## STRUCTURES AND REACTIVITIES OF NITROGEN-CONTAINING DERIVATIVES OF CARBONYL COMPOUNDS XXXIII.\* UV SPECTRA AND STRUCTURES OF 4-BENZYLIDENEAMINO-1,2,4-TRIAZOLES

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A number of products of the condensation of aminotriazole with substituted benzaldehydes were synthesized. Their UV spectra in ethanol and concentrated sulfuric acid are presented. The change in the UV spectra on passing from one solvent to another is explained by the change in the conjugation of the N-N bond. The basicities of the nitrogen atoms were compared by the Pariser-Parr-Pople method.

In this paper we have studied the structures of the products of the condensation of aminotriazole with substituted benzaldehydes by means of electronic spectral and quantum-chemical methods.

The conformation of 4-benzylideneamino-1,2,4-triazoles at the N-N bond is caused by steric interactions and the competitive effect of two forms of conjugation  $-\pi - \pi$  (A) and  $\pi - p$  (B). A change in one of the competitive components can affect the conformation of a molecule and its spectrum.

Data on the absorption of 4-benzylideneamino-1,2,4-triazoles (I-XIII) in ethanol and concentrated sulfuric acid are presented in Table 1. In ethanol there are two quite intense bands: a long-wave band at 273-359 nm and a short-wave band at 214-244 nm.

The long-wave band is determined to a considerable degree by the transfer of an electron from the upper filled molecular orbital to a lower vacant molecular orbital. As seen in Table 2, in planar case A this transition is accompanied by transfer of electron charge from the benzene ring to the azomethine bond



Fig. 1. UV spectra: 1) benzylideneaminotriazole in ethanol; 2) benzylideneaminotriazole in conc.  $H_2SO_4$ ; 3)  $\alpha$ -methylbenzylideneaminotriazole in ethanol.

\*See [1] for communication XXXII.

and from the triazole ring to the same bond. On rotation of the triazole ring its participation in this transition decreases, and one can judge the degree of coplanarity of the molecule from the position of the maximum of the longwave band. We note that even in the case of planar conformation A, the energy of conjugation of the triazole ring and the azomethine bond is insignificant, since the order of the N-N bond is extremely low, as seen from our calculated molecular diagram.

The benzylideneaminotriazole molecule can arbitrarily be considered to be the combination of two chromophore systems:  $K_b$ , which is the conjugated system of the benzene ring with substituent R and the CH=N group, and  $K_t$ , which is the system of the triazole ring and the nitrogen of the azomethine bond [2].

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			Amax, nM	(ۥ10-4)	
Comp.	ĸ	N N C	H		¢cH−
		ethanol	conc. H <sub>2</sub> SO <sub>4</sub>	ethanol	conc. H <sub>2</sub> SO <sub>4</sub>
Ι	Н	214(0,65); 278(1,01)	295(1,95)	215(3,75); 278(2,15)	220(0,92); 295(2,03)
II	p-Cl	218(1,23); 285(2,51)	218(0,55); 320(2,05)	215(1,99); 283(3,83)	235(0,37); 320(3,59)
III	<i>m</i> -Cl	215(1,72); 274(1,86)	295(1,69)	215(3,71); 284(2,59)	295(1,44)
N	<i>p</i> -Br	219(1,26); 286(2,67)	225(0,47); 330(1,23)	220(1,45); 287(3,80)	$230(2,13); \ 330(6,08)$
>	p-NO <sub>2</sub>	297(1,99)	287(1,71)	220(1,62); 284(1,35)	$220(1,25); \ 280(2,50)$
١٨	m-NO <sub>2</sub>	262 (2,65)	255(1,95)	220(2,16); 258(2,18)	250(2,04)
ΝI	$p-N(CH_3)_2$	244(1,25); 359(4,09)	258(0,95); 275(0,85)	255(1,00); 375(4,78)	260(1,82); 275(1,82)
VIII	<i>p</i> -CH (CH <sub>3</sub> ) <sub>2</sub>	219(1,29); 287(2,26)	220(2,29); 330(2,51)	220(2,14); 290(2,17)	325(2,04)
IX	<i>p</i> -OCH <sub>3</sub>	227(1,16); 307(2,35)	226(2,82); 308(3,89)	225(1,70); 320(2,35)	235(0,67); 364(2,87)
×	HO-d	229(1,08); 310(2,00)	229(0,51); 334(2,29)	220(1,72); 318(2,33)	226(0,49); 344(2,29)
IX	HO- <i>o</i>	215(1,32); 278(1,51)	280(1,56); 390(0,46)	220(1,65); 281(1,45)	295(1,78); 400(0,32)
IIX	HO-m	215(1,47); 280(1,98)	225(0,52); 295(1,44)	220(7,76); 259(1,14)	302(1,49)
XIII	$p-N(CH_3)_{3I}$	273(1,95)	255(1,17); 275(0,89)		

