BENZOPYRIDOFULVENES

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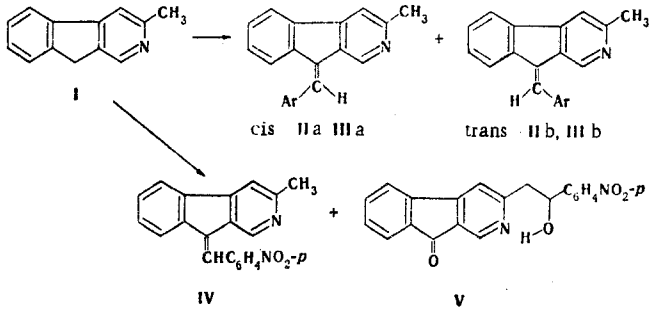
A group of benzopyridofulvenes was obtained by condensation of 3-methyl-2-azafluorene and 4-azafluorene with anisaldehyde, veratraldehyde, and p-nitrobenzaldehyde. It was established that they are produced in the form of geometrical isomers, which could be isolated in the case of the 9-(o-methoxy) and 9-(m,p-dimethoxy) derivatives of 3-methyl-2-azafluorene. One isomer of the analogous benzylidene derivative and 3-[β-hydroxy-β-(p-nitrophenyl)ethyl]-2-azafluorenone were obtained in the condensation of this azafluorene with p-nitrobenzaldehyde. The dimethoxybenzylidene derivatives of both azafluorenes were reduced to dimethoxybenzyl derivatives. The geometrical isomers of a substituted indenoindolizine were obtained from the mixture of isomers of N-phenacyl-9-(m,p-dimethoxybenzylidene)-4-azafluorene bromide and dimethyl acetylenedicarboxylate.

Numerous analogous derivatives of fluorene have been studied in detail [1]. The available information on benzopyridofulvenes, which was obtained mainly in our laboratory, is limited. Having a practicable method for the synthesis of some azafluorenes at our disposal, we turned to a study of their condensation with aromatic aldehydes in order to obtain various benzopyridofulvenes, to establish the configuration of their geometrical isomers, and to search for physiologically active compounds among them. It was established that one of the compounds of this type – 9-benzylidene-4-azafluorene – has considerable bactericidal activity [2].

3-Methyl-9-(o-methoxybenzylidene)-2-azafluorene (II) and 3-methyl-9-(m,p-dimethoxybenzylidene)-2-azafluorene (III) were obtained by condensation of 3-methyl-2-azafluorene (I) [3] with o-anisaldehyde and veratraldehyde, respectively. These compounds are produced in the form of relatively stable geometrical isomers, the isolation of which is accomplished by means of chromatography. In [4] it was conditionally assumed that the cis isomer in the benzopyridofulvene series is the isomer in which the phenylene fragment of the azafluorene and the aryl ring are on the same side of the multiple bond.



IIa, b Ar = $C_6H_4(OCH_3)$-o; IIIa, b Ar = $C_6H_3(OCH_3)_2$-m, p

The assignment of the isolated isomers to cis and trans forms was made on the basis of the following data. The cis isomers (IIa and IIIa) have lower chromatographic mobilities than the trans isomers (IIb and IIIb). In the trans isomers the nitrogen atom of the pyridine ring is shielded by the adjacent aryl ring, a consequence of which should be weakening of the interaction of these isomers with the adsorbent and, consequently, their increased chromatographic mobilities as compared with the cis isomers. The shift of the signal of the α proton of trans isomer IIb (8.53 ppm) to strong field as compared with the analogous signal of cis isomer IIa

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TABLE 1. Chemical (δ) and Specific (Δ_{Eu}) Shifts of the Signals of the Protons of the Isomers of II and III*

