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peri-Amino Ketones of the Acenaphthene and Acenaphthylene Series

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Abstract—*peri*-Amino-substituted methyl and aryl ketones of the acenaphthene and acenaphthylene series were subjected to protonation and acylation at the nitrogen atom, dehydrogenation, and reactions with aldehydes. Conformations of substituents in the *peri* positions and probability for their participation in intra- and intermolecular transformations were determined on the basis of spectral data and quantum-chemical calculations.

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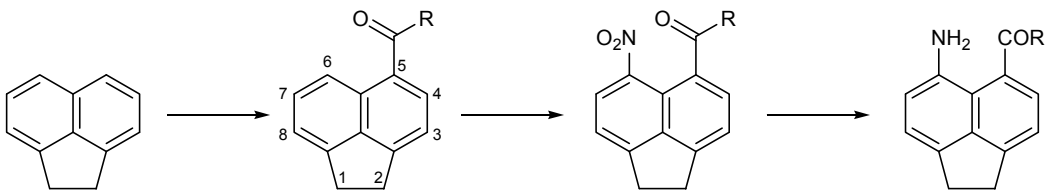
peri-Amino-substituted alkyl and aryl naphthyl ketones with a free amino group were not isolated, for they readily undergo heterocyclization *in statu nascendi* with formation of benzo[*cd*]indole derivatives [1–3]. By contrast, *peri*-amino ketones of the acenaphthene series are relatively stable compounds due to "contracting" effect of the ethylene bridge, which makes the opposite *peri* positions in the naphthalene core more distant from each other and thus increases the distance between the substituents constituting the *peri*-amino carbonyl fragment. First representatives of acenaphthene *peri*-amino ketones were synthesized according to Scheme 1 as early as 1966 [4, 5]; however, their properties and transformations have not been studied so far.

In the present work we examined the IR and ^{1}H NMR spectra of methyl and aryl ketones **IVa**–**IVc**, estimated the probability for participation of the amino group in intra- and intermolecular transformations, and performed dehydrogenation of the ethylene bridge (Scheme 2). As substrates we used previously synthesized methyl and phenyl acenaphthenyl ketones **IVa** and **IVb** [4, 5] and 5-amino-6-(*p*-methoxybenzoyl)-naphthalene (**IVc**) obtained in the present work.

We traced variations of some spectral parameters of intermediate compounds during the transformation of acenaphthene (**I**) into previously unknown *peri*-amino *p*-methoxyphenyl ketone **IVc**. In going from acenaphthene (**I**) to 5-(*p*-methoxybenzoyl)acenaphthene (**IIc**) the 6-H signal in the ^{1}H NMR spectrum shifts downfield from δ 7.58 to 7.98 ppm due to magnetically anisotropic effect of the carbonyl group in the *peri* position. The position of the carbonyl stretching vibration band in the IR spectrum of ketone **IIc** (1635 cm^{-1}; mineral oil) suggests strong conjugation of the carbonyl group with the aromatic fragments in the crystalline

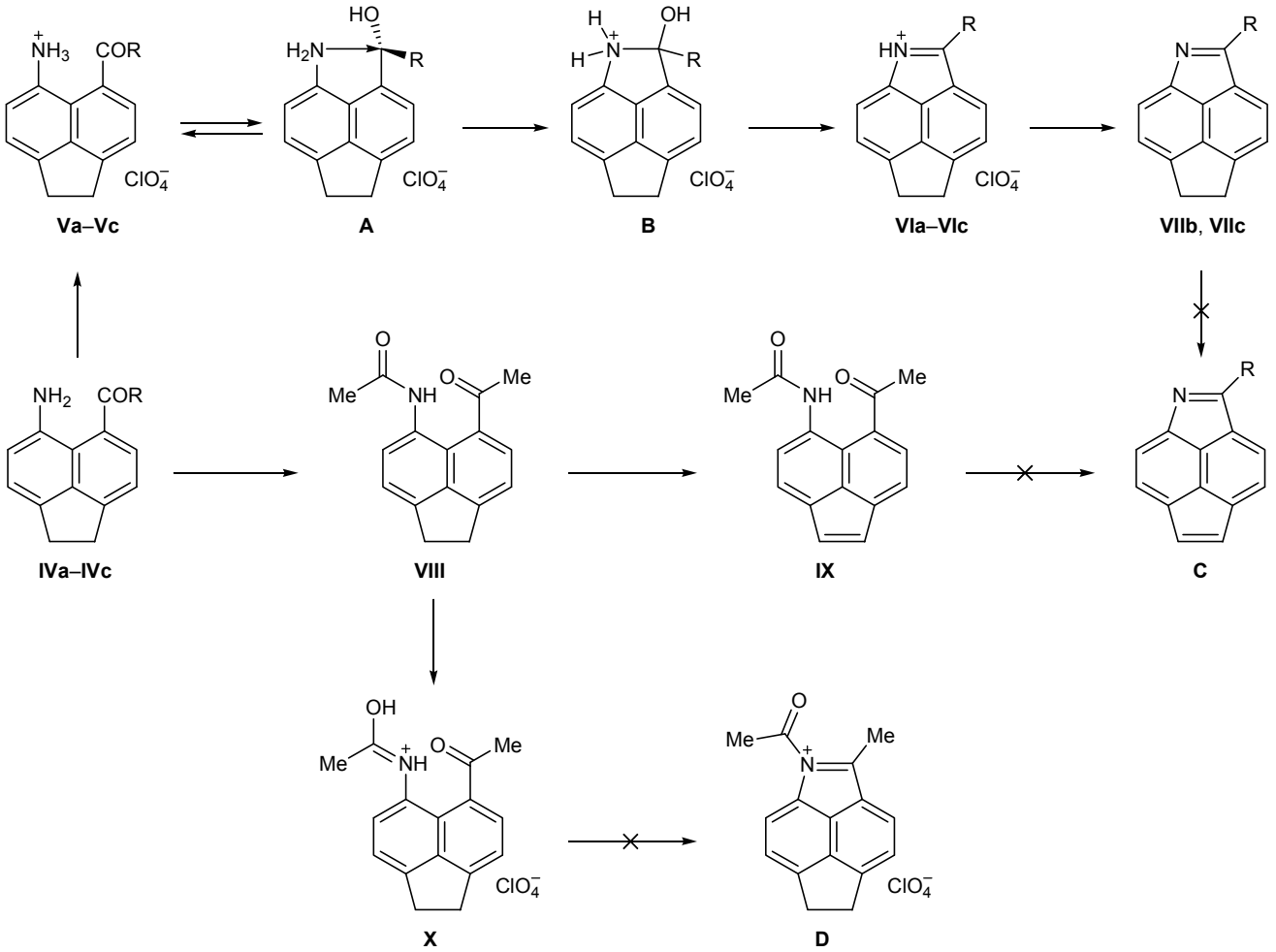
Scheme 1.



I **IIa–IIc** **IIIa–IIIc** **IVa–IVc**

R = Me (**a**), Ph (**b**), 4-MeOC$_6$H$_4$ (**c**).

Scheme 2.



