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X-ray Structure Determination of Products resulting from Trapping of Hydroxynitrilium Ions

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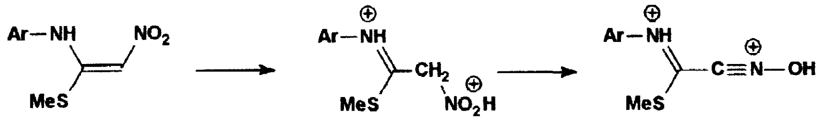
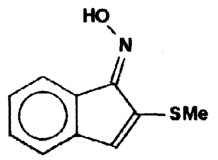
Abstract: X-ray diffraction study of bis(S-methyl) 1-*N*-phenylimino-2-hydroxyimidodithiooxalate **5a** and S-methyl-α-(hydroxyimino)-*N*-(4-fluorophenyl)phenylthioglyoxyimidate **5b** resulting from trapping hydroxynitrilium ions derived from 1-arylamino-1-methylthio-2-nitroethenes with MeSH or PhH shows that the thioimidate group is *E*-configured meanwhile the hydroxyimino groups possess the nucleophilic entering group and the OH in the *syn* configuration, in agreement with theoretical considerations.

INTRODUCTION

Arylaminonitroethene compounds are known for instance for their non-linear optical properties[1a] but mainly as useful synthons in organic chemistry in the field of heterocyclic synthesis because they are keen to undergo various cyclocondensation reactions.[1b,c] 1-Arylamino-1-methylthio-2-nitroethenes **1** can also undergo cyclization in superacids to afford compounds such as **2**, or react intermolecularly with various nucleophiles to form substituted oximes.[2,3] Reactions of 1-arylamino-1-methylthio-2-nitreoethenes **1** were studied by mean of ^{1}H and ^{13}C NMR at low temperature [3]. It was shown that **1** are firstly *C,O*-diprotonated to transient cations **3**, then transformed into conjugated hydroxynitrilium ions **4** that may react with methanethiol or benzene to afford **5a** or **5b** respectively. Compounds **5a,b**, which have their imine CN double bonds conjugated are prone to fast imine *Z/E* equilibrium in organic solvents.



1 **3** **4**



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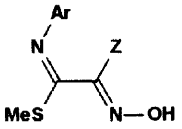

5a,b

a: Ar = phenyl Z = MeS
b: Ar = 4F-phenyl Z = phenyl

As a way to determine configurations of representative products, an X-ray diffraction study was undertaken on *S*-methyl *N*-arylthioimidate compounds **5a** and **5b**

RESULTS AND DISCUSSION

As previously described,[3] compound **5a** was prepared from a solution of 1-phenylamino-1-methylthio-2-nitroethene in triflic acid and quenching with MeSH, meanwhile **5b** was obtained from 1-(4'-fluorophen-1'-

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yl)amino-1-methylthio-2-nitroethene in triflic acid and trapping *in situ* with C_6H_6. Both products were crystallized from a mixture of CH_2Cl_2: petroleum ether.

Table 1: Details of Crystallographic Data Collections [4]

characteristics *	**5a**	**5b**
crystal color	yellow prisms	gold
chemical formula	$C_{10}H_{12}N_2OS_2$	$C_{15}H_{13}FN_2OS$
formula weight	240.34	288.34
crystal system	monoclinic	monoclinic
space group	$P\ 2_1/a$	C 2/c
a	12.941(7)	29.378(7)
b	6.986(1)	9.372(5)
c	13.671(3)	10.668(5)
α	90.0	90.0
β	109.32(5)	90.89(3)
γ	90.0	90.0
θ range for cell parameters	$1° \le \theta \le 25°$	$13° \le \theta \le 19°$
volume of unit cell	1166.3(8) $Å^3$	2937.(1) $Å^3$
Z	4	8
D_c ($g.cm^{-3}$)	1.34	1.30
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ (mm^{-1})	4.14	2.17
maximum value of *θ*	$2\theta_{max.} = 50°$	$2\theta_{max.} = 60°$
h	0 → 15	-34 → 26
k	-8 → 8	-13 → 11
l	-16 → 15	-12 → 12
residual **: R; R_w	0.032; 0.029	0.099; 0.119
no. of parameters **	176	183
Δρ: max.; min. ($eÅ^{-3}$)	0.30; -0.38	0.53;-0.62

* : a, b, c in Å and α, β, γ in °. ** **5a**: 1837 and **5b**: 1922 reflections such as $I \ge 3\sigma(I)$.

