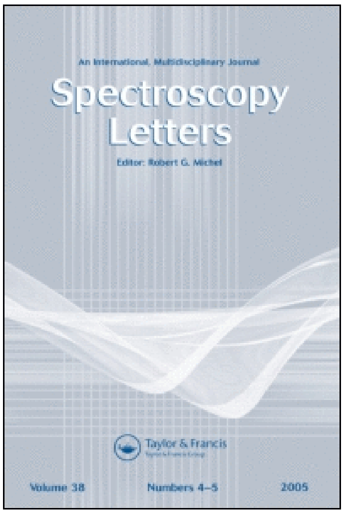

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CNDO/S Method Interpretation of the Ultraviolet Spectra of 1-3-Diazole and 1-3-Diazine, i.e. Pyrimidine-2-thione and 2-Methylthiopyrimidine

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CNDO/S METHOD INTERPRETATION OF THE ULTRAVIOLET SPECTRA OF 1-3-DIAZOLE AND 1-3-DIAZINE, i.e. PYRIMIDINE-2-THIONE AND 2-METHYLTHIOPYRIMIDINE.

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ABSTRACT

The existence of pyrimidine-2-thione in the thione form is confirmed by CNDO/S calculations. 2-methylthiopyrimidine is calculated, and all the transitions are in agreement with the experimental values.

INTRODUCTION

The pyrimidine-2-thione molecule can be found in two protomeric forms : the 2-mercaptopyrimidine and the pyrimidine-2-thione itself.

A CNDO/S calculation of the various transitions was carried out in order to confirm the existence of this molecule in the thione form in the most diluted solutions used in ultraviolet spectroscopy.

Moreover, the attribution of the absorption bands of the 2-methylthiopyrimidine molecule was done.

METHOD OF CALCULATION

The ultraviolet spectra have been described elsewhere (1).

The geometry of the pyrimidine cycle was estimated according to the results previously obtained (2), and is given in the Appendix.

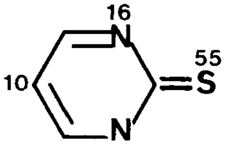
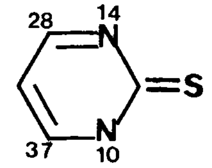
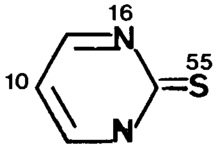
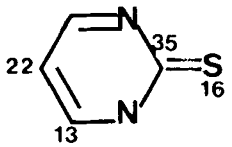
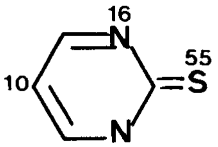
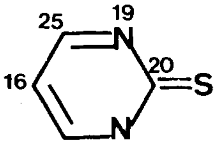
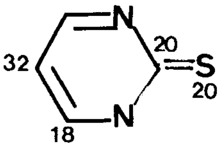
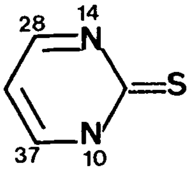
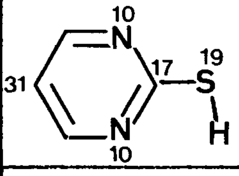
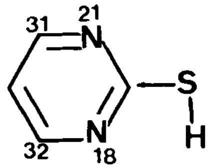
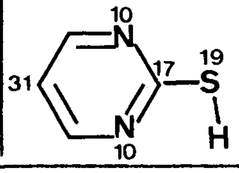
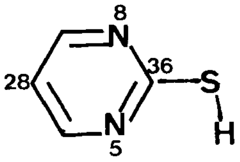
The parameterization of the CNDO/S method which was used is described in the literature (3, 4, 5).

In our calculations, the configuration interaction was limited to the 30 lower energy configurations. The d orbitals of the sulphur atom were taken into account, and they were treated as proposed by H.V. Schulte and A. Schweig (3). The parameters given by these authors for the sulphur atom were utilized.

RESULTS AND DISCUSSION

a) The results of the CNDO/S calculation carried out for the molecule in the NH form and the SH form are illustrated in Scheme 1.
The comparison of these results with the experimental data obtained in methylene chloride can be done with Table 1.

