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Synthesis of 5-Aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines

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Abstract — Previously unknown derivatives of tetrahydro[*a*]phenanthridine containing annelated benzoquinoline and cyclohexene nuclei were prepared by condensation of azomethines of the 2-naphthylamine series with cyclohexanone. The possibility of synthesis of such compounds without preliminarily preparing Schiff bases was demonstrated. The effect of substituents in the aromatic ring of the azomethine on the yield of the target products was elucidated. The IR, UV, ^{1}H NMR, and mass spectra of the synthesized compounds were discussed.

Quinoline derivatives, while being a well-documented class of compounds, are attracting ever increasing attention. This is explained by the preparation on the basis of natural and synthetic quinoline bases of antitumor [1, 2] and antomicrobial agents [3, 4]. Moreover, these compounds are structural analogs of alkaloids [5], enzyme inhibitors [6], and antibiotics [7, 8].

Of particular interest among quinoline bases are derivatives of 5,6-benzoquinoline whose nucleus is a structural unit of lysergic acid and its physiologically active analogs [9, 10]. The presence of alternating benzene rings and heterorings makes possible varying physicochemical properties of the molecule, thus varying its physiological activity.

The aim of the present work was to develop synthetic procedures for 5-aryl-1,2,3,4-tetrahydrobenzo-[*a*]phenanthridines incorporating both benzoquinoline and cyclohexene nuclei.

As shown in [11], phenylmethylene-2-naphthylamine and its derivatives react with cyclohexanone, yielding 5,6-benzoquinoline derivatives. The condensation was performed in the presence of nitrobenzene under pressure (in ampule) at 140–145°C. The reaction under mild conditions (without heating, in the presence of a small amount of catalyst) gave a mixture of the corresponding β-arylaminoketone [(aryl)(2-naphthylamino)methyl]cyclohexanone, and a cyclization product, a hydroxy derivative of tetrahydrobenzoquinoline, 2-aryl-3,4-(1,2-cyclohexahexanediyl)-4-hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline. β-Arylaminoketones are also considered as intermediate products in the Baeyer synthesis of quinoline bases [12].

In the present work we accomplished a selective synthesis of 5-aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine by reaction of azomethines of the 2-naphthylamine series with cyclohexanone or by reaction of 2-naphthylamine, an aldehyde, and cyclohexanone. Azomethines **IVa**–**IVu** were prepared by reactions of 2-naphthylamine (**I**) with benzaldehydes **IIIa**–**IIIu** in alcoholic solution under heating for 10–20 min. The yields, melting points, and elemental analyses of the products are listed in Table 1.

The IR spectra of azomethines **IVa**–**IVu** display a characteristic band of N=CH stretching vibrations in the range 1632–1605 cm^{-1}. The spectra of **IVe, IVj**, and **IVn** show strong bands at 1535 and 1370 cm^{-1} [$\nu(NO_2)$], and the spectra of **IVh, IVq**, and **IVs**, a broad band of hydroxyl stretching vibrations at 3450–3430 cm^{-1}. Stretching vibrations of the C–F bond in **IVb** appear at 1150 cm^{-1}, of the C–Br bond in **IVd, IVm**, and **IVs**, at 670–520 cm^{-1} (a medium band), and of the C–Cl bond in **IVc**, at 830 cm^{-1}.

Compounds **IVa**–**IVu** are fairly stable to electron impact. The base peak in the mass spectra of most azomethines is a molecular ion peak (M^+). The most important fragmentation pathways of the molecular ion involve generation of an $[M - 1]^+$ ion and of $[M - HCN]^+$ or $[(M - 1) - HCN]^+$ ions (weak peaks).

Tetrahydrobenzo[*a*]phenanthridines **VI** were synthesized refluxing a solution of an azomethine and cyclohexanone (1:3) in ethanol for 1–6 h in the presence of catalytic amounts of HCl. In the absence of catalyst the reaction almost fails: Either the starting materials are recovered or strong tarring of the reaction mixture occurs. Sometimes the reaction was performed without preliminarily preparing azomethines. In these cases, equimolar amounts of 2-naphthylamine and a substituted benzaldehyde **IIIv**–**III**α was ref-

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Table 1. Yields, melting points, and elemntal analyses of arylmethylene-2-naphthylamine **IVa**–**IVu**