Bond lengths, valence and torsion angles.

Values of the main bond lengths, valence angles and torsion angles are reported in table 2 and 3:

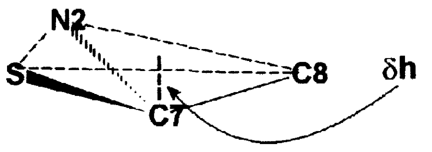
Table 2: Selected Bond Lengths (Å) and Angles (°) with esd's in Parentheses

5a		**5b**		**5a**		**5b**	
S(1)-C(9)	1.791(2)	S(1)-C(9)	1.796(6)	C(9)-S(1)-C(7)	140.07(8)	C(9)-S(1)-C(7)	102.5(2)
S(1)-C(7)	1.739(1)	S(1)-C(7)	1.749(3)	S(1)-C(7)-N(2)	124.2(1)	S(1)-C(7)-N(2)	122.6(3)
C(7)-N(2)	1.277(2)	C(7)-N(2)	1.274(4)	C(7)-N(2)-C(1)	118.9(1)	C(7)-N(2)-C(1)	118.2(3)
N(2)-C(1)	1.433(2)	N(2)-C(1)	1.425(4)	S(1)-C(7)-C(8)	110.4(1)	S(1)-C(7)-C(8)	112.5(2)
C(7)-C(8)	1.498(2)	C(7)-C(8)	1.493(5)	N(2)-C(7)-C(8)	125.3(1)	N(2)-C(7)-C(8)	124.7(3)
C(8)-N(1)	1.277(2)	C(8)-N(1)	1.282(4)	C(7)-C(8)-S(2)	120.6(1)	C(7)-C(8)-C(10)	117.8(3)
C(8)-S(2)	1.750(1)	C(8)-C(10)	1.483(5)	C(7)-C(8)-N(1)	116.9(1)	C(7)-C(8)-N(1)	115.3(3)
N(1)-O(1)	1.398(2)	N(1)-O(1)	1.386(4)	S(2)-C(8)-N(1)	122.5(1)	C(10)-C(8)-N(1)	126.9(3)
S(2)-C(10)	1.792(2)	C(4)-F	1.363	C(8)-S(2)-C(10)	102.48(8)		
				C(8)-N(1)-O(1)	110.6(1)	C(8)-N(1)-O(1)	114.1(3)
				N(1)-O(1)-H	106.0(13)	N(1)-O(1)-H	99.4(3)

Table 3: Selected Torsion Angles (°)

5a		**5b**	
C(9)-S(1)-C(7)-N(2)	-1.6	C(9)-S(1)-C(7)-N(2)	-4.2
S(1)-C(7)-N(2)-C(1)	176.4	S(1)-C(7)-N(2)-C(1)	176.1
C(7)-N(2)-C(1)-C(2)	124.4	C(7)-N(2)-C(1)-C(2)	-66.8
N(2)-C(7)-C(8)-N(1)	110.8	N(2)-C(7)-C(8)-N(1)	126.2
S(1)-C(7)-C(8)-S(2)	107.6	S(1)-C(7)-C(8)-C(10)	121.9
O(1)-N(1)-C(8)-S(2)	-1.3	O(1)-N(1)-C(8)-C(10)	1.0
N(1)-C(8)-S(2)-C(10)	164.5	N(1)-C(8)-C(10)-C(14)	-52.5
C(8)-N(1)-O(1)-H	169.3	C(8)-N(1)-O(1)-H	-158.7
C(8)-C(7)-N(2)-C(1)	-7.5	C(8)-C(7)-N(2)-C(1)	-8.3

The CN double bonds are in the range 1.274-1.282 Å, close from values for oximes; 1.281 Å or formaldoxime;[5] 1.276 Å but less than expected for usual thioimidates;[6] 1.302 Å. It is noteworthy that in **5a** both hydroxyimino and imino CN double bonds have the same bond length; 1.277 Å, probably because they have nearly the same surroundings. In **5a** and **5b**, both hydroxyimino and imino CN double bonds are not conjugated [7] because of the high N=C(7)-C(8)=N torsion angle value respectively of 110.8 and 126.2°(more than 50° from planarity). This lack of conjugation is probably the cause of the elongation of the CC single bond with lengths of respectively 1.493 and 1.498 Å, values that may be compared to those observed, for instance, in unconjugated acid esters;[6] 1.488 Å. This lack of conjugation probably causes a loss in π-electron delocalization energy, however, this effect is probably compensated by the fact that, in this conformation, the hydroxyimino groups and the S-methylthioimidate groups, separately, are nearly planar.