SCHEMA 1

Nature of the transition	Main configuration squared coefficient	Occupied molecular orbital	Virtual molecular orbital
$\pi \longrightarrow \pi^*$ 3.29 eV 376.0 nm	0,98		
$\pi \longrightarrow \pi^*$ 4.58 eV 270.5 nm	0,88		
$\pi \longrightarrow \pi^*$ 5.83 eV 212.5 nm	0,71		
$\pi \longrightarrow \pi^*$ 6.07 eV 204.1 nm	0.66		
$\pi \longrightarrow \pi^*$ 4.87 eV	0.71		
$\pi \longrightarrow \pi^*$ 5.72 eV	0,92		

The numbers adjoined to the figures of the molecules are the squared coefficients of the atomic orbitals involved in the corresponding molecular orbital multiplied by 10^2.

TABLE 1

Pyrimidine-2-thione		
Nature of the transition	Theoretical	Experimental CH_2Cl_2
$\pi \rightarrow \pi^*$ 3.29 eV	376.0 0.1581	384 3.366
$\pi \rightarrow \pi^*$ 4.58 eV	270.5 0.5669	293.5 4.364
$\pi \rightarrow \pi^*$ 5.83 eV	212.5 0.0999	235.8 4.436
$\pi \rightarrow \pi^*$ 6.07 eV	204.1 0.2739	

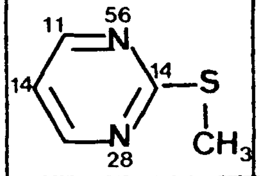
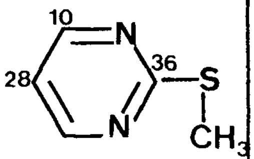
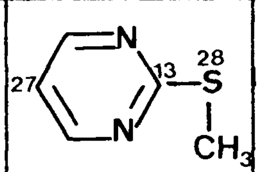
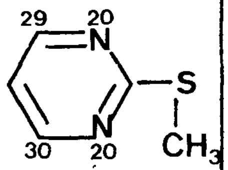
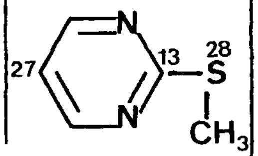
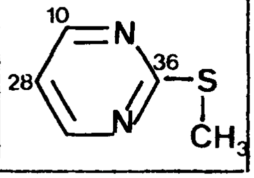
The first number corresponds to the value of the transition in n.m., the second value represents the oscillator strength for theoretical and log ε for experimental.

We conclude that the molecule is in the thione form. All the transitions observed for pyrimidine-2-thione are typified by a $\pi \rightarrow \pi^*$ transition. The first transition, calculated at 3.29eV (376 nm), is found at 384 nm in the presence of methylene chloride. It essentially involves the exocyclic sulphur in the occupied molecular orbital, whereas the whole

cycle is involved in the virtual molecular orbital.
The sulphur atom is therefore more charged in its ground state than in its excited state. Consequently it is more stabilized in protic solvents - this gives proof to the hypsochromic effect experimentally observed when ethanol is substituted for methylene chloride (1).
The second transition calculated at 4.58eV (270.5 nm) is found at 293.5 nm in the presence of methylene chloride.
Finally, the last $\pi \longrightarrow \pi^*$ transition calculated at 5.83eV (212.5 nm) corresponds to a charge transfer between the sulphur atom in its ground state and the entire cycle in its excited state.

b) The results of the CNDO/S calculation carried out for the 2-methylthiopyrimidine molecule are reported in Scheme 2. The comparison between calculated and experimental results is given in Table 2.
First of all, a $n \longrightarrow \pi^*$ type transition (4.43eV) can be observed, which appears experimentally as a shoulder. It characterizes the electron pairs of the nitrogen atom, and is found for many pyrimidine derivatives.
The following $\pi \longrightarrow \pi^*$ type transition is calculated at 4.80eV. This transition, as well as the last $\pi \longrightarrow \pi^*$ transition calculated at 5.57eV, characterizes the $S \text{——} Me$ radical.

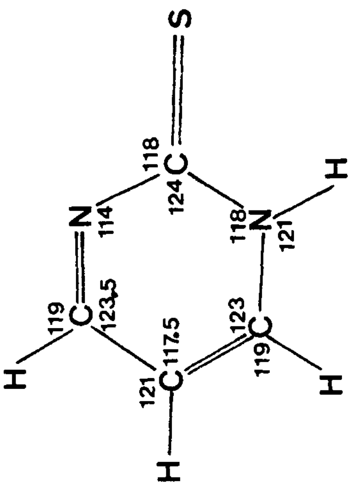
SCHEMA 2

Nature of the transition	Main configuration squared coefficient	Occupied molecular orbital	Virtual molecular orbital
$n \rightarrow \pi^*$ 4.43 eV	0,50		
$\pi \rightarrow \pi^*$ 4.80 eV	0,70		
$\pi \rightarrow \pi^*$ 5.57 eV	0.94		

The numbers adjoined to the figures of the molecules are the squared coefficients of the atomic orbitals involved in the corresponding molecular orbital multiplied by 10^2.