Comp.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N (Hlg)		C	H	N (Hlg)
IVa	95	97	88.34	5.60	6.08	$C_{17}H_{13}N$	88.31	5.63	6.06
IVb	90	110	–	–	5.65	$C_{17}H_{12}FN$	81.92	4.82	5.62 (7.63)
IVc	90	119	76.99	4.52	5.26 (13.24)	$C_{17}H_{12}ClN$	76.98	4.52	5.28 (13.22)
IVd	90	128	65.76	3.89	4.50 (25.81)	$C_{17}H_{12}BrN$	65.80	3.87	4.52 (25.81)
IVe	90	122	73.88	4.37	10.15	$C_{17}H_{12}N_2O_2$	73.91	4.35	10.14
IVf	84	79–80	88.00	6.59	5.40	$C_{19}H_{17}N$	88.03	6.56	5.41
IVg	80	99–100	83.08	5.73	5.37	$C_{18}H_{15}NO$	83.08	5.75	5.36
IVh	70	228–230	82.61	5.23	5.64	$C_{17}H_{13}NO$	82.59	5.26	5.67
IVi	65	145	85.43	5.66	4.17	$C_{24}H_{19}NO$	85.45	5.64	4.15
IVj	60	94	73.89	4.38	10.11	$C_{17}H_{12}N_2O_2$	73.91	4.35	10.14
IVk	57	87–88	88.13	6.10	5.70	$C_{18}H_{15}N$	88.16	6.12	5.72
IVl	50	60	83.04	5.76	5.38	$C_{18}H_{15}NO$	83.08	5.75	5.36
IVm	53	102–103	65.83	3.89	4.54 (25.80)	$C_{17}H_{12}BrN$	65.80	3.87	4.52 (25.81)
IVn	60	100	73.89	4.37	10.16	$C_{17}H_{12}N_2O_2$	73.91	4.35	10.14
IVo	40	59	85.48	5.28	4.31	$C_{23}H_{17}NO$	85.45	5.26	4.33
IVp	40	131–132	78.31	5.82	4.79	$C_{19}H_{17}NO_2$	78.35	5.84	4.81
IVq	40	182	77.52	4.90	5.35	$C_{17}H_{13}NO_2$	77.57	4.94	5.32
IVr	45	172	77.59	4.92	5.30	$C_{17}H_{13}NO_2$	77.57	4.94	5.32
IVs	38	162	62.60	3.67	4.27 (24.55)	$C_{17}H_{12}BrNO$	62.58	3.68	4.29 (24.53)
IVt	35	108–109	81.54	5.99	3.79	$C_{25}H_{22}NO_2$	81.52	5.98	3.80
IVu	45	122	78.52	4.74	5.11	$C_{18}H_{13}NO_2$	78.54	4.72	5.09

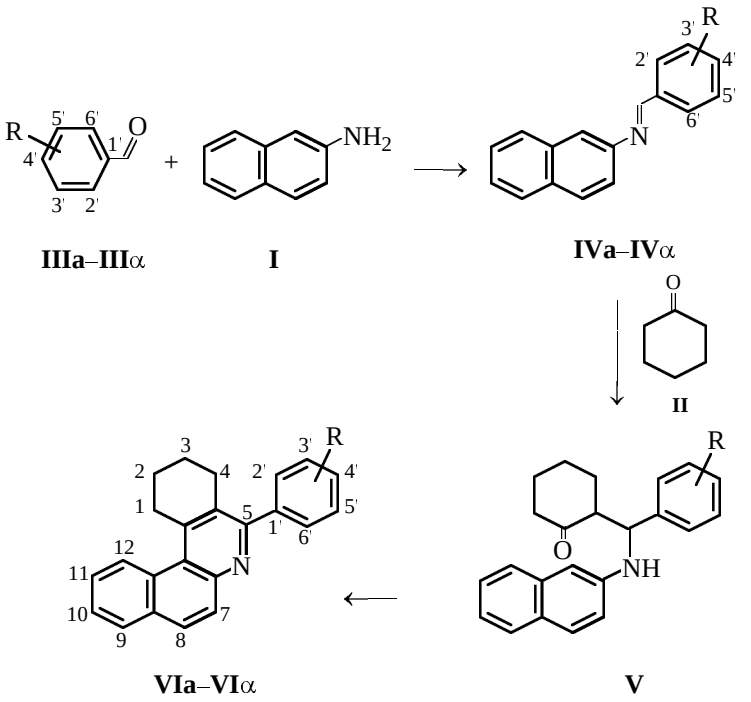
luxed in ethanol solution for 1–2 h, and, after cooling, not isolating the resulting Schiff base (most commonly, a viscous liquid), a triple excess of cyclohexanone (with respect to the Schiff base) and a catalytic amount of HCl were added. Refluxing was continued for an additional 1.5–6 h. The reaction products were mostly isolated as crystals.

