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Pyran Derivatives *peri*-Fused to Acenaphthene and Acenaphthylene

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Abstract—*peri*-Acyloxyacenaphthenyl bromomethyl ketones prepared by bromination of *peri*-acyloxyacenaphthenyl methyl ketones reacted with sodium methoxide to give 2-acyl-3-hydroxyacenaphtho[5,6-*bc*]pyran derivatives, while their reaction with piperidine afforded acenaphtho[5,6-*bc*]pyran-3-on. Heating of the latter in acetic anhydride produced 3-acetoxyacenaphtho[5,6-*bc*]pyran which was subjected to dehydrogenation to obtain a new heteroaromatic system.

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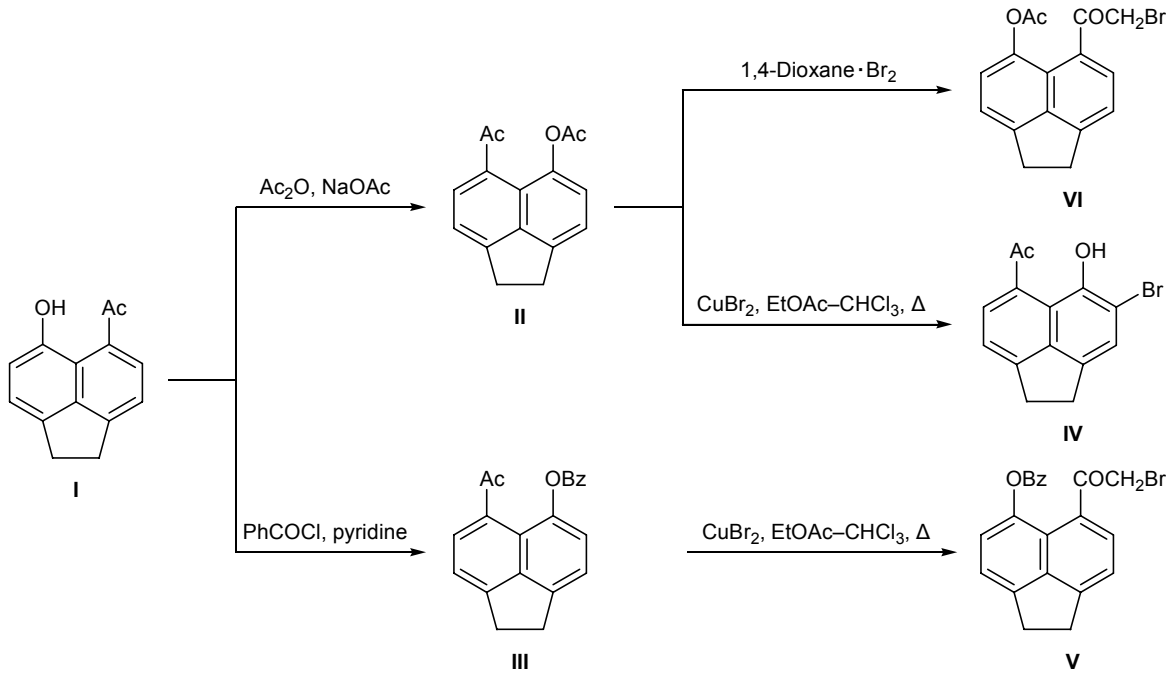
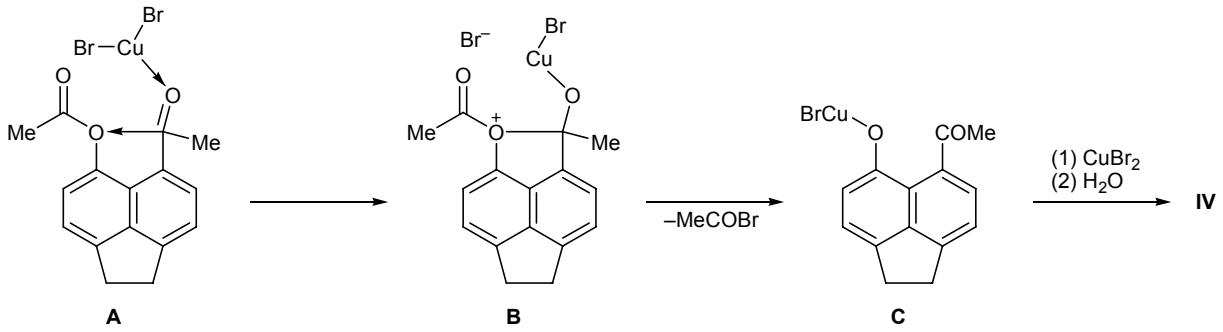
Compounds possessing pronounced antibacterial properties comparable with those of strong antibiotics were found among *peri*-fused pyran derivatives [1, 2]. *peri*-Fused bis-pyran systems like 1,6- and 1,8-dioxapyrenes exhibited unusual photobiological and genotoxic activity [3, 4], readily formed charge-transfer complexes [5], and were used as building blocks for the synthesis of so-called organic metals [6]. We previously synthesized 2-acylnaphtho[1,8-*bc*]pyran-3-ones and coordination compounds based thereon, which showed strong yellow–orange fluorescence and were proposed as effective chemosensors and highly sensitive analytical reagents for qualitative and quantitative determination of heavy metals [7]. Naphtho[1,8-*bc*]-pyran-3-ones were obtained by bromination of *peri*-acyloxynaphthyl alkyl ketones at the side alkyl chain

Scheme 1.



