LETTERS TO THE EDITOR

UV SPECTRA AND STRUCTURES OF COMPLEXES OF AZOLES WITH TRINITROPHENOL AND TRINITROANISOLE

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We have observed the appearance of a new band with a maximum at 400-420 nm and an inflection at 390 nm in the electronic absorption spectra during the reaction of a number of azoles (L) of varying basicity [imidazole (I), benzimidazole (II), 3,5-dimethylpyrazole (III), 1,3,5-trimethylpyrazole (IV), triazole (V), benzotriazole (VI), 1,2-naphthotriazole (VII), benzothiazole (VIII), and 3,5-dimethylisoxazole (IX)] with trinitrophenol (HA) in dioxane. The inflection at 390 nm is related to the trinitrophenoxide anion (A^-), as confirmed by a study of HA in alkaline alcohol and aqueous solutions.

The appearance of a band at 400-420 nm, in analogy with the data in [1], is associated with the formation of complexes due to an intermolecular hydrogen bond of the $L\cdots H-A$ type (H complexes) rather than with complexing of the $\pi-\pi$ type. The latter should have been accompanied by the appearance of low-intensity absorption bands at considerably higher wavelengths [2].

The compositions of the H complexes (1 : 1) and their stability constants (K_{st} in liters per mole) were determined by spectrophotometry: for I 7700, II 3000, III 230, IV 250, V 15, VIII 1.25, and IX < 1. The K_{st} values for the complexes with I and II are in agreement with the data in [3] regarding their high degree of ionic character. A small bathochromic shift of the absorption bands of the H complexes is observed as the pK_a values of the azoles decrease. Aromatic annelation of the low-basicity azoles apparently leads to simultaneous complexing involving the p and π system of the donor. This is accompanied by an appreciable bathochromic shift of the indicated band (for example, in the case of V-VII).

The spectra of the complexes of the azoles with symmetrical trinitroanisole (CH_3A) are identical to the spectra of picric acid complexes, whereas the spectral characteristics of the two free acceptors differ substantially. In addition, the same trend of the dependence of the stability constants on the basicities is observed for the trinitroanisole complexes as for the picrates of the azole series: for I 1000, II 600, IV 10, V 1, and IX < 1.

With allowance for the material set forth above and the results of a study of the reaction of CH_3A with pyridine [4], we propose the possibility of transfer of a methyl group from trinitroanisole to the pyridine nitrogen atom of the zole ring.

LITERATURE CITED

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