S-methyl thioimidate function

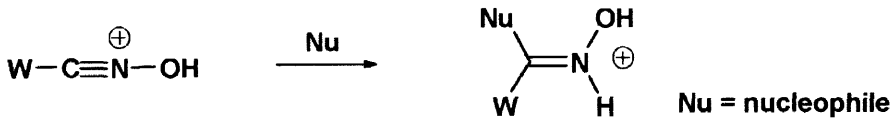
The S-methyl thioimidate functions are slightly pyramidal, with C(7) out of the plane at only δh = 0.026 Å in **5a** and 0.030 Å in **5b**. The hydroxyimino groups are planar: in **5a** the C(8) is only 0.002 Å out of the N(1)S(2)C(7) plane , as does the C(8) in **5b** which is only at 0.002 Å out of the N(1)C(10)C(7) plane .

The torsion angles made by the aromatic rings about the N(2)-C(1) bonds and the plane defined by C(7)=N(2)-C(1) of the thioimidate groups have the values of 55.6 and 66.8° in **5a** and in **5b** respectively. The higher value in **5b** accounts for the difference in steric hindrance between substituents bonded to the C(8) hydroxyimino carbon: the phenyl ring being bulkier than the MeS group.

In **5b** the mean plane of both aromatic rings are not parallel but make an angle of 37.4°.

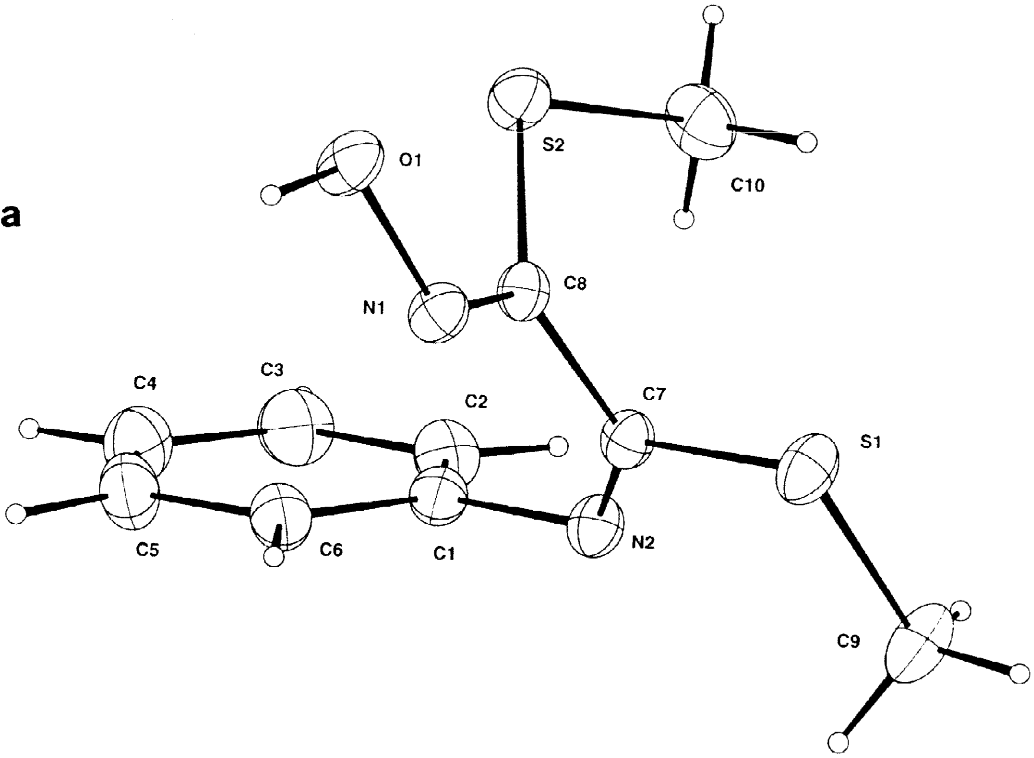
Hydroxyimino group.

