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PHYSICOCHEMICAL PROPERTIES AND STRUCTURES OF 4-AZAFLUORENONES AND  
2,3-BENZO-4-AZAFLUORENONES

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The quantum-chemical characteristics and the results of a comparative analysis of the IR and electronic absorption spectra and the polarographic reduction of methyl-containing 4-azafluorenones (structural analogs of the alkaloid onychine - 1-methyl-4-azafluorenone) and condensed benzo-4-azafluorenones are presented.

Some physicochemical properties of azafluorenones (ketoindenopyridines), which are iso-electronic analogs of fluorenones, were examined in [1]; however, detailed studies of these compounds have not yet been made. In the present communication we present the results of a comparative study of the IR and electronic absorption spectra and polarography of 4-azafluorenones (5H-indeno[1,2-b]pyridin-5-ones) and 2,3-benzo-4-azafluorenones (6H-indeno[3,2-b]-quinolin-6-ones) and give an analysis of them with the use of the calculated quantum-chemical characteristics of the molecules of the investigated compounds (see middle of following page).

IR Absorption Spectra. It is known [10] that a change in the  $\nu_{C=O}$  frequency and the integral intensity  $A(C=O)$  of molecules that do not participate in hydrogen and donor-acceptor bonds is determined primarily by conjugation and the inductive effect; the intensity of the absorption band is a more sensitive parameter. It has been shown [10, pp. 168, 327; 11] that conjugation of the carbonyl group with a multiple bond and phenyl rings decreases  $\nu(C=O)$  by 25-30  $cm^{-1}$ , while the intensity of the band increases by ~30%.

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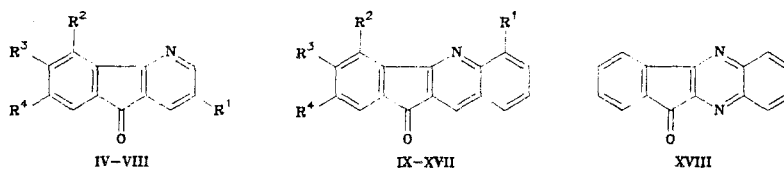
Patrice Lumumba International-Friendship University, Moscow 117,923. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, Vol. 24, No. 3, pp. 361-366, March, 1988. Original article submitted September 30, 1986.

TABLE 1. Frequencies [ $\nu(\text{C}=\text{O})$ ] and Integral Intensities [ $A(\text{C}=\text{O})$ ] of the Carbonyl Bands of the Investigated Compounds in Solution  $\text{CCl}_4$

Compound	Compound name	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$	$A(\text{C}=\text{O}) \times 10^4, \text{ liter/mole} \cdot \text{cm}^2$
I	2,3-Dimethyl-1-cyclopentanone	1750	2.5 [13]
II	2,3,4-Trimethylcyclopent-2-en-1-one	1697	3.1 [14]
III	Fluorenone	1720	3.00
IV	2-Methyl-4-azafluorenone	1723	2.83
V	5-Methyl-4-azafluorenone	1721	3.10
VI	7-Methyl-4-azafluorenone	1721	2.92
VII	2,7-Dimethyl-4-azafluorenone	1722	2.99
VIII	2,7-Dimethyl-6-nitro-4-azafluorenone	1732	2.76
IX	6H-Indeno[3,2-b]quinolin-6-one	1722	2.91
X	1-Methyl-6H-indeno[3,2-b]quinolin-6-one	1723	3.20
XII	9-Methyl-6H-indeno[3,2-b]quinolin-6-one	1721	3.01
XIV	1,9-Dimethyl-6H-indeno[3,2-b]quinolin-6-one	1722	3.21
XV	8,9-Dimethyl-6H-indeno[3,2-b]quinolin-6-one	1721	3.18
XVI	8,10-Dimethyl-6H-indeno[3,2-b]quinolin-6-one	1721	3.26
XVII	1,8,10-Trimethyl-6H-indeno[3,2-b]quinolin-6-one	1722	3.25
XVIII	6H-Indeno[3,2-b]quinoxalin-6-one	1731	4.66