R = Me (**a**), Ph (**b**), 4-$MeOC_6H_4$ (**c**).

state. The carbonyl stretching vibration band in the IR spectrum of *peri*-nitro ketone **IIIc** is located at a higher frequency (1650 cm^{-1}).

The geometric parameters of compounds **IVa**–**IVc** were calculated in terms of the density functional theory with B3LYP/6-31G** basis set using Gaussian 03 software; some results are presented in Table 1. It is seen that the plane of the carbonyl group in molecules **IVa**–**IVc** is turned through an angle of 26–43° relative to the acenaphthene core: the torsion angles $H^1NC^6C^{12}$ and $H^2NC^6C^7$ are 37–41 and 12–14°, respectively (Table 1). The configuration of bonds at the nitrogen atom indicates that the lone electron pair on the nitrogen does not lie in the naphthalene ring plane. The $N–H^1\cdots O$ angle in molecules **IVa**–**IVc** ranges from 147 to 149°. These data show that (1) the seven-membered H-chelate ring in isolated molecule of each amino ketone **IVa**–**IVc** is neither planar nor coplanar to the acenaphthene core and (2) partial conjugation between the naphthalene π-electron system, on the one hand, and the carbonyl group or *p* electrons of the amino group, on the other, is conserved.

The conclusions drawn on the basis of the calculation results were confirmed experimentally. The ^1H NMR spectra contained an upfield broadened two-proton singlet at δ 4.25–4.51 ppm from the NH_2 group, indicating the absence of intramolecular hydrogen bond, while conjugation of the *peri*-substituents with the naphthalene ring induced downfield (δ 7.41–7.78 ppm) and upfield (δ 6.83–6.86 ppm) displacement of signals from protons in the *ortho* positions with respect to the above substituents relative to the signals from protons in positions *3* and *8*.

The chemical shifts of the *ortho* protons in the ^1H NMR spectra do not correlate with the calculated electron densities (Table 1). A probable reason is sol-

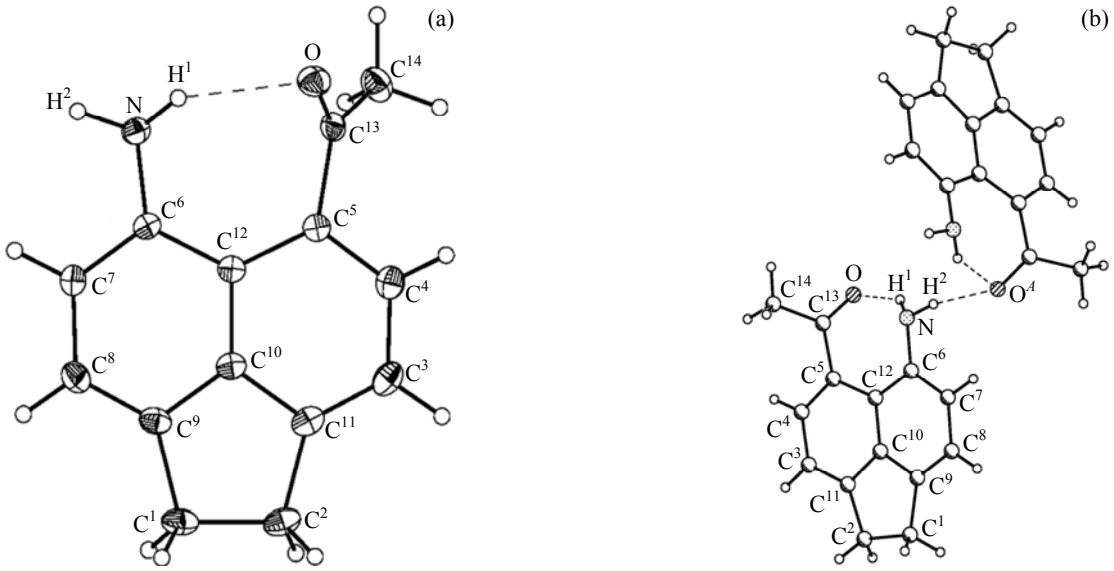


Fig. 1. (a) Intra- and (b) intermolecular hydrogen bonds in the crystalline structure of compound **IVa**.

vent effect which changes configuration of the substituents. This assumption is indirectly supported by considerable difference between the experimental and calculated torsion angles $H^1NC^6C^{12}$ and $H^2NC^6C^7$ (Table 1).

Comparison of the calculation results and experimental NMR data allowed us to draw one more important conclusion: the formation of strong intramolecular hydrogen bond requires that the seven-membered H-chelate ring be planar and coplanar to the naphthalene core and that the angle $N–H^1\cdots O$ be close to straight. Contracting effect of the ethylene bridge leads to in-plane distortion of the naphthalene skeleton, so that the distance between the *peri*-carbon atoms in positions *5* and *6* increases to 2.620–2.657 Å (Table 1), which is considerably longer than the corresponding interatomic distance in naphthalene (2.450 Å). In addition, the bonds between C^5 and C^6 and the corresponding substituents in compounds **IVa**–**IVc** deviate in opposite directions. As a result, the nitrogen atom becomes remote from the sp^2-hybridized carbonyl carbon atom by a considerable distance (>3 Å), which (in combination with noncoplanar conformations of the *peri* substituent) provides the possibility for rotation or at least rocking oscillation of the amino group. Presumably, such rotation is responsible for averaging of signals from two magnetically nonequivalent protons in the amino group, observed in the ^{1}H NMR spectrum as signal broadening.

Table 1 also contains the X-ray diffraction data for methyl ketone **IVa**; some experimental parameters considerably differ from the corresponding calculated values, which may be due to specificity of crystal packing. Figure 1 shows a fragment of crystal packing of compound **IVa**. It is seen that both hydrogen atoms in the amino group are involved in intra- and intermolecular interactions with the carbonyl oxygen atom. Judging by the $NH\cdots O$ distances (2.076 and 2.247 Å, respectively), these interactions may be regarded as weak intra- and intermolecular hydrogen bonds.

Treatment of *peri*-amino ketones **IVa**–**IVc** with perchloric acid in acetic acid or methanol at room temperature resulted in the formation of ammonium perchlorates **Va**–**Vc** which did not undergo heterocyclization (Scheme 2). Optimization of the geometric parameters of cation **Va** at the B3LYP/6-31G** level of theory with no account taken of counterion and solvent effects showed that one hydrogen atom in the protonated amino group participates in the formation of planar seven-membered H-chelate ring which is coplanar to the acenaphthene core (the torsion angles $OC^{13}C^5C^{12}$ and $H^1NC^6C^{12}$ are equal to zero (Table 2).

Replacement of the methyl group by aryl (compounds **Vb** and **Vc**) leads to appreciable change in the conformations of the ammonium and carbonyl substituents in the *peri* positions. The above torsion angles in cations **Vb** and **Vc** are 21–23 and 19–20°, respectively, indicating some deviation of the seven-membered H-chelate ring from planar structure (Table 2). The NH^1O angle (162–165°) is much closer to the straight angle (as compared to amino precursors **IV**; Table 1),

and fairly similar distances N–H^1 and $H^1\cdots O$ suggest that the proton involved in intramolecular hydrogen bond is located almost in the middle between two electronegative atoms. According to the calculations, the barrier to proton transfer to the carbonyl oxygen atom in system **Vc** is equal to zero (cf. the distances O–H and N–H in **Va** and **Vb** and **Vc**; Table 2).

