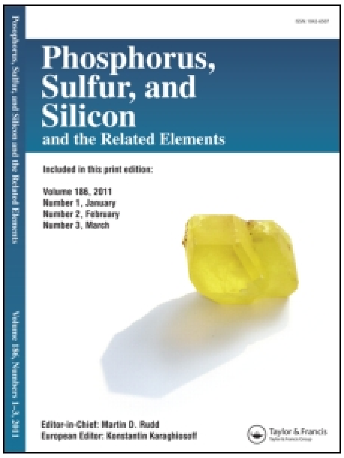

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ON THE GEOMETRICAL ISOMERISM AND HYDROGEN BONDING IN β-SULFINYLENAMINES

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ON THE GEOMETRICAL ISOMERISM AND HYDROGEN BONDING IN β-SULFINYLENAMINES

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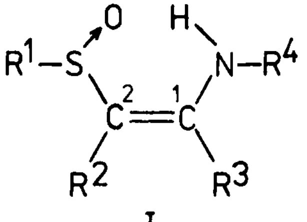
Abstract Geometrical isomerism in β-sulfinylenamines was probed by means of correlation between the NOEs and relevant internuclear distances. The intramolecular hydrogen bond is discussed on the basis of 17-O NMR.

INTRODUCTION

The problem of configurational assignments and the presence of intramolecular hydrogen bonding (HB) in secondary β-sulfinylenamines I has recently been raised in several laboratories[1-4].



I

Parent secondary β-sulfinylenamines, alkyl substituted or unsubstituted on a double bond, appear in solution as a single enamine isomer, accompanied by the imine form(s). Although in some contributions[5,6] the Z geometry for secondary β-sulfinylenamines was suggested, as the one being stabilized by intramolecular hydrogen bond, systematic NMR investigations show[1] rather low frequency position of the NH resonance (ca. 4 - 5 ppm) in only one enamine isomer in $CDCl_3$ solution. In order to get better insight into a problem we have undertaken the observation of the acceptor part of the HB using ^{17}O NMR which was recently shown as a very sensitive probe of the hydrogen bond[7,8]. We also present a method of choosing the proper geometry using the correlation of homonuclear NOEs, acquired by irradiaton of several sites in a molecule, and the internuclear distances[9], established from MM calculations[10] in both Z and E forms.

RESULTS AND DISCUSSION

The ^1H NMR spectrum of the compound Ia ($R_1=R_4=t$-Bu, $R_2=R_3=H$) shows, in $CDCl_3$ solution, two sets of signals, assigned to Z/E mixture (1:4) on the basis of vicinal coupling constants. Other β-sulfinylenamines, unsubstituted on a double bond, should be considered as the E isomers[1,5].

This criterion can not be used for the α or β-alkylsubstituted β-sulfinylenamines. Homonuclear NOE is a method of choice in this case. In principle, the multispin system can not be analysed as an assembly of independent two spin systems. The routine program for irradiation of several multiplets allows testing of each intramolecular relaxation pathway for each proton. The sum of NOEs, for a given proton, observed in various irradiation lists should show linear dependence on the sum of respective NOE growth rates ρ expressed by the known equation:[9]

$$\rho_{IS} = \gamma_I^2 \gamma_S^2 \hbar \tau_c r_{IS}^{-6}$$

where r_{IS} is the interproton distance. Short irradiation time, equal for all multiplets, should be used in order to secure the linear growth of NOE and to avoid the spin diffusion effects. In Table 1 the data for the compound Ib is shown. Minimum strain energy conformations for Z and E forms were calculated using MM approach and these conformations were the source of internuclear distances. The average distance were considered in the case of interaction of equivalent group of protons with CH or NH proton.

TABLE 1 NOEs and interproton distances in Ib (R^1=Et, R^2=Me, R^3=H, R^4=-CαHMePh)[a, b]

Nuclear interaction	NOE % Forward	Reverse	r_Z Å	r_E Å
$C_\alpha H \Leftrightarrow C^1H$	5.1^{*}	5.3^{**}	2.48	2.79
$C_\alpha H \Leftrightarrow C_\alpha CH_3$	0.8	8.5^{**}	2.70	2.70
$C^1H \Leftrightarrow NH$	0.9^{***}	1.9^{*}	2.95	2.96
$NH \Leftrightarrow C^2CH_3$	4.6	2.0^{***}	4.63	2.92
$C_\alpha CH_3 \Leftrightarrow NH$	5.0^{***}		2.99	2.92
$C_\alpha CH_3 \Leftrightarrow C^1H$	1.3^{*}		4.61	4.66

Observation site		NH	C^1H	CαH	Correlation coefficient
NOE_{tot}		7.9	8.3	13.8	
Σr^{-6}	Z	0.003018	0.00588	0.006848	$R_8 = 0.8$
	E	0.004704	0.003718	0.004724	$R_8 \doteq 0.4$

a) The measurements were performed in CDCl3 solution at -20°C using 1.6 s irradiation time.

b) NOEs included in NOE_{tot} for a given proton are marked uniformly.

These MM calculations also show that minimum energy conformations of the Z forms of the α- or β-alkylsubstituted β-sulfinyl enamines have the strain energy lower by ca. 1.4 - 4.5 kcal than minimum energy conformations of the E forms, even if the hydrogen bond energy is not considered in calculation procedure. On the other hand, the same calculations show, that in the series of unsubstituted β-sulfinylenamines the strain energy of the best conformation is lower in E isomer than in Z isomer. These differences are qualitatively in agreement with the experiment which shows, that in the α- or β-substituted β-sulfinylenamines only one isomer is present in solution and they point to the Z geometry.

The evidence for intramolecular hydrogen bond is the unambiguous proof of Z geometry in a studied system. In Table 2 preliminary ^{17}O NMR data is exemplified.

Low frequency shift of ca. 10 - 50 ppm has been observed on the formation of intramolecular HB in ketones[8] and in nitrogen oxides[7]. If one assumes that **Ic** and **Ie** are intermolecularly hydrogen bonded than 20 ppm low frequency shift when going to **Id** and **If**, respectively can be interpreted in terms of intramolecular hydrogen bond in the latter compounds. The γ - effect of the CH_3 group on the C^2 carbon atom in **Id** and **If** is only few ppm to lower frequencies. The steric compression shift, which may be expected in Z forms, results in high frequency shift of ^{17}O resonance[7].

TABLE 2 ^{17}O NMR chemical shifts in **I** (0.7 mole solution in CDCl3, 25°C, ppm vs. external H2O)

COMPOUND	R^1	R^2	R^3	R^4	$\delta(^{17}O)$
Ic	Me	H	H	Bn	50
Id	Me	Me	H	*t*-Bu	30
Ie	Ph	H	H	Bn	37
If	Ph	Me	H	*t*-Bu	16

In conclusion, both presented experiments are in agreement as regards the geometry of alkyl substituted β-sulfinylenamines and they find qualitative support in theoretical MM calculations.

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