Compound	Shifts	1-H	3-CH_3	4-H	5-H
cis †, 116—118°	δ	8,74	2,58	7,19	7,60
	Δ_{Eu}	19,77	22,42	10,62	4,42
trans †, 128—129°	δ	8,57	2,51	7,06	7,60
	Δ_{Eu}	19,00	17,48	8,40	3,51
IIa, cis, 57—60°	δ	8,78	2,52	7,27	7,51
	Δ_{Eu}	18,2	23,37	12,3	4,39
IIb, trans, 128—129°	δ	8,53	2,43	7,27	7,53
	Δ_{Eu}	16,9	16,3	7,4	3,07
IIIa, cis, 125—126°	δ	8,70	2,52	7,52	7,68
	Δ_{Eu}	10,6	10,46	2,88	3,32
IIIb, trans, 158—159,5°	δ	8,80	2,46	7,44	7,57
	Δ_{Eu}	5,60	2,45	3,06	1,03

*Studies of the PMR spectra of 9-benzylidene-3-methyl-2-azafluorene and II and III in the presence of $Eu(DPM)_3$ showed that the specific shifts (Δ_{Eu}) for the cis isomers are greater than the corresponding specific shifts for the trans isomers.
†These compounds were described in [4].

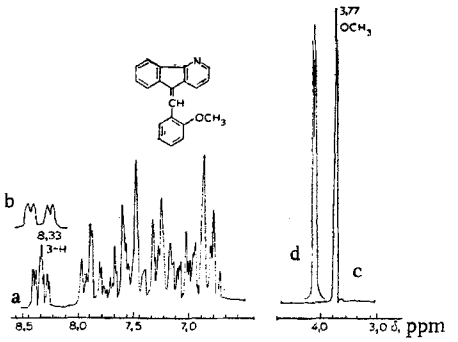


Fig. 1. PMR spectra of VIII: a) without the addition of a paramagnetic shift reagent (PSR); b) signals of the 3-H protons in the presence of a PSR ([PSR]/[substrate] = 0.045); c) signal of the OCH_3 protons without the addition of a PSR; d) signal of the OCH_3 protons in the presence of a PSR ([PSR]/[substrate] = 0.433).

(8.78) (Table 1) is also associated with shielding of the pyridine ring by the aryl ring. It was experimentally established that the amount of trans isomers IIb and IIIb formed is approximately three times the amount of cis isomers IIa and IIIa. The cis isomers of this type are less stable than the corresponding trans isomers. Signals of the trans isomers are observed in the PMR spectra of isomers IIa and IIIa recorded some time after the compounds are dissolved. The higher stability of the trans isomers as compared with the cis isomers is evidently due to their stabilization as a result of interaction of the unshared pair of electrons of the nitrogen atom with the π-electron system of the aryl ring, as proposed in [4]. The presence in it of electron-donor methoxy groups promotes this interaction.

The condensation of azafluorene I with p-nitrobenzaldehyde proceeds ambiguously. In addition to 3-methyl-9-(p-nitrobenzylidene)-2-azafluorene (IV), a relatively significant amount of 3-[β-hydroxy-β-(p-nitrophenyl)ethyl]-2-azafluorenone (V) is formed. Under the reaction conditions azafluorene I is oxidized to 3-methyl-2-azafluorenone, which then undergoes condensation at the α-methyl group with p-nitrobenzaldehyde. The formation of V via this pathway was proved by alternative synthesis by condensation of 3-methyl-2-azafluorenone [3] with p-nitrobenzaldehyde in the presence of sodium methoxide. The PMR spectrum of V does not contain signals of a methyl group. The molecular weight determined by mass spectrometry and the analytical data are in agreement with its formula. The insolubility of V in organic solvents and its high melting point (207-208°C) constitute evidence for its chelate structure with a partially quaternized nitrogen atom. According to the chromatographic data, benzopyridofulvene IV is an individual substance that melts over a narrow range.

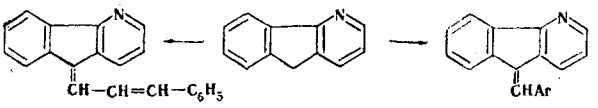
TABLE 2.