TABLE 2. Frequencies and Intensities of the Absorption Bands of 4-Azafluorenones IV, V, and VIII and Ketoindenoquinolines IX, X, XII, and XIV-XVII at  $1612-1633 \text{ cm}^{-1}$  in  $\text{CCl}_4$

Compound	Frequency, $\text{cm}^{-1}$	Apparent coefficient of extinction, $\epsilon$ , liters/mole $\cdot$ cm	Compound	Frequency, $\text{cm}^{-1}$	Apparent coefficient of extinction, $\epsilon$ , liters/mole $\cdot$ cm	Compound	Frequency, $\text{cm}^{-1}$	Apparent coefficient of extinction, $\epsilon$ , liters/mole $\cdot$ cm
IV	1622	108	X	1631	585	XV	1631	758
V	1618	76	XII	1629	790	XVI	1630	725
VIII	1612	63	XIV	1633	734	XVII	1631	624
IX	1629	682						



IV  $\text{R}^1=\text{CH}_3, \text{R}^2=\text{R}^3=\text{R}^4=\text{H}$ ; V  $\text{R}^1=\text{R}^3=\text{R}^4=\text{H}, \text{R}^2=\text{CH}_3$ ; VI  $\text{R}^1=\text{R}^2=\text{R}^3=\text{H}, \text{R}^4=\text{CH}_3$ ;  
 VII  $\text{R}^1=\text{R}^4=\text{CH}_3, \text{R}^2=\text{R}^3=\text{H}$ ; VIII  $\text{R}^1=\text{R}^4=\text{CH}_3, \text{R}^2=\text{H}, \text{R}^3=\text{NO}_2$ ; IX  $\text{R}^1=\text{R}^2=\text{R}^3=\text{R}^4=\text{H}$ ;  
 X  $\text{R}^1=\text{CH}_3, \text{R}^2=\text{R}^3=\text{R}^4=\text{H}$ ; XI  $\text{R}^1=\text{R}^2=\text{R}^3=\text{H}, \text{R}^4=\text{CH}_3$ ; XII  $\text{R}^1=\text{R}^2=\text{R}^4=\text{H}, \text{R}^3=\text{CH}_3$ ;  
 XIII  $\text{R}^1=\text{R}^4=\text{CH}_3, \text{R}^2=\text{R}^3=\text{H}$ ; XIV  $\text{R}^1=\text{R}^3=\text{CH}_3, \text{R}^2=\text{R}^4=\text{H}$ ; XV  $\text{R}^1=\text{R}^2=\text{H}, \text{R}^3=\text{R}^4=\text{CH}_3$ ;  
 XVI  $\text{R}^1=\text{R}^3=\text{H}, \text{R}^2=\text{R}^4=\text{CH}_3$ ; XVII  $\text{R}^1=\text{R}^2=\text{R}^4=\text{CH}_3, \text{R}^3=\text{H}$

The keto group in azafluorenones and fluorenones is included in a five-membered ring that is condensed with benzene rings. The planar structure of fluorenone [12] and, in analogy with it, probably, azafluorenones suggests a certain degree of conjugation of the  $\text{C}=\text{O}$  groups with the benzene rings. The cyclopentanone molecule, in the spectrum of which  $\nu(\text{C}=\text{O}) = 1750 \text{ cm}^{-1}$ , can be taken as a model of the unconjugated  $\text{C}=\text{O}$  group in a five-membered ring. Conjugation of an exocyclic  $\text{C}=\text{O}$  group in a five-membered ring with a benzene ring as, for example, in the 2,3-benzocyclopentanone molecule, decreases  $\nu(\text{C}=\text{O})$  by  $\sim 35 \text{ cm}^{-1}$  as compared with  $\nu(\text{C}=\text{O})$  in cyclopentanone (Table 1). In addition, it is known that conjugation of the  $\text{C}=\text{O}$  group in cyclic ketones leads to an increase in the integral intensity  $A(\text{C}=\text{O})$  of the band by 0.3-0.8 practical units [4, 11].