The calculated parameters correspond to a strong intramolecular hydrogen bond. The formation of bridging hydrogen bonds is also confirmed by the AIM and NBO analyses. On the other hand, if the calculated conformation of **Va**–**Vc** were present in solution, the ^{1}H NMR spectra would contain a very downfield signal from H^1 (at about δ 15–16 ppm) and less downfield signal from H^2 and H^3 (at δ ~10 ppm). In the real ^{1}H NMR spectra of **Va** and **Vc** in deuterated nitrobenzene we observed only a very diffuse three-proton signal from the H_3N^+ group at δ 10.0–10.3 ppm, i.e., these protons are degenerate. The observed pattern may be rationalized in terms of reversible exchange interaction of a proton in the H_3N^+ group with the solvent and rotation of the NH_2 group thus released. Protonation of the amino group induces more than 1-ppm downfield shift of signal from proton in the *ortho* position with respect to the ammonium substituent, as compared to analogous signal of *peri*-amino ketones **IVa**–**IVc**, which correlates with the calculated charge on the corresponding carbon atom in **Va** and **Vc** (Table 2).

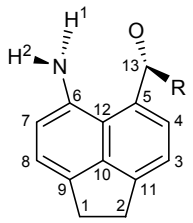
The position of the carbonyl stretching vibration band (~1630 cm^{-1}) in the IR spectrum of acetylacenaphthenylammonium salt **Va** (mineral oil) suggests formation of fairly strong intramolecular hydrogen bond in the condensed phase. Stretching vibrations of the H_3N^+ group give rise to two broad bands centered at 3550 and 3180 cm^{-1} and a "plateau" at ~2700 cm^{-1}. The latter is typical of *peri*-substituted ketones with strong intramolecular hydrogen bond [6].

The effect of an electron-withdrawing substituent on the nitrogen atom on the conformation of the *peri*-amino carbonyl fragment was studied by analyzing spectral parameters and calculated data for *peri*-acetylamino-substituted methyl ketone **VIII**. This compound was synthesized by treatment of a suspension of *peri*-amino ketone **IVa** in water with acetic anhydride. Analogous analysis was performed with acenaphthylene methyl ketone **IX** which was prepared by dehydrogenation of the ethylene bridge in **VIII** by the action of tetrachloro-1,4-benzoquinone (chloranil). The difference in the electronic structures of compounds **VIII** and **IX** is that the *peri* substituents in the latter could be conjugated with each other through the aromatic bond system.

According to the calculations, both acenaphthene and acenaphthylene ketones **VIII** and **IX** are characterized by slightly distorted (from planar structure) seven-membered H-chelate ring where the NH hydrogen atom and the carbonyl oxygen atom deviate insignificantly toward the same side of the naphthalene ring plane and toward each other (see the corresponding torsion angles in Table 2).

The calculated conformations of the *peri* substituents and the H···O distances that are shorter than the

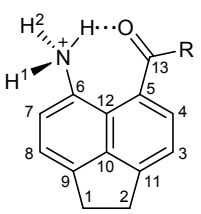
Table 1. Angles (deg) and interatomic distances (Å) in structures **IVa**–**IVc**, calculated at the DFT B3LYP/6-31G** level of theory



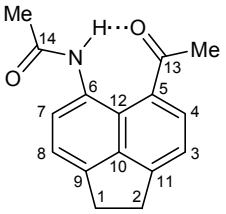
Angle or bond	R = Me (**IVa**)[a]	R = Ph (**IVb**)	R = *p*-$MeOC_6H_4$ (**IVc**)
NC^6C^{12}	122.6 (121.63)	122.0	121.9
$C^6C^{12}C^5$	129.7 (128.94)	129.1	129.0
$C^{12}C^5C^{13}$	125.9 (123.94)	124.8	124.7
$C^9C^{10}C^{11}$	110.6 (111.61)	111.0	111.1
$OC^{13}C^5C^{12}$	26.1 (54.07)	40.3	42.6
$H^1NC^6C^{12}$	37.7 (47.35)	40.6	40.4
$H^2NC^6C^7$	14.1 (8.32)	12.2	12.3
N–$H^1\cdots$O	149.3 (144.4)	146.9	147.1
$H^1\cdots O$	1.786 (2.076)	1.859	1.863
$H^2\cdots O$	3.477 (3.625)	3.544	3.548
$N\cdots C^{13}$	3.119 (2.975)	3.037	3.027
$C^6\cdots C^5$	2.623 (2.588)	2.607	2.606
$C^9\cdots C^{11}$	2.327 (2.325)	2.332	2.332
N···O	2.710 (2.867)	2.767	2.772
Atom no.	Calculated charges on the naphthalene carbon atoms		
3	–0.16	–0.16	–0.16
4	–0.12	–0.11	–0.11
7	–0.11	–0.11	–0.11
8	–0.16	–0.16	–0.16

[a] Selected experimental X-ray diffraction data are given in parentheses.

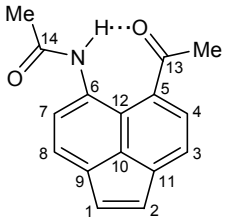
Table 2. Angles (deg), distances (Å), and charges on atoms in cations **Va**–**Vc** and N-acetyl-substituted acenaphthene and acenaphthylene derivatives **VIII** and **IX**, calculated at the B3LYP/6-31G** level of theory



Va–Vc



VIII



IX

Angle or bond	**Va** (R = Me)	**Vb** (R = Ph)	**Vc** (R = *p*-MeOC$_6$H$_4$)	**VIII**[a]	**IX**, [**IX**]·H$_2$O[a]
NC^{6}C^{12}	121.6	120.7	120.5	120.3 (120.9)	120.4 (124.5)
C^{6}C^{12}C^5	132.5	131.9	131.2	132.2 (130.2)	131.1 (130.9)
C^{12}C^{5}C^{13}	126.5	125.5	126.4	127.9 (124.5)	127.4 (123.8)
C^{9}C^{10}C^{11}	110.2	110.6	110.5	107.7 (111.1)	110.3 (109.4)
NH^{1}O	171.7	164.8	161.9	164.1 (147.4)	159.4 (58.7)
OC^{13}C^{5}C^{12}	0.0	21.5	22.8	15.2 (31.1)	23.1 (40.8)
H^{1}NC^{6}C^{12}	0.0	19.4	20.4	9.1 (41.5)	22.0 (138.4)
H^{2}NC^{6}C^7	60.0	82.2	87.3		
C^{14}NC^{6}C^7				7.3 (45.8)	18.6 (130.2)
H^{3}NC^{6}C^7	60.0	38.2	32.0		
N–H^1	1.151	1.148	1.409	1.025 (0.913)	1.021 (0.826)
H^1···O	1.327	1.337	1.091	1.624 (1.895)	1.675 (3.185)
N···O	2.472	2.463	2.469	2.625 (2.709)	2.655 (2.845)
H^2···O	3.003	2.877	2.824		
H^3···O	3.003	3.095	3.138		
N···C^{13}	3.173	3.099	3.092	3.200 (3.062)	3.139 (3.130)
C^6···C^5	2.648	2.634	2.631	2.681 (2.614)	2.646 (2.614)
C^9···C^{11}	2.324	2.328	2.326	2.300 (2.329)	2.323 (2.308)
Atom no.	Calculated charges on the naphthalene carbon atoms[b]				
3	–0.14	–0.15	–0.15	–0.16	–0.15
4	–0.12	–0.12	–0.12	–0.12	–0.13
7	–0.08	–0.08	–0.08	–0.09	–0.11
8	–0.15	–0.15	–0.15	–0.17	–0.16

