UDC 547.836:543.422

N. S. Prostakov, L. M. Kirillova, Hanna Bu Habib, and L. A. Murugova

Previously unknown unsymmetrical azines with arylidene and azafluorenylidene fragments were obtained. Some of the geometric isomers of 3-methyl-9-benzylidene(4-methoxybenzylidene)hydrazono-2-azafluorenes were isolated. The longwave absorption bands in the electronic spectra of these compounds were interpreted on the basis of the experimental and calculated data (the PPP method).

In connection with the fact that azines containing the azafluorene fragment are unknown we undertook the synthesis of a series of unsymmetrical arylidenehydrazonoazafluorenes. Azines III-XII were obtained by the condensation of 3-methyl-2-azafluorenone hydrazone (I) and also 4-azafluorenone hydrazone (II) [1] with benzaldehyde, anisaldehyde, salicylaldehyde, vanillaldehyde, and veratraldehyde.

Theoretically eight geometric isomers of the arylidenehydrazonoazafluorenes (four each with the s-cisoid and s-transoid configurations) are possible. In practice, however, only the last isomers can exist, i.e., two of them with the Z configuration of the arylideneaza-methine fragment in relation to the nitrogen-containing ring and two with the E configuration.

By TLC it was established that two geometric isomers of the azines III-V were present in the obtained samples, but it was not possible to separate them by column chromatography. The individual geometric isomers were isolated by fractional crystallization of the azine III [(IIIa) mp 158-159°C, (IIIb) mp 107-108°C] and the azine IV [(IVa) mp 134-136°C, (IVb) mp 138-140°C]. The individual isomers of the azines III, IV have different colors and different types of crystals; IIIa, IVa form yellow velvety flakes, and IIIb, IVb form shiny orange crystals.



I, III—VII R=CH₃, 2 **aza;** II, VIII—XII R=H, 4 **aza;** III, VIII $\Lambda r = C_6H_5$; IV, IX $\Lambda r = \rho-CH_3OC_6H_4$; V, X $\Lambda r = o-HOC_6H_4$; VI, XI $\Lambda r = (p-OH)(m-CH_3O)C_6H_3$; VII, XII $\Lambda r = \gamma,m-(CH_3O)_2C_6H_3$

In the IR spectra of isomers IIIa, b in tablets with potassium bromide a difference is observed in the region corresponding to the stretching vibrations of the C=C and C=N bonds (Table 1).* The bands at 1618, 1580, and 1500 cm⁻¹ in the spectrum of the isomer IIIa belong to the skeletal vibrations of the azafluorene fragment. In the spectrum of iosmer IIIb, in addition to the same absorption bands, there is a band of medium intensity at 1638 cm⁻¹, which is usually assigned to the stretching vibrations of highly perturbed C=N bonds of the azine fragment [2].

In the IR spectra of compounds IV-XII (Table 1) there is also an absorption band in the region of 1633-1638 cm⁻¹, on the basis of which it can be supposed that all these azines have the same structure as the isomer IIIb.

A feature of the IR spectrum of the azine (V) is the presence of absorption bands in the regions of 2600 and at ~3100 cm⁻¹, which can be explained by the coexistence of the conformers

*The authors express their gratitude to Doctor of Chemical Sciences B. E. Zaitsev for taking part in the discussion of the IR and electronic absorption spectra of the compounds.

P. Lumumba People's Friendship University, Moscow, 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 248-253, February, 1986. Original article submitted December 26, 1984.