It is apparent from Table 1 that the maxima of the  $\nu(\text{C}=\text{O})$  absorption bands of the stretching vibrations of the carbonyl groups of 4-aza- and 2,3-benzo-4-azafluorenones lie over the narrow range  $1720-1723 \text{ cm}^{-1}$ , while the integral intensities [ $A(\text{C}=\text{O})$ ] range from 2.80 to 3.26 practical units. The presence of a nitro group in the benzene ring leads to an increase in  $\nu(\text{C}=\text{O})$  to  $1732 \text{ cm}^{-1}$ . Consequently, the measured  $\nu(\text{C}=\text{O})$  and  $A(\text{C}=\text{O})$  values in the IR spectra of azafluorenones provide evidence that the  $\text{C}=\text{O}$  group in these compounds exists in conjugation

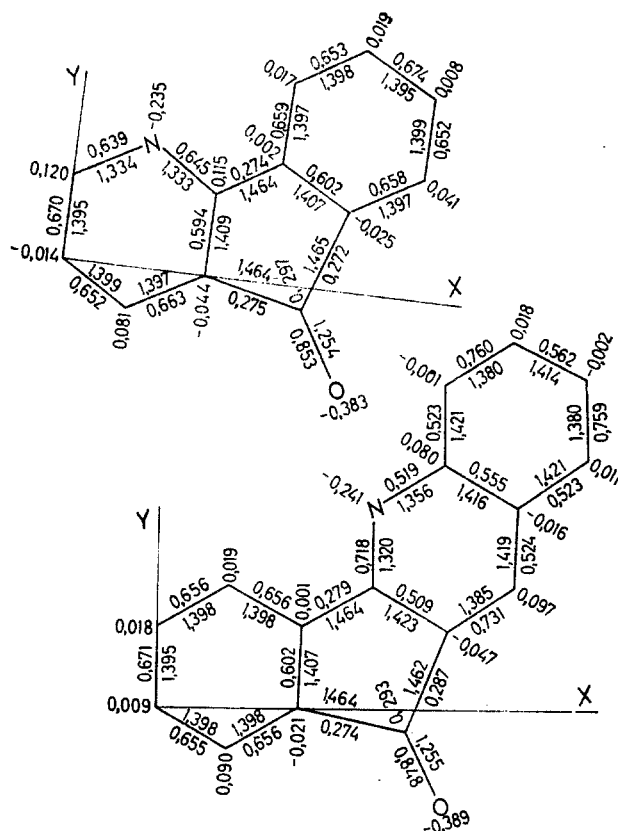


Fig. 1. Molecular diagrams of 4-azafluorenone and 2,3-benzo-4-azafluorenone.

tion, which has approximately the same effect on the vibration of the C=O group as in unsaturated ketones.

A distinctive feature of the IR spectra of 4-azafluorenones (AF) as compared with the spectra of 2,3-benzo-4-azafluorenones (BAF) consists in differences in the positions of the maxima and intensities of the bands of stretching vibrations of the aromatic rings: the frequencies of the vibrations of the C=C and C=N bonds in the spectra of AF are  $7\text{--}21\text{ cm}^{-1}$  lower than in the spectra of BAF; however, the intensities of these bands in the spectra of AF are lower by a factor of  $\sim 5\text{--}10$  than in the spectra of BAF (Table 2).