[a] X-Ray diffraction data are given in parentheses.
[b] The charge on the H^1 atom is +0.43 for all cations.

sum of the corresponding van der Waals radii (Table 2) indicate formation of fairly strong intramolecular hydrogen bond, which does not contradict the experimental spectral parameters. In the ^{1}H NMR spectra of **VIII** and **IX** in DMSO-d_6, the proton involved in intramolecular hydrogen bond resonates at δ 9.68 and 10.10 ppm, respectively. The corresponding signal of acenaphthylene derivative **IX** in chloroform-*d* appears in a weaker field, at δ 10.70 ppm. In the IR spectra of **VIII** and **IX** (mineral oil) stretching vibrations of the N–H bond give rise to absorption band at 3275 cm^{-1}.

Some structural parameters of *N*-acylamino ketones **VIII** and **IX**, determined by X-ray analysis, differ considerably from those calculated by quantum-chemical method (Table 2; Figs. 2, 3). Insofar as the calculations were performed for isolated molecule in the gas phase, the observed differences may be assigned to specificity of crystal packing, the more so as compound **IX** crys-

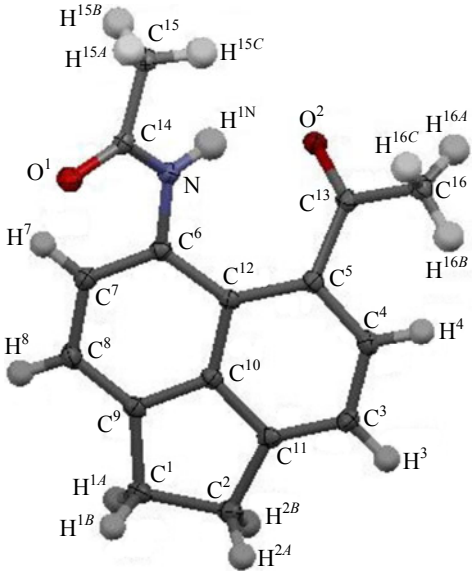


Fig. 2. Structure of the molecule of *N*-(6-acetylacenaphthen-5-yl)acetamide (**VIII**) according to the X-ray diffraction data.

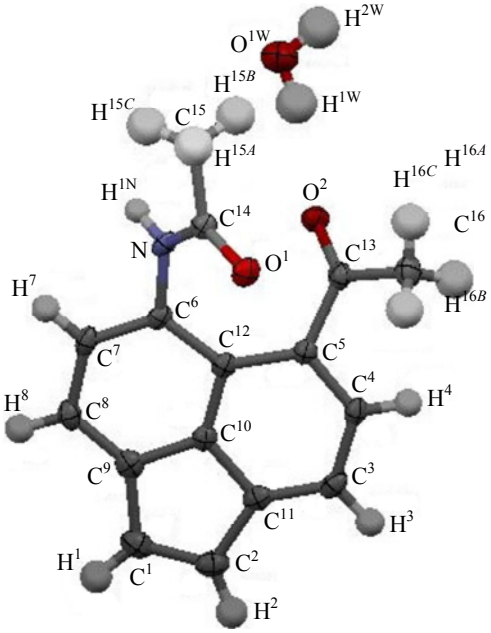
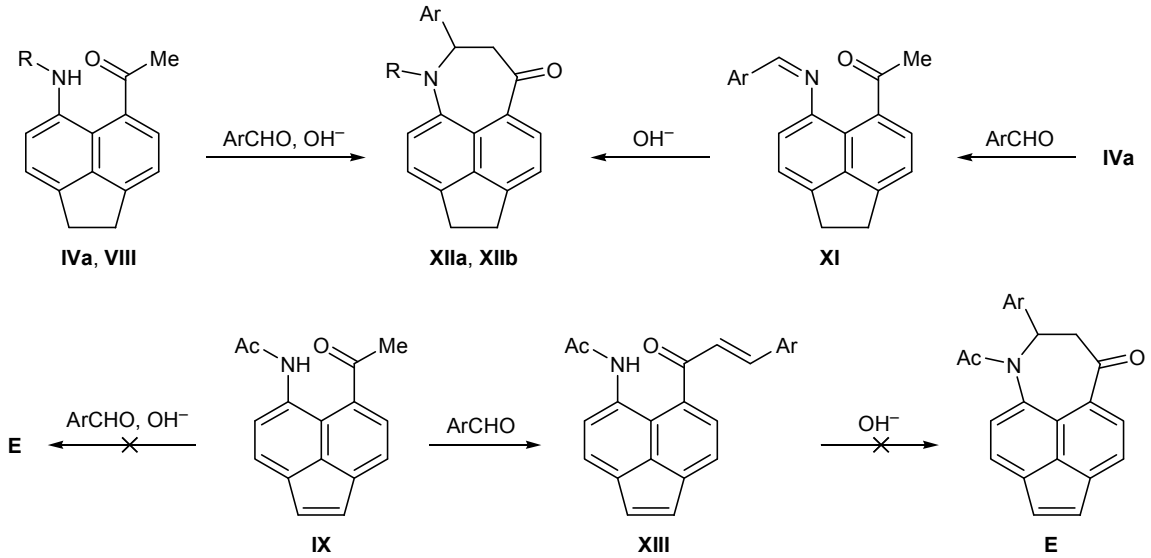


Fig. 3. Structure of the molecule of *N*-(6-acetylacenaphthylen-5-yl)acetamide (**IX**) according to the X-ray diffraction data.

tallizes as monohydrate. According to the X-ray diffraction data (unlike the calculation results), no planar seven-membered H-chelate ring is formed in the crystalline structure of *peri*-acetylamino-substituted acenaphthenyl methyl ketone **VIII** (cf. the corresponding torsion angles in Table 2). Although the carbonyl oxygen atom and NH hydrogen atom are located at the same side of the naphthalene ring plane, the distances between these atoms and between the nitrogen and oxygen atoms are considerably longer than the calculated ones, and these distances rule out formation of a strong intramolecular hydrogen bond in crystal. On the other hand, fairly strong intramolecular hydrogen bond exists in solution (see above). Comparison of the calculated and experimental (X-ray diffraction) data for compound **IX** seems to be inappropriate, for ketone **IX** crystallizes together with a water molecule. In this case, one hydrogen atom in water molecule is involved

Scheme 3.



R = H (**a**), Ac (**b**), Ar = 4-MeOC$_6$H$_4$.

