THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME TETRAZOLE DERIVATIVES

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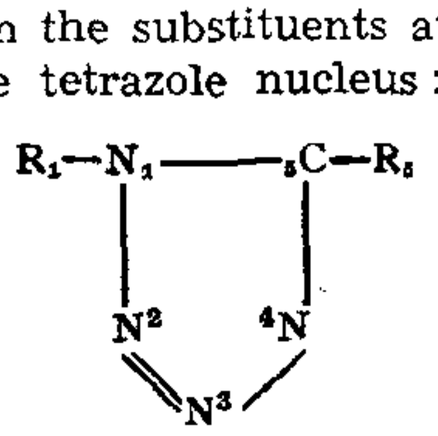
ALTHOUGH there have been extensive studies in the chemistry of the tetrazole system, the spectroscopic information on tetrazole derivatives is rather limited.[1] Schueler *et al.*[2] have investigated the ultraviolet absorption spectra of some tetrazole derivatives and correlated the spectra with the pharmocological action of the compounds. Elpern and Nachod[3] have studied the ultraviolet spectra of substituted 5-aryl tetrazoles with the substituents in different positions. The spectra of the hydrochlorides and methiodides of the basic disubstituted tetrazoles have also been reported by Elpern.[4] Lieber and co-workers[5,6] have studied the ultraviolet absorption spectra of 1, 3-disubstituted-5-iminotetrazoles, 1, 4-disubstituted-iminotetrazoles and related compounds and also 5-nitroaminotetrazole and its salts. In this communication, the ultraviolet absorption spectra of fifteen tetrazole derivatives are reported and discussed in terms of the resonance conjugation brought about between the substituents at 1 and 5 positions and the tetrazole nucleus:



(I)

Most of the compounds used in the present study were prepared by Lieber and co-workers during their earlier investigations.[7,8] These compounds were further purified before use. All absorption spectra were recorded in 95% ethanol using a Cary recording spectrophotometer and also a Beckman, model DU spectrophotometer. The wavelengths (λ_{max}) in mμ and the molar extinction coefficients (ϵ_{max}) corresponding to the absorption maxima are listed in Table I.

Tetrazole itself does not exhibit any absorption band in the near ultraviolet region[2] and consequently there will be absorption in Type I compounds only if R_1 and R_5 have strong resonance interaction with the tetrazole nucleus. From the results in Table I it can be seen that while there is no absorption when R_5 is a saturated hydrocarbon substituent or a halogen, a rather intense band is observed at 218 mμ when R_5 is an amino group. When the hydrogens in this amino group are substituted by saturated hydrocarbon substituents as in compound 4 [I, $R_1 = H$, $R_5 = N(C_2H_5)_2$], an appreciable bathochromic shift of the 218 mμ band is observed; however, the intensity of the band remains the same. This is in accordance with the earlier observation[5] that the introduction of a methyl group into the 5-amino position of either 1- or 2-methyl-5-aminotetrazole effects a bathochromic shift in the absorption maximum. When the substituent on the 5-amino group is a strongly resonating group as in compounds 7 (I, $R_1 = H$, $R_5 = NHC_6H_5$) and 9 [I, $R_1 = H$, $R_5 = NH(4\text{-}CH_3O_6H_4)$], in addition to a large bathochromic shift, a strong hyperchromic effect is noticed. It is interesting to find that 5-phenylaminotetrazole (compound 7) exhibits an absorption band at a λ_{max} greater than that of 5-phenyltetrazole (compound 5). These observations are explained by the proposal that the tetrazole ring is electronegative and withdraws

TABLE I

Ultraviolet absorption spectra of some tetrazole derivatives (I)

