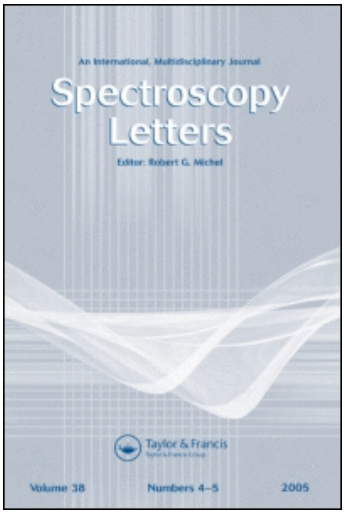

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Electronic Interactions in Heterocyclic Compounds: 2-Substituted Benzoxazoles

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ELECTRONIC INTERACTIONS IN HETEROCYCLIC COMPOUNDS: 2-SUBSTITUTED BENZOXAZOLES.

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ABSTRACT

The determination of a valence-bond model for the $\nu_{C=N}$ vibration in 2-substituted benzoxazoles is possible using a quantitative method,based on integrated infrared intensities.

By comparison with the parent compounds,2-substituted benzothiazoles,we are able to conclude that the electronic interactions in benzoxazoles may conduct to similar correlations than those already described for benzothiazoles.

INTRODUCTION

The attribution of the $\nu_{C=N}$ skeleton vibration in 2-substituted benzothiazoles has been already confirmed(1). It was then possible to definite a valence-bond model for resonance interactions in these compounds (2),through correlations with HAMMETT's σ constants(3).We intend here to compare the $\nu_{C=N}$ intensities of the two parent compounds.

EXPERIMENTAL

2-chlorobenzoxazole and 2-methylbenzoxazole are commercial compounds;2-diethylaminobenzoxazole and

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2-methoxybenzoxazole are prepared following known methods (4,5).

All compounds were recorded on a PE 225 spectrophotometer, between 1650 and 1400 cm^{-1}. The path length of NaCl cells used (150 microns) were determined exactly by the interference method (6). The absorption of the solvents (spectroscopic grade CCl_4 or $CHCl_3$) was compensed to have a regular base line in the studied spectral range. Concentrations are calculated to give an absorption with a maximum between 40 and 80 %.

Spectra are recorded twice at two concentrations, giving an integrated intensity which is the average of four integrations.

$A = c^{-1}.e^{-1}.\int a.d\nu$ (A in $l^{-1}.mole^{-1}.cm^{-2}$)

c= concentration ($mole.l^{-1}$)

e= path length (cm)

a= optical density relative to the base line

$d\nu$ = integration interval (cm^{-1})

A five scale expansion gives a good precision for the integration every cm^{-1}.

RESULTS AND DISCUSSION

The comparison with their sulfur homologous seems to be a good approach to the estimation of intramolecular interactions in benzoxazoles. It would have been possible to investigate the 2-substituted oxazoles, as we did for the couple thiazole/benzothiazole (1). However, if the valence bond model is the same, as we expect, it is more convenient, in a first approach, to use the "benzo" compounds.

We would have liked to use in our calculations the parameters for benzoxazole and 2-fluorobenzoxazole. But this was not possible for two reasons:

a) Benzoxazole gives band overlapping in the studied area;

b) 2-fluorobenzoxazole is too reactive and must be stored at -10°C as a petroleum ether solution (7).

Table I gives the spectroscopic data found for benzoxazoles and those already described for benzothiazoles (2), respectively designed as BO and BT.

Infrared measurements for substituted BT compounds

TABLE I: IR DATA FOR 2-SUBSTITUTED BO AND BT DERIVATIVES

	BO					
	$\nu_{C=N}$		ϵ_A		A_{BO}	$A_{BT}^{d)}$
	this work	litt.	this work	litt.		
CH_3 (a)	1578	id(c)	179	97	1480	1650
Cl (a)	1526	id(c)	789	806	2330	3050
OCH_3 (a)	1549	--	888	--	7980	8670
NEt_2 (b)	1512	--	447	--	13370	14200

a) Solvent CCl_4
b) Solvent $CHCl_3$
c) Reference 8
d) Reference 2

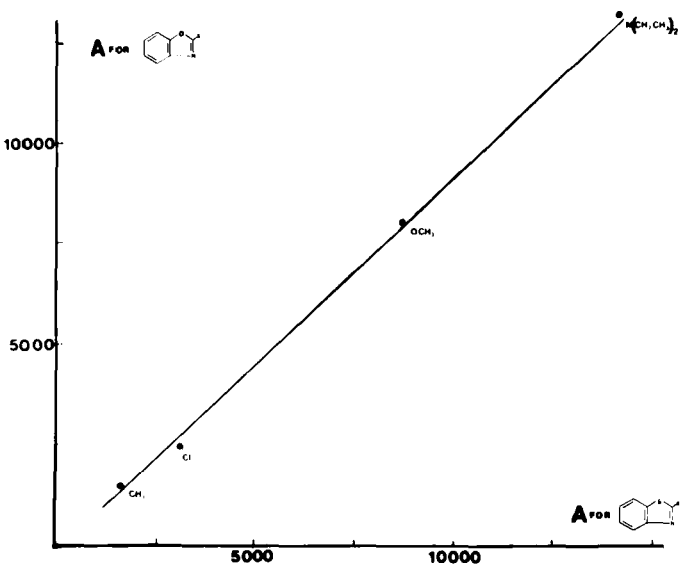

Fig. 1

Relation $A_{BO} = f(A_{BT})$

have confirmed (2) that the infrared intensity A is a function of the σ_R^o resonance parameter corresponding to the 2-substituent (9).

It can be seen from Fig.1 that there is also a linear correlation between A_{BO} and A_{BT}. Using a least square method it is possible to write :

$$A_{BO} = 0,96\ A_{BT} - 1,05 \quad (r = 0,999).$$

This relation was established for donor substituents, covering a large σ_R^o scale. These experimental results show that intramolecular interactions in 2-substituted benzoxazoles are similar to those in 2-substituted benzothiazoles. We are going to examine other benzoxazoles to determine a more general relation (10).

CONCLUSION

IR quantitative methods confirm to be a good tool for evaluation of intramolecular interactions in benzoheterocyclic systems.

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