Both **5a** and **5b** have hydroxyimino groups nearly planar with OH and MeS / Ph in the *syn* configuration as shown by the torsion angle O-N=C-Nu (with Nu the first atom in SMe or Ph) respectively of -1.3° and 1.0°. Such a configuration is expected for the kinetic product resulting from nucleophilic addition of methanethiol or benzene on the conjugated CN triple bond of hydroxynitrilium ion **3**.[8]



Apparently for both compounds, hydroxyimino group *Z/E* interconversion is very slow in these experimental conditions, and therefore the hydroxyimino configurations so observed are those of the kinetic products formed *in situ*, in agreement with the postulated mechanism of formation.

5a



5b

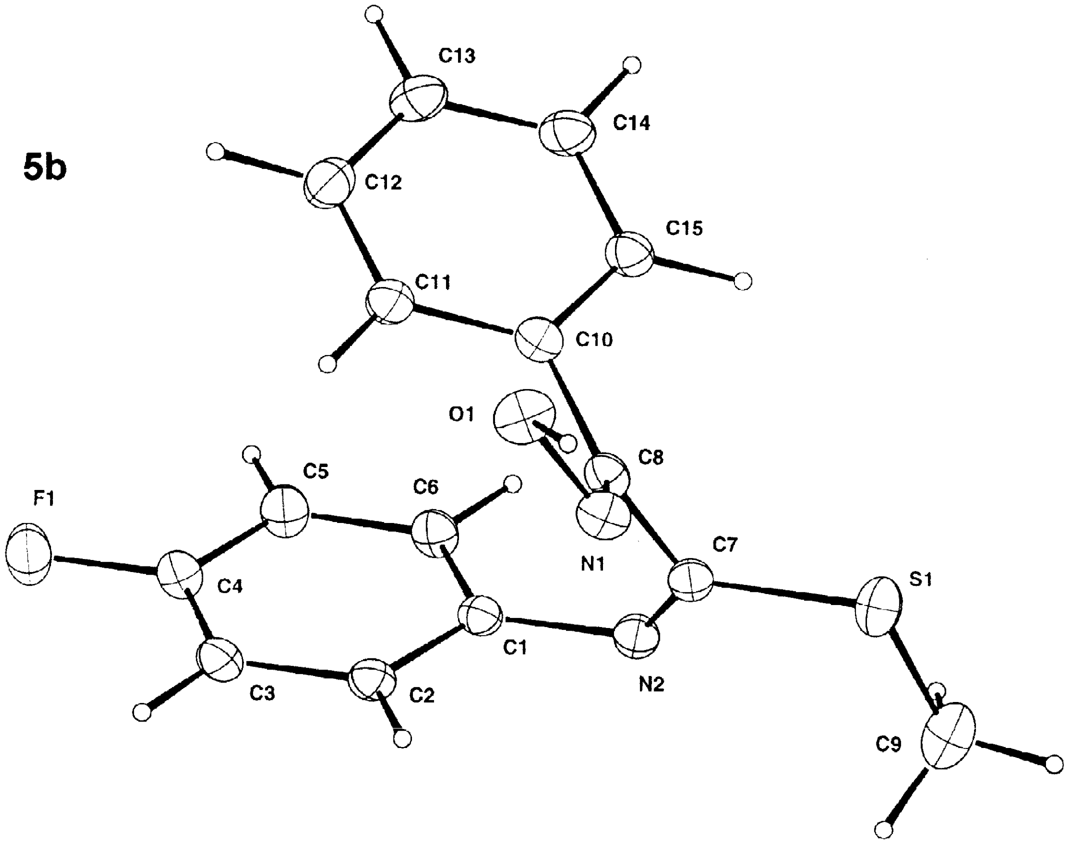


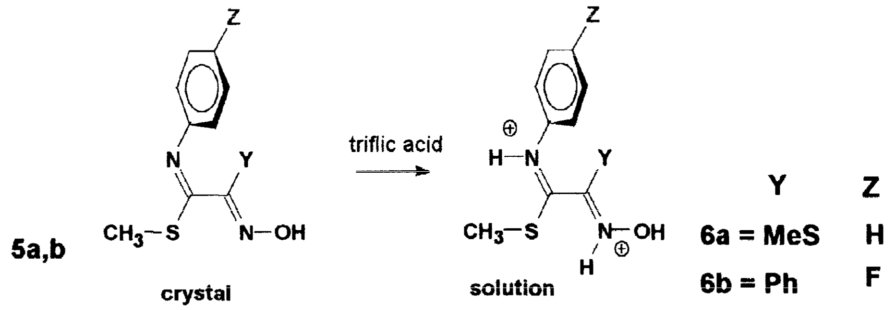
Figure 1: CAMERON drawing [11] of hydroxyimino derivatives **5a** and **5b**.

