ELECTRONIC ABSORPTION SPECTRA OF 3-CHLORO- AND 3-AMINO-1,2,4-TRIAZOLE DERIVATIVES

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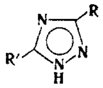
The manifestation of acid–base interactions in the electronic absorption spectra of 32 1,2,4-triazole derivatives was studied. Ionization of the heteroring does not have a substantial effect on the energies of the electron transitions of 3-chloro-5-substituted 1,2,4-triazoles but causes changes in the extinctions of the absorption bands of 3-amino-5-substituted triazoles.

The electronic absorption spectra of 1,2,4-triazole have been investigated [1], and the effects of substituents in the spectra of its nitro and amino derivatives have been discussed [2-4].

We have obtained the electronic absorption spectra of 3-chloro- and 3-amino-1,2,4-triazole derivatives (Table 1) in order to accumulate data on the effect of substituents on the character of the electronic transitions and on the dependence of the spectra on the acidity of the medium.



I–XXXII

I–XVII R=Cl; XVIII–XXXII R=NH$_2$; I R′=H; II R′=CH$_3$; III R′=C$_2$H$_5$; IV R′=*n*-C$_3$H$_7$; V R′=*i*-C$_3$H$_7$; VI R′=Br; VII R′=Cl; VIII R′=COOCH$_3$; IX R′=CONH$_2$; X R′=C$_6$H$_5$; XI R′=*m*-CH$_3$C$_6$H$_4$; XII R′=*p*-CH$_3$C$_6$H$_4$; XIII R′=*o*-BrC$_6$H$_4$; XIV R′=*o*-ClC$_6$H$_4$; XV R′=*o*-NO$_2$C$_6$H$_4$; XVI R′=*m*-NO$_2$C$_6$H$_4$; XVII R′=*p*-NO$_2$C$_6$H$_4$; XVIII R′=H; XIX R′=CH$_3$; XX R′=C$_2$H$_5$; XXI R′=*n*-C$_3$H$_7$; XXII R′=*i*-C$_3$H$_7$; XXIII R′=NH$_2$; XXIV R′=COOCH$_3$; XXV R′=CONH$_2$; XXVI R′=C$_6$H$_5$; XXVII R′=*m*-CH$_3$C$_6$H$_4$; XXVIII R′=*p*-CH$_3$C$_6$H$_4$; XXIX R′=*o*-BrC$_6$H$_4$; XXX R′=*o*-NO$_2$C$_6$H$_4$; XXXI R′=*m*-NO$_2$C$_6$H$_4$; XXXII R′=*p*-NO$_2$C$_6$H$_4$

The UV spectra of 3-chloro-1,2,4-triazole (I) in water and ethanol have an absorption maximum at 197 nm, which is shifted only slightly in acidic and alkaline media. The introduction of electron-donor and electron-acceptor substituents in the 5 position of the heteroring (II–VII), like ionization of these compounds, gives rise to an increase in the absorption coefficient of this band without changing its position. In the case of carbomethoxy or carbamido derivatives VIII and IX, in addition to a short-wave maximum, a long-wave band appears at 220–230 nm; in the case of IX in aqueous KOH one observes a 20 nm bathochromic shift for this band.

5-Aryl derivatives of 3-chloro-1,2,4-triazole (X–XVII) are characterized by a band at 200 nm with an extinction coefficient of 20–25 · 10^3 and long-wave absorption at 230–300 nm, the position of which depends on the substituent in the phenyl ring (Table 1). Ionization of 3-chloro-5-aryl-1,2,4-triazoles leads to a bathochromic shift of the long-wave band. Interactions associated with the addition of a proton or splitting out of a proton do not have a substantial effect on the character of the spectra of these derivatives. The certain bathochromic shift of the long-wave band observed in the case of 3-chloro-5-carbamido- and 5-nitroaryl-1,2,4-triazoles is evidently explained by ionization of the amino and nitro groups and by a change in the energies of the electron transitions associated with these groups.