Scheme 2.



with subsequent base-catalyzed heterocyclization of α-bromoalkyl ketones thus formed [8].

In the present work we followed the same approach to synthesize a series of pyran derivatives in which the pyran ring is *peri*-fused to acenaphthene and acenaphthylene ring systems. As starting compound we used 1-(6-hydroxyacenaphthen-5-yl)ethanone (**I**) [9], which was converted into esters **II** and **III** by conventional methods (Scheme 1).

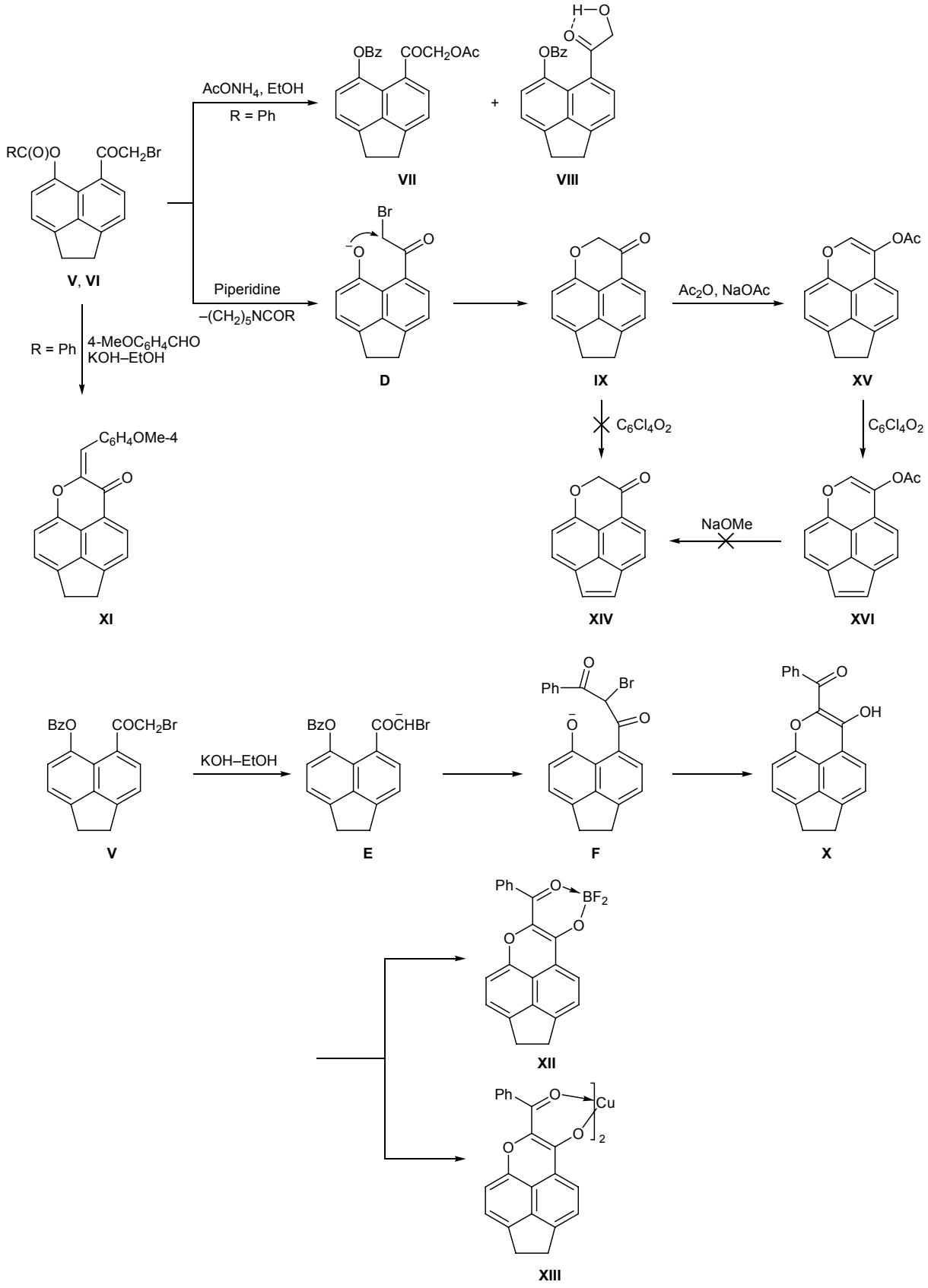
We found that *peri*-acetoxy- and *peri*-benzoyloxy-substituted acenaphthenyl methyl ketones differently reacted with such brominating agent as copper(II) bromide. The reaction of acetate **II** with $CuBr_2$ in ethyl acetate–chloroform involved cleavage of the ester group and bromination at the aromatic ring (**II** → **IV**), whereas benzoate **III** reacted with conservation of the ester group, and bromination involved the side chain (**III** → **V**). Presumably, bromination at the aromatic ring is preceded by attack by copper(II) bromide at the ketone carbonyl oxygen atom, and the next steps are elimination of acetyl bromide and intramolecular rearrangement (**A** → **B** → **C**; Scheme 2). Analogous reaction path in the case of benzoyloxy derivative **III** is likely to be hindered by reduced electrophilicity of the benzoyl group.

