Tetrahedron. Vol. 24, pp. 5569 to 5574. Pergamon Press 1968. Printed in Great Britain

ELECTRONIC ABSORPTION SPECTRA OF CONDENSED THIAZOLES AND OXAZOLES

A. GASCO, E. BARNI and G. DIMODICA
Istituto Chimico della Università di Torino, Italia

(*Received in the UK* 5 *March* 1968; *accepted for publication* 25 *March* 1968)

Abstract—The UV spectra of angular and linear naphthothiazoles and naphthoxazoles have been recorded. The linear correlation between the frequency of the ρ bands and the frontier orbital energies, calculated using simple HMO methods, are considered to afford evidence of the nature of the chromophore responsible for the absorption.

INTRODUCTION

FROM consideration of the UV spectra of benzothiazole and benzoxazole derivatives it was suggested[1] that, if a 2-alkyl substituent was present, the chromophore responsible for the absorption was the benzene ring which was weakly perturbed by conjugation of the lone-pair electrons of the X heteroatom in the azole ring. A similar conclusion was reached from a study of the UV spectrum of 2-methylbenzoselenazole.[2] The UV spectra of naphtho-X-azoles (X = S, O) have been recorded in order to investigate the generality of this hypothesis.

RESULTS AND DISCUSSION

The spectra of 2-methylnaphtho[1.2-d]thiazole (I), 2-methylnaphtho[2.1-d]thiazole (II), and 2-methylnaphtho[2.3-d]thiazole (III) are shown in Fig. 1 while the main spectral parameters are summarized in Table 1. There are appreciable differences between the spectra of the angular and linear isomers. The latter show a hyperchromic red shift of the α band (λ_{max} = 346 nm; log ε = 3·42) and a red shift of the

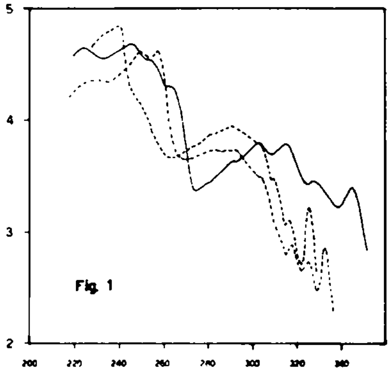

FIG. 1 Spectra of: – – – – 2-Methylnaphto[1.2-d]thiazole (I)
—·—·— 2-Methylnaphto[2.1-d]thiazole (II)
——— 2-Methylnaphto[2.3-d]thiazole (III)

TABLE 1

Compound		λ_{max}	log ε
2-Methylnaphto[1.2-d]thiazole	(I)	326	3·23
		318	3·11
		311	3·48
		292	3·95
		235	4·84
2-Methylnaphto[2.1-d]thiazole	(II)	333	2·86
		326	2·74
		318	2·89
		292	3·75
		288	3·75
		283	3·75
		257	4·62
		250	4·62
		230	4·36
2-Methylnaphto[2.3-d]thiazole	(III)	346	3·42
		329	3·50
		316	3·80
		304	3·80
		292	3·65
		263	4·31
		254	4·54
		246	4·68
		225	4·66
2-Methylbenzothiazole (a)	(VIII)	252	3·87
2-Methylnaphto[1.2-d]oxazole	(IV)	321	3·67
		315	3·44
		308	3·51
		301	3·36
		288	3·78
		284	3·79
		277	3·84
		222	4·78
2-Methylnaphto[2.1-d]oxazole	(V)	326	3·40
		318	3·12
		312	3·24
		305	3·02
		290	3·42
		280	3·67
		270	3·69
		261	3·62
		244	4·60
		237	4·71
		233	4·69
2-Methylnaphto[2.3-d]oxazole	(VI)	326	3·38
		300	3·95
		288	3·86
		235	4·75
2-Methylbenzoxazole (a)	(VII)	231	3·97

ρ band (329–292 nm). The spectra of the corresponding 2-methylnaphtho[1.2-d]-oxazole (IV), 2-methylnaphtho[2.1-d]oxazole (V) and 2-methylnaphtho[2.3-d]-oxazole (VI) are shown in Fig. 2 and the spectral parameters are also shown in Table 1. Again the linear isomers differ from the angular isomers in that the ρ band is again shifted towards the red with partial overlap of the α-band.*