Based on published data [11–13], we suggest intermediate formation of arylaminoketones and tetrahydrobenzoquinolines. However, arylaminoketone could be isolated only in the case of 5-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (**VIo**). 2-[(4,5-Dimethoxyphenyl)(2-naphthylamino)-methyl]cyclohexanone (**V**) (mp 197°C) formed after 10-min refluxing in ethanol of (3,4-dimethoxyphenyl)-methylene-2-naphthylamine (**IVo**) and a triple excess of cyclohexanone in the presence of a catalytic amount of HCl. The IR spectrum revealed in the product a secondary amino group (3240 cm^{-1}) and a CO group (1574 cm^{-1}). The reduced intensities of the amino and carbonyl absorption bands are apparently explained by intramolecular H bonding, which agrees with published data [14]. Moreover, 2-[(4,5-dimethoxyphenyl)(2-naphthylamino)methyl]cyclohexanone (**V**) is readily available for hydramine cleavage under the action of HCl to give 2-naphthylamine and 2-(3,4-dimethoxyphenylmetylene)cyclohexanone, whereas tetrahydrobenzo[*a*]phenanthridines are stable and undergo no chemical transformations upon prolonged refluxing in HCl.

The reaction occurs by Scheme 1.

The reaction is made possible by the mobility of the hydrogen atom α to the carbonyl group of cyclohexanone. In the presence of acid catalyst, the nucleophilic substitution of cyclohexanone occurs in such a way that its mobile hydrogen atom adds at the nitrogen atom and the rest molecule, at the carbon atom of the azomethine bond, resulting in arylaminoketone formation. The arylaminoketone undergoes cyclization followed by dehydration to give the final product, 5-aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine **VIa**–**VI**α. As the catalyst we used concentrated hydrochloric acid whose role is to activate the ketone molecule and to polarize the azomethine bond. The electronic nature of substituents in the azomethine molecule has a considerable effect on the polarization and activity of the azomethine bond. Acceptor substituents in the *para* position of the aldehyde part of the azomethine, via π conjugation of the benzene ring and the azomethine bond increase the positive charge

Scheme 1.



IIIa–**III**α **I** **IVa**–**IV**α

II

VIa–**VI**α **V**

R = H (**IIIa, IVa, VIa**), 4'-F (**IIIb, IVb, VIb**), 4'-Cl (**IIIc, IVc, VIc**), 4'-Br (**IIId, IVd, VId**), 4'-NO_2 (**IIIe, IVe, VIe**), 4'-CH_2CH_3 (**IIIf, IVf, VIf**), 4'-OCH_3 (**IIIg, IVg, VIg**), 4'-OH (**IIIh, IVh, VIh**), 4'-$OCH_2C_6H_5$ (**IIIi, IVi, VIi**), 2'-NO_2 (**IIIj, IVj, VIj**), 2'-CH_3 (**IIIk, IVk, VIk**), 2'-OCH_3 (**IIIl, IVl, VIl**), 3'-Br (**IIIm, IVm, VIm**), 3'-NO_2 (**IIIn, IVn, VIn**), 3'-OC_6H_5 (**IIIo, IVo, VIo**), 3',4'-di-OCH_3 (**IIIp, IVp, V, VIp**), 2',4'-di-OH (**IIIq, IVq, VIq**), 3',4'-di-OH (**IIIr, IVr, VIr**), 5'-Br-2'-OH (**IIIs, IVs, VIs**), 4'-$OCH_2C_6H_5$-3'-OCH_3 (**IIIt, IVt, VIt**), 3',4'-OCH_2O (**IIIu, IVu, VIu**), 2'-CF_3 (**IIIv, IVv, VIv**), 3'-OH (**IIIw, IVw, VIw**), 2',3'-di-OCH_3 (**IIIx, IVx, VIx**), 2',5'-di-OCH_3 (**IIIy, IVy, VIy**), 4'-OH-3'-OCH_2CH_3 (**IIIz, IVz, VIz**), 3'-$OCH_2C_6H_5$-4'-OH (**III**α**, IV**α**, VI**α).

on the azomethine carbon atom and facilitates addition of the anion of cyclohexanone. Here, therefore, the yield is markedly higher than with electron-donor substituents.