The presence of a bromine atom in the *ortho* position with respect to the hydroxy group induced a downfield shift of the hydroxy proton signal in the ^{1}H NMR spectrum of compound **IV** (δ 12.60 ppm) as compared to hydroxy ketone **I** (δ 11.60 ppm) [10]. These findings suggest stronger intramolecular hydrogen bond in **IV** due to effect of bulky *ortho*-substituent on the hydroxy group. The IR spectra of *peri*-hydroxy ketones **I** and **IV** in the condensed phase are characterized by the presence of low-frequency OH stretching vibration band at 2670 (**I**) and 2609 cm^{-1} (**IV**). The carbonyl stretching vibration frequency is also reduced to 1633 (**I**) and 1627 cm^{-1} (**IV**). The observed low-frequency shifts are determined by formation of a strong intramolecular hydrogen bond. We previously revealed formation of a planar seven-membered H-chelate ring (which is coplanar to the naphthalene core) in the crystalline structure of *peri*-hydroxy ketone **I** [10]. Presumably, analogous structure is intrinsic to 7-bromo derivative **IV**. We succeeded in synthesizing *peri*-acetoxy-substituted naphthenyl bromomethyl ketone **VI** using 1,4-dioxane–bromine complex as brominating agent.

In the IR spectra of bromomethyl ketones **V** and **VI** the carbonyl stretching vibration band is displaced to higher frequencies due to negative inductive effect of the bromine atom (1710–1715 cm^{-1} against 1680–1690 cm^{-1} in the spectra of methyl ketones **II** and **III**). Compounds **V** and **VI** characteristically displayed a two-proton singlet at about δ ~4.5 ppm due to protons in the bromomethyl group.

The reactions of bromomethyl ketones **V** and **VI** with bases were governed by the substrate and reagent nature (Scheme 3). Benzoyloxynaphthenyl ketone **V** reacted with ammonium acetate to form a complex mixture of products. We succeeded in isolating from the product mixture two compounds, **VII** and **VIII**, resulting from nucleophilic substitution of bromine by acetoxy and hydroxy groups. Regardless of the nature of the acyloxy group, the reaction of bromomethyl ketones **V** and **VI** involved cleavage of the ester moiety (**V**, **VI** → **D**), followed by intramolecular nucleophilic replacement of the bromine atom with formation of acenaphtho[5,6-*bc*]pyran-3-one (**IX**). Treatment of benzoyloxynaphthenyl ketone **V** with strong bases, e.g., potassium hydroxide, induced deprotonation of the methylene group (**V** → **E**) with subsequent intramolecular rearrangement (**E** → **F**) and heterocyclization (**F** → **X**). The reaction of ketone **V** with 4-methoxybenzaldehyde under analogous conditions led to the formation of 2-(4-methoxybenzylidene) derivative **XI** (Scheme 3).

Scheme 3.


RC(O)O
COCH2Br
V, VI
AcONH4, EtOH
R = Ph
OBz
COCH2OAc
VII
OBz
VIII
Piperidine
–(CH2)5NCOR
Br
D
IX
Ac2O, NaOAc
OAc
XV
R = Ph
4-MeOC6H4CHO
KOH–EtOH
C6H4OMe-4
XI
C6Cl4O2
XIV
C6Cl4O2
NaOMe
XVI
BzO
COCH2Br
V
KOH–EtOH
BzO
COCHBr
E
Ph
Br
F
Ph
OH
X
Ph
BF2
XII
Ph
Cu
2
XIII

The reactions of bromomethyl ketones **V** and **VI** with ammonium acetate and piperidine were not selective, and individual compounds **VII**, **VIII**, and **XII** were isolated from multicomponent reaction mixtures in fairly poor yields (20–30%). The yield of 2-benzoylacenaphthopyran **X** was 70%; however, this compound turned out to be unstable. It underwent decomposition in organic solvents and over chromatographic sorbents (aluminum oxide, silica gel) to give products which were not isolated and identified. Therefore, its ^{1}H NMR spectrum cannot be regarded as informative. Structure **X** shown in Scheme 3 was postulated by analogy with more stable derivatives of the naphthalene series [8]. The presence of a ketoenol fragment in molecule **X** was confirmed by the ability of this compound to form difluoridoboron and copper chelates **XII** and **XIII**.