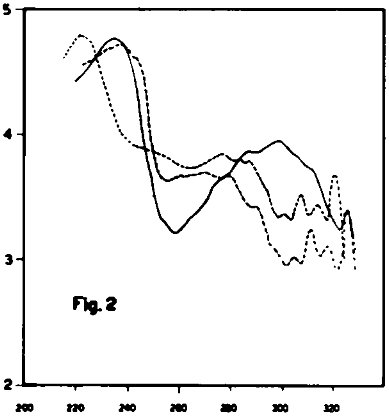

FIG. 2 Spectra of: – – – – 2-Methylnaphto[1.2-d]oxazole (IV)
–·–·–· 2-Methylnaphto[2.1-d]oxazole (V)
——— 2-Methylnaphto[2.3-d]oxazole (VI)

It is clear that the hypothesis discussed above[1,2] cannot be applied to these compounds for, if the absorption was due to the perturbed naphthalene ring, it would be expected to find shifts of the α and ρ bands similar to those found in mono-substituted naphthalenes.[4] However, in this instance the ρ bands are shifted less in the [2.1-d] isomer than in the [1.2-d] isomer and in contrast the α-bands of the [2.1-d] isomers are shifted more than those of the [1.2-d] isomers. An alternative suggestion to be considered is that the molecule as a whole is responsible for the absorption. In order to prove the validity of this hypothesis we have calculated, using a simple HMO method, the energy levels of naphthothiazoles and naphthoxazoles. In the case of the oxazole derivatives the parameters suggested by Streitwieser[5] were used for the calculations. The coulomb integrals for C atoms adjacent to the hetero-atoms were corrected to take account of the inductive effect and in particular, the Me group being treated as an heteroatom, a correction factor of $-0{\cdot}2$ was introduced. In the case of the thiazole derivatives α_s and β_{c-s} were assumed to have the values $\alpha_s = \alpha_c + \beta$, and $\beta_{c-s} = 0{\cdot}8\,\beta$.[6]

In Fig. 3 molecular diagrams are given for all the compounds we have examined. The frontier orbital energies are given in Figs 4 and 5. If the basic chromophoric group is that of the naphtho-X-azole it should be possible to correlate the energy difference between the 1 and 1′ orbitals with the wave number of the ρ bands; the plot of these values are shown in Figs 4 and 5.* It is of interest to note that the ρ band

---

* Spectra of 2-methylnaphthoxazoles in heptane were reported by Pushkina and Postovskii.[3]

† The choice of $\bar{\nu}$ values used in the calculations is somewhat arbitary because the fine structure of the ρ bands is not consistent in the various compounds. The values chosen correspond to the centre of the absorption region (Table 1).