It is known [15] that the sharp change in the frequencies and intensities of the bands in the IR absorption spectra of compounds that contain aromatic and heteroaromatic rings is due to an increase in the degree of localization of the  $\text{C}\cdots\text{N}$  and  $\text{C}\cdots\text{C}$  bonds and a decrease in the symmetry of the rings. This is in agreement with the change in the calculated (by us) values of the lengths, bond orders, and  $\pi$  charges on the atoms of AF and BAF in the pyridine and quinoline fragments, respectively. From molecular diagrams and Table 3 it is apparent that the two C=N bonds in the N-aromatic ring of AF are virtually equivalent [ $r(\text{C}=\text{N}) = 1.333$  and  $1.334\text{ \AA}$ ] and that the  $\text{C}\cdots\text{C}$  bond orders differ by only 0.070. At the same time, in BAF molecules the lengths and orders of the two C=N bonds differ by  $\Delta r = 0.026\text{ \AA}$  and  $\Delta p = 0.199\text{--}0.209$ , respectively, as compared with  $\Delta r = 0.045\text{ \AA}$  and  $\Delta p = 0.250\text{--}0.266$  for the C=C bonds (Fig. 1). The increase in the intensities of the bands of vibrations of the heteroaromatic fragments in the IR spectra of BAF as compared with the IR spectra of AF can also be associated with redistribution of the electron density on the atoms of the vibrating bonds. According to the calculations, the sum of the charges on the  $\text{C}\cdots\text{N}\cdots\text{C}$  fragments in AF is equal to zero, as compared with  $0.31\text{ e}$  in BAF (Fig. 1).

**Electronic Absorption Spectra.** The long-wave band at  $370\text{--}390\text{ nm}$  is related to a  $^1(n \rightarrow \pi^*)$  transition localized on the carbonyl group. Evidence in favor of this is as follows: a) the absence of absorption in this region in the spectrum of a model compound that does not contain a carbonyl group; b) the weak intensity of the band ( $\epsilon \approx 400$ ) as a consequence of prohibition of the  $^1(n \rightarrow \pi^*)$  transition; c) the decrease in the intensity of the band in a

TABLE 3. Electronic Absorption Spectra of 6H-Indeno[3,2-b]quinolinones XI and XII