In the ^{1}H NMR spectrum of 6-benzoyloxy-5-(hydroxyacetyl)acenaphthene (**VIII**) the hydroxy proton resonated as a broadened singlet, and protons in the neighboring methylene group gave a doublet, indicating spin–spin coupling in the HO–CH_2 fragment. The downfield position of the OH signal (δ 11.10 ppm) is rationalized by formation of intramolecular hydrogen bond with closure of five-membered H-chelate ring. 5-Acetoxyacetyl-6-benzoyloxyacenaphthene (**VII**) displayed more complex pattern in the ^{1}H NMR spectrum, and it was difficult to identify protons of the naphthalene core therein. This may be due to the presence of conformers (e.g., those with the *peri*-substituents oriented at the same and opposite sides of the naphthalene ring plane).

Our attempt to perform dehydrogenation of naphthopyranone **IX** to obtain fused acenaphthylene derivative **XIV** was unsuccessful. Heating of ketone **IX** with tetrachlorobenzoquinone in boiling toluene or chlorobenzene was accompanied by strong tarring, and we isolated from the reaction mixture only a small amount of the initial compound. We presumed that introduction of a double bond into the pyran ring should facilitate aromatization and obtained 3-acetoxy derivative **XV**. In fact, dehydrogenation of **XV** gave expected fused acenaphthylene **XVI**. However, the latter did not undergo deacetylation upon treatment (30 min) with sodium methoxide in methanol at ~35°C. Instead of expected naphthopyranone **XIV** we isolated only initial compound **XVI**.

Acenaphthene derivative **XV** is almost colorless, whereas acenaphthylene derivative **XVI** is orange. This is consistent with their electronic absorption spectra (Fig. 1). A solution of **XV** in acetonitrile almost does not absorb in the visible region; its absorbance above ~405–410 nm is negligible, while compound **XVI** in acetonitrile absorbs up to ~480 nm. In addition, the long-wave absorption maximum of compound **XVI** is located at λ 405 nm against 345 nm for pyran **XV**, indicating extension of conjugated bond system in going from acenaphthene to acenaphthylene derivative.

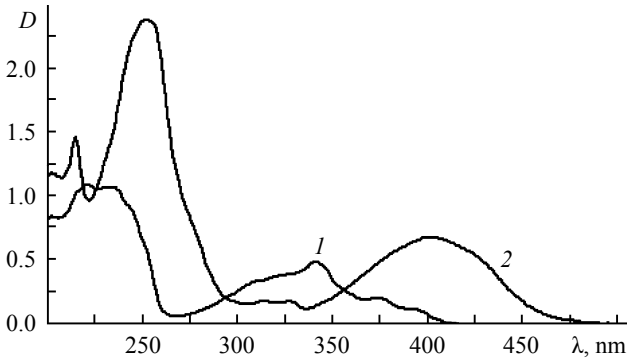


Fig. 1. Electronic absorption spectra of compounds (*1*) **XV** and (*2*) **XVI** in acetonitrile.

peri-Fused heterocyclic compounds **XV** and **XVI** are luminophors (Fig. 2). 3-Acetoxyacenaphtho[5,6-*bc*]pyran (**XV**) shows yellow–green emission at λ 436 nm upon UV irradiation, and compound **XVI** is characterized by orange luminescence at λ 518 nm.

Comparison of the chemical shifts of the peripheral protons (in the naphthalene ring and heteroring) in the ^{1}H NMR spectra clearly illustrates that molecule **XVI**

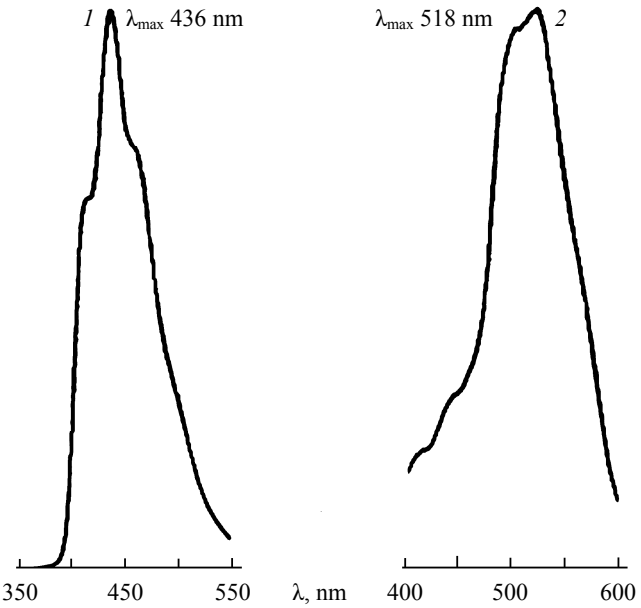
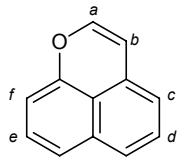
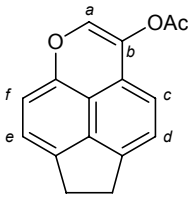


Fig. 2. Luminescence spectra of compounds (*1*) **XV** and (*2*) **XVI** in acetonitrile (λ_{excit} 320 nm).