CONCLUSION

The characteristic transition of the thiocarbonyl group in pyrimidine-2-thione is of $\pi \rightarrow \pi^*$ type. For this transition, the charge of the exocyclic sulphur atom in the excited state is smaller than the charge of the same atom in the ground state. This finding is in accordance with the hypsochromic displacement observed when ethanol is substituted for methylene chloride.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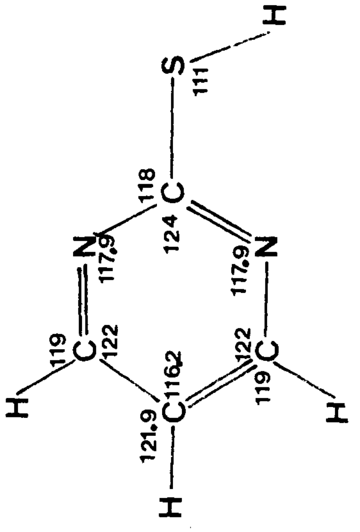
118
124
114
118
121
123,5
119
117,5
121
123
119
H
N
C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117,9
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116,2
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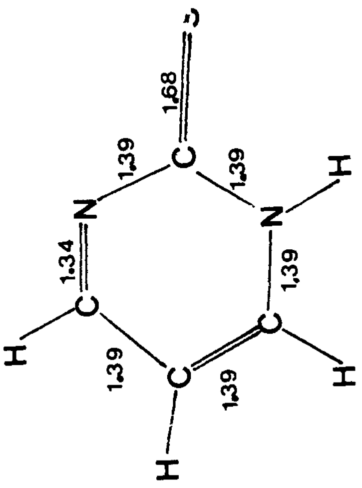
122
119
N
C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1,39
1,39
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1,39
H
N
C

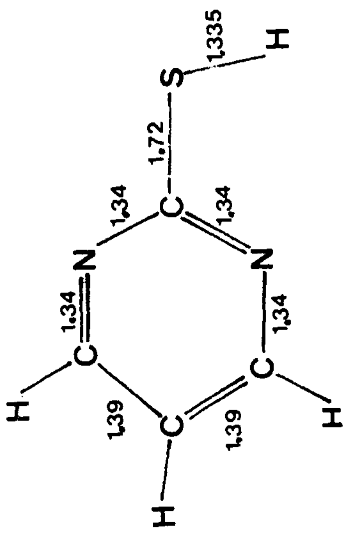
H
S
1,335
1,72
1,34
1,34
1,34
1,34
1,39
1,39
N
C

TABLE 2

2-methylthiopyrimidine		
Nature of the transition	Theoretical	Experimental EtOH
$n \rightarrow \pi^*$ 4.43 eV	279.3 0.0000	287 (e) 3.103
$\pi \rightarrow \pi^*$ 4.80 eV	257.8 0,0473	251 4,021
$\pi \rightarrow \pi^*$ 5.57 eV	222,4 0.4541	220 3.414

The first number corresponds to the value of the transition in n.m., the second value represents the oscillator strength for theoretical and log ε for experimental.

The CNDO/S calculation confirms the existence of the pyrimidine-2-thione molecule in the thione form in the solutions used for ultraviolet spectroscopy.

REFERENCES

1 - J. KISTER, D. BOUIN-ROUBAUD, L. BOUSCASSE and J. METZGER, Spectroscopy Letters, 13 (1), 1, (1980).

2 - D. BOUIN-ROUBAUD, Thesis, University of Aix-Marseille III, (1980).

3 - Y. W. SCHULTE and A. SCHWEIG, Theoret. Chim. Acta, 33, 19, (1974).

4 - J. Del. BENE and H. H. JAFFE, J. Chem. Phys., 48, 1807, (1968).

5 - M. RAJZMANN and P. FRANCOIS, Q.C.P.E. n° 382, (1979).

6 - L. E. LYONS and J. C. MACKIE, J. Chem. Soc., (1963), p. 3665.

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APPENDIX

Geometry of molecules.

The distances are given in angstroms, the angles in degrees.