It can be proposed that *ortho*-substituents produce a steric effect on the reaction center of the azomethine group. An *ortho*-nitro substituent sightly reduces the yield of the target product, regardless of the fact that the electronic effect of this group favors the reaction. A stronger steric effect is observed in *o*-methyl (**IVk**), *o*-methoxy (**IVl**), and *o*-trifluoromethyl (**IVv**) derivatives of phenylmethylene-2-naphthylamines.

Disubstituted azomethines require more severe conditions to convert into a phenanthridine derivative. Thus, the reactions with 5-bromo-2-hydroxy- and 2,5-dimethoxy-substituted azomethines **IVs, IVy** were performed for 6 h at increased concentration of the catalyst. The yields of the target products were no higher than 13%.

Tetrahydrobenzo[*a*]phenanthridines **VIa**–**VI**α are high-melting white or light yellow crystals. Their physicochemical characteristics are listed in Table 2. Compounds **VIc**–**VIe**, and **VIn** have been described in [11].

The absence in the IR spectra of compounds **VIa**–**VIf** (Table 3) of bands in the range 1725–1650 cm^{-1}, characteristic of carbonyl stretching vibrations, as well as of bands in the range 3400–3300 cm^{-1}, characteristic of amino group, suggests that one deals here with a cyclic tertiary amine. Methylene groups of the cyclohexene ring give two bands at 2920–2880 cm^{-1}, and the bands of stretching vibrations of aromatic CH bonds are at 3065–3050 cm^{-1}. A strong band in the region of 2860 cm^{-1} (OCH_3) is present in the spectra of **VIg, VIl, VIo, VIt, VIx**, and **VIy**. Compounds **VIe, VIj**, and **VIn** give bands at 1365 and 1530 cm^{-1}, related respectively to symmetric and antisymmetric vibrations of the N–O bond.

The UV spectra of tetrahydrobenzo[*a*]phenanthridines **VIa**–**VI**α (Table 4) are typical of azophenan-

Table 2. Yields, melting points, and elemental analyses of 5-aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines **VIa**–**VI**α

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N (Hlg)		C	H	N (Hlg)
VIa	80	122–124	89.31	6.17	4.52	$C_{23}H_{19}N$	89.32	6.15	4.53
VIb	85	258–260	–	–	4.30	$C_{23}H_{18}FN$	84.40	5.50	4.28
VIc	80	200–202	80.45	5.22	4.06 (10.20)	$C_{23}H_{18}ClN$	80.47	5.25	4.05 (10.23)
VId	80	220	71.13	4.61	3.62 (20.58)	$C_{23}H_{18}BrN$	71.13	4.65	3.60 (20.62)
VIe	74	240–242	77.95	5.13	7.88	$C_{23}H_{18}N_2O_2$	77.97	5.08	7.91
VIf	55	198–199	89.00	6.84	4.13	$C_{25}H_{23}N$	89.02	6.83	4.15
VIg	42	182–183	84.93	6.20	4.17	$C_{24}H_{21}NO$	84.96	6.19	4.13
VIh	40	292–294	84.90	5.87	4.29	$C_{23}H_{19}NO$	84.92	5.85	4.31
VIi	35	149–150	86.73	6.00	3.40	$C_{30}H_{25}NO$	86.75	6.02	3.37
VIj	66	238–239	78.00	5.04	7.90	$C_{23}H_{18}N_2O_2$	77.97	5.08	7.91
VIk	46	175–176	89.13	6.50	4.33	$C_{24}H_{21}N$	89.16	6.50	4.34
VIl	44	224–226	84.96	6.20	4.15	$C_{24}H_{21}NO$	84.96	6.19	4.13
VIm	63	248–250	71.10	4.61	3.63 (20.59)	$C_{23}H_{18}BrN$	71.13	4.65	3.60 (20.62)
VIn	74	226–230	77.98	5.06	7.95	$C_{23}H_{18}N_2O_2$	77.97	5.08	7.91
VIo	40	254	79.27	5.72	3.51	$C_{29}H_{23}NO$	79.30	5.74	3.50
VIp	50	214–216	82.33	6.21	3.78	$C_{25}H_{23}NO_2$	82.30	6.23	3.80
VIq	20	224	80.90	5.56	4.11	$C_{23}H_{19}NO_2$	80.94	5.57	4.11
VIr	46	294–296	80.92	5.55	4.13	$C_{23}H_{19}NO_2$	80.94	5.57	4.11
VIs	13	271	68.28	4.47	3.48	$C_{23}H_{18}BrNO$	68.31	4.45	3.46
VIt	18	192–193	83.57	6.04	3.20	$C_{31}H_{27}NO_2$	83.60	6.07	3.15
VIu	20	251–252	81.57	5.35	3.94	$C_{24}H_{19}NO_2$	81.59	5.38	3.97
VIv	45	101–102	–	–	3.70	$C_{24}H_{18}F_3N$	76.39	4.77	3.71
VIw	50	268	84.90	5.87	4.28	$C_{23}H_{19}NO$	84.92	5.85	4.31
VIx	20	157	82.32	6.25	3.76	$C_{25}H_{23}NO_2$	82.30	6.23	3.80
VIy	10	145	82.31	6.23	3.80	$C_{25}H_{23}NO_2$	82.30	6.23	3.80
VIz	54	237–238	82.29	6.20	3.80	$C_{25}H_{23}NO_2$	82.30	6.23	3.80
VIα	50	260–261	83.54	5.82	3.23	$C_{30}H_{25}NO_2$	83.52	5.80	3.25