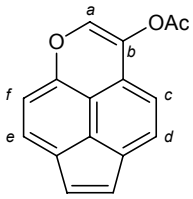
Chemical shifts (δ, ppm) of protons in the naphthalene ring and heteroring in the ^{1}H NMR spectra of compounds **XV**–**XIX**



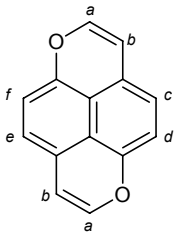
XVII



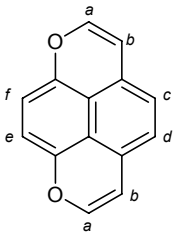
XV



XVI



XVIII



XIX

Proton	**XVII**	**XV**	**XVI**	**XVIII**	**XIX**
a	6.71	6.77	7.73	6.14	6.17
b	5.91	–	–	5.40	5.35
c	6.67	6.62	7.42	6.16	6.01
d	7.19	7.00	8.04	6.08	6.01
e	7.24	6.93	8.10	6.16	6.18
f	6.72	6.44	7.30	6.08	6.18
Range	5.91–7.24	6.44–7.00	7.30–8.10	5.40–6.16	5.35–6.18

becomes aromatic as the amount of π-electrons in the peripheral contour attains 14: signals of these protons shift downfield relative to those observed for nonaromatic heterocyclic systems **XV** and **XVII** [11] having an odd number of π-electrons (13) at the periphery. By contrast, the existence of an 18π-electron peripheral contour makes structures **XVIII** and **XIX** [3, 11] antiaromatic, and signals from all peripheral protons in their molecules are located in the ^{1}H NMR spectra in a stronger field relative to those of both aromatic (**XVI**) and nonaromatic systems (**XV**, **XVII**).

These data clearly confirm the assumption [12–16] that just peripheral electrons determine aromatic, nonaromatic, or antiaromatic character of carbo- and heterocyclic systems. Comparison of the data for acetoxy derivatives **XV** and **XVI** with those of compounds **XVII**–**XIX** which lack acetoxy substituent may be regarded as appropriate, taking into account weak effect of acetoxy group on their spectral parameters. It is sufficient to consider the chemical shifts of protons in positions *a*, *c,* and *f* (that are distant from the ethylene bridge) of **XV** and **XVII** and their electronic absorption spectra (see Fig. 1 and the data of [17, 18]).

In the ^{1}H NMR spectra of all acenaphthene derivatives obtained in the present work signals from protons in the naphthalene ring in the *ortho* positions with respect to the ethylene bridge are broadened due to long-range spin–spin couplings. Therefore, all aromatic protons can be identified unambiguously.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker DPX-250 and Varian Unity-300 spectrometers at 250 and 300 MHz, respectively, using tetramethylsilane as internal reference. The IR spectra (attenuated total reflectance) were measured on a Varian Excalibur 3100 FT-IR spectrometer. The electronic absorption spectra were obtained from solutions in acetonitrile on a Varian Cary 100 Scan UV-Vis spectrophotometer, and the luminescence spectra (acetonitrile) were measured on a Hitachi 6010 spectrofluorimeter.

6-Acetylacenaphthen-5-yl acetate (II). A small amount (on a tip of spatula) of anhydrous sodium acetate was added to a solution of 0.67 g (3 mmol) of 1-(6-hydroxyacenaphthen-5-yl)ethanone (**I**) in 6 ml of acetic anhydride, and the mixture was heated for 30 min under reflux. The mixture was cooled and poured into 20 ml of cold water. When hydrolysis of acetic anhydride was complete, the precipitate was filtered off and dried in air. Yield 0.6 g (75%), dark brown crystals, mp ~60°C. Chromatographic purification (aluminum oxide, chloroform) followed by recrystallization from light petroleum ether with addition of a few drops of benzene gave light yellow crystals with mp 79–80°C. IR spectrum, ν, cm^{-1}: 1767 (C=O, ester), 1693 (C=O, ketone), 1588. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, $COCH_3$), 2.60 s (3H, $OCOCH_3$), 3.40 m (4H, CH_2CH_2), 7.24 d (1H, 4-H,

$J_{3,4}$ = 8.19 Hz), 7.30 br.d (1H, 8-H, $J_{7,8}$ = 7.85 Hz), 7.33 br.d (1H, 3-H, $J_{3,4}$ = 8.19 Hz), 7.47 d (1H, 7-H, $J_{7,8}$ = 7.85 Hz). Found, %: C 75.25; H 5.70. $C_{16}H_{14}O_3$. Calculated, %: C 75.58; H 5.55.