Com-		Absorption bands, cm ⁻¹ (in tablets with KBr)						
pound*	Ar	0 – H	C = N	C=C Skeletal	C0			
IIIa	C ₆ H ₅			1618 vs 1588 m, 1553 m, 1490 m				
IIIb	C ₆ H ₅		1638 s	1612 vs . 1590 m , 1565 P 1500 W	· · · ·			
IV	p-CH ₃ OC ₆ H ₄		1638 s	1617 VS 1592 m , 1570 VS , 1552 m , 1520 S , 1500 W	1255 vs ., 1170 vs			
V	o-HOC ₆ H4	3400 m 3120 m 3070 sb 2600 mb	1638 s	1612 vs , 1565 m), 1547 m, 1500 w	1260 vs ,1165m			
VI	(p-HO) (m-CH ₃ O)C ₆ H ₃	3450 mb, 2710 s, 2570 sb, 2420 sb	1636 s	1615 vs , 1598 s 1585 s , 1570 s 1555 s , 1513 vs	1268 vs 1230 vs 1168 s 1150s 1128 s			
VII	$p.m-(CH_3O)_2-C_8H_3$		1638 m	1613 vs , 1590 sh 1555 m , 1520 vs	1280 VS 1140 S , 1031 S			
VIII	C ₆ H ₅		1638 s	1610 ^m , 1590 s. 1575 s 1558 m, 1500w				
ιx	p-(CH ₃ O)-C ₀ H ₄	_	1639 s	1615 vs , 1590 s , 1600 sh , 1575 m 1550 m , 1525 vs	1265 vs 1178 vs			
Х	0-HOC ₆ H ₄	3070 sb , 2740 s , 2620 sb	1633 s	1610 ^{vs} , 1590s, 1575 ^m , 1550m	1310 vs, 1260 vs			
XI	$(p-HO)(m-CH_3O)-C_6H_3$	3100 usb	1636 s	1618vs, 1590s 1580sh, 1560m, 1523vs	1303 vs, 1275 vs, 1210 s 1180 vs			
ХП	$p,m-(CH_3O)_2-C_6H_3$		1633 s'	1605 s 1590 s , 1575 s 1550 m , 1520 vs	1273 vs, 1240 s 1170 m, 114C vs, 1030 vs			

TABLE 1. IR Spectra of the Azines of Azafluorenes III-XII

*IIIa, b, IV-VII R = CH₃, VIII-XII R = H.

A [with a strong intramolecular hydrogen bond (the band at 2600 cm⁻¹)] and B (the bands at $\sim 3100 \text{ cm}^{-1}$).



For a more detailed investigation of the electronic structure of the azines III-XII we used their electronic absorption spectra and quantum-chemical calculations.

The experimental data for azines III-XII (Table 2) indicate that the electronic absorption spectra are not a simple superimposition of two unconnected azafluorene (Φ_1) and arylidenehydrazone (Φ_2) systems. This becomes clear during comparison with the spectra of the initial compounds, i.e., the hydrazones I and II, in which the long-wave maximum of the azafluorene fragment undergoes of bathochromic shift to ~320 nm ($\Delta\lambda$ ~ 20 nm) on account of the auxochromic effect of the =N-NH₂ group. The introduction of the arylidenehydrazone group, however, leads to an even larger shift of the long-wave absorption band to 360 nm, which indicates that the $\pi-\pi$ conjugation, which is only possible in the flat conformers, increases in the investigated systems.

During the quantum-mechanical calculations we used the modified program in [3-5] with allowance for the configurational interaction of 25 singly excited states, with variation in the resonance integrals $\beta_{\mu\nu}$ and bond lengths $r_{\mu\nu}$, and with self-consistency in a linear relationship to the bond orders $P_{\mu\nu}$ using the standard parameters for C, N, and O. The two-center Coulombic intetrals $\gamma_{\mu\nu}$ were calculated by means of the Matago-Nishimoto formula [6].