threne structures. The condensation of the benzoquinoline nucleus with an alicycle produces a bathochromic shift of absorption maxima and increase in their intensity compared with unsubstituted benzoquinoline, which has also been noted in [15].

The long-wave band has vibrational structure. When there is an electron-acceptor substituent in the *para* position of the benzene ring (compounds **VIc**–**VIe**), the long-wave maxima smoothen and suffer a bathochromic shift, except for compound **VIb**, the fluorine substituent in which produces a hypsochromic shift [16].

EXERIMENTAL

The IR spectra were measured on a UR-20 spectrophotometer in KBr. The ^{1}H NMR spectra were obtained on Bruker AC-300 (300 MHz) or Tesla BS-567 (100 MHz) for 2–5% solutions in DMSO-d_6, internal reference TMS. The mass spectra were recorded on an MX-1320 instrument. The UV spectra were taken on a Specord UV-Vis spectrophotometer for 1×10^{-4} M ethanol solutions.

5-Aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines VIa–VIα**.** Method I (for **VIa**–**VIu**). *a*. Aldehyde **IIIa**–**IIIu**, 0.1 mol, and 0.1 mol of 2-naphthylamine (**I**) in 50 ml of benzene was heated under reflux with a Dean–Stark trap for 1–2 h. The solvent was then removed by distillation, and the residue was recrystallized from ethanol to obtain arylmethylene-2-naphthylamine **IVa**–**IVu** (Table 1).

b. Cyclohexanone (**II**), 0.03 mol, and 5–6 drops of conc. HCl acid were added to a solution of 0.01 mol of Schiff base **IVa**–**IVu** in 50 ml of ethanol, and the mixture was heated under reflux for 1–6 h, depending on substitution pattern in the benzene ring of arylmethylene-2-naphthylamine. The crystals that formed

Table 3. ^{1}H NMR and mass spectra of 5-aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines **VIa**–**VI**α