6-Acetylacenaphthen-5-yl benzoate (III). Freshly distilled benzoyl chloride, 0.6 ml (4 mmol), was added to a solution of 0.67 g (3 mmol) of 1-(6-hydroxyacenaphthen-5-yl)ethanone (**I**) in 3 ml of anhydrous pyridine, and the mixture was kept for 2 h at 0°C. The mixture was then poured into ice water acidified with hydrochloric acid; after 2 h, the precipitate was filtered off and dried in air. Yield 0.8 g (85%), mp 98–99°C (from ethanol). IR spectrum, ν, cm^{-1}: 1736 (C=O, ester), 1683 (C=O, ketone), 1599. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, $COCH_3$), 3.20 m (4H, CH_2CH_2), 7.10–8.15 m (9H, H_{arom}). Found, %: C 79.50; H 5.37. $C_{21}H_{16}O_3$. Calculated, %: C 79.73; H 5.10.

1-(7-Bromo-6-hydroxyacenaphthen-5-yl)ethanone (IV). A solution of 0.32 g (1.26 mmol) of compound **III** in a small amount of chloroform was added to a suspension of 0.47 g (2.1 mmol) of copper(II) bromide in 5 ml of ethyl acetate. The mixture was heated for 3 h under reflux with continuous stirring and filtered, the filtrate was evaporated, and the dry residue was purified by chromatography on aluminum oxide using benzene as eluent. Yield 0.27 g (72%), orange powder, mp 161–162°C (from ethanol). IR spectrum, ν, cm^{-1}: 2609 (OH), 1627 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.80 s (3H, CH_3), 3.38 m (4H, CH_2CH_2), 7.26 br.d (1H, 3-H, $J_{3,4}$ = 7.55 Hz), 7.57 br.s (1H, 8-H), 8.22 d (1H, 4-H, $J_{3,4}$ = 7.55 Hz), 12.60 s (1H, OH). Found, %: C 57.57; H 3.90; Br 27.31. $C_{14}H_{11}BrO_2$. Calculated, %: C 57.76; H 3.81; Br 27.44.

6-(Bromoacetyl)acenaphthen-5-yl benzoate (V). A solution of 0.6 g (1.9 mmol) of compound **III** in a small amount of chloroform was added to a suspension of 0.8 g (3.6 mmol) of copper(II) bromide in 10 ml of ethyl acetate. The mixture was heated for 3 h under reflux with continuous stirring and filtered, the filtrate was evaporated, and the dry residue was purified by chromatography on aluminum oxide using chloroform as eluent. Yield 0.65 g (87%), yellow powder, mp 120–121°C. IR spectrum, ν, cm^{-1}: 1735 (C=O, ester), 1711, 1678 (C=O, ketone), 1599. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.45 m (4H, CH_2CH_2), 4.35 s (2H, CH_2), 7.30–7.70 m (7H, H_{arom}), 8.22 d (2H, H_{arom}). Found, %: C 63.54; H 3.70; Br 20.41. $C_{21}H_{15}BrO_3$. Calculated, %: C 63.82; H 3.83; Br 20.22.

6-(Bromoacetyl)acenaphthen-5-yl acetate (VI). 1,4-Dioxane–bromine complex, 0.379 g (1.5 mmol), was added in portions under continuous stirring to a solution of 0.382 g (1.5 mmol) of compound **II** in dioxane. The solution was evaporated, and the residue was dried in air and subjected to chromatography on aluminum oxide using chloroform as eluent; a fraction with R_f 0.8 was collected. Yield 0.35 g (70%), orange powder, mp 124–125°C (from alcohol). IR spectrum, ν, cm^{-1}: 1758 (C=O, ester), 1715, 1693 (C=O, ketone), 1590. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s (3H, CH_3), 3.40 m (4H, CH_2CH_2), 4.50 s (2H, CH_2), 7.25–7.45 m (4H, H_{arom}). Found, %: C 57.34; H 3.67; Br 23.49. $C_{16}H_{13}BrO_3$. Calculated, %: C 57.68; H 3.93; Br 23.98.