Table 3. Crystallographic and structure refinement parameters for compounds **IVa**, **VIII**, and **IX**

Parameter	**IVa**	**VIII**	**IX**
Formula	$C_{14}H_{13}NO$	$C_{16}H_{15}NO_2$	$C_{16}H_{14}NO_{2.5}$
Molecular weight	211.25	253.29	260.28
Temperature, K	120	120	120
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	*Pbca*	*P*-1	*Pbca*
$Z(Z')$	8(1)	2(1)	8(1)
a, Å	13.5853(12)	6.3447(5)	12.5798(11)
b, Å	8.7637(8)	8.8113(7)	9.6502(9)
c, Å	18.1318(16)	12.0186(10)	21.3532(19)
α, deg	90	100.462(2)	90
β, deg	90	104.987(2)	90
γ, deg	90	103.306(2)	90
V, Å^3	2158.7(3)	610.49(9)	2592.2(4)
d_{calc}, g cm^{-3}	1.300	1.378	1.334
μ, cm^{-1}	0.82	0.91	0.91
$F(000)$	896	268	1096
θ_{max}, deg	28.00	26.00	28.99
Total number of reflections	17049	5095	25202
R_{int}	0.0841	0.0516	0.0674
Number of independent reflections	2573	2358	3436
Number of reflections with $I>2\sigma(I)$		1898	2385
Number of refined parameters	154	178	188
R_1	0.0418	0.0406	0.0530
wR_2	0.0976	0.1204	0.1060
Goodness of fit	1.013	1.012	1.011
Residual electron density d_{max}/d_{min}, e A^{-3}	0.216/–0.159	0.202/–0.269	0.777/–0.254

in weak ($d_{HO-H\cdots O=C}$ = 2.057 Å) hydrogen bond with the carbonyl oxygen atom, as if it is wedged between the *peri*-substituents thus making the latter more distant from each other and considerably changing the conformation of the entire *peri*-acylamino ketone fragment. The result is that the distance between the NH hydrogen atom and carbonyl oxygen atom reaches 3.185 Å, which excludes formation of hydrogen bond although these atoms appear at the same side of the naphthalene ring plane.

Heating of amino ketones **IV** with perchloric acid or of ammonium perchlorates **V** in acetic acid lead to their heterocyclization with formation of acenaphtho-[5,6-*bc*]pyrrolium salts **VI**. A probable heterocyclization path is shown in Scheme 2: **IV**→**V**→**A**→**B**→**VI**. Deprotonation of 2-aryl-substituted salts **VI** gave the corresponding free bases **VIIb** and **VIIc**, whereas we failed to isolate 2-methyl-substituted analog **VIIa** because of fast tarring. By treatment of *N*-acetylamino ketone **VIII** with perchloric acid we obtained O-protonated perchlorate **X** which, unlike protonated *peri*-amino ketones **V**, did not undergo heterocyclization to structure **D** on heating (Scheme 2). Our attempts to effect dehydrogenation of free bases **VII** with tetrachloro-1,4-benzoquinone or acid-catalyzed heterocyclization of acenaphthylene derivative **IX** with a view to obtain a new 14π-electron heterocyclic system **C** were unsuccessful. In all cases, unchanged initial compounds were recovered from the reaction mixtures.

By heating *peri*-amino methyl ketone **IVa** with *p*-methoxybenzaldehyde in ethanol we obtained the corresponding Schiff base **XI** which underwent base-catalyzed intramolecular ring closure with formation of acenaphthoazepinone **XIIa** (Scheme 3). Compound

XIIa, as well as its *N*-acetyl derivative **XIIb**, can be synthesized in one step by reaction of *peri*-amino ketones **IVa** and **VIII** with *p*-methoxybenzaldehyde in the presence of alkali. Under analogous conditions, acenaphthylene *peri*-acetylamino ketone **IX** gave rise to *trans*-chalcone **XIII** instead of expected heterocyclization product **E**, and no heterocyclization of **XIII** occurred even on prolonged heating.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on Bruker DPX-250 (250 MHz) and Varian Unity-300 (300 MHz) spectrometers using hexamethyldisiloxane as internal reference (for atom numbering, see Scheme 1). The products were purified by chromatography on aluminum oxide using chloroform as eluent. The X-ray diffraction data for compounds **IVa**, **VIII**, and **IX** were acquired on a Smart Apex II CCD diffractometer (MoK_α irradiation, graphite monochromator, ω-scanning) at the X-Ray Analysis Center, Chemistry and Materials Science Department, Russian Academy of Sciences (Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences). The structures were solved by the direct method and were refined by the least-squares procedure with respect to F^2_{hkl} in full-matrix anisotropic approximation. Hydrogen atoms in all structures were localized by the Fourier difference syntheses of electron density. The principal crystallographic and refinement parameters are listed in Table 3. All calculations were performed using SHELXTL PLUS software package [7]. Quantum-chemical calculations in terms of the density functional theory (B3LYP/6-31G** and B3LYP/6-311-G**) with account taken of zero point vibration energy were performed using Gaussian 03 software [8].

Acenaphthen-5-yl(4-methoxyphenyl)methanone (IIc). Aluminum chloride, 3.7 g (27.7 mmol), was added in small portions under stirring at room temperature to a suspension of 2.85 g (18.5 mmol) of acenaphthene (**I**) and 3 ml (27.7 mmol) of *p*-methoxybenzoyl chloride in 5 ml of tetrachloroethane. The mixture was stirred for 2 h, poured into water, and left overnight. Tetrachloroethane was removed by steam distillation, and the light brown material was recrystallized from alcohol. Yield 4.62 g (87%), slightly colored powder, mp 105°C (from ethanol). IR spectrum, ν, cm^{-1}: 1635 (C=O), 1600, 1560. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.47 br.s (4H, CH_2CH_2), 3.90 s (3H, OCH_3), 6.96 d.d (2H, 3′-H, 5′-H, ^3J = 9.11, ^4J = 2.19 Hz), 7.31 br.d (1H, 3-H, $J_{3,4}$ = 7.70 Hz), 7.37 br.d (1H, 8-H, $J_{8,7}$ = 6.91 Hz), 7.51 t (1H, 7-H, $J_{7,8}$ = 6.91, $J_{7,6}$ = 6.90 Hz), 7.66 d (1H, 6-H, $J_{6,7}$ = 6.91 Hz), 7.87 d.d (2H, 2′-H, 6′-H, ^3J = 9.11, ^4J = 2.19 Hz), 7.98 d (1H, 4-H, $J_{4,3}$ = 7.70 Hz).

4-Methoxyphenyl(6-nitroacenaphthen-5-yl)-methanone (IIIc). Compound **IIc**, 4.5 g (15.6 mmol), was dissolved in 6 ml of tetrachloroethane, 2.3 ml of nitric acid (d = 1.45 g/cm^3) was slowly added dropwise under stirring, and the mixture was stirred for 40 min, washed with water to remove excess nitric acid, and subjected to steam distillation to remove tetrachloroethane. The product was recrystallized from acetic acid. Yield 4.15 g (80%), mp 226–227°C. IR spectrum, ν, cm^{-1}: 1650 (C=O), 1607, 1560. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.53 br.s (4H, CH_2CH_2), 3.90 s (3H, OCH_3), 6.98 d.d (2H, 3′-H, 5′-H, ^3J = 8.79, ^4J = 2.19 Hz), 7.42 br.d (1H, 3-H, $J_{3,4}$ = 7.71 Hz), 7.46 br.d (1H, 8-H, $J_{8,7}$ = 7.22 Hz), 7.75 d (1H, 7-H, $J_{7,8}$ = 7.22 Hz), 7.97 d.d (2H, 2′-H, 6′-H, ^4J = 8.79, ^4J = 2.19 Hz), 8.14 d (1H, 4-H, $J_{4,3}$ = 7.71 Hz).