Compound	mp, °C	R_f, ether–heptane (3:1)	PMR spectra, δ, ppm	IR spectra, ν, cm^{-1}	UV spectra, λ_{max}, nm (log ε)	Found				Empirical formula	Calculated			
						C, %	H, %	N, %	M^+		C, %	H, %	N, %	M
VIII	119—121	0,52	8,33 (1H, 3-H), 7,96—6,69 (11H, aromatic H), 3,73 (3H, s, OCH_3)	2830$\nu_{s\ C-H}$ (OCH_3), 1642$\nu_{C=C}$, 1253$\nu_{as\ C-O-C}$, 1025$\nu_{s\ =C-O-C}$	212 (4,46); 231 (4,56); 289 (4,26); 340 (4,16)	82,4	5,4	5,1	285	$C_{20}H_{15}NO$	84,2	5,3	4,9	285
IX	123—125	0,64	8,33 (1H, 3-H), 8,0–6,69 (11H, aromatic H), 3,77 (3H, s, OCH_3), 3,71 (3H, s, OCH_3)	2840$\nu_{s\ C-H}$ (OCH_3), 1624$\nu_{C=C}$, 1234$\nu_{as\ C-O-C}$, 1024$\nu_{s\ =C-O-C}$	242 (4,0); 301 (3,62); 311 (3,64); 364 (3,72)	78,4	6,4	4,3	315	$C_{21}H_{17}NO_2$	80,0	5,4	4,4	315
X	91—92	0,77*	8,26 (1H, 3-H), 7,89—6,7 (11H, aromatic H), 5,84 (1H, m, —CH=), 5,15 (2H, m $=CH_2$)	2925, 2908ν_{CH_2} (OCH_2), 1636$\nu_{C=C}$, 1260$\nu_{as\ =C-O-C}$ 1030$\nu_{s\ =C-O-C}$	212 (4,56); 230 (4,66); 310 (4,25); 340 (4,14)	84,5	5,3	4,4	311	$C_{22}H_{17}NO$	84,9	5,5	4,5	311
XI	196—212†	—	8,44 (1H, 3-H), 8,2—6,78 (11H, aromatic H)	1513ν_{as} NO_2, 1334ν_s NO_2	205 (4,52); 226 (4,61); 266 (4,36); 306 (4,31); 346 (4,24)	75,7	3,8	9,0	300	$C_{19}H_{12}N_2O_2$	76,0	4,0	9,3	300

*Ether.

†From acetone.

One must evidently assign to it a cis form in which the dipole moment is considerably lower than in the trans form.



VII VI VIII–XI

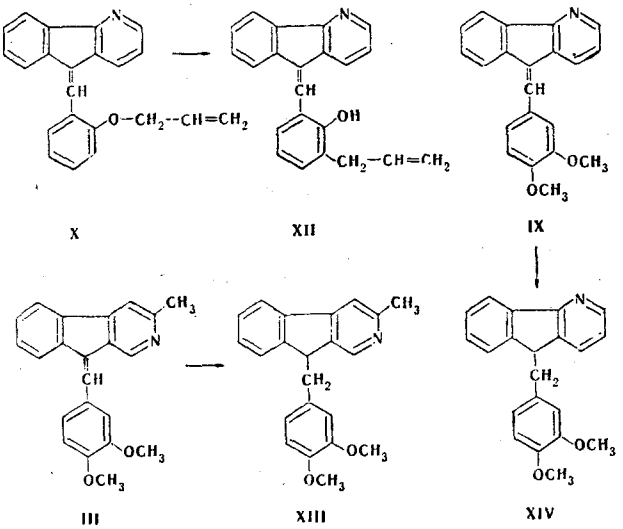
VIII Ar = $C_6H_4(OCH_3)$-o; IX Ar = $C_6H_3(OCH_3)_2$-m; p; X Ar = $C_6H_4(OCH_2CH=CH_2)$-o;

XI Ar = $C_6H_4NO_2$-p.

A second group of similar compounds was synthesized from 4-azafluorene (VI) [5]. 9-Cinnamylidene-4-azafluorene (VII) and benzopyridofulvenes VIII-XI were obtained by condensation of VI with various aldehydes.

