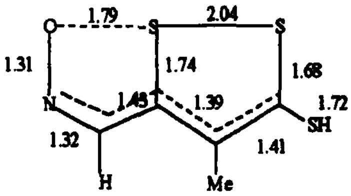


BOND ORDERS

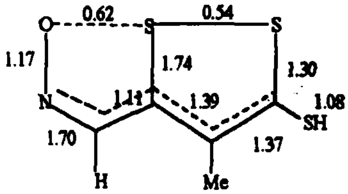
CHARGES

SCHEME XI

tomic distances are in agreement with X-ray crystallographic data of compounds of this type,[19,20] the only discrepancy being the length of the S—O link which seems underestimated by the calculations.



INTERATOMIC DISTANCES



BOND ORDERS

SCHEME XII

ACKNOWLEDGEMENTS

We thank Mister G. Bouer for his kind assistance in the preparation of the manuscript.

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