6-Aminoacenaphthen-5-yl(4-methoxyphenyl)-methanone (IVc). A suspension of 1.46 g of Raney nickel in 10 ml of methanol was added to a suspension of 3.038 g (9.12 mmol) of compound **IIIc** in 50 ml of methanol, and 5 ml of hydrazine hydrate was added in portions under stirring (each next portion was added when hydrogen no longer evolved after addition of the preceding portion). The reaction was performed until initial nitro ketone **IIIc** dissolved completely (~90 min). The mixture was filtered from the catalyst through a small layer of aluminum oxide on a Schott filter, the filtrate was poured into water, and the yellow precipitate was filtered off. Yield 1.5 g (54%), mp 166–167°C (from ethanol). IR spectrum, ν, cm^{-1}: 3447, 3354 (NH_2), 1620 (C=O), 1600, 1560. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.38 centrosymmetric m (4H, CH_2CH_2, J = 8.00, 7.03, 2.05 Hz), 3.87 s (3H, OCH_3), 4.25 br.s (2H, NH_2), 6.83 d (1H, 7-H, $J_{7,8}$ = 7.40 Hz), 6.94 d.d (2H, 3′-H, 5′-H, ^3J = 8.93, ^4J = 2.05 Hz), 7.20 br.d (1H, 8-H, $J_{8,7}$ = 7.40 Hz), 7.21 br.d (1H, 3-H, $J_{3,4}$ = 7.02 Hz), 7.41 d (1H, 4-H, $J_{4,3}$ = 7.02 Hz), 7.91 d.d (2H, 2′-H, 6′-H, ^3J = 8.93, ^4J = 2.05 Hz).

6-Aminoacenaphthen-5-yl(phenyl)methanone (IVb). 5-Benzoyl-6-nitroacenaphthene, 5 g (17 mmol), was dispersed in 70 ml of methanol, 2.1 g (36 mmol) of Raney nickel in 15 ml of methanol was added, and 8.3 ml (166 mmol) of hydrazine hydrate was then add-

ed in portions under stirring (each next portion was added when hydrogen no longer evolved after addition of the preceding portion). The progress of the reaction was monitored by thin-layer chromatography. When the reaction was complete, the mixture was poured into water, the precipitate was filtered off, dried in air, dissolved in chloroform, and subjected to column chromatography on aluminum oxide (8×4 cm), a fraction with R_f 0.8 (TLC, development with iodine vapor) being collected. Yield 3.5 g (78%), yellow powder, mp 148–149°C [6]. IR spectrum, ν, cm^{-1}: 3420, 3340 (NH_2), 1640 (C=O), 1615, 1600, 1580. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.38 centrosymmetric m (4H, CH_2CH_2, J = 7.91, 6.52, 1.90 Hz), 4.30 br.s (2H, NH_2), 6.86 d (1H, 7-H, $J_{7,8}$ = 7.40 Hz), 7.21 br.d (1H, 3-H, $J_{3,4}$ = 6.96 Hz), 7.23 br.d (1H, 8-H, $J_{8,7}$ = 7.40 Hz), 7.44 d (1H, 4-H, $J_{4,3}$ = 6.96 Hz), 7.48 d (2H, 3′-H, 5′-H, ^3J = 7.69 Hz), 7.60 t (1H, 4′-H, J = 7.47, 7.32 Hz), 7.92 d (2H, 2′-H, 6′-H, ^3J = 7.10 Hz).

1-(6-Aminoacenaphthen-5-yl)ethanone (IVa). Yield 93%, mp 121–122°C [5]. IR spectrum, ν, cm^{-1}: 3410, 3320 (NH_2), 1660 (C=O) 1600, 1580. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.80 s (3H, CH_3), 3.34 centrosymmetric m (4H, CH_2CH_2, J = 8.02, 6.37, 3.74 Hz), 4.51 br.s (2H, NH_2), 6.84 d (1H, 7-H, $J_{7,8}$ = 7.40 Hz), 7.18 br.d (1H, 8-H, $J_{8,7}$ = 7.40 Hz), 7.22 br.d (1H, 3-H, $J_{3,4}$ = 7.22 Hz), 7.78 d (1H, 4-H, $J_{4,3}$ = 7.22 Hz).

6-(4-Methoxybenzoyl)acenaphthen-5-ylammonium perchlorate (Vc). Compound **IVc**, 0.303 g (1 mmol), was dispersed in 0.7 ml of acetic acid, and 0.1 ml of 72% perchloric acid was added dropwise under stirring. After 1–2 min, abundant solid separated, the mixture was diluted with diethyl ether, and the precipitate was filtered off and washed with diethyl ether. Yield 0.395 g (98%), mp 176–178°C. IR spectrum, ν, cm^{-1}: 3052, 2620 (NH_3^+), 1625 (C=O), 1600, 1090 (ClO_4^-). ^1H NMR spectrum ($C_6D_5NO_2$), δ, ppm: 3.40 s (4H, CH_2CH_2), 3.80 s (3H, CH_3), 6.87 d (2H, 3′-H, 5′-H, ^3J = 8.79 Hz), 7.46 d (1H, 3-H, $J_{3,4}$ = 7.47 Hz), 7.56 d (1H, 8-H, $J_{8,7}$ = 7.76 Hz), 8.00 d (2H, 2′-H, 6′-H = 8.79 Hz), 8.03 d (1H, 7-H, $J_{7,8}$ = 7.76 Hz), 8.24 d (1H, 4-H, $J_{4,3}$ = 7.47 Hz), 10.00 br.s (3H, NH_3^+).

Perchlorates **Va** and **Vb** were synthesized in a similar way.

6-Acetylacenaphthen-5-ylammonium perchlorate (Va). Yield 84%, mp 207–208°C. IR spectrum, ν, cm^{-1}: 3550, 3180, 2690 (NH_3^+), 1640 (C=O), 1600, 1100 (ClO_4^-). ^1H NMR spectrum ($C_6D_5NO_2$), δ, ppm: 3.05 s (3H, CH_3), 3.30 s (4H, CH_2CH_2), 7.41 d (1H, 3-H, $J_{3,4}$ = 7.55 Hz), 7.50 d (1H, 8-H, $J_{8,7}$ = 7.54 Hz), 8.20 d (1H, 7-H, $J_{7,8}$ = 7.48 Hz), 8.51 d (1H, 4-H, $J_{4,3}$ = 7.55 Hz), 10.30 br.s (3H, NH_3^+).