TABL.	E 2.	Electro	onic	Absorpt	ion	Spect	tra	a ot	the	Unsymme	etric	cal A-	
zine	s of	3-Methy	1-2-8	azafluor	ene	III-V	/11	and	14-	Azafluo	rene	VIII-	
XII	(aza	fluorene	-N	N=CH-Ar;	for	the	R	and	Ar	values,	see	Table	1)

, pund	960	$\%$ ethanol λ_m	_{lax} , nm (lgε)	I	96% ethanol + sulfuric (2N), λ_{max} , acid nm (Ige)					
Comp	A	В	С	D	A	В	с	D		
111	208 (4,70), 220 sh (4,52)	258 (4,69), 264 (4,68)	340 (4,55), 354 (4,57)	388 sh (410)	215 (4,48)	242 (4,53), 270 (4,53)	295 (4,14), 310 (4,29)	368* (4,40). 380 (4,10)		
IV	213 (5,17)	248 (4,54)		367 (4,52)	223 (4,59)	237 (4,35), 273 (4,59)	295 sh (4,43), 330 (4,20)	403* (4,31)		
V	212 (4,61), 220 (4,58)	260 (4,65)	340 (4,30)	378 (4,34)	217 (4,37)	242 (4,37), 263 (4,50)	297 (4,16), 315 (4,11), 324 (4,32)	400* (4,15)		
VI	216 (4,58), 226 (4,55)	260 (4,64)	294 (3,04)	390 (4,43)	212 (4,21)	233 (4,49), 270 (4,43)	298 (4,26), 312 (4,25)	364 (3,61), 424* (4,35)		
VII	216 (4,59), 225 (4,57)	260 (4,65)	287 (4,07)	380 (4,44)	207 (4,61)	233 (4,63)	272 (4,61), 313 (4,45)	410* (4,38)		
VIII	207 (4,52)	$\begin{array}{c} 237 \ (4,54),\\ 243 \ (4,55),\\ 246 \ \mathbf{sh} \\ (4,51),\\ 264 \ \mathbf{sh} \\ (4,35) \end{array}$	293 (4,34), 304 (4,38), 315 (4,40)	335 (4,44), 345 (4,47), 357 sh (4,34)	206 (4,58)	241 (4,54)	293 sh (4,22), 303 (4,32)	330 (4,36), 345* (4,52)		
IX	213 (4,50)	246 (4,52), 240 (4,53), 247 (4,52)	300 (4,16), 315 (4,14)	367 (4,50)	212* (4,53), 220 (4,67)	234* (4,50)	253 (4,48), 305 (4,27), 317 (4,80)	387* (4,45)		
х	217 (4,53), 227 (4,56), 240 (4,48)	267 (4,32)	310 (4,30)	340 (4,25 <u>)</u> , 375 (4,28)	217 (4,48)	236 (4,34), 253 (4,37)	329 (4,39)	390* (4,27)		
XI	212 (4,47), 227 (4,53)	250 (4,38)	287 (4,16)	384 (4.34), 500* (3,30)	$\begin{vmatrix} 212 & (4,29) \\ 232 & (4,52) \end{vmatrix}$	280 (4,22)	323 (4,46)	412* (4,15)		
XII	214 (4,56), 228 (4,60)	252 (4,47), 267 (4,38)	287 (4,29). 313 (4,19)	387 (4,43)	212 (4,66), 230 (4,68)	277 (4,44)	324 (4,54)	395* (4,36)		

*The bands disappear from the spectrum with the addition of acid to the solution in ethanol.

During the calculations the =N-N= group was taken as structurally similar to the =CH-CH=group. It was assumed that sp^2 hybridization is realized for the nitrogen atoms while the interaction between the unshared electron pairs in the hybrid orbitals in the trans position to each other can be disregarded. The π bonds are formed by overlap of the p_Z atomic orbitals of the nitrogen and carbon atoms. The calculations were made for the theoretically most probable four Z and E isomers with the s-transoid configuration in relation to the N-N bond in azines III and VIII not containing substituents in the arylidene fragment and, therefore, selected as models. Since the calculated and experimental spectra of the two isomers differ little, during the interpretation of the spectra and the electronic structure of these compounds we started from the calculated data for one arbitrarily chosen isomer.