Angle between x-axis and direction of polarization (calc.), deg

Compound	Absorption maximum, $\lambda$ , nm		Oscillator force (calc.), f	Angle between x-axis and direction of polarization (calc.), deg	Mass of excited configurations, %
	calc.	experimental (in ethanol)			
IX	358	} ~ 340 350 sh (3,9)*	0,033	30	62 ( $\psi_n \rightarrow \psi_m$ )**; 24 ( $\psi_{n-1} \rightarrow \psi_m$ )
	350		0,016	25	48 ( $\psi_{n-1} \rightarrow \psi_m$ ); 23 ( $\psi_n \rightarrow \psi_{m+1}$ )
	310	} 289 (5,06)	0,118	-70	60 ( $\psi_{n-2} \rightarrow \psi_m$ ); 24 ( $\psi_n \rightarrow \psi_{m+2}$ )
	295		0,094	84	62 ( $\psi_n \rightarrow \psi_{m+1}$ ); 22 ( $\psi_{n-1} \rightarrow \psi_{m+1}$ )
	286		1,590	35	38 ( $\psi_{n-1} \rightarrow \psi_{m+1}$ ); 27 ( $\psi_n \rightarrow \psi_m$ ); 18 ( $\psi_{n-1} \rightarrow \psi_m$ )
	249		254 (4,58)	0,678	30
	237	229 (4,67)	0,080	52	43 ( $\psi_{n-3} \rightarrow \psi_m$ ); 42 ( $\psi_{n-2} \rightarrow \psi_{m+1}$ )
	227	} 223 (4,67)	0,070	-76	50 ( $\psi_{n-3} \rightarrow \psi_{m+1}$ ); 16 ( $\psi_{n-4} \rightarrow \psi_m$ )
	225		0,520	-15	33 ( $\psi_n \rightarrow \psi_{m+2}$ ); 25 ( $\psi_{n-2} \rightarrow \psi_{m+1}$ )
	210	212 (4,70)	0,633	72	37 ( $\psi_n \rightarrow \psi_{m+3}$ ); 27 ( $\psi_{n-2} \rightarrow \psi_{m+2}$ )
XI	367	} ~ 340- 355 sh (3,1)	0,025	63	57 ( $\psi_n \rightarrow \psi_m$ ); 28 ( $\psi_{n-1} \rightarrow \psi_m$ )
	357		0,021	74	39 ( $\psi_{n-1} \rightarrow \psi_m$ ); 34 ( $\psi_n \rightarrow \psi_{m+1}$ )
	316	318 sh (4,8)	0,475	19	37 ( $\psi_n \rightarrow \psi_{m+1}$ ); 24 ( $\psi_{n-2} \rightarrow \psi_m$ )
	300	} 292 (5,02)	0,176	10	43 ( $\psi_{n-2} \rightarrow \psi_m$ ); 25 ( $\psi_n \rightarrow \psi_{m+1}$ )
	292		1,140	-77	66 ( $\psi_{n-1} \rightarrow \psi_{m+1}$ ); 24 ( $\psi_n \rightarrow \psi_m$ )
253	256 (3,98)	0,242	68	48 ( $\psi_{n-3} \rightarrow \psi_m$ ); 10 ( $\psi_n \rightarrow \psi_m$ )	
XII	234	} 231 (4,86)	0,173	18	50 ( $\psi_{n-3} \rightarrow \psi_m$ ); 25 ( $\psi_{n-4} \rightarrow \psi_m$ )
	229		0,035	47	35 ( $\psi_{n-2} \rightarrow \psi_{m+1}$ ); 24 ( $\psi_{n-4} \rightarrow \psi_m$ )
	226	} 225 (4,84)	0,060	-10	71 ( $\psi_n \rightarrow \psi_{m+2}$ ); 10 ( $\psi_n \rightarrow \psi_{m+2}$ )
	220		0,140	34	45 ( $\psi_{n-3} \rightarrow \psi_{m+1}$ ); 27 ( $\psi_{n-4} \rightarrow \psi_{m+2}$ )

\*The  $\log \epsilon$  values are given in parentheses.

\*\*The  $\psi_n$  orbital is the highest occupied MO, and  $\psi_m$  is the lowest vacant MO.

TABLE 4. Data from the Polarographic Reduction of X, XI, and XIII in Solution in Acetonitrile with 0.05 M  $N(C_2H_5)_4ClO_4$  as the Inert Electrolyte

Compound	Half-wave potentials relative to a saturated calomel electrode			Current constants		
	$-E'_{1/2}$	$-E''_{1/2}$	$-E'''_{1/2}$	$A_1$	$A_2$	$A_3$
X	1,51	2,08	2,51	1,37	1,87	5,8
XI	1,47	2,16	2,60	1,48	3,22	5,6
XIII	1,49	2,05	2,50	1,41	2,62	5,0

proton-donor medium. In some cases the vibrational structure of the  $^1(n \rightarrow \pi^*)$  transition is slightly resolved, and the difference between the vibrational components is  $\sim 1273 \text{ cm}^{-1}$ , which corresponds to the frequency of the stretching vibration of the carbonyl group in the excited state.

According to the calculations, the diffuse shoulder at  $\sim 340$ - $355 \text{ nm}$  in the spectra of BAF and its derivatives corresponds to two long-wave  $^1(\pi, \pi^*)$  transitions (Table 3). In the spectra of solutions in acetonitrile one observes a slightly resolved vibrational structure of these bands with a difference in the frequencies of the components of  $1560 \text{ cm}^{-1}$ , which corresponds to the stretching vibrations of aromatic bonds. The observed structure of the electronic-vibrational bands virtually coincides with the well-resolved structure of the long-wave band in the electronic spectrum of ketoindenoquinoline IX, which makes it possible to satisfactorily analyze the  $^1(\pi, \pi^*)$  bands of BAF. The electron transition at  $358 \text{ nm}$  from the ground state to the first excited state is accompanied by a shift of the  $\pi$ -electron charge to the ketone bond ( $\Delta Q_{C=O} = 0.356$ - $0.393 \bar{e}$ ) from the aromatic rings ( $\Delta Q = 0.153$ - $0.183 \bar{e}$ ) and the quinoline fragment ( $\Delta Q = 0.183$ - $0.267 \bar{e}$ ).