As compared with triazole I, one observes a hyperchromic change in the principal band ($\lambda_{max}^{H_2O}$ 203 nm, ε^{H_2O} 5100) for 3-amino-1,2,4-triazole (XVIII) in water. It was shown for 3-amino-1,2,4-triazole and its

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TABLE 1. Electronic Absorption Spectra of 3,5-Disubstituted 1,2,4-Triazoles

Compound	λ_{max} (ε)		
	In C_2H_5OH	In 0,1 M HCl	In 0,1 M KOH
I	197 (2540)	200 (1470)	203 (1960)
II	197 (3050)	198 (2600)	205 (2570)
III	198 (3140)	197 (3790)	205 (2700)
IV	197 (4460)	197 (3940)	204 (2860)
V	198 (3920)	197 (3790)	204 (3050)
VI	197 (4250)	199 (4060)	205 (3340)
VII	201 (3520)	201 (3500)	206 (2900)
VIII	199 (5940)	198 (6230)	208 (4280)
	233 (5300)	227 (4960)	230 (5590)
IX	200 (6480)	204*	207 (7270)
	222 (7260)	220*	240 (7480)
X	200 (23070)	201 (7460)	205 (16290)
	209 sh		
	214 sh		
	251 (16960)	248 (5541)	256 (14940)
	262 sh	261 sh	264 sh
	275 sh		
XI	202 (21930)	203*	205 (18180)
	211 sh		
	216 sh		
	249 sh		
	255 (18780)	254*	258 (17110)
	265 sh		268 sh
	278 sh		279 sh
XII	202 (24620)	205*	207 (18530)
	210 sh		
	216 sh		
	249 sh		
	255 (20910)	254*	258 (17200)
	265 sh		
	278 sh	278 sh	
XIII	206 (21820)		204 (16680)
	245 (6960)		210 (15950)
			245 (5780)
XIV	202 (22410)	201*	204 (17390)
	252 (14710)	249*	257 (12580)
	262 sh		
XV	199 (22680)	197*	204 (18990)
	217 sh	218*	
	259 sh		241 (11030)
			295 sh
XVI	199 (21030)		203 (12920)
	218 sh		
	248 (20400)		259 (19160)
XVII	199 (21030)		203 (14790)
	219 (10280)		226 (7980)
	296 (15820)		328 (12800)
XVIII	207 (6060)	200 (6960)	207 (3610)
XIX	204 (6010)	202 (9440)	208 (3880)
XX	204 (6380)	202 (8950)	206 (4900)
XXI	204 (6620)	202 (9660)	207 (4800)
XXII	203 (6860)	201 (9920)	206 (4790)
XXIII	196 sh		
	208 (6320)	207 (7400)	209 (4940)
XXIV	200*	199 (10770)	205 (4900)
	252*	247 (5380)	263 (5180)
XXV	196 (15850)†	200 (11250)	205 (7300)
	202 sh		
	247 (2350)	242 (4850)	265 (5630)
XXVI	198 (43180)	197 (31000)	202 (17430)
	220 sh	205 sh	221 (8990)
	259 (12880)	251 (12650)	274 (10350)
XXVII	201 (37940)	201 (30440)	203 (20450)
	226 sh		226 sh
	262 (9090)	253 (11420)	274 (10040)
XXVIII	200 (36750)	199 (30190)	201 (23890)
	223 sh	207 sh	223 sh
	260 (10060)	256 (15780)	273 (10690)
XXIX	200 (43240)	201 (29590)	204 (18900)
	202 sh		
	224 sh	224 sh	224 sh
	269 sh	244 (6610)	262 (4100)
XXX	198 (32920)	201 (23240)	204 (17070)
	210 sh	220 sh	216 sh
	247 sh	247 sh	254 (7790)
XXXI	205*	203*	208 (13950)
	216*		226 sh
	261*	254*	273 (16690)
XXXII	196*	199*	
	214*	224*	216 sh
	233*		238 (6570)
	267*	301*	364 (9420)

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* Not completely soluble.