6-Benzoylacenaphthen-5-ylammonium perchlorate (Vb). Yield 73%, mp 212–213°C. IR spectrum, ν, cm^{-1}: 3090, 2700 (NH_3^+), 1625 (C=O), 1600, 1100 (ClO_4^-). ^1H NMR spectrum (CF_3COOH), δ, ppm: 3.35 s (4H, CH_2CH_2), 7.20–7.91 m (9H, H_{arom}).

2-(4-Methoxyphenyl)-5,6-dihydroindeno-[6,7,1-*cde*]indolium perchlorate (VIc). One drop of 72% perchloric acid was added to a suspension of 0.21 g (0.52 mmol) of perchlorate **Vc** in 1.5 ml of acetic acid, the mixture was heated for 1 h under reflux, 0.3 ml of acetic anhydride was added, and the mixture was heated under reflux for 40 min more. The mixture was cooled, and the precipitate was filtered off and washed with diethyl ether. Yield 0.17 g (85%), mp 247°C (decomp.). IR spectrum, ν, cm^{-1}: 1600, 1580, 1100 (ClO_4^-).

Perchlorates **VIa** and **VIb** were synthesized in a similar way.

2-Methyl-5,6-dihydroindeno[6,7,1-*cde*]indolium perchlorate (VIa). Yield 82%, mp 226–227°C. IR spectrum, ν, cm^{-1}: 3170 (NH^+), 1630 (C=N), 1480, 1100 (ClO_4^-). ^1H NMR spectrum ($C_6D_5NO_2$), δ, ppm: 3.42 s (3H, CH_3), 3.62 m (4H, CH_2CH_2), 7.67 d (1H, 3-H, $J_{3,4}$ = 7.54 Hz), 7.90 d (1H, 8-H, $J_{8,7}$ = 7.40 Hz), 8.31 d (1H, 7-H, $J_{7,8}$ = 7.40 Hz), 8.74 d (1H, 4-H, $J_{4,3}$ = 7.54 Hz), 13.22 br.s (1H, NH^+).

2-Phenyl-5,6-dihydroindeno[6,7,1-*cde*]indolium perchlorate (VIb). Yield 88%, mp 232–234°C. IR spectrum, ν, cm^{-1}: 1600, 1580, 1100 (ClO_4^-).

2-(4-Methoxyphenyl)-5,6-dihydroindeno-[6,7,1-*cde*]indole (VIIc). Perchlorate **VIc**, 0.3 g (0.78 mmol), was dispersed in 5 ml of diethyl ether, 0.12 ml (1.2 mmol) of triethylamine was added, and the mixture was stirred for 5 min at room temperature. The mixture was evaporated to dryness, and the residue was dissolved in chloroform and subjected to chromatography on aluminum oxide, the first fraction with R_f 0.8 being collected. Yield 0.21 g (95%), yellow powder, mp 167–168°C. IR spectrum, ν, cm^{-1}: 1625 (C=N), 1600, 1560. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.55 centrosymmetric m (4H, CH_2CH_2), 3.90 s (3H, OCH_3), 7.08 d.d (2H, 3′-H, 5′-H, ^3J = 8.93, ^4J = 2.05 Hz), 7.42 br.d (1H, 7-H, $J_{7,8}$ = 7.03 Hz), 7.53 br.d (1H, 4-H, $J_{4,3}$ = 7.03 Hz), 7.88 d (1H, 8-H, $J_{8,7}$ = 7.03 Hz), 8.26 d (1H, 3-H, $J_{3,4}$ = 7.03 Hz), 8.36 d.d (2H, 2′-H, 6′-H, ^3J = 8.93, ^4J = 2.05 Hz).

2-Phenyl-5,6-dihydroindeno[6,7,1-*cde*]indole (VIIb) was synthesized in a similar way. Yield 91%, mp 157–158°C. IR spectrum, ν, cm^{-1}: 1625 (C=N), 1560. ^1H NMR spectrum, ($CDCl_3$), δ, ppm: 3.60 centrosymmetric m (4H, CH_2CH_2), 7.46 br.d (1H, 7-H, $J_{7,8}$ = 7.07 Hz), 7.50–7.62 m (4H, 4-H, H_{arom}), 7.96 d (1H, 8-H, $J_{8,7}$ = 7.07 Hz), 8.31 d (1H, 3-H, $J_{3,4}$ = 7.14 Hz), 8.40 d (2H, H_{arom}, J = 8.13 Hz).

***N*-(6-Acetylacenaphthen-5-yl)acetamide (VIII).** Amino ketone **IVa**, 0.568 g (2.7 mmol), was dispersed in 5 ml of water on heating to 40–50°C, 1 ml of acetic anhydride was added, the mixture turned homogeneous, and a solid separated in 3–5 min and was filtered off. Yield 0.554 g (81%), light yellow powder, mp 161–162°C (from ethanol); published data [1]: mp 160.2–161°C. IR spectrum, ν, cm^{-1}: 3280 (NH), 1673 (C=O, amide), 1647 (C=O, ketone). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (3H, $NCOCH_3$), 2.6 s (3H, $COCH_3$), 3.36 m (4H, CH_2CH_2), 7.34 d (1H, 7-H, $J_{7,8}$ = 7.17 Hz), 7.39 s (2H, 3-H, 4-H), 7.5 d (1H, 8-H, $J_{8,7}$ = 7.18 Hz), 9.68 br.s (1H, NH). Found, %: C 75.51; H 6.12; N 5.75. $C_{16}H_{15}NO_2$. Calculated, %: C 75.89; H 5.93; N 5.53.

***N*-(6-Acetylacenaphthylen-5-yl)acetamide (IX).** *N*-Acetylamino ketone **VIII**, 0.3 g (1.2 mmol), was dissolved in 2 ml of *o*-dichlorobenzene, 0.438 g (1.8 mmol) of tetrachloro-1,4-benzoquinone was added, and the mixture was heated for 2 h under reflux. The mixture was evaporated to dryness, and the residue was dissolved in chloroform and subjected to chromatography on aluminum oxide. Yield 0.04 g (13%), yellow powder, mp 107–108°C. IR spectrum, ν, cm^{-1}: 3270 (NH), 1670 (C=O, amide), 1650 (C=O, ketone). ^1H NMR spectrum, δ, ppm: in $CDCl_3$: 2.23 s (3H, NCOMe), 2.84 s (3H, COMe), 6.88 d (1H, 2-H, $J_{2,1}$ = 5.3 Hz), 7.11 d (1H, 1-H, $J_{1,2}$ = 5.3 Hz), 7.62 d (1H, 3-H, $J_{3,4}$ = 7.6 Hz), 7.66 d (1H, 7-H, $J_{7,8}$ = 7.2 Hz), 8.10 d (1H, 8-H, $J_{8,7}$ = 7.3 Hz), 8.30 d (1H, 4-H, $J_{4,3}$ = Hz), 10.7 br.s (1H, NH); in DMSO-d_6: 2.00 s (3H, COMe), 2.60 s (3H, NCOMe), 7.05 d (1H, 2-H, $J_{2,1}$ = 5.3 Hz), 7.15 d (1H, 1-H, $J_{1,2}$ = 5.3 Hz), 7.47 d (1H, 7-H, $J_{7,8}$ = 7.3 Hz), 7.70–7.83 m (3H, 3-H, 4-H, 8-H), 10.1 s (1H, CONH). Found, %: C 76.15; H 5.41; N 5.77. $C_{16}H_{13}NO_2$. Calculated, %: C 76.49; H 5.18; N 5.58.

