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CHEMISTRY OF NITROSOIMINES. IX.[1] ESCA STUDY OF 3-SUBSTITUTED 2-NITROSOIMINO-2,3-DIHYDROBENZOTHIAZOLES : MESOIONIC STRUCTURE

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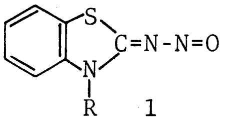
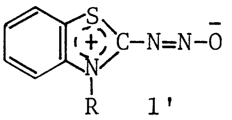
Core electron binding energies of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1**) and related compounds were measured by ESCA to show large contribution of mesoionic structures for **1** and this was also supported by observed chemical shifts (NMR) of 3-methyl groups of benzothiazolines.

Nitrosoimines ($R^1R^2C=N-N=O$) are thermally unstable and decompose into the corresponding carbonyl compounds and nitrogen even at low temperatures, unless they are stabilized by resonance and/or protected by bulky groups.[2] The stability of nitrosoimines contained in heterocycles has been attributed to the contribution of mesoionic structure (**1'**) as studied by UV.[3]

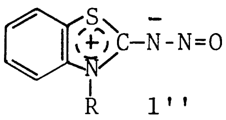
We report here more direct evidence for the contribution of mesoionic structures as studied by ESCA[4] and also supported by NMR.



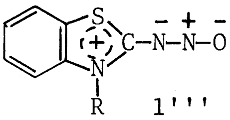
1



1'



1''



1'''

Core electron binding energies of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1a** and **1b**) and related compounds are shown in Table 1.

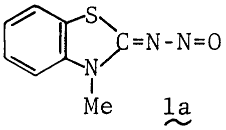
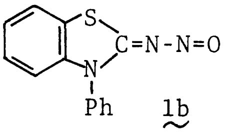
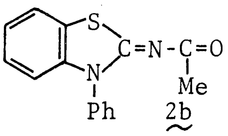
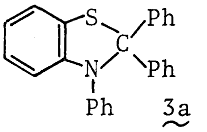
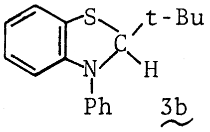
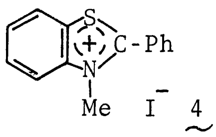
Observed binding energies (eV) of **2b** show two N 1s peaks due to two kinds of nitrogen atoms: nitrogen with lower binding energy (398.6) and that with higher binding energy (400.6). The former nitrogen (corresponding to the imino nitrogen) should be negatively charged and the latter (corresponding to the thiazoline nitrogen) should be positively charged, because the neutral nitrogen (3a and 3b) has the binding energy between the two and the thiazolium nitrogen (4) has higher binding energy than the two.

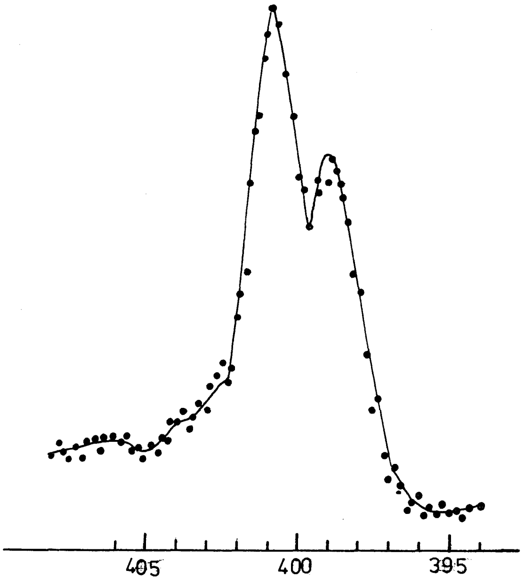
It is therefore concluded for the title compound (1) that the imino nitrogen [398.9 (1a), 398.8 (1b)] should be negatively charged and the thiazoline and the nitroso nitrogens [400.8 (1a), 400.8 (1b)] should be positively charged. This fact that the imino nitrogen in these conjugated systems (1 and 2) is really negatively charged is rather unexpected because the corresponding nitrogen of amides or nitrosamines should be positively charged.

The oxygen atom of 1 is considerably negatively charged (ca 0.2-0.3 charge unit) as supported by reported charge densities of oxygens of benzoquinone and its derivatives obtained from observed binding energies.5)

These facts are depicted as mesoionic structures (1'-1''').

Table 1 Core electron binding energies (eV) of benzothiazolines

Compounds	N 1s		O 1s	C 1s
 1a	398.9	400.8	531.4	284.4
	(1 : 2)*			
 1b	398.8	400.8	531.2	284.6
	(1 : 2)			
 2b	398.6	400.6	531.3	285.3
	(1 : 1)			
 3a	399.1			284.4
 3b	399.4			284.7
 4	401.7			285.2



Binding energy (eV)

Fig. 1 N 1s spectrum of 1a

* Values in parentheses in Table 1 show relative intensities.