Experimentally, three absorption bands with the principal maxima in the regions of 210, 250, and 360 nm are mainly observed in the electronic absorption spectra of azines III and VIII. On the slope of the long-wave absorption band it is possible to distinguish a shoulder with $\lambda_{\max} \approx 370$ nm. From comparison of the experimental and calculated data and also analysis of the configuration interaction matrix (CIM) it is possible to conclude that the long-wave absorption bands in the spectra of arylidenehydrazono-2(4)-azafluorenes III and VIII are formed by the two so $\rightarrow s^{1}\pi\pi \star$ and so $\rightarrow s^{2}\pi\pi \star$ electronic transitions. The first transition, polarized along the y axis (the long axis of the molecule), is due to the extent of 98% to the transition of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The second transition, $s_{0} \rightarrow s^{2}\pi\pi \star$, can also be considered a single-electron transition with the major contribution from the $\Psi_{m-1\rightarrow n}$ configuration (96%). This transition is polarized along the x axis and has an intensity and order of magnitude lower than the $s_{0} \rightarrow s^{1}\pi\pi \star$ transition.

Our calculated λ_{max} values both for the first two electronic transitions and for the others agree well with the experimental data. One of the possible reasons for the small quite

TABLE 3. Total Charges, $\Sigma q(e)$, Calculated by the PPP Method, the Change in Electron Density, $\Delta q(e)$, at the Fragments, and the Intramolecular Charge Transfer (ICT) (e) of Compounds III and VIII



(1) (2) (3)										
Com- pound	5 n	Param- eters	Fragments					TOT		
		<u> </u>	A	в	с	D	N ₍₁₎	N ₍₂₎	СН(3)	101
111	s ₀ s*1	$\Sigma q \Sigma q \Delta q$	0,039 0,093 0,054	$\begin{array}{c} 0,122 \\ -0,054 \\ 0,176 \end{array}$	$ \begin{vmatrix} -0.013 \\ 0.018 \\ -0.031 \end{vmatrix} $	0,044 0,105 -0,061	-0,165 -0,145 -0,020	-0,188 -0,119 -0,069	0,161 0,099 0,062	0,238 (e)
VIII	s ₀ s* ₁	$\Sigma q \Sigma q \Delta q$	0,045 0,134 -0,089	0,183 0,063 0,120	-0,076 -0,025 -0,051	$0,043 \\ 0,085 \\ -0,042$	$-0,166 \\ -0,193 \\ 0,027$	$-0,188 \\ -0,139 \\ -0,049$	0,160 0,075 0,085	0,232 (e)

*A minus sign at Δq signifies a decrease in electron density at the molecular fragment during the $s \rightarrow s^{1}_{\pi\pi}$ transition.

permissible increase in the λ_{max} values of the $s_0 \rightarrow s_{\pi\pi\pi}^*$ transition compared with the experimental λ_{max} values of the long-wave absorption band ($\Delta \lambda = \lambda_{calc} - \lambda_{expt}$ amounts to ~20 nm) may be conformational mobility of the investigated azines in the solutions.

Analysis of the molecular diagrams shows that the π -electron density in the ground state of the molecules (s_0) is concentrated predominantly at the nitrogen atoms, and the nitrogen of the azafluorene fragment (Φ_1) has the largest π charge. The transition to the first singlet excited state (the s_0 \rightarrow s¹ $\pi\pi\pi$ transition) is accompanied by intramolecular charge transfer (ICT) predominantly from the heteroatoms of the arylidenehydrazone group (Φ_2) and the carbon atoms of fragments A and C to the atoms of the five-membered ring B. The ICT values for this transition Δq are given in Table 3. For compound III compared with VIII the electronwithdrawing characteristics of ring B are somewhat less clearly defined, since Δq_B for them amounts to 73.8 and 51.7%, respectively. The methine carbon atom C(3), which is electrondeficient in the s_0 state of the molecules and for which Δq amounts to ~30%, also acts as an electron acceptor. The donor is the benzene ring D.

The calculated values of the C=N and N-N bond lengths (1.30 and 1.35 Å, respectively) agree satisfactorily with the data from electron diffraction in the gas phase for the planar trans conformation of the acetaldehyde azine molecules, according to which $r_{C=N} = 1.27$ and $r_{N-N} = 1.41$ Å [7].