Comp. no.	^{1}H NMR spectrum, δ, ppm (*J*, Hz)				Mass spectrum, *m*/*z* (I_{rel}, %)
	C^1–H^2	4H (C^2–H^2, C^3–H^2)	C^4–H^2	aromatic protons and protons in R	
VIa	3.60 m	1.80 m	2.85 m	7.59–8.20 m, 8.60–8.80 m	309 (100), 233 (52), 232 (20)
VIb	3.65 m	1.85 m	2.90 m	7.39–7.50 m, 7.65–7.83 m, 7.87 s, 8.02–8.21 m, 8.82–8.90 m	328 (20), 327 (92), 326 (100), 298 (10), 251 (21), 109 (23)
VIc[a]	3.80 m	1.78 m	2.78 m	7.01 d (8.0), 7.30 d (7.0), 7.56 m, 7.60–7.79 m, 7.85 m, 7.98–8.20 m, 8.78–8.92 m	344 (10), 343 (80), 342 (100), 232 (15), 111 (10)
VId	3.59 m	1.81 m	2.82 m	7.45–7.58 m, 7.64–7.80 m, 7.90–8.12 m, 8.23–8.90 m	389 (15), 388 (95), 387 (100), 232 (13), 156 (20)
VIe[a]	3.52 m	1.82 m	2.82 m	7.68–7.89 m, 7.99–8.11 m, 8.30–8.50 m, 8.80–8.85 m	354 (100), 308 (43), 277 (30)
VIf[a]	3.80 m	1.90 m	2.50 m	7.48 d (5.8), 7.52 d (6.0), 7.81–7.89 m, 8.00–8.20 m, 8.55–8.80 m, 9.40 d (6.2), 1.35 m (3H, CH_2CH_3), 2.55 q (2H, CH_2CH_3)	337 (100), 322 (80), 308 (30), 260 (20)
VIg	3.58 m	1.79 m	2.82 m	7.00 m, 7.08 m, 7.45 m, 7.54 m, 7.60–7.80 m, 7.85 m, 7.92–8.12 m, 8.70–8.89 m, 3.82 s (3H, OCH_3)	340 (52), 339 (100), 308 (70), 262 (25)
VIh[a]	3.52 m	1.75 m	2.85 m	6.88–6.94 m, 7.77–7.43 m, 7.63–7.70 m, 7.81 d (7.3), 7.60 d (8.0), 8.00–8.08 m, 9.50 s (1H, OH)	326 (15), 325 (63), 324 (100), 308 (15), 248 (20), 155 (12), 139 (28)
VIi	3.60 m	1.70 m	3.10 m	6.90–7.20 m, 7.30–7.60 m, 7.63–7.80 m, 7.83–8.10 m, 8.70–8.90 m, 5.19 s (2H, OCH_2)	416 (20), 415 (80), 337 (40), 338 (100), 322 (50), 308 (42)
VIj	3.60 m	1.70 m	2.70 m	7.55–8.28 m, 8.70–8.92 m	354 (100), 308 (50), 276 (37)
VIk	3.60 m	1.80 m	3.16 m	7.20–7.40 m, 7.60–7.80 m, 7.85 m, 7.92–8.15 m, 8.75–8.93 m, 2.00 s (3H, CH_3)	324 (30), 323 (100), 308 (25)
VIl	3.55 m	1.75 m	3.10 m	7.10–7.40 m, 7.50–7.90 m, 8.70–8.90 m, 3.80 s (3H, OCH_3)	340 (25), 339 (100), 338 (92), 308 (75), 234 (33), 152 (34), 139 (50), 40 (35), 36 (62)
VIm	3.60 m	1.60 m	2.80 m	7.42–7.80 m, 7.85–7.90 m, 7.97–8.12 m, 8.72–8.90 m	389 (20), 388 (90), 387 (100), 232 (10), 156 (15)
VIn	3.65 m	1.75 m	2.80 m	7.62–7.95 m, 8.00–8.19 m, 8.25–8.49 m, 8.70–8.90 m	355 (20), 354 (100), 308 (30), 276 (25)
VIo	3.55 m	1.80 m	2.80 m	7.00–8.05 m, 8.70–8.90 m	402 (70), 401 (100), 324 (20), 308 (15)
VIp[a]	3.59 m	1.83 m	2.89 m	7.02–7.13 m, 7.15 s, 7.62–7.75 m, 7.85 d (9.2), 8.00 d (9.0), 8.05–8.12 m, 8.82 d (7.3), 3.8 s (3H, OCH_3), 3.88 s (3H, OCH_3)	369 (100), 354 (30), 339 (45), 307 (20), 292 (13)
VIq	3.50 m	1.60 m	2.85 m	6.80–7.00 m, 7.60–8.10 m, 8.70–8.85 m, 9.06 br.s (2OH)	341 (60), 340 (100), 307 (13), 264 (18), 139 (13)
VIr	3.55 m	1.75 m	2.80 m	6.90–7.55 m, 7.80–8.12 m, 8.8 m, 9.05 br.s (2OH)	341 (66), 340 (100), 307 (13), 264 (18), 139 (20)
VIs	3.40 m	1.80 m	2.72 m	6.90–7.05 m, 7.30–7.50 m, 7.60–7.80 m, 7.82–7.90 m, 7.95–8.15 m, 8.72–8.90 m, 10.01 br.s (1H, OH)	405 (20), 404 (95), 405 (100), 387 (10), 324 (15), 307 (30), 80 (25)
VIt	3.60 m	1.85 m	2.88 m	6.88 s, 7.10 s, 7.20–7.70 m, 7.84–7.95 m, 8.70–8.84 m, 5.22 s (2H, OCH_2), 3.93 s (3H, OCH_3)	446 (80), 445 (100), 430 (27), 414 (18), 369 (53), 338 (32)
VIu	3.59 m	1.80 m	2.85 m	7.10 s, 7.15 d (7.4), 7.70–7.82 m, 7.90 s, 8.00–8.20 m 8.80–8.99 m, 6.20 s (2H, OCH_2O)	353 (10), 352 (15), 272 (50), 143 (12), 135 (100), 77 (10)