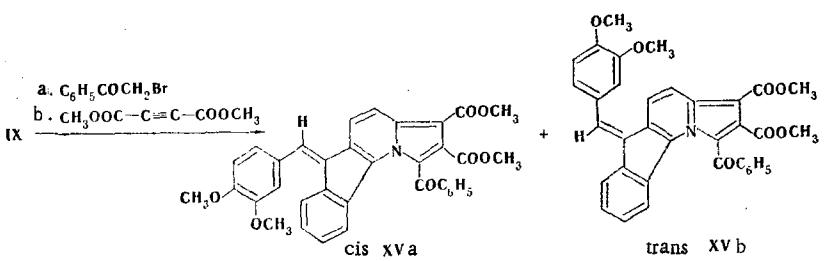
We were unable to isolate the cis and trans forms of these benzopyridofulvenes, and perhaps one cannot separate them by chromatography. According to the data from their PMR spectra measured with the use of a paramagnetic-shift reagent [$Eu(DPM)_3$], they all exist in the form of mixtures of isomers (Fig. 1). The relative stabilities of the isomers of benzopyridofulvenes are consequently associated with the change in the position of the nitrogen atom in the azafluorene system.

The benzopyridofulvenes obtained in this study are of interest for the synthesis from them of compounds that contain fragments of natural alkaloids, and they therefore may be of biological interest. 9-(o-Hydroxy-m-allylbenzylidene)-4-azafluorene (XII) was obtained from allyloxybenzylidene derivative X by thermal Claisen rearrangement. The 0.86 ppm shift ($\Delta\delta$) to strong field of the signal of the methylene group in the allyl fragment is evidence for this rearrangement.



X XII IX

III XIII XIV



cis XV a trans XV b

3-Methyl-9-(m,p-dimethoxybenzylidene)-2-azafluorene (III) was reduced by means of benzyl alcohol [6] to 3-methyl-9-(m,p-dimethoxybenzyl)-2-azafluorene (XIII), which to a certain extent is similar to papaverine with respect to its structural fragments. Compound XIII was also obtained directly from azafluorene I and veratraldehyde. In the PMR spectrum of XIII the $-CHCH_2-$ fragment gives a spectrum of the AX_2 type [$\delta_{(CH)}$ 4.06, $\delta_{(CH_2)}$ 2.91 ppm; $J_{(H-C-C-H)}$ =7 Hz]. 9-(m,p-Dimethoxybenzyl-4-azafluorene (XIV) was obtained via similar pathways from 9-(m,p-dimethoxybenzylidene)-4-azafluorene (IX). According to preliminary data, the hydrochloride of XIII has growth-regulating activity.

The synthesis of a new indenoindolizine system was accomplished on the basis of benzopyridofulvene IX. Compound IX was treated with bromoacetophenone (we could not isolate the quaternary salt in crystalline form), and the mixture was then treated with acetylenedicarboxylic acid ester (ADAE) in the presence of triethylamine. 2,3-Dicarbomethoxy-1-benzoyl-6-(m,p-dimethoxybenzylidene)indeno[1,2-e]indolizine (XV) is formed as a result of 1,3-dipolar cycloaddition of ADAE to 9-(m,p-dimethoxybenzylidene)-4-azafluorenium benzoylmethylid. It was established by thin-layer chromatography (TLC) that the ylid isolated in the case of treatment of N-phenacyl-9-(m,p-dimethoxybenzylidene)-4-azafluorenium bromide with potassium carbonate is converted to indenoindolizine XV on reaction with ADAE.

Since benzopyridofulvene IX is a mixture of configurational isomers (according to the PMR spectra), XV is produced in the form of geometrical isomers. They were isolated by chromatography, and XVa was designated as the cis isomer, and XVb was designated as the trans isomer. The observed difference ($\Delta\delta$) in the chemical shifts of the protons in the γ position of the pyridine ring during an examination of the PMR spectra of isomers XVa and XVb is 0.20 ppm; this difference is due to the anisotropic effect of the aryl ring in the trans isomer.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Specord recording spectrophotometer. Chromatography was carried out on activity II aluminum oxide. The PMR spectra were recorded with a Hitachi–Perkin-Elmer R-22 spectrometer with hexamethyldisiloxane as the internal standard. The molecular weights of the compounds were measured with an MKh-1303 mass spectrometer.