The introduction of electron-donating substituents (-OCH₃ and -OH) into the arylidene fragment (compounds IV-VI, IX-XII) leads to a bathochromatic shift of the long-wave bands in the electronic spectra by 20 nm (Table 2). This fact can be considered experimental evidence for the existence of $\pi-\pi$ conjugation. In addition, this is demonstrated by the spectral data on the protonation of compounds III-XII (Table 2). With the addition of sulfuric acid to al-cohol solutions of compounds III-XII, there is a bathochromic shift of the long-wave absorption bands by 20-30 nm in their spectra; the intensity of this band then decreases, and it disappears. This process can be considered an equilibrium process, since isobestic points are observed in the spectra. As known, a bathochromic shift in an acidic medium is typical of $\pi-\pi^*$ absorption bands. This is consistent with our calculated data and incidates that the nitrogen atom of the azofluorene fragment is evidently protonated initially and the hydrazo group is then protonated.

Quantum-chemical calculation of the electronic absorption spectra of the NH cations of the azafluorenium fragments in compounds III and VIII in terms of the same PPP method showed that the energy of the $s_0 \rightarrow s_{\pi\pi\pi}^{i}$ transitions does in fact increase the result of the increase in the electronegativity of the heteroatom during protonation of the nitrogen and the associated relative approach of the HOMO and LUMO levels. The theoretical bathochromic shifts of the long-wave absorption bands corresponding to these electronic transitions must amount to 30 and 40 nm for compounds. III and VIII, respectively, which agrees qualitatively with the experimental data (Table 2).

EXPERIMENTAL

The IR spectra were recorded in tablets with potassium bromide on a UR-20 instrument. The electronic spectra were obtained on a Specord UV-vis spectrophotometer in 96% ethanol with subsequent acidification by concentrated sulfuric acid. The concentration of the solutions was varied in the range of 10^{-3} - 10^{-5} M. The thickness of the quartz cuvette was 1.0 cm. The absorbent for TLC was Silufol UV-254, and the eluant was ethyl acetate.

<u>3-Methyl-9-benzylidenehydrazono-2-azafluorene (III).</u> A solution of 0.5 g (2.4 mmoles) of hydrazone I, 0.5 g (5 mmoles) of benzaldehyde in 20 ml of ethanol, and 5 ml of benzene was boiled for 1 h. After distillation of the solvents the residue was dissolved in chloroform and deposited on aluminum oxide with ether as eluant to remove the benzoic acid. We obtained 0.32 g (46%) of a mixture of the isomers of the azine (III). Found %: C 80.7; H 5.1; N 14.0; M^+ 297. C₂₀H₁₅N₃. Calculated: C 80.8; H 5.1; N 14.1; M 297.

By fractional crystallization from hexane we obtained IIIa [orange crystals, mp 158-159°C, R_f 0.52 (ethyl acetate)] and IIIb [yellow needle crystals, mp 107-108°C, R_f 0.67 (ethyl acetate)].

<u>3-Methyl-9-(p-methoxybenzylidene)hydrazono-2-azafluorene (IV)</u>. A reaction mixture of 0.1 g (0.5 mmole) of hydrazone I, 0.2 g (1.5 mmoles) of anisaldehyde, 12 ml of ethanol, and 2 ml of benzene was boiled for 3 h. After cooling 10 ml of heptane was added. The precipitate was filtered off, washed with hexane, and dried. We obtained 0.12 g (73%) of a mixture of the isomers of azine IV. Found %: C 76.9; H 5.3; N 12.9; M⁺ 327. C₂₁H₁₇N₃O. Calculated: C 77.1; H 5.2; N 12.8; M 327.

By fractional crystallization from hexane we isolated yellow crystals [mp 134-136°C, R_f 0.6 (ethylacetate)] and then orange crystals [mp 138-140°C, R_f 0.75 (ethyl acetate)]. A mixed melting test with the two types of crystals melted at 135-139°C.