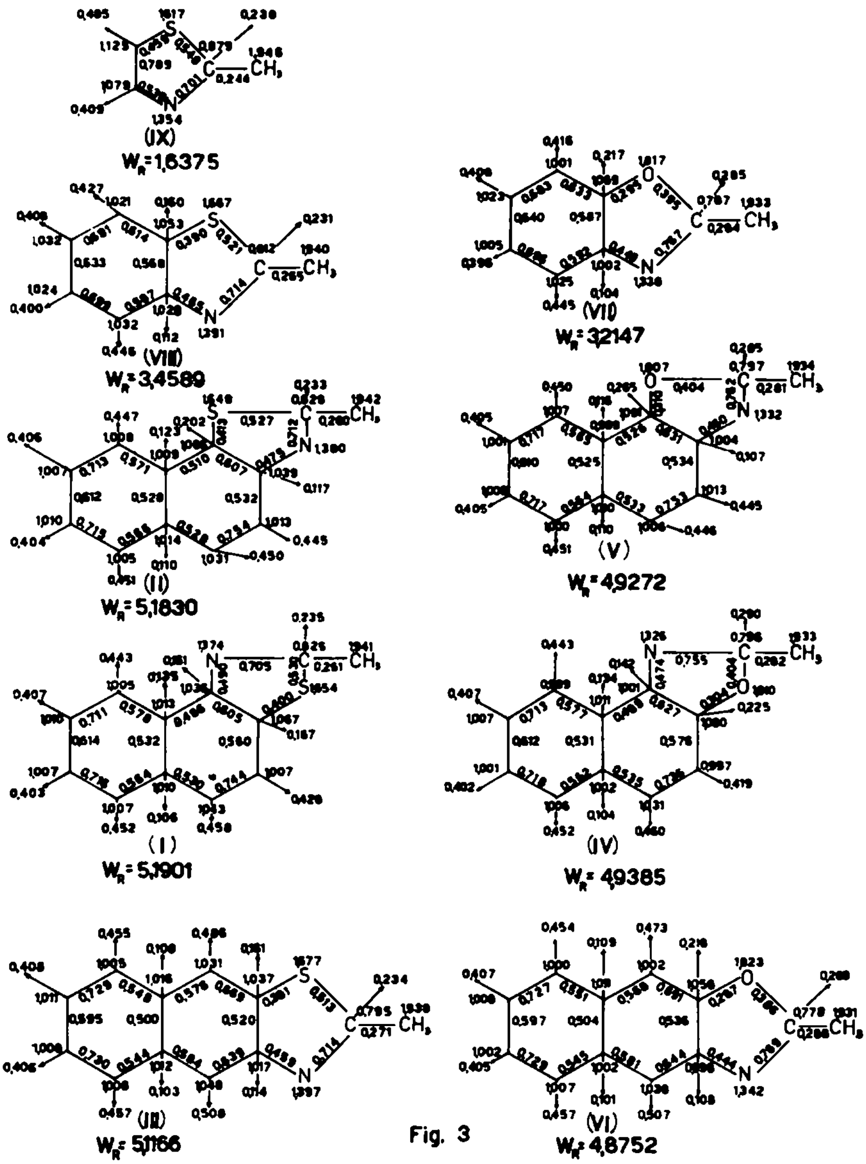

FIG. 3 Molecular diagrams of thiazole and oxazole derivatives. W_r = resonance energy.

of 2-methylbenzoxazole (VII), 2-methylbenzothiazole (VIII) and the band at 230 nm of 2-methylthiazole (IX),[7] which can be reasonably considered as a ρ-band, lie on the regression lines.

The results reported above support this alternative hypothesis suggested by us.

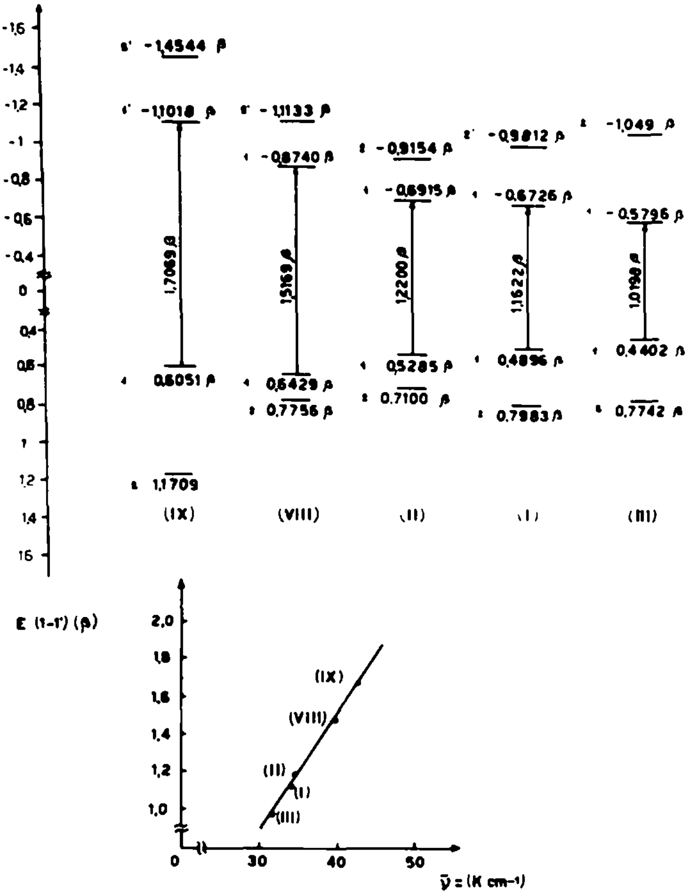

FIG. 4 Frontier orbital energies and plot of frontier orbital energies versus wave numbers of thiazolo derivatives.