According to the calculations, the very intense band in the experimental spectra of the compounds with  $\lambda_{\max} = 289\text{-}295\text{ nm}$  ( $\log \epsilon \approx 5.0$ ) is due to three electron transitions, the oscillator forces of which differ markedly (Table 3). In the experimental spectra the bands of these transitions are overlapped. The transition with the highest calculated value of the oscillator force  $f = 1.3\text{-}1.5$  lies at  $299\text{-}285\text{ nm}$  and is in agreement with the experimental observations. The assignment of the remaining bands is given in Table 3.

A distinctive feature of the experimental electronic spectra of benzoazafluorenones as compared with the spectra of azafluorenones is inversion of the intensities of the absorption bands: for the first class of compounds the bands at  $280\text{-}300\text{ nm}$  are approximately five times more intense than the bands at  $210\text{-}260\text{ nm}$ , while the relationship of the intensities of these bands is reversed for the second class of compounds. This peculiarity in the electronic spectra can be used for the identification of AF and BAF.

Since the maxima of absorption bands in the electronic spectra are determined by the difference in energy levels (molecular orbitals) of the ground and excited states, to evaluate the conjugation in a molecule one must know the change in the energies of these orbitals.

The band of the  ${}^1(n\pi^*)$  transition characterizes the conjugation of the  $\text{C}=\text{O}$  group with phenyl rings. The energy of the nonbonding orbitals  $n$  in which the unshared pairs of electrons ( $\text{Py}^2$ ) of the oxygen atoms of carbonyl groups are located changes very little in series of saturated, conjugated linear, and cyclic ketone-containing groups. Thus, according to the data from the photoelectronic spectra, the bond energy of the  $n$  orbitals is  $9.30\text{ eV}$  ( $1\text{ eV} = 8065.5\text{ cm}^{-1}$ ) in isopropyl methyl ketone,  $9.25\text{ eV}$  in cyclopentanone,  $9.28\text{ eV}$  in fluorenone, and  $9.10\text{-}9.25\text{ eV}$  in anthraquinone. Consequently, the average value of the energy of the  $n$  orbital of the ketone group in saturated and unsaturated ketones is approximately constant ( $E_n \approx 9.28\text{ eV} = 74,813\text{ cm}^{-1}$ ). Taking this into account, one can, using the experimental values of the maxima of the  $(n\pi^*)$  transitions, trace the change in the energy of the lowest vacant  $\pi$ -molecular orbital ( $\psi_m$ ) in the electronic spectra of carbonyl-containing compounds. Thus on passing from saturated ketones, for example, from cyclopentanone ( $\nu_{n\pi^*} = 34,850\text{ cm}^{-1}$ ) to conjugated ketones the energy of  $\psi_m$  decreases: by  $3000\text{ cm}^{-1}$  on passing to 1,2-cyclopentanone, by  $4850\text{ cm}^{-1}$  on passing to benzophenone, by  $5800\text{ cm}^{-1}$  on passing to fluorenone, by  $9470\text{ cm}^{-1}$  on passing to 4-azafluorenone, and by  $9600\text{ cm}^{-1}$  on passing to 2,3-benzo-4-azafluorenone. The significant increase in the decrease in the energy of  $\psi_m$  ( $\Delta E \approx 4850\text{ cm}^{-1}$ ) on passing from benzophenone to AF and BAF constitutes evidence for substantial interaction of the  $\pi$  bond of the  $\text{C}=\text{O}$  group with the phenyl rings in the first excited state. Since the decrease in the energy of  $\psi_m$  for fluorenone is close to that for AF and BAF, it may be assumed that the indicated conjugation in the first excited state is approximately the same in fluorenone, AF, and BAF.