<u>3-Methyl-9-(o-hydroxybenzylidene)hydrazono-2-azafluorene (V).</u> A mixture of the isomers of azine V was obtained similarly with a yield of 70% from hydrazone I and salicyladehyde; mp 143-145°C (from hexane), R_f 0.72 and 0.57 (ethyl acetate). Found %: C 76.4; H 4.9; N 13.6; M⁺ 313. C₂₀H₁₅N₃O. Calculated: C 76.7; H 4.8; N 13.4; M 313.

 $\frac{3-\text{Methyl-9-(p-hydroxy-m-methoxybenzylidene)hydrazono-2-azafluorene (VI).} A solution of 0.7 g (3.3 mmoles) of the hydrazone I and 0.56 g (3.7 mmoles) of vanillin in 10 ml of ethanol was boiled for 10 h. The orange-red crystals which separated were recrystallized from a 5:1 mixture of n-butanol and chloroform. We obtained 1.0 g (90%) of azine VI; mp 208-210°C. Found %: C 73.6; H 5.2; N 12.5; M⁺ 343. C₂₁H₁₇N₃O₂. Calculated: C 73.5; H 4.9; N 12.2; M 343.$

<u>3-Methyl-9-(p,m-dimethoxybenzylidene)hydrazono-2-azafluorene (VII)</u>. In the reaction we used $\overline{0.4 \text{ g}}$ (2 mmoles) of hydrazone I, 0.42 g (2.4 mmoles) of veratraldehyde, 20 ml of ethanol, and 10 ml of benzene. The mixture was boiled for 30 h, and after cooling 15 ml of heptane was added. The precipitated azine VII [0.55 g (81%)] was crystallized from heptane; mp 138-140°C, R_{f} 0.75 (ethyl acetate). Found %: C 73.9; H 5.4; N 12.2; M⁺ 357. C₂₂H₁₉N₃O₂. Calculated: C 73.9; H 5.3; N 11.8; M 357.

9-Benzylidene-, 9-p-Methoxybenzylidene-, 9-o-Hydroxybenzylidene-, 9-p-Hydroxy-m-methoxybenzylidene-, and 9-m, p-Dimethoxybenzylidenehydrazono-4-azafluorenes (VIII)-(XII). The compounds were obtained from hydrazone II and the respective aldehydes by similar methods and with the reagents in the same molar ratios as in the syntheses of azines III-VII. Azine VIII formed orange crystals; mp 104-108°C (from heptane), yield 80%. Found %: C 80.5; H 4.8; N 14.9; M⁺ 283; C₁₉H₁₉N₃. Calculated: C 80.6; H 4.6; N 14.8; M 283. Azine IX formed orange crystals; mp 148-150°C (from heptane), Rf 0.71 (2:1 ethyl acetate-heptane), yield 84%. Found %: C 76.4; H 4.8; N 13.6; M⁺ 313. C₂₀H₁₅N₃O. Calculated: C 76.7; H 4.8; N 13.4; M 313. Azine X formed yellow crystals; mp 158-160°C (from heptane), yield 75%. Found %: C 76.3; H 4.5; N 13.8; M⁺ 299. C₁₉H₁₃N₃O. Calculated: C 76.3; H 4.4; N 14.1; M 299. Azine XI formed orange crystals; mp 211-212°C (5:1 butanol-chloroform), yield 72%. Found %: C 70.3; H 6.0; N 11.5; M⁺ 329. C₂₀H₁₅N₃O₂ «C₂H₅OH. Calculated: C 70.4; H 5.6; N 11.2; M 329. Azine XII formed yellow-orange crystals; mp 115-118°C (from heptane), yield 63%. Found %: C 73.5; H 4.9; N 12.2; M⁺ 343. C₂₁H₁₇N₃O₂. Calculated: C 73.7; H 4.9; N 12.3; M 343.

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