TABLE 1. UV Spectra

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TABLE 2. Energy Levels and Populations of the Fragments of the 4-Benzylideneamino-1,2,4-triazole Molecule

	Energy, eV.	$\sum_{m} c^{2}_{im}$ values for fragments			
Orbital		N = N = N - N = N = N = N = N = N = N =	—N=C—	-	
Upper vacant Lower occupied	2,634 10,194	0,106 0,271	0,550 0,245	0,344 0,484	

TABLE 3. Analysis of the Components of the Energy of Protonation ( $\Delta \Delta E = \Delta E_1 - \Delta E_0$ ) of the 4-Benzylideneamino-1,2,4-triazole Molecule

		V		AAE - 17		
Variant	A	В	С	D	F	AAE. ev
I	-0,957	1,068	0,495	0,520	-1,492	-0,377
II	-2,780	1,311	0,964	0,470	1,207	1,172
III	-0,954	0,734	0,531	-0,261	0,747	1,320

TABLE 4. Characteristics of 4-Benzylideneamino-1,2,4-triazoles

		Provinie el formaula	N,	%	Viold 0	Methiodide	
Comp.•	comp.* Mp, °C Empirical for		found	calc.	11eiu, %	mpt	
I II IV V VI VII VIII IX X XII XIII	171 202 176 215 230 218 194 133 143 239 207 231	$\begin{array}{c} C_9H_8N_4\\ C_9H_7N_4Cl\\ C_9H_7N_4Cl\\ C_9H_7N_4Br\\ C_9H_7N_5O_2\\ C_9H_7N_5O_2\\ C_1H_{15}N_5\\ C_{12}H_{14}N_4\\ C_{10}H_{10}N_4O\\ C_9H_8N_4O\\ C_9H$	32,5 26,9 21,8 32,1 32,6 26,6 27,7 29,8 29,7 29,6 18 3	32,5 27,1 27,1 21,8 32,2 32,5 26,1 27,7 29,8 29,8 29,8 29,8 29,8	93 89 79 87 89 87 92 70 81 76 71 84 64	180 195 202 211 185 190 194 160 207 194 177 197	
		0121111.15	10,0	,0	· · ·		

\*Compounds I, III, VIII, IX, X, XI, XII, and XIII were recrystallized from ethanol; II, IV, VI, and VII were recrystallized from propanol; and V was recrystallized from acetic acid.

† All of the methiodides were recrystallized from water.



The short-wave band owes its origin to the aminotriazole chromophore ( $K_t$ ), since it is known that triazole compounds do not absorb above 214 nm, and in systems with conjugation the absorption maximum undergoes a bathochromic shift (4-phenyl-1,2,4-triazole absorbs at 224 nm [3]). The long-wave intense band should be assigned to the absorption of the  $K_b$  chromophore as a consequence of its great similarity to the band of benzylideneaniline ( $\lambda_{max}$  226 nm,  $\varepsilon$  17,000 [4]).

The introduction of substituents into the benzene ring in each case induces a definite shift of the  $K_b$  and  $K_t$  bands. When a para nitro group is introduced, the general character of the spectrum is retained, but the  $K_b$  band is shifted ( $\lambda_{max}$  297 nm,  $\epsilon$  19,950). When a p-N(CH<sub>3</sub>)<sub>2</sub> group is introduced, the spectrum changes substantially. The band ascribed to the  $K_b$  system undergoes a pronounced bathochromic shift



 $(\lambda_{\max} 359 \text{ nm})$ , and its intensity increases appreciably ( $\epsilon 40,930$ ). The band is typical for a  $\pi \rightarrow \pi^*$  transition, and it can be assumed that it is associated with an electron shift along the entire almost coplanar molecule. The high intensity of the K<sub>b</sub> band is apparently associated with the same direction of the electron shifts of the quasi-autonomous K<sub>b</sub> and K<sub>t</sub> systems (D).



Since the system of VII is syn-polarized, the bathochromic effect here is observed to a greater extent than in I [2].

The bathochromic shift of the K<sub>t</sub> band is a maximum in the case of the  $p-N(CH_3)_2$  group ( $\lambda_{max} 244$  nm,  $\epsilon$  12,500). The shift of this band can be explained only by assuming that  $\pi - \pi$  conjugation is realized at the N-N bond in these compounds, during which the system is not completely planar, which is apparent from an examination of the spectra of the conjugate acids.