The reduction of ketoindenoquinolines X, XI, and XIII on a dropping mercury electrode in an aprotic solvent (acetonitrile) with  $\text{N}(\text{C}_2\text{H}_5)_4\text{ClO}_4$  ( $0.05\text{ M}$ ) as the inert electrolyte occurs in several steps, thereby fitting into the general scheme of the reduction of aromatic ketones in an aprotic medium (Table 4). The first step consists in the addition of one electron, as indicated by the value of current constants  $A_1$ , and is close to reversible, as one can judge from the dependence of the slope of the polarographic wave on the potential. The electron adds to the  $\text{CO}$  group, on the carbon atom of which, according to the results of quantum-chemical calculations, the maximum positive charge is concentrated (Fig. 1).

It might be expected that the reduction of AF would occur more rapidly than in the case of benzophenone owing to the presence of benzene and quinoline rings condensed with the fragment that bears the carbonyl group; this is in agreement with the data of Hoytink [17] regarding the reduction of condensed aromatic compounds and is confirmed by the half-wave potentials of the first waves  $E'_{1/2}$  (Table 4). The AF compounds have more negative  $E'_{1/2}$  values as compared with fluorenone, since the acceptor effect of the carbonyl group is greater than that of the condensed quinoline fragment. The effect of  $\text{CH}_3$  substituents in the outer condensed rings of AF is not substantial, as indicated by the close  $E'_{1/2}$  values of the compounds (Table 4). The subsequent reduction of the anion radicals and dianions also indicates an insubstantial difference in the investigated AF, although a regularity with respect to the  $E''_{1/2}$  and  $E'''_{1/2}$  values is observed here: V is reduced more readily, IV is reduced with somewhat greater difficulty, and III is reduced least readily.

## EXPERIMENTAL

4-Azafluorenones IV-VIII and 2,3-benzo-4-azafluorenones IX-XV (Table 1) were synthesized by the methods in [2, 3]. The substances were purified chromatographically prior to recording of their spectra. The spectra were recorded with a UR-20 spectrometer. The error in determination of the maxima of the absorption bands was  $\pm 2 \text{ cm}^{-1}$ , while the error in the determination of the integral intensities was  $\pm 10\%$ . The intensities of the bands were determined from the formula [4]

$$A = \pi/2 \Delta\nu_{1/2}^2 \ln(T_0/T) \nu_{\text{max}}/c \cdot l,$$

where  $\Delta\nu_{1/2}^2$  is the half width of the band in reciprocal centimeters,  $c$  is the concentration in moles per liter, and  $l$  is the layer thickness in centimeters. The  $A$  values are given with respect to four to five experimental measurements in practical units ( $10^4$  liters/mole  $\cdot$   $\text{cm}^2$ ).

The electronic absorption spectra were recorded with a Specord UV-vis spectrophotometer under standard conditions in quartz cuvettes with a layer thickness of 1 cm. The polarographic measurements were made with an OH-102 electronic recording polarograph (Radelkis, Hungary) at  $25 \pm 0.1^\circ\text{C}$  with the use of the mercury pool as the anode on a dropping mercury cathode with capillary characteristics  $m = 2.692 \text{ mg/sec}$  and  $\tau = 3.46 \text{ sec}$  (for open circuit). The potentials were monitored by means of an R307 high-resistance potentiometer. The solvent (acetonitrile) was purified by the method in [5]; the inert electrolyte  $\text{N}(\text{C}_2\text{H}_5)_4\text{ClO}_4$  was prepared from  $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$  and  $\text{Mg}(\text{ClO}_4)_2$  and was purified by the method in [6]. The quantum-chemical calculations were made by the Pariser-Parr-Pople (PPP) method [7, 8] using the program in [9].

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