Table 3. (Contd.)

Comp. no.	^{1}H NMR spectrum, δ, ppm (*J*, Hz)				Mass spectrum, *m*/*z* (I_{rel}, %)
	C^1–H^2	4H (C^2–H^2, C^3–H^2)	C^4–H^2	aromatic protons and protons in R	
VIv[a]	3.60 m	1.80 m	2.50 m	7.50 d (7.3), 7.62–7.80 m, 7.88 d (9.0), 7.94–8.15 m 8.73–8.92 m	378 (10), 377 (100), 376 (80), 308 (20), 232 (30), 145 (40)
VIw	3.55 m	1.79 m	2.80 m	6.80–7.00 m, 7.20–7.40 m, 7.60–7.90 m, 7.93–8.19 m, 8.70–8.84 m, 9.60 s (1H, OH)	326 (10), 325 (80), 324 (100), 308 (20), 248 (18), 155 (9), 139 (30)
VIx[a]	3.53 m	1.90 m	2.50–2.60 m, 2.85–3.00 m	6.61 d (7.5), 6.90 d (9.6), 7.30 d (9.0), 7.53–7.60 m, 7.80–8.01 m, 8.80–8.90 m, 3.52 s (3H, OCH_3), 3.90 s (3H, OCH_3)	369 (100), 354 (25), 339 (40), 292 (30)
VIy[a]	3.60 m	1.80 m	2.50–2.80 m 2.84–2.95 m	6.75 d (7.5), 6.83–7.00 m, 7.52–7.60 m, 7.75 d (6.6), 7.84 d (7.0), 7.85–8.00 m, 8.73–8.77 m, 3.62 s (3H, OCH_3), 3.75 s (3H, OCH_3)	326 (30), 325 (85), 324 (100), 308 (15), 248 (20), 155 (15), 139 (40)
VIz	3.56 m	1.70 m	2.90 m CH_3),	7.0 s, 7.20 d (8.3), 7.60–7.85 m, 7.90–8.22 m, 8.70–8.90 m, 1.33 m (3H, OCH_2CH_3), 4.09 q (2H, OCH_2 · 9.60 s (1H, OH)	369 (100), 352 (70), 334 (20), 317 (15)
VIα	3.50 m	1.75 m	2.50 m	6.88–7.70 m, 7.90–8.20 m, 8.80–8.90 m, 9.20 (1H, OH), 5.19 s (2H, OCH_2)	431 (100), 414 (20), 337 (15), 324 (10), 308 (25)

[a] The ^{1}H NMR spectra were obtained on a Bruker AC-300 spectrometer (300 MHz).