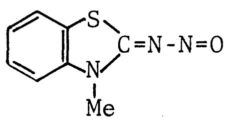
The binding energies can roughly be correlated with the units of charge obtained from the Pauling electronegativity relations.6) Thus a difference of 2.0 eV for the binding energies of two kinds of nitrogen atoms in **1** may well be thought to correspond to a charge difference of 0.40 charge unit.

A comparable value (2.4 eV = 0.46 unit charge) for the difference of unit charge of two nitrogens in 3-methyl-2-phenyl-1,3,4-thiadiazole-5-thiones, a betaine, has been reported.7)

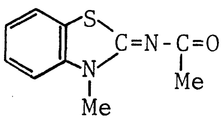
The above conclusion is supported by observed chemical shifts (NMR : δ from TMS in CDCl$_3$) of 3-methyl group of benzothiazolines and further insight for charge distribution of benzothiazolines can be obtained.

The values for **3**8) and **9**9) (δ 2.59-2.99) are for neutral nitrogens and quite constant values for **5**, **6**, **7** and **8**10) (δ 3.30-3.50) show large contribution of canonical structure shown as **1''**. The lowest values (δ 3.90 and 3.85) for **1a** and **2a** are reflection of further resonance contribution by nitroso and by the carbonyl11) groups as shown by **1'** and **1'''**.

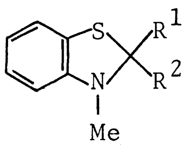
The compounds, **3**, **7**, **8** and **9**, were obtained by reaction of **1** with the corresponding Grignard reagents.12)



1a 3.90

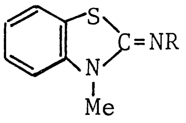


2a 3.85



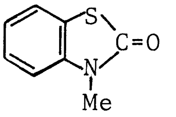
3c R^1=R^2=Ph 2.59

3d R^1=t-Bu, R^2=H 2.99

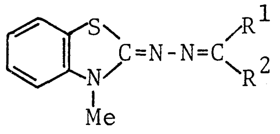


5a R=H 3.40

5b R=Me 3.41

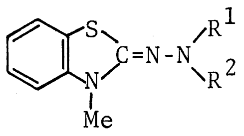


6 3.43



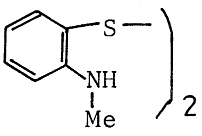
7a R^1=Ph, R^2=H 3.53

7b R^1=Me, R^2=Et 3.44



8a R^1=t-Bu, R^2=H 3.44

8b R^1=R^2=PhCH$_2$ 3.31



9 2.76, 2.69

References and Notes

1) For part VIII see: K. Akiba, M. Hisaoka, and N. Inamoto, Chem. Lett., 1974, 1267.

2) K. Akiba, S. Matsunami, C. Eguchi, and N. Inamoto, Bull. Chem. Soc. Japan, 47 935 (1974). C. J. Thoman, S. J., and I. M. Hunsberger, J. Org. Chem., 33, 2852 (1968).

3) K. Akiba, I. Fukawa, N. Nomura, and N. Inamoto, Bull. Chem. Soc. Japan, 45, 1867 (1972).

4) The spectra were measured on a McPherson ESCA 36 electron spectrometer. The Al-K$_{\alpha1,2}$ line (1486.6 eV) provided the activation energy. The instrument was adjusted so that the Au-4f$_{7/2}$ line fell at 84.0 eV. Accuracy ± 0.2 eV.

5) T. Ohta, M. Yamada, and H. Kuroda, Bull. Chem. Soc. Japan, 47, 1158 (1974).

6) G. J. Leigh, J. N. Murrell, W. Bremser, and G. G. Proctor, Chem. Commun., 1970, 1661.

7) M. Patsch and P. Thiele, Angew. Chem. Internat. Ed., 10, 569 (1971).

8) The corresponding chemical shifts of six compounds (**3**) lie between 2.59 and 2.99.

9) **9** shows two singlets, and each corresponds to 3H.

10) The corresponding chemical shifts of eight compounds (**8**) lie between 3.30 and 3.48.

11) Carbonyl absorption of **2a** (IR: $\nu_{C=O}$, 1605 cm^{-1}) lies at very low frequency due to strong contribution of mesoionic structure.

12) K. Akiba, T. Kawamura, M. Hisaoka, and N. Inamoto, Chem. Lett., 1973, 201 and unpublished results.

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