3-Methyl-9-(o-methoxybenzylidene)-2-azafluorene (II). A 0.11-g (4.8 mg-atom) sample of sodium was added to a solution of 0.6 g (3.3 mmole) of azafluorene I in 20 ml of methanol, and 0.45 g (3.3 mmole) of o-anisaldehyde was added to the refluxing solution. The mixture was then maintained at room temperature for 7 days, after which 30 ml of water was added, and the liberated oily substance was chromatographed to give 0.24 g (24.3%) of isomer IIb as colorless crystals with mp 128-129°C (from heptane) and R_f 0.4 [ether–heptane (3:1)]. PMR spectrum (in CCl_4), δ: 8.53 (1H, s, 1-H), 6.65-7.77 (9H, aromatic), 3.78 (3H, s, OCH_3), and 2.49 ppm (3H, s, CH_3). IR spectrum, ν: 2840 (CH_3 in OCH_3), 1643 (C=C), 1246 (ν_{as} C–OCH_3), 1023 cm^{-1} (ν_s C–OCH_3). UV spectrum, λ_{max} (log ε): 213 (4.8); 232 (4.88); 258 (4.69); 286 (4.2); 347 nm (4.53). Found: C 84.2; H 5.9; N 4.4%; M^+ 299. $C_{21}H_{17}NO$. Calculated: C 84.3; H 5.7; N 4.7%; M 299. The picrate of IIb was obtained as yellow crystals with mp 271.5-273°C (from alcohol). Found: N 10.6%. $C_{21}H_{17}NO \cdot C_6H_3N_3O_7$. Calculated: N 10.6%.

After elution of isomer IIb, we isolated 0.07 g (7.1%) of isomer IIa as pale-yellow crystals with mp 57-60°C (from heptane) and R_f 0.33 (in the same system). PMR spectrum, δ: 8.78 (1H, s, 1-H), 6.55-7.6 (9H, aromatic), 3.72 (3H, s, OCH_3), and 2.52 ppm (3H, s, CH_3). Found: C 84.4; H 5.8; N 4.7%. $C_{21}H_{17}NO$. Calculated: C 84.3; H 5.7; N 4.7%. The picrate of IIa was obtained as red crystals with mp 246.5-247.5°C (from alcohol). Found: N 10.6%. $C_{21}H_{17}NO \cdot C_6H_3N_3O_7$. Calculated: N 10.6%.

3-Methyl-9-(m,p-dimethoxybenzylidene)-2-azafluorene (III). A solution of 1 g (5.5 mmole) of azafluorene I in 30 ml of ether was added to 10 ml of a 10% solution of potassium ethoxide, and a solution of 1.1 g (6.6 mmole) of veratraldehyde in 30 ml of ether was added to the refluxing solution. The mixture was refluxed for 1.5 h and allowed to stand at room temperature for 3 days. Water (30 ml) was added, and the mixture was extracted with ether. The extract was dried with magnesium sulfate and evaporated, and the residual viscous mass was chromatographed to give 0.64 g (35.4%) of isomer IIIb as orange crystals mp 158-159.5°C (from alcohol–hexane) and R_f 0.43 (ether). PMR spectrum (in CCl_4), δ: 8.80 (1H, s, 1-H), 6.68-7.66 (8H, aromatic), 3.77 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), and 2.46 ppm (3H, s, CH_3). IR spectrum, ν: 2844 (ν_s CH_3 in OCH_3), 1638 (C=C), 1245 (ν_{as} C–OCH_3), 1037 cm^{-1} (ν_s C–OCH_3). Found: C 80.0; H 6.0; N 4.5%; M^+ 329. $C_{21}H_{19}NO_2$. Calculated: C 80.2; H 5.8; N 4.3%; M 329.