6-(Acetoxyacetyl)acenaphthen-5-yl benzoate (VII) and 6-(hydroxyacetyl)acenaphthen-5-yl benzoate (VIII). Ammonium acetate, 0.12 g (1.6 mmol), was added to a solution of 0.2 g (0.5 mmol) of compound **V** in 3 ml of ethanol. The mixture was heated for 30 min under reflux, and the red oily material was separated and subjected to chromatography on aluminum oxide using chloroform as eluent. The first fraction (R_f 0.9) contained compound **VII**. Yield 35 mg (18%), light yellow powder, mp 111–112°C. IR spectrum, ν, cm^{-1}: 1740 (C=O, ester), 1721 (PhC=O), 1697 (C=O, ketone). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.85 s (3H, CH_3), 3.46 m (4H, CH_2CH_2), 5.03 s (2H, CH_2), 7.30–7.42 m (3H, H_{arom}), 7.48–7.58 m (3H, Ph) 7.62–7.70 m (1H, H_{arom}), 8.18–8.24 m (2H, Ph). Found, %: C 73.36; H 4.63. $C_{23}H_{18}O_5$. Calculated, %: C 73.79; H 4.85. The second fraction (R_f 0.6) contained compound **VIII**. Yield 22 mg (13%), yellow powder, mp 131–132°C. IR spectrum, ν, cm^{-1}: 3430 (OH), 1738 (C=O, ester), 1659, 1637 (C=O, ketone). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.40 m (4H, CH_2CH_2), 5.20 d (2H, HOC**H**$_2$, ^3J = 4.32 Hz), 7.18 d (1H, 4-H, $J_{3,4}$ = 7.6 Hz), 7.31 d (1H, 8-H, $J_{7,8}$ = 7.5 Hz), 7.35 d (1H, 3-H, $J_{3,4}$ = 7.6 Hz) 7.46–7.58 m (3H, Ph), 7.88–7.95 (2H, Ph), 8.33 d (1H, 7-H, $J_{7,8}$ = 7.5 Hz), 11.10 br.s (1H, OH). Found, %: C 75.45; H 4.57. $C_{21}H_{16}O_4$. Calculated, %: C 75.89; H 4.85.

6,7-Dihydroindeno[6,7,1-*def*]chromen-3(2*H*)-one (IX). *a*. Piperidine, 0.3 ml, was added dropwise to a hot solution of 0.456 g (1.4 mmol) of compound **VI** in a mixture of 27 ml of hexane and 9 ml of benzene. The mixture was heated for 1 h under reflux and cooled, the precipitate of piperidinium bromide was filtered off, the filtrate was evaporated, and the residue was purified by chromatography on aluminum oxide using chloroform as eluent; a fraction with R_f 0.8 was

collected. Yield 0.104 g (36%), yellow–green powder, mp 155–156°C. IR spectrum, ν, cm^{-1}: 1677 (C=O), 1613, 1502. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.45 m (4H, CH_2CH_2), 4.95 s (2H, CH_2), 7.03 d (1H, 9-H, $J_{9,8}$ = 7.5 Hz), 7.25 d (1H, 8-H, $J_{8,9}$ = 7.5 Hz), 7.40 d (1H, 5-H, $J_{5,4}$ = 7.4 Hz), 8.05 d (1H, 4-H, $J_{4,5}$ = 7.4 Hz). Found, %: C 80.38; H 4.56. $C_{14}H_{10}O_2$. Calculated, %: C 79.98; H 4.79.

b. Compound **IX** was synthesized in a similar way from 0.452 g (1.1 mmol) of bromomethyl ketone **V**. Yield 0.038 g (16%), yellow powder, mp 156–157°C (from ethanol).

3-Hydroxy-6,7-dihydro[6,7,1-*def*]chromen-2-yl(phenyl)methanone (X). A solution of 0.2 g (0.5 mmol) of compound **V** in 10 ml of ethanol was cooled with an ice bath, 2 ml of 5% potassium hydroxide was added, and a dark red solid separated. After 25–30 min, the mixture was acidified with dilute (1:1) hydrochloric acid, and the precipitate turned bright red. It was filtered off, washed with water, and dried in air. Yield 0.1 g (70%), red powder, mp 156–157°C. Found, %: C 80.65; H 4.17. $C_{21}H_{14}O_3$. Calculated, %: C 80.24; H 4.49.

2-(4-Methoxybenzylidene)-6,7-dihydroindeno[6,7,1-*def*]chromene-3(2*H*)-one (XI). A suspension of 0.2 g (0.5 mmol) of compound **V** in 7 ml of methanol was added to a solution of 0.06 ml (0.5 mmol) of 4-methoxybenzaldehyde and 0.03 g (0.6 mmol) of sodium methoxide in 3 ml of methanol. The mixture turned orange, and it was heated until the initial bromomethyl ketone dissolved completely (the solution turned red). The mixture was cooled, acidified with dilute (1:1) hydrochloric acid to weakly acidic reaction, and diluted with water, and the red precipitate was filtered off, washed with water, dried, and purified by chromatography on aluminum oxide using chloroform as eluent. Yield 0.08 g (48%), red powder, mp 204–205°C. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1585, 1563, 1505. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.45 m (4H, CH_2CH_2), 3.88 s (3H, OCH_3), 6.99 d (2H, C_6H_4, J = 9.0 Hz), 7.15 s (1H, CH), 7.22 d (1H, 9-H, $J_{9,8}$ = 7.6 Hz), 7.28 d (1H, 8-H, $J_{9,8}$ = 7.6 Hz), 7.45 d (1H, 5-H, $J_{5,4}$ = 7.3 Hz), 7.90 d (2H, C_6H_4, J = 9.0 Hz), 8.20 d (1H, 4-H, $J_{4,5}$ = 7.3 Hz). Found, %: C 80.68; H 4.67. $C_{22}H_{16}O_3$. Calculated, %: C 80.47; H 4.91.

