HETEROCYCLIC NITRO COMPOUNDS

VIII.* UV SPECTRA OF NITRO DERIVATIVES OF 1,2,4-TRIAZOLE

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The UV spectra of a number of 3(5)-nitro-1,2,4-triazoles at 220-350 nm were studied. A dependence of the position of the K band in the spectra of 3-nitro-5-R-triazoles on the nature of the substituent (R) is shown, and transfer of the effect of direct polar conjugation through the triazole ring was detected. Correlation dependences between the frequency and $\sigma_n^+(\sigma_n^+ - \sigma^0)$ constants were found in the series of 1-methyl-3-nitro-5-R-triazoles.

The UV spectra of 1,2,4-triazoles have received comparatively little study. According to the data in [2], absorption is observed at 186.2 nm in the UV spectrum of unsubstituted 1,2,4-triazole, and absorption bands are absent in the long-wavelength region. The introduction of substituents which are capable of conjugation with the triazole ring (phenyl and acetyl) induces a bathochromic shift with a simultaneous increase in the absorption intensity [2-4].

The introduction of a nitro group into the 1,2,4-triazole molecule causes a bathochromic shift of the absorption band of the triazole ring at 215-230 nm (log ε 3.8-4.0) and the appearance of a new absorption band at 250-340 nm (log ε 3.6-3.9), which is apparently due to conjugation of the nitro group with the triazole ring (K band) [5, 6]. In contrast to the long-wave maximum, the short-wave maximum has little sensitivity to the nature of the substituent and to ionization of the triazole ring [6].

In this paper we examine the effect of substituents on the position of the long-wave absorption band of neutral nitrotriazole molecules.

First of all, we note that the introduction of both electron-donating and electron-accepting substituents results in a bathochromic shift of the absorption maximum as compared with unsubstituted 3-nitrotriazole (see, for example, compounds 1, 2, 6, and 7 in Table 1).

The position of the nitro group also affects λ_{max}; thus, in the spectra of 1-methyl-3-nitro-5-substituted triazoles (compounds 4, 15, 24, and 25) the absorption maximum is shifted by 12-16 nm to the short-wave region in comparison with the spectra of the isomeric 1-methyl-3-substituted-5-nitrotriazoles (compounds 3 and 10-12). The position of the absorption maximum in the series of 1-methyl-3-nitro-5-R-1,2,4-triazoles (compounds 4, 14, and 27) is considerably more sensitive to the effect of the electron-donating substituents than to the effect of electron-accepting substituents.

In our opinion, the reason for this difference is the compatibility of the effect of electron-donating and electron-accepting groups when they are simultaneously present in the ring and the coincidence of the polarization created by them with the direction of polarization of the ring itself. This compatibility is destroyed in compounds with two electron-accepting groups. A similar picture was observed in the benzene series [7].

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* See [1] for communication VII.

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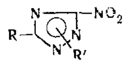
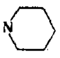
TABLE 1. Absorption Maxima in the UV Spectra of 3(5)-Nitro-1,2,4-triazoles



Compound	R	R′	λ_{max}, nm	lg ε
1	H	H	230	3,73
2	CH_3	H	258	3,61
3	H	2-CH_3	270	3,66
4	H	1-CH_3	255	3,74
5	H	4-CH_3	260	3,75
6	NO_2	H	255	3,79
7	COOH	H	250	3,62
8	COOH	2-CH_3	265	3,68
9	COO^-	2-CH_3	270	3,68
10	$COOCH_3$	2-CH_3	262	3,63
11	CH_3	2-CH_3	279	3,67
12	Cl	2-CH_3	277	3,62
13	C_6H_5	2-CH_3	320	3,54
14	NO_2	1-CH_3	250*	3,88
15	CH_3	1-CH_3	262,5	3,70
16	NH_2	1-CH_3	330	3,48
17	$NHCH_3$	1-CH_3	345	3,45
18	$N(CH_3)_2$	1-CH_3	348	3,32
19	$N(C_2H_5)_2$	1-CH_3	352	3,33
20		1-CH_3	335	3,30
21	CH_3O	1-CH_3	288	3,64
22	C_2H_5O	1-CH_3	290	3,57
23	C_6H_5O	1-CH_3	280	3,27
24	$COOCH_3$	1-CH_3	250*	3,77
25	Cl	1-CH_3	262,5	3,67
26	Br	1-CH_3	265	3,64
27	N_3	1-CH_3	290	3,63

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* Shoulder.

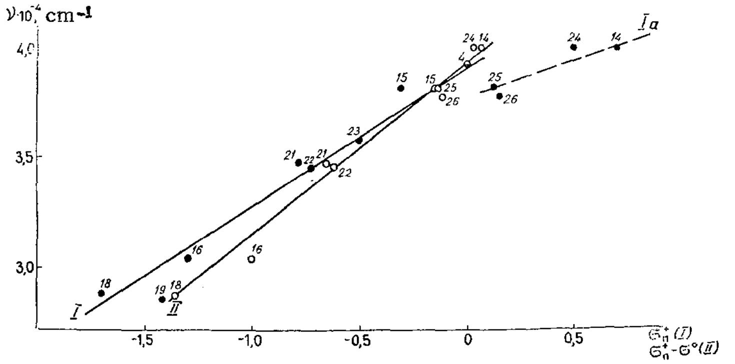

Fig. 1. Dependence between the absorption frequencies and the substituent constants in 1-methyl-3-nitro-5-R-triazoles: I and Ia) σ_n^+; II) ($\sigma_n^+ - \sigma^0$) (The numbering of the points corresponds to that in Table 1.)

The magnitudes of the wave numbers for the series satisfactorily correlates with the σ_n^+ constants of electron-donating substituents (Fig. 1, Line I):

$$\nu = 6970\sigma_n^+ + 39558 \ (r = 0.986).$$

Electron-accepting substituents are grouped about another line (Ia).

If one constructs the dependence between the frequency and the $\sigma_n^+ - \sigma^0$ difference (which characterizes a purely resonance effect of a substituent [8]), electron-donating and electron-accepting substituents fall on the same line (line II):

$$\nu = 8110(\sigma_n^+ - \sigma^0) + 39345 \ (r = 0.992).$$

The correlation dependences found indicate the major role of the C-effects and the possibility of direct polar conjugation through the triazole ring.

In contrast to 1-methyl-3-nitro-5-substituted triazoles, the dependence between the position of the absorption maximum and the character of the substituent is not so clearly expressed in the 1-methyl-5-nitro-3-substituted triazole series (compounds 3, 8, and 13). However, even here one can note that compounds with +C substituents (compounds 11-13) have maxima which are shifted to the longer-wave region as compared with other members of the series. The small number of examples does not make it possible to draw more definite conclusions.

EXPERIMENTAL

All of the compounds studied in this investigation were obtained via methods described in [1, 9-13] and were additionally crystallized. The measurements of ethanol solutions were made with an SF-4A spectrophotometer. The concentrations used were ~ 10^{-4} M, and the layer thickness was 1 cm.

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