1-[6-(4-Methoxybenzylideneamino)acenaphthen-5-yl]ethanone (XI). Amino ketone **IVa**, 0.478 g (2.27 mmol), was dissolved on heating in 1 ml of ethanol, 0.31 ml (2.27 mmol) of *p*-methoxybenzaldehyde was added, the mixture was heated for 3–4 min under reflux and cooled, and the precipitate was filtered off. Yield 0.608 g (82%), yellow powder, mp 109–110°C (from ethanol). IR spectrum, ν, cm^{-1}: 1680 (C=O), 1620 (C=N), 1607. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.50 s (3H, COMe), 3.40 m (4H, CH_2CH_2), 3.90 s (3H, OMe), 7.02 d (2H, 3′-H, 5′-H, ^3J = 8.75 Hz), 7.20 d (1H, 7-H, $J_{7,8}$ = 7.40 Hz), 7.28 br.s (2H, 3-H, 4-H), 7.33 d (1H, 8-H, $J_{8,7}$ = 7.40 Hz), 7.86 d (2H, 2′-H, 6′-H, ^3J = 8.75 Hz), 8.53 s (1H, N=CH). Found, %: C 80.00; H 5.89; N 4.47. $C_{22}H_{19}NO_2$. Calculated, %: C 80.24; H 5.76; N 4.26.

2-(4-Methoxyphenyl)-2,3-dihydroacenaphtho[5,6-*bc*]azepin-4(1*H*)-one (XIIa). Amino ketone **IVa**, 0.162 g (0.77 mmol), was dispersed in 1 ml of ethanol, 0.104 ml (0.77 mmol) of *p*-methoxybenzaldehyde and 0.4 ml of 30% aqueous sodium hydroxide were added, and the mixture was heated to 50–60°C and kept for 2 h at room temperature. The solution was cooled, and the precipitate was filtered off. Yield 76%, orange–red powder, mp 109–110°C. IR spectrum, ν, cm^{-1}: 3420 (NH), 1700 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.1–3.2 d.d (1H, 3-H, J = 16.7 Hz), 3.34–3.44 m (4H, CH_2CH_2), 3.5–3.6 d.d (1H, 3-H, J = 16.7 Hz), 3.84 s (3H, OMe), 4.36 br.s (1H, NH), 4.70–4.76 d (1H, 2-H, J = 11.1 Hz), 6.75–6.85 d (1H, 10-H, J = 7.4 Hz), 6.90–6.95 d (2H, C_6H_4, J = 8.6 Hz), 7.10–7.15 d (1H, 9-H, J = 7.4 Hz), 7.30–7.35 d (1H, 6-H, J = 7.4 Hz), 7.34–7.38 (2H, C_6H_4, J = 8.6 Hz), 8.13–8.17 d (1H, 5-H, J = 7.4 Hz). Found, %: C 80.42; H 5.68; N 4.45. $C_{22}H_{19}NO_2$. Calculated, %: C 80.24; H 5.78; N 4.26.

1-Acetyl-2-(4-methoxyphenyl)-2,3-dihydroacenaphth[5,6-*bc*]azepin-4(1*H*)-one (XIIb). A mixture of 0.3 g (1.2 mmol) of 6-acetylamino-5-acetylacenaphthene **VIII**, 0.16 ml (1.2 mmol) of *p*-methoxybenzaldehyde, 0.6 ml of 30% aqueous sodium hydroxide, and 2 ml of ethanol was stirred for 3 h at room temperature. The precipitate was filtered off and dried in air. Yield 0.25 g (62%), light yellow powder, mp 172–173°C. IR spectrum, ν, cm^{-1}: 1687 (1-C=O), 1647 (C^4=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.1–3.2 d.d (1H, 3-H, J = 13.7 Hz), 3.4–3.5 m (4H, CH_2CH_2), 3.43–3.53 d.d (1H, 3-H, J = 13.7 Hz), 3.7 s (3H, OMe), 6.44–6.50 d.d (1H, 2-H, J = 9.9 Hz), 6.72–6.76 d (2H, C_6H_4, J = 8.75 Hz), 7.12–7.16 d (1H, 10-H, J = 7.25 Hz), 7.22–7.26 d (2H, C_6H_4, J = 8.75 Hz), 7.27–7.30 d (1H, 9-H, J = 7.25 Hz), 7.36–7.40 d (1H, 6-H, J = 7.25 Hz), 7.96–8.00 d (1H, 5-H, J = 7.25 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.0, 30.0, 31.0, 48.0, 55.0, 56.5, 76.5, 77.0, 77.5,

113.6, 119.6, 119.8, 128.4, 130.2, 131.2, 131.6, 132.4, 132.8, 140.0, 146.0, 152.0, 158.5, 170.5, 200.0. Found, %: C 77.86; H 5.62; N 3.87. $C_{24}H_{21}NO_3$. Calculated, %: C 77.63; H 5.66; N 3.77.

(2*E*)-1-(6-Acetylaminoacenaphthylen-5-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (XIII). *N*-(6-Acetylacenaphthylen-5-yl)acetamide, 0.5 g (1.99 mmol), was dissolved in 5 ml of ethanol on slight heating, 0.24 ml (1.99 mmol) of *p*-methoxybenzaldehyde and 1 ml of 30% aqueous sodium hydroxide were added, and the mixture was heated for 5 min under reflux. The mixture was cooled, the precipitate was filtered off, dried in air, and dissolved in chloroform, and the solution was subjected to chromatography on aluminum oxide to isolate a red fraction with R_f 0.7. Yield 0.507 g (69%), red–orange powder, mp 176–177°C. IR spectrum, ν, cm^{-1}: 3300 (NH), 1673 (C=O, amide), 1640 (COCH=CH), 1600. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.15 s (3H, $NCOCH_3$), 3.85 s (3H, OCH_3), 6.90 d (1H, 2-H, $J_{2,1}$ = 5.26 Hz), 6.92 d (2H, 3′-H, 5′-H, ^3J = 8.77 Hz), 7.07 d (1H, 1-H, $J_{1,2}$ = 5.27 Hz), 7.22 d [1H, C(O)CH=C**H**, J = 15.78 Hz], 7.55 d (2H, 2′-H, 6′-H, ^3J = 8.77 Hz), 7.62 d [1H, C(O)C**H**=CH, J = 15.78 Hz], 7.63 d (1H, 7-H, $J_{7,8}$ = 7.01 Hz), 7.64 d (1H, 3-H, $J_{3,4}$ = 7.72 Hz), 7.82 d (1H, 8-H, $J_{8,7}$ = 7.01 Hz), 8.18 d (1H, 4-H, $J_{4,3}$ = 7.72 Hz), 9.80 br.s (1H, NH). Found, %: C 77.65; H 5.31; N 3.51. $C_{24}H_{19}NO_3$. Calculated, %: C 77.95; H 5.14; N 3.79.

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