A bathchromic shift of the  $K_b$  band relative to the spectrum in ethanol is observed in the spectra of the conjugate acids (Table 1). As a consequence of protonation of the unshared pair of electrons of the imino  $N_6$  atom, one of the conjugation competitors vanishes, and the molecule tends to take on a planar structure of the A type [4, 5].

An example of a compound in which only conformation B with complete absence of  $\pi - \pi$  conjugation is realized as a consequence of steric hindrance is  $\alpha$ -methylbenzylideneaminotriazole, which is structurally close to a tetrasubstituted hydrazone in which the unshared pair of the nitrogen atom is completely removed from conjugation [6]. The K<sub>b</sub> band of this compound ( $\lambda_{max}$  253 nm,  $\varepsilon$  10,330, see Fig. 1) practically coincides with the analogous band of benzylidenemethylamine ( $\lambda_{max}$  245 nm,  $\varepsilon$  16,000).

Becker's investigations [7] and our study of the basicities by the MO method (see below) indicate that the  $N_1$  and  $N_2$  atoms of the triazole ring are more basic than the  $N_6$  atom of the azomethine bond. The UV spectra of monomethylated compounds practically coincide with the spectra of the starting compounds in both alcohol and concentrated sulfuric acid. If the bathochromic shift of the methylated compounds in sulfuric acid is explained by protonation of the imino nitrogen atom ( $N_6$ ), it can then be assumed that methylation proceeds in the triazole ring.

We made a quantum-chemical calculation of the energy of protonation of the 4-benzylideneamino-1,2,4-triazole molecule ( $\Delta E = E_{pr} - E_{un}$ ) with the approximations of the Pariser-Parr-Pople method using the program in [8]. The electron structure and energy of the unprotonated molecule were found under the usual approximations of the method in [8, 9], while several variants were used to examine the protonated molecule. In one of them (variant I), we restricted ourselves to the increase in the integral of the core of the protonated atom ( $U_{N^+} = -26.46 \text{ eV}$ ), disregarding the direct interaction of the positive charge of the proton with the remaining part of the molecule.

Variant II is a model in which the proton is localized on the nitrogen atom being attacked and interacts with the p orbitals of the entire molecule. In this case, the charge of the core of the protonated atom is two, while in the unprotonated molecule it is one.

Variant III involves a self-consistent examination of a system consisting of the 1s orbital of hydrogen, the trigonal orbital of the nitrogen atom being attacked (unshared pair), and the  $\pi$  system of the molecule. The charge of the proton, which is distributed between the 1s orbital of hydrogen and the unshared pair of nitrogen, interacts with all of the atoms of the molecule.

The energy differences for protonation of the N<sub>1</sub> and N<sub>6</sub> atoms and their components ( $\Delta \Delta E = \Delta E_1 - \Delta E_6 = \Delta \Delta A + \Delta \Delta B + \Delta \Delta C + \Delta \Delta D + \Delta \Delta F$ ), which we previously used for an analysis of substituent effects,

are presented in Table 3. In contrast to Variant I, the other two variants predict a higher basicity for the nitrogen atoms of the triazole ring and the appropriate orientation for methylation in the triazole ring.

As seen from Table 3, the reason for such an orientation is primarily associated with the difference in the coulombic components of the protonation energy ( $\Delta\Delta F$ ). During attack of the triazole ring, the proton falls within the negative field of two nitrogen atoms, while it is repulsed by the positive field of the adjacent atoms during attack of the azomethine bond. Allowance for this circumstance changes the sign of the energy difference of the coulombic interaction (variants II and III), and the azomethine nitrogen becomes relatively less basic.

## EXPERIMENTAL

Benzylideneaminotriazoles (I-XIII). Equimolar amounts of 4-amino-1,2,4(4H)-triazole [11] and the substituted aldehyde (0.1 mole each) were mixed with 20 ml of ethanol, 3 drops of concentrated HCl were added, and the mixture was allowed to stand for 24 h. The crystals were separated, washed with alcohol, and recrystallized from an appropriate solvent (Table 4).

Methiodides of the Benzylideneaminotriazoles. These were synthesized by heating the base and a small excess of methyl iodide on a water bath for 5-8 h in dimethylformamide-dioxane (1:3 by volume).

 $\alpha$ -Methylbenzylideneaminotriazole. A solution of 16.8 g of aminotriazole and 24.0 g of acetophenone was refluxed with a Dean-Stark adapter until the water was completely removed. The mixture was then cooled, and the precipitated colorless crystals were separated, dried, and recrystallized from ethanol to give 84% of a product with mp 123°. Found %: N 30.0. C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>. Calculated %: N 30.1.

The spectral measurements were made with an SFD-2 spectrophotometer in 10-mm thick quartz cuvettes. The solvents were absolute ethanol and concentrated  $H_2SO_4$ .

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