Compound No.	R_1	R_5	λ_{max}	$\epsilon_{max} \times 10^{-3}$
1	H	C_2H_5*	..	..
2	H	Br†	..	..
3	H	NH_2‡	218	3·42
4	H	$N(C_2H_5)_2$	234	3·42
5	H	C_6H_5	240	15·70
6	C_6H_5	NH_2	225	6·21
7	H	NHC_6H_5	249·5	17·51
8	$4\text{-}CH_3C_6H_4$	NH_2	229	8·08
9	H	$NH(4\text{-}CH_3C_6H_4)$	250	16·69
10	$4\text{-}ClC_6H_4$	NH_2	227	10·40
11	$3\text{-}ClC_6H_4$	NH_2	242·5	5·91
12	$4\text{-}OHC_6H_4$	NH_2	234	11·17
13	$4\text{-}OCH_3C_6H_4$	NH_2	234	13·47
14	$4\text{-}NH_2C_6H_4$	NH_2	256	14·60
15	$4\text{-}NO_2C_6H_4$	NH_2	264	8·88

* Even a concentration of $2{\cdot}22 \times 10^{-2}$ moles per litre did not result in U.V. absorption. † Even a concentration of $2{\cdot}61 \times 10^{-3}$ moles per litre did not result in U.V. absorption. ‡ Monohydrate (Fairmount Chemical).

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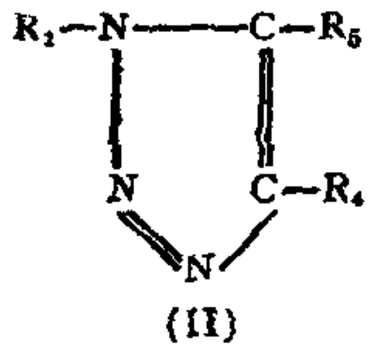
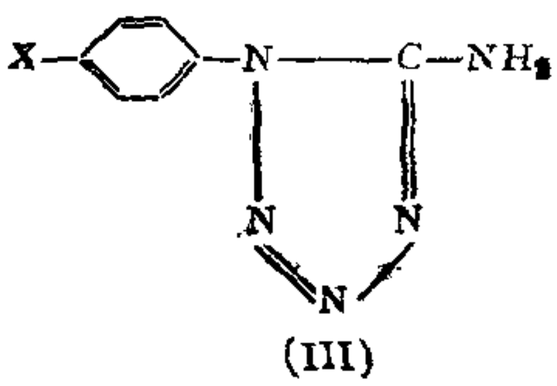
electrons from the 5-amino group in substituted 5-aminotetrazoles.[9] From the spectra of the isomeric compounds 6 (I, $R_1 = C_6H_5$, $R_5 = NH_2$) and 7 (I, $R_1 = H$, $R_5 = NHC_6H_5$) as well as 8 (I, $R_1 = 4\text{-}CH_3C_6H_4$, $R_5 = NH_2$) and 9 [I, $R_1 = H$, $R_5 = NH(4\text{-}CH_3C_6H_4)$], we see that there is an increase in the λ_{max} and ϵ_{max} of the absorption band when the resonating group is shifted from position-1 to position-5. Similar observations have been made in the case of the isomeric substituted 5-amino-1, 2, 3-triazoles[10] (II):



(II)

However, in substituted 5-amino-1, 2, 3-triazoles, in addition to the substituents at 1- and 5-positions, the substituent in position-4 also influences the ultraviolet absorption characteristics. In general it appears that in tetrazole derivatives, I, there is a greater bathochromic effect when R_5 is a resonating group than R_1. Schueler *et al.*[2] have drawn a similar conclusion from their results.

The 1-substituted phenyl-5-aminotetrazoles can be regarded as substituted benzenes:



(III)

The intensity and the position of the absorption bands of the compounds of Type III depend markedly on the nature of the substituent, X, on the phenyl group. A strongly interacting group like the nitro group as in compound 15 (I, $R_1 = 4\text{-}NO_2C_6H_4$, $R_5 = NH_2$) shifts the absorption maximum to a very large extent. When the substituents are electron-donating groups, the λ_{max} of Type III compounds increases approximately in proportion to the increase in the electron-donating power of the substituent, X. This proportionality indicates that the 1-(5-aminotetrazoyl) group is an electron-withdrawing group capable of strong resonance interaction.[11]

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LADY TATA MEMORIAL TRUST—SCHOLARSHIPS AND GRANTS FOR 1957-58

THE Trustees of the Lady Tata Memorial Trust announce on the death anniversary of Lady Meherbai Dorabji Tata, 18th June 1957, the awards of scholarships and grants for the year 1957-58.

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