Table 4. UV spectra 5-aryl-1,2,3,4-tetrahydrobenzo[*a*]phenanthridines (**VIa**–**e**)

Comp. no.	λ_{max}, nm (log ε)
VIa	203 (4.58), 215 (4.60), 258 (4.68), 275 (4.51), 292 (4.12), 318 (3.50), 336 (3.67), 352 (3.98)
VIb	210 (4.58), 248 (4.70), 272 (4.58), 290 (4.29), 308 (3.00), 329 (3.06), 341 (3.10)
VIc	203 (4.57), 213 (4.61), 250 (4.72), 274 (4.64), 290 (4.32), 326 (3.46), 349 (3.71), 357 (3.80)
VId	205 (4.59), 216 (4.63), 253 (4.80), 348 (3.74), 359 (4.00)
VIe	207 (4.54), 215 (4.60), 250 (4.70), 277 (4.62), 289 (4.30), 349 (3.68), 360 (4.02)
VIf	206 (4.51), 217 (4.58), 248 (4.73), 275 (4.65), 292 (4.31), 320 (3.40), 340 (3.70), 354 (3.90)
VIg	263 (4.64), 278 (4.49), 340 (3.70), 358 (3.73)
VIh	215 (4.34), 252 (4.60), 272 (4.52), 294 (4.30), 318 (3.50), 346 (3.65), 352 (3.71)
VIi	213 (4.30), 256 (4.62), 273 (4.50), 296 (4.27), 315 (3.38), 348 (3.50), 356 (3.82)
VIj	208 (4.52), 214 (4.59), 253 (4.68), 275 (4.60), 287 (4.33), 313 (3.40), 330 (3.80), 348 (4.00)
VIk	206 (4.48), 212 (4.50), 250 (4.60), 271 (4.62), 290 (4.32), 312 (3.37), 340 (3.75), 352 (3.90)
VIl	213 (4.34), 253 (4.63), 276 (4.64), 289 (4.25), 311 (3.50), 336 (3.70), 354 (3.80)
VIm	206 (4.52), 215 (4.60), 252 (4.78), 274 (4.60), 295 (4.32), 346 (3.70), 357 (4.00)
VIn	207 (4.50), 214 (4.57), 252 (4.65), 275 (4.60), 287 (4.33), 312 (3.39), 330 (3.68), 346 (3.94)
VIo	203 (4.56), 215 (4.58), 253 (4.64), 274 (4.00), 290 (4.28), 310 (3.42), 328 (3.67), 350 (3.92)
VIp	203 (4.61), 218 (4.61), 254 (4.70), 323 (3.52), 338 (3.73), 352 (3.78)
VIq	211 (4.30), 252 (4.59), 272 (4.52), 293 (4.28), 319 (3.50), 346 (3.68), 352 (3.70)
VIr	210 (4.30), 252 (4.57), 272 (4.51), 291 (4.27), 317 (3.50), 345 (3.64), 350 (3.68)
VIs	213 (4.20), 260 (4.55), 274 (4.50), 295 (4.20), 319 (3.43), 347 (3.52), 354 (3.70)

Table 4. (Contd.)

Comp. no.	λ_{max}, nm (log ε)
VIt	212 (4.10), 256 (4.34), 270 (4.28), 349 (3.30), 356 (3.80)
VIu	206 (4.30), 217 (4.08), 252 (4.28), 272 (4.00), 294 (4.15), 315 (3.70), 330 (3.27), 355 (3.50)
VIv	208 (4.28), 214 (4.34), 256 (4.58), 270 (4.10), 291 (4.10), 313 (3.49), 337 (3.42), 354 (3.60)
VIw	216 (4.28), 250 (4.62), 270 (4.50), 296 (4.00), 315 (3.51), 348 (3.60), 353 (3.70)
VIx	205 (4.60), 217 (4.58), 253 (4.64), 294 (4.10), 320 (3.40), 330 (3.70), 350 (3.80)
VIy	206 (4.58), 215 (4.53), 254 (4.60), 293 (4.00), 322 (3.43), 332 (3.70), 350 (3.78)
VIz	213 (4.30), 255 (4.40), 290 (4.20), 319 (3.50), 346 (3.20), 352 (3.70)
VIα	210 (4.40), 262 (4.57), 276 (4.53), 290 (4.26), 315 (3.60), 347 (3.50), 354 (3.72)

were separated, washed with 25% ammonia, dried, and recrystallized from ethanol.

Method II (for **VIv**–**VIα**). Aldehyde **IIIv**–**IIIα** and 0.01 mol of 2-naphthylamine (**I**) in 50 ml ethanol were heated on a water bath at 90°C for 1–2 h. After cooling, 0.03 mol of cyclohexanone **II** and 5–6 drops of HCl were added, and heating was continued for an additional 1.5–2 h. The precipitate that formed was separated, washed with 25% ammonia, dried, and recrystallized from ethanol.

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