3-Hydroxy-6,7-dihydro[6,7,1-*def*]chromen-2-yl(phenyl)methanone complex with BF_3 (XII). Boron trifluoride–diethyl ether complex, 4–5 drops (~0.1 ml), was added to a solution of 0.032 g (0.1 mmol) of compound **X** in 2 ml of benzene, a violet solid instantaneously separated, and the mixture turned violet. The mixture was diluted with petroleum ether, and the precipitate was filtered off. Yield 0.029 g (80%), dark red (almost black) powder, mp 259°C (decomp.). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.45 m (4H, CH_2CH_2), 7.02 d (1H, 9-H, $J_{9,8}$ = 7.8 Hz), 7.25 d (1H, 8-H, $J_{8,9}$ = 7.8 Hz), 7.38 br.d (1H, 5-H, $J_{5,4}$ = 7.3 Hz), 7.50–7.70 m (3H, Ph), 8.01 d (1H, 4-H, $J_{4,5}$ = 7.3 Hz), 8.36–8.43 (2H, Ph). Found, %: C 69.25; H 3.88; F 10.60. $C_{21}H_{13}BF_2O_3$. Calculated, %: C 69.65; H 3.62; F 10.49.

3-Hydroxy-6,7-dihydro[6,7,1-*def*]chromen-2-yl(phenyl)methanone copper complex (XIII). A saturated aqueous solution of copper(II) acetate was added to an approximately equal volume of a saturated solution of 0.04 g (0.13 mmol) of compound **X** in diethyl ether. The mixture was shaken for ~30 min, and the dark red precipitate was filtered off and dried. Yield 0.074 g (84%), red powder, mp 210°C (decomp.). IR spectrum, ν, cm^{-1}: 1624, 1585, 1546, 1503, 1477, 1447, 1411, 1375. Found, %: C 73.69; H 4.07. $C_{42}H_{26}CuO_6$. Calculated, %: C 73.13; H 4.28.

6,7-Dihydroindeno[6,7,1-*def*]chromen-3-yl acetate (XV). A solution of 0.114 g (0.5 mmol) of compound **IX** in 3 ml of acetic anhydride containing a catalytic amount of sodium acetate was heated for 30 min under reflux. The mixture was cooled and poured into water, and the precipitate was filtered off, washed with water, and subjected to chromatography on Silokhrom using chloroform as eluent. Yield 0.075 g (55%), bright yellow powder, mp 85–86°C. IR spectrum, ν, cm^{-1}: 1757 (C=O), 1696, 1651, 1604, 1586. UV spectrum, λ_{max} (logε), nm: 202 (4.21), 221 (4.32), 233 (4.31), 341 (3.96), 374 (3.58). Luminescence spectrum: $\lambda_{excit}/\lambda_{max}$ 320/436 nm. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 3.25 m (4H, CH_2CH_2), 6.44 d (1H, 9-H, $J_{9,8}$= 7.0 Hz), 6.62 d (1H, 4-H, $J_{4,5}$ = 7.6 Hz), 6.77 s (1H, 2-H), 6.93 d (1H, 8-H, $J_{8,9}$ = 7.0 Hz), 7.00 d (1H, 5-H, J = 7.6 Hz). Found, %: C 76.47; H 4.91. $C_{16}H_{12}O_3$. Calculated, %: C 76.18; H 4.79.

Indeno[6,7,1-*def*]chromen-3-yl acetate (XVI). 2,3,5,6-Tetrachloro-1,4-benzoquinone, 0.068 g (0.28 mmol), was added to a solution of 0.07 g (0.28 mmol) of compound **XIV** in 2 ml of *o*-dichlorobenzene. The solution turned green and was heated for 40 min under reflux. After cooling, the colorless precipitate was filtered off, the filtrate was cooled and evaporated, and the residue was subjected to chromatography on silica gel using chloroform as eluent. Yield 0.035 g (50%), orange powder, mp 113–114°C. IR spectrum, ν, cm^{-1}: 1762 (C=O), 1639, 1595. UV

spectrum, λ_{max} (logε), nm: 202 (4.13), 215 (4.23), 252 (4.44), 313 (3.32), 328 (3.30), 402 (3.89). Luminescence spectrum: $\lambda_{excit}/\lambda_{max}$ 320/518 nm. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (3H, CH_3), 7.30 d (1H, 9-H, $J_{9,8}$ = 7.3 Hz), 7.41 d (1H, 7-H, $J_{7,6}$ = 4.9 Hz), 7.42 d (1H, 4-H, $J_{4,5}$ = 7.8 Hz), 7.49 d (1H, 6-H, $J_{6,7}$ = 4.90 Hz), 7.73 s (1H, 2-H), 8.04 d (1H, 5-H, $J_{5,4}$ = 7.80 Hz), 8.10 d (1H, 8-H, $J_{8,9}$ = 7.3 Hz). Found, %: C 76.41; H 4.24. $C_{16}H_{10}O_3$. Calculated, %: C 76.79; H 4.03.

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