S-methyl thioimidate ester function.

X-ray crystal analysis shows that the *S*-methyl thioimidate ester function of **5a,b** are *E*-configured. However, in solution in organic solvents they undergo fast *E-Z* equilibrium as indicated from NMR spectra. In solution, the *E*-isomer is usually more stable than the *Z*-isomer, but the position of the equilibrium is mainly sensitive to the bulkiness of the substituent bonded to the central carbon and to a lesser extend, to the nature of the solvent.[9,10] Free activation energy to *E-Z* interconversion in organic solvents are close to 15 kcal.mol^{-1} (e.g. $\Delta G^{\pm}$ = 15.7 and 15.0 kcal.mol^{-1} in Y-C(SMe)=N-Ph with Y = $PhCH_2$ and Ph respectively in deuterated methanol [9b]) and probably lower in the present case. Addition of triflic acid causes *N*-protonation of the S-methyl thioimidate ester function that increases the activation barrier to rotation about the partial CN double bond, for which values higher than 20 kcal.mol^{-1} are reported (e.g. $\Delta G^{\pm}$ = 21.8 and 24.0 kcal.mol^{-1} in Y-C(SMe)=NH^+-Ph respectively with Y= Ph and *o*-Tol in trifluoroacetic acid [9c]). This high activation energy barrier explains why it is possible to observe a sole cation **6a** or **6b** by directly dissolving crystals of **5a** or **5b** in triflic acid [3] and hence, the configuration of the protonated S-methyl thioimidate ester function resulting from this dissolution is the same as the one in the crystal.

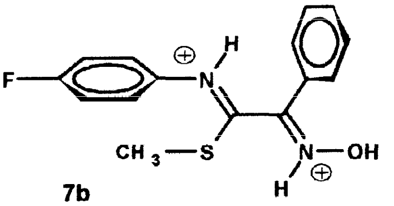
Application: configuration of their N,N-diprotonated forms.

As a consequence of all those observations, the configurations of previously described cations **6a,b** [3] can now be attributed (Scheme 1), as well as the configuration of the minor ion **7b**.



Scheme 1: *N,N*-diprotonation of **5a,b** in triflic acid.

For example, when **5b** is dissolved in an organic solvent such as $CDCl_3$, a fast *Z/E* imine isomerization occurs that may be "frozen" by addition of triflic acid in excess. Then, two protonated forms can be observed by NMR, the major one is **6b** and the minor one **7b** with a *Z*-protonated thioimidate group in which anisotropic effects of the phenyl rings cause deshielding of some aromatic protons and shielding of the MeS group: $\Delta\delta_H$= 0.52 ppm,[3] a value close to the $\Delta\delta_H$ = 0.53 ppm observed for Ph-C(SMe)=$\overset{+}{N}H$-Ph in trifluoroacetic acid.[9c]



7b

CONCLUSION

The present X-ray crystallographic analysis allowed us to determine the configuration of both products which was not possible before because of fast *Z/E*-imine interconversion in solution causing broadening of nmr signals. This study indicates that both compounds are *E*-configured at the level of the thioimidate group, the hydroxyimino group being configured in such a way that the OH and the MeS / Ph are in a *cis*-configuration, as expected from the kinetic product resulting from a nucleophilic addition on the CN triple bond of the precursor hydroxynitrilium ion. These results are in agreement with their previous mechanism of formation. Further studies are underway in this field and would be published soon.

EXPERIMENTAL

Crystal data for **5a** and **5b** were recorded at room temperature with a Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and an X-ray tube with a Mo anticathode (λ = 0.71069 Å). Two standard reflections were measured every four hours and an orienting control after each 400 reflections. A total of 4306 reflections were measured for **5a** and 4195 for **5b**. An empirical absorption correction was carried out and i) 2056 reflections merged, (R equivalent = 5.55 %), 1837 independent reflections such as $I \geq 3\sigma(I)$ were used in structural analyses of **5a** and ii) 2969 reflections merged, (R equivalent = 1.68 %) with 1922 independent reflections such as $I \geq 3\sigma(I)$ were used in structural analyses of **5b**. The structure was solved using direct methods [12] and refined using least square calculation.[13]

AKNOWLEDGEMENT

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