EXPERIMENTAL

Materials. 2-Methylnaphto-X-azoles were prepared and purified according to literature data which are summarized in Table 2.

TABLE 2. PREPARATION OF 2-METHYLNAPHTO-X-AZOLES

Compound		Ref.
2-Methylnaphto[1.2-d]thiazole	(I)	*a*
2-Methylnaphto[2.1-d]thiazole	(II)	*b*
2-Methylnaphto[2.3-d]thiazole	(III)	*c*
2-Methylnaphto[1.2-d]oxazole	(IV)	*d*
2-Methylnaphto[2.1-d]oxazole	(V)	*d*
2-Methylnaphto[2.3-d]oxazole	(VI)	*e*

[a] P. Jacobson, *Ber. Dtsch. Chem. Ges.* **20**, 1895 (1887); [b] P. Jacobson, *Ibid.* **21**, 2624 (1888); [c] I. G. Farbenind. A.G.Ger. 642,379, Mar. 5 (1937); *Chem. Abstr.* **31**, 35058 (1937); [d] N. I. Fisher and F. M. Hamer, *J. Chem. Soc.* 962 (1934); [e] K. Fries, R. Walter and K. Schilling, *Liebigs Ann.* **516**, 248 (1935).

Dotted values were used in calculations of wave numbers. (a) Taken from Ref. 2.

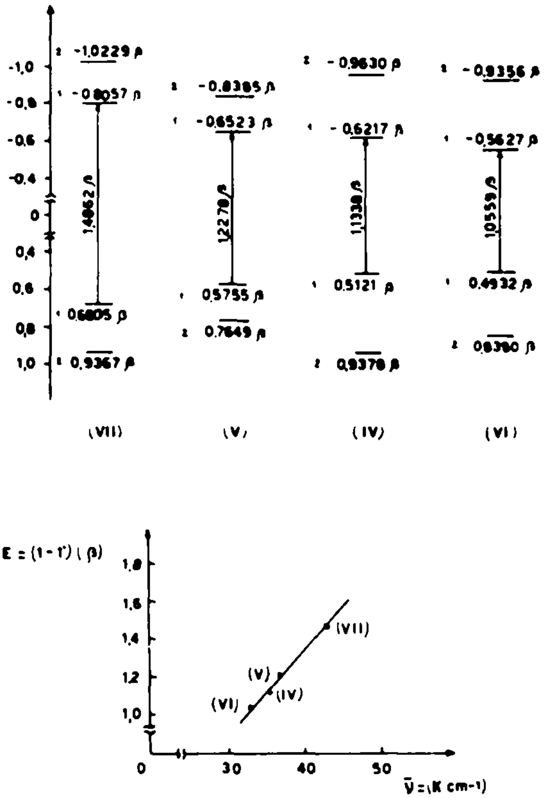

FIG. 5 Frontier orbital energies and plot of frontier orbital energies versus wave numbers of oxazolo derivatives.

Measurement of spectra. Spectra were recorded in 95% EtOH with a Bechman DU Spectrophotometer. *Calculations.* The calculations of molecular diagrams were performed on a IBM 360/44 computer.

REFERENCES

[1] R. Passerini and A. Cerniani, *J. Chem. Soc.* 2261 (1954).

[2] Y. Maroni-Barnaud, H. Wahl and P. Maroni, *Bull. Soc. Chim.* 1741 (1961).

[3] L. N. Pushkina and I. Ya. Postovskii, *Zh. Obsh. Khim.* 34, 424 (1964).

[4] A. Gasco, G. Di Modica and E. Barni, *Ann. Chim. Roma*, 58, 385 (1968).

[5] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists.* Wiley, New York (1961).

[6] R. Zahradnik, in A. R. Katritzky, *Advances in Heterocyclic Chemistry* Vol. 5. Academic Press, New York, London (1965).

[7] R. Kuhn and F. Drawert, *Liebigs Ann.* 590, 55 (1954).