After elution of isomer IIIb, we isolated 0.2 g (11%) of isomer IIIa as yellow crystals with mp 125-126°C (from octane–acetone) and R_f 0.30 (in the same system). PMR spectrum (in CCl_4), δ: 8.70 (1H), 6.66-7.73 (8H, aromatic), 3.79 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), and 2.52 ppm (3H, s, CH_3). Found: C 79.9; H 5.9; N 3.9%; M^+ 329. $C_{21}H_{19}NO_2$. Calculated: C 80.2; H 5.8; N 4.3%; M 329.

3-Methyl-9-(p-nitrobenzylidene)-2-azafluorene (IV) and 3-[β-Hydroxy-β-(p-nitrophenyl)ethyl]-2-azafluorenone (V). A 0.2-g (9 mg-atom) sample of sodium was added to a solution of 1 g (5.5 mmole) of azafluorene I in 35 ml of methanol, the mixture was heated to 60°C, 0.9 g (6 mmole) of p-nitrobenzaldehyde was added, and the mixture was allowed to stand at room temperature for 4 days. It was then filtered to give 0.4 g (21%) of

V as orange crystals with mp 207-208°C (from acetone) and R_f 0.58 (ether). PMR spectrum (in CF_3COOH), δ: 8.86 (1H, s, α-H), 7.42-8.45 (9H, m, aromatic), 5.53 (1H, m, CH), and 3.64 ppm (2H, d, CH_2). IR spectrum, ν: 3170 (associated OH), 1714 (CO), 1460 (CH_2), 1524 (ν_{as} NO_2), and 1344 cm^{-1} (ν_s NO_2). Found: C 69.3; H 3.8; N 8.1%; M^+ 346. $C_{20}H_{14}N_2O_4$. Calculated: C 69.3; H 4.0; N 8.1%; M 346.

After separation of V, 80 ml of water was added to the mother liquor, and the mixture was extracted with ether. The ether was removed from the extract, and the residue was chromatographed to give 0.12 g (7%) of benzopyridofulvene IV as bright-yellow crystals with mp 140-142°C (from hexane) and R_f 0.82 (ether). PMR spectrum (in $CDCl_3$), δ: 8.37 (1H, s, α-H), 7.11-8.18 (10H, m, aromatic H), signals at 8.13 (2H) and 7.41 (2H) corresponding to the AA'BB' four-spin system characteristic for p-substituted benzene, and 2.47 ppm (3H, s, CH_3). IR spectrum, ν: 1610 (C=C), 1525 (ν_{as} NO_2), and 1344 cm^{-1} (ν_s NO_2). UV spectrum, λ_{max} (log ε): 214 (4.52), 224 (4.54), 262 (4.52), 356 nm (4.16). Found: C 76.2; H 4.3; N 8.6%; M^+ 314. $C_{20}H_{14}N_2O_2$. Calculated: C 76.4; H 4.4; N 8.9%; M 314. Chromatography yielded 0.3 g of a mixture of I, IV, and V.

B) A similar method gave 0.6 g (56%) of orange crystals of V, with mp 207-208°C (from acetone) and R_f 0.58 (ether), from 0.6 g (3.1 mmole) of 3-methyl-2-azafluorenone, 0.61 g (4 mmole) of p-nitrobenzaldehyde, and 0.1 g (0.004 g-atom) of sodium in 35 ml of methanol. Found: C 69.6; H 4.2; N 8.0%. $C_{20}H_4N_2O_4$. Calculated: C 69.3; H 4.0; N 8.1%.