†Solutions in H_2O.

derivative [4] that they exist in the amino form in any medium. On the basis of data on the pK_a values of 3-amino-1,2,4-triazole derivatives, it has been assumed that the center of basicity in them is the heteroring nitrogen atom rather than the amino group [5].

The λ_{max} values of the bands in the 200-nm region of the spectra of the cations and anions of aminotriazoles with nonaromatic substituents in the 5 position (XVIII-XXIII) remain unchanged as compared with the spectra of neutral molecules, and the extinction coefficients increase in aqueous HCl and decrease in aqueous KOH. The long-wave bands of triazoles XXIV and XXV experience a bathochromic shift in alkaline media.

We note the appearance of bands at 370 (ε 5.8) and 435 nm (ε 4.5) in the spectrum of an alkaline solution of 3,5-diamino-1,2,4-triazole XXIII; the explanation for this is difficult.

Three bands with maxima at 198, 220, and 259 nm are observed in the electronic spectrum of 3-amino-5-aryl-1,2,4-triazole XXVI. In acidic solutions the long-wave band undergoes a hypsochromic shift, the band at 220 nm vanishes, and the extinction of the short-wave band decreases from 43,000 to 31,000 units. In alkali the extinction of the band at 200 nm decreases to 17,000 units, and the longest-wave band is shifted bathochromically. Similar effects are noted in the spectra of triazoles XXVII, XXVIII, and XXXI. The long-wave band of triazole XXXII is shifted bathochromically in both acidic and alkaline media, and this may constitute evidence for the participation of the nitro groups in an acid–base interaction.

The decrease in the extinction coefficient of the short-wave π-π^* band in the spectra of 5-aryl-substituted triazoles in aqueous HCl and KOH solutions is evidently associated with disruption of the conjugation between the benzene and heterocyclic rings as a result of ionization of the latter.

EXPERIMENTAL

The electronic absorption spectra were obtained with a Specord UV-vis Spectrophotometer. The synthesis of the 1,2,4-triazoles was described in [6-8].

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THERMOYLYSIS OF 1-PHENYL-5-ALKYLSULFONYLTETRAZOLE IN THE PRESENCE OF ARYLHYDRAZINES. AN INSTANCE OF MIGRATION OF AN ALKYLSULFONYL GROUP IN A 1,3-DIPOLE

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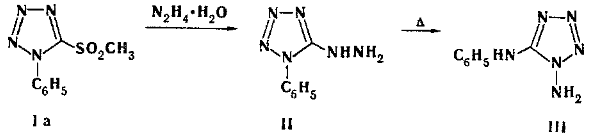
When 1-phenyl-5-alkylsulfonyltetrazoles are heated with arylhydrazines, the heteroring is cleaved to give nitrogen and 1-arylamino-2-phenyl-3-alkylsulfonylguanidine. According to the proposed scheme, the intermediate product of nucleophilic addition of the arylhydrazine to the tetrazole decomposes to give nitrogen and a 1,3-dipole, which is stabilized by migration of an alkylsulfonyl group.

It has previously been shown that the product of replacement of the methylsulfonyl group of 1-phenyl-5-methylsulfonyltetrazole (Ia) by a hydrazino group on heating (100-130°C) is recyclized to the isomeric 1-amino-5-anilinotetrazole (III) [1]:



It seemed of interest to ascertain the scope of this transformation for the reaction of sulfone Ia with other nucleophilic agents, particularly arylhydrazines. It was found that the reaction with phenylhydrazine commences only at 170° and proceeds vigorously at 180-190° with nitrogen evolution. A reaction product with empirical formula $C_{14}H_{16}N_4O_2S$ was isolated in 30% yield from the reaction mixture. The IR spectrum of crystals of the product contain two high-intensity bands at 1253 and 1112 cm^{-1}, which are characteristic for the SO_2 group in sulfones [2]; there are similar bands in the spectrum of starting sulfone Ia (1312 and 1160 cm^{-1}). Absorption bands of stretching and deformation vibrations of NH groups are observed in the IR spec-

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