9-(o-Methoxybenzylidene)-4-azafluorene (VIII). A 10-ml sample of a 10% solution of potassium ethoxide was added to a solution of 1 g (6 mmole) of azafluorene VI in 50 ml of ethanol, 1 g (7.3 mmole) of o-anisaldehyde was added to the mixture at 60°C, and the resulting mixture was refluxed for 3 h. After 3 days, 100 ml of water was added, and the precipitate was dissolved in chloroform and chromatographed. The residue isolated from the eluate was crystallized from hexane. The condensation of azafluorene VI with veratraldehyde, o-allyloxybenzaldehyde, and p-nitrobenzaldehyde was carried out similarly. The characteristics of benzopyridofulvenes VIII-XI are presented in Table 2. Condensation of azafluorene VI with cinnamaldehyde gave 9-cinnamylidene-4-azafluorene (VII) with mp 114-120°C (from hexane). IR spectrum, ν: 1620 (C=C) and 964 cm^{-1} (trans-C-H). UV spectrum, λ_{max} (log ε): 210 (4.84), 240 (5.13), 250 (4.58), 281 (4.64), 307 (4.56), 316 (4.6), 374 nm (5.23). Found: C 89.3; H 5.2; N 5.3%; M^+ 281. $C_{21}H_{15}N$. Calculated: C 89.7; H 5.3; N 5.0%; M 281.

Compounds VII-XI are yellow substances.

9-(o-Hydroxy-m-allylbenzylidene)-4-azafluorene (XII). A 0.48-g (1.54 mmole) sample of benzopyridofulvene X was heated at 220-230°C for 1 h, after which the residue was dissolved in ether and chromatographed to give, successively, 0.1 g of starting X and 0.08 g (21%) of XII with mp 212-213°C (from chloroform). In the PMR spectrum the protons of the vinyl group form an ABC spin system: the two quartets at 5.30 and 5.26 ppm, which belong to the CH_2 protons of this group, and a multiplet at 6.09 ppm, which is related to CH of the same group. The character of the splitting of the latter signal constitutes evidence that the ABC system is a part of a more complex $ABCX_2$ spin system, i.e., an allyl group. PMR signals (δ): 3.58 (2H, d, α-CH_2 of an allyl group) and 7.02-851 ppm (11H, aromatic). IR spectrum, ν: 2670, 2560 (>$\overset{+}{N}$-H), and 1645 cm^{-1} (C=C). UV spectrum, λ_{max} (log ε): 216 (5.21), 219 (5.28), 309 (4.87), 332 nm (4.67). Found: N 4.5%; M^+ 311. $C_{22}H_{17}NO$. Calculated: N 4.5%; M 311.

3-Methoxy-9-(m,p-dimethoxybenzyl)-2-azafluorene (XIII). A) A 0.21 g (0.07 mole) sample of the mixture of isomers of benzopyridofulvene III, 0.74 g (6.8 mmole) of benzyl alcohol, and 0.7 g (12.5 mmole) of potassium hydroxide were mixed, and the mixture was heated to 210°C, after which it was heated at 170-190°C for 25 min. A portion of the solid residue was dissolved in 15 ml of chloroform, and the solution was passed through a layer of aluminum oxide (elution with ether) to give 0.093 g (40%) of XIII with mp 112-113°C (from octane) and R_f 0.3. PMR spectrum (CCl_4), δ: 8.11 (1H, s, 1-H), 6.47-7.56 (8H, m, aromatic), 4.06 (1H, t, 9-H), 3.46 and 3.39 (6H, two s, two CH_3 in two OCH_3), 2.91 (2H, d, CH_2), and 2.46 ppm (3H, s, CH_3). IR spectrum, ν: 2840 (ν_s CH_3 in OCH_3), 1240 (ν_{as} C-OCH_3), 1022 cm^{-1} (ν_s C-OCH_3). Found: C 79.4; H 6.5; N 4.0%; M^+ 331. $C_{21}H_{21}NO_2$. Calculated: C 79.8; H 6.3; N 4.2%; M 331. The hydrochloride of XIII was obtained as yellow crystals with mp 221-224°C (from alcohol). Benzoic acid was isolated from the chloroform-insoluble residue of the reaction mass after acidification.

B) A mixture of 1.35 g (7.5 mmole of azafluorene I, 2.7 g (16 mmole) of veratryl alcohol, 0.15 g (2.7 mmole) of potassium hydroxide, and a few crystals of veratraldehyde was heated to 185°C, after which it was heated to 225°C for 15 min. The solid residue was treated with 15 ml of chloroform, and the solution was chromatographed with a column filled with aluminum oxide to give 1.6 g (64.5%) of XIII with mp 112-113°C (from octane) and R_f 0.3.

Similar methods were used to obtain XIV, with mp 109-111°C (from octane) and R_f 0.6, in 60 and 95% yields, respectively. PMR spectrum, δ: 8.26 (1H, q, 3-H) and 7.84 ppm (1H, q, 1-H); signals that form an ABX spin system – 3.94 (1H, m, 9-H) and two quartets at 3.04 and 2.63 ppm, which belong to the protons of the CH_2 group – are present at strong field; 4.44 (2H, d, with splitting of OCH_2); singlets at 3.60 and 3.69 ppm belonging to the protons of the OCH_3 group. IR spectrum (in KBr), ν: 2840 (CH_3 in OCH_3), 1240 (ν_{as} C–OCH_3), 1030 cm^{-1} (ν_s C–OCH_3). UV spectrum, (log ε): 212 (4.52), 252 (3.9), 284 (4.0), 308 nm (4.12). Found: C 79.6; H 6.2; N 4.1%; M^+ 317. $C_{21}H_{19}NO_2$. Calculated: C 79.5; H 6,0; N 4.4%; M 317.

Isomers of 2,3-Dicarbomethoxy-1-benzoyl-6-(3,4-dimethoxybenzylidene)indene[1,2-e]indolizine (XVa and XVb). A mixture of a 0.73 g (2.3 mmole) sample of the mixture of isomers of benzopyridofulvene IX, 0.52 g (2.5 mmole) of bromoacetophenone, and 25 ml of acetonitrile was refluxed for 4 h, after which the acetonitrile was removed by distillation, and the residue was refluxed for 6 h with 0.62 g (4.3 mmole) of ADCE and 0.6 g (6 mmole) of triethylamine in 25 ml of chloroform. Water (50 ml) was added. The residue from the chloroform solutions after drying with magnesium sulfate and evaporation was chromatographed (elution with chloroform) to give 0.08 g (6%) of isomer XVb as orange crystals with mp 209-210°C (from heptane) and R_f 0.62 (chloroform). PMR spectrum (in $CDCl_3$), δ: 8.13 (1H, d, 5-H), 7.0-8.04 (14H, m, aromatic H), 3.91 (3H, s, CH_3), 3.82 (6H, s, CH_3), and 3.28 ppm (3H, s, CH_3). IR spectrum (in KBr), ν: 2840 (CH_3 in OCH_3), 1743, 1703 (CO), 1634 (C=C), 1250 (ν_{as} C–OCH_3), 1023 cm^{-1} (ν_s C–OCH_3). Found: N 2.2%; M^+ 573. $C_{35}H_{27}NO_7$. Calculated: N 2.4%; M 573. Subsequent elution gave 0.01 g (0.8%) of a mixture of isomers XVb and XVa with R_f 0.62 and 0.52. At the end of the chromatographic process we isolated 0.2 g (15.2%) of isomer XVa as yellow crystals with mp 218-221°C [from heptane–chloroform (2:1)] and R_f 0.52 (chloroform). PMR spectrum (in $CDCl_3$), δ: 8.33 (1H, d, 5-H), 6.8-8.0 (14H, m, aromatic), 3.90 (3H, s, CH_3), 3.82 (3H, s, CH_3), 3.79 (3H, s, CH_3), and 3.26 ppm (3H, s, CH_3). IR spectrum (in KBr), ν: 2840 (CH_3 in OCH_3), 1740, 1700 (CO), 1630 cm^{-1} (C=C). Found: C 73.0; H 4.4; N 2.5%; M^+ 573. $C_{35}H_{27}NO_7$. Calculated: C 73.3; H 